DX

179051

STUDIES OF 1,2-QUINONE MONOOXIMES AND THEIR METAL COMPLEXES

Terrance Augustine Thomas

A thesis submitted to the University of North London
in partial fulfilment of the requirements for the
degree of Doctor of Philosophy.

THIS RESEARCH PROGRAMME WAS CARRIED OUT IN
COLLABORATION WITH SMITHKLINE BEECHAM PHARMACEUTICALS

AUGUST 1993

Dedicated to my wife Judy, and my Mum

Declaration

Whilst registered as a candidate for this degree, the author has not been registered for any other award.

T. A. Thomas

Terrance A. Thomas

STUDIES OF 1,2-QUINONE MONOOXIMES AND THEIR METAL COMPLEXES

Abstract:

The chemistry of 1,2-quinone monooximes has been reviewed. The synthesis of 5-amino, 5-alkylamino and 5-acylamino substituted 1,2-benzoquinone monooximes was systematically studied. Thus, it has been found that 5-amino-1,2-benzoquinone-2-oxime (5-AqoH), 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime (5-Et-4-MeqoH), 5-hexylamino-1,2-benzoquinone-2-oxime (5-HxqoH) and 5-heptylamino-1,2-benzoquinone-2-oxime (5-HptqoH) were best prepared by the reaction of the corresponding phenol with sodium nitrite in the presence of concentrated hydrochloric acid. Under these conditions, N-nitrosation was inhibited and the 1,2-benzoquinone-2-oxime hydrochlorides were formed. The 5-acylamino-1,2-benzoquinone-2-oximes, 5-propionylamino-1,2-benzoquinone-2-oxime (5-PrqoH), 5-butyrylamino-1,2-benzoquinone-2-oxime (5-BuqoH), 5-pentanoylamino-1,2-benzoquinone-2-oxime (5-PeqoH), and 5-heptanoylamino-1,2-benzoquinone-2-oxime (5-HpqoH) were obtained from their metal complexes, since the direct reaction of the phenol with sodium nitrite failed to give the compounds giving the corresponding 1,4-benzoquinone-4-oximes, 3-propionylamino-1,4-benzoquinone-4-oxime (3-PrqoH), 3-butyrylamino-1,4-benzoquinone-4-oxime (3-BuqoH), 3-pentanoylamino-1,4-benzoquinone-4-oxime (3-PeqoH) and 3-heptanoylamino-1,4-benzoquinone-4-oxime (3-HpqoH) instead. Spectroscopic analysis has shown the compounds to exist in the quinone oximic rather than in the nitrosophenolic form. X-ray crystallographic studies of 5-HxqoH, 5-Et-4-MeqoH and 5-Et-4-MeqoH.HCl have shown all three compounds to have some 1,4-oxime-imino character.

The synthesis of nickel(II), copper(II), palladium(II) and platinum(II) complexes of the acylamino and alkylamino substituted 1,2-benzoquinone-2- oximes both by the direct and nitrosation methods was examined. The nitrosation method gave rise to complexes $Ni(qo)_2.nH_2O$, $Cu(qo)_2.nH_2O$ and $Pd(qo)_2$ but failed to give the corresponding platinum complexes. The latter were only obtained by the direct method. The nickel(II) and copper(II) complexes reacted with pyridine and 2,2-dipyridyl to give adducts of the type $Ni(qo)_2(py)_2$ and $Cu(qo)_2(py)$ and $M(qo)_2(dipy)$ respectively. The palladium and platinum complexes however failed to react with either of the Lewis bases. Magnetic moment studies showed the hydrated complexes and Lewis base adducts to be magnetically dilute and thus monomeric. Such studies, as well as IR and LSIMS mass spectral analysis of the anhydrous complexes $Ni(qo)_2$ and $Cu(qo)_2$, showed them to be associated both in the solid state and in solution.

The reaction of selected 1,2-quinone monooximes (qoH) and metal 1,2-quinone monooximates ($M(qo)_2$; qoH = 1,2-naphthoquinone-1-oxime

(1-nqoH), 1,2-naphthoquinone-2-oxime (2-nqoH), 3-butyrylamino-1,2-benzoquinone-2-oxime, 4-chloro-1,2-benzoquinone-2-oxime (4-ClqoH), 4-bromo-1,2-benzoquinone-2-oxime (4-BrqoH), 5-acetylamino-1,2-benzoquinone-2-oxime (5-AcqoH), 5-hydroxy-1,2-benzoquinone-2-oxime (5-HqoH); M = Ni and Cu) with dimethyl acetylenedicarboxylate (DMAD) was systematically examined.

The reaction of 1-nqoH and 5-HqoH gave rise to nucleophilc addition products *cis*- and *trans*-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime, *trans*-(O-dicarbomethoxyethenyl)-5-hydroxy-1,2-benzoquinone-2-oxime. The yields were enhanced by the presence of small amounts of alkali and alkaline earth metal chlorides. With $M(1\text{-nqo})_2$ and $M(Buqo)_2$ (M = Ni, Cu) 1,4-oxazines were the only products formed. However, $M(4\text{-Clqo})_2$ and $M(4\text{-Brqo})_2$ 1,4-benzoxazinones and 1,4-benzoxazines were isolated. The reaction of the structurally related 1,2-dioximes and metal 1,2-dioximates $M(dmgH)_2$ and $M(dagH)_2$, ($dmgH_2$ = dimethylglyoxime; $dagH_2$ = 1,2-diaminoethanedione dioxime; M = Ni, Cu) with DMAD was also examined. The dimethylglyoxime and its metal complexes failed to afford any adducts while the 1,2-diaminoethanedione dioxime and its metal complexes gave nucleophilic addition products *cis*- and *trans*-bis(O-1,2-dicarboxyethenyl)-1,2-diaminoethanedione dioxime. Mechanisms for the reaction of DMAD with both the quinone monooximes and the 1,2-dioximes have been proposed.

Acknowledgements

I wish to express my sincerest gratitude to Professor John Charalambous for the invaluable support he gave during this work. None of this would have been possible without his contribution.

I would also like to thank Dr. E. G. Brain for his many suggestions, Dr. Oliviero Carugo at the University of Pavia, Italy and Mr. Nick Choi at the University of North London for their help with the X-ray crystallographic studies.

Whilst pursuing this work, the author was supported by a research scholarship jointly funded by the A.G. Leventis Foundation and the University of North London.

Abbreviations

5-AcqoH	5-Acetylamino-1,2-benzoquinone-2-oxime
5-BuqoH	5-Butyrylamino-1,2-benzoquinone-2-oxime
5-PrqoH	5-Propionylamino-1,2-benzoquinone-2-oxime
5-PeqoH	5-Pentanoylamino-1,2-benzoquinone-2-oxime
5-HpqoH	5-Heptanoylamino-1,2-benzoquinone-2-oxime
5-HxqoH	5-Hexylamino-1,2-benzoquinone-2-oxime
5-HptqoH	5-Heptylamino-1,2-benzoquinone-2-oxime
5-AqoH	5-Amino-1,2-benzoquinone-2-oxime
5-Et-4-MeqoH	5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime
3-AcqoH	3-Acetylamino-1,4-benzoquinone-4-oxime
3-PrqoH	3-Propionylamino-1,4-benzoquinone-4-oxime
3-BuqoH	3-Butyrylamino-1,4-benzoquinone-4-oxime
3-PeqoH	3-Pentanoylamino-1,4-benzoquinone-4-oxime
3-HpqoH	3-Heptanoylamino-1,4-benzoquinone-4-oxime
3-HxqoH	3-Hexylamino-1,4-benzoquinone-4-oxime
3-HptqoH	5-Heptylamino-1,4-benzoquinone-4-oxime
1-nqoH	1,2-naphthoquinone-1-oxime
2-nqoH	1,2-naphthoquinone-2-oxime
5-HqoH	5-Hydroxy-1,2-benzoquinone-2-oxime
t.g.a	Thermal gravimetric analysis
IR	Infra-red
NMR	Nuclear magnetic resonance
TLC	Thin layer chromatography
m.p.	melting point

b.p.	boiling point
EGDE	Ethyleneglycol dimethylether
DMAD	Dimethyl acetylenedicarboxylate
py	pyridine
dipy	2,2-dipyridyl
$dmgH_2$	dimethylglyoxime
$dagH_2$	1,2-diaminoethanedione dioxime
Fig.	Figure

CONTENTS

Chapter Two

THE SYNTHESIS AND CHARACTERISATION OF ACYLAMINO AND ALKYLAMINO SUBSTITUTED 1,2-BENZOQUINONE MONOOXIMES.

CHAPTER ONE

CHAPTER 1

The Synthesis, Structure, and Properties of 1,2-Quinone Monooximes and Their Metal Complexes.

1.1. Introduction.

1,2-Quinone monooximes (Fig. 1.1), which are isomeric with 2-nitrosophenols (Fig. 1.2), have been known for some time.[1] Structural studies of these compounds (discussed later) show that in most cases, there is a predominance of quinone oximic character. Hence, in this thesis the compounds will be referred to as quinone monooximes though this does not imply that any specific compound exists exclusively in that form.

Figure 1.1.

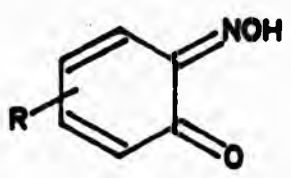
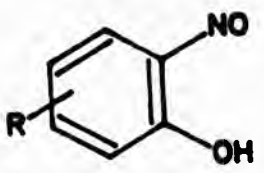


Figure 1.2.



Quinone monooximes, and more so their transition metal complexes have attracted considerable interest in a wide spectrum of areas. In the case of the uncoordinated 1,2-quinone monooximes, their close structural resemblance to the ligand in the naturally occurring siderophore ferroverdin,[2,3] and their own ability to chelate iron, holds some possibility for their use in the treatment of human iron overload disorders.[4,5] In addition, their propensity to selectively precipitate certain metal ions has been exploited for the purposes of metal

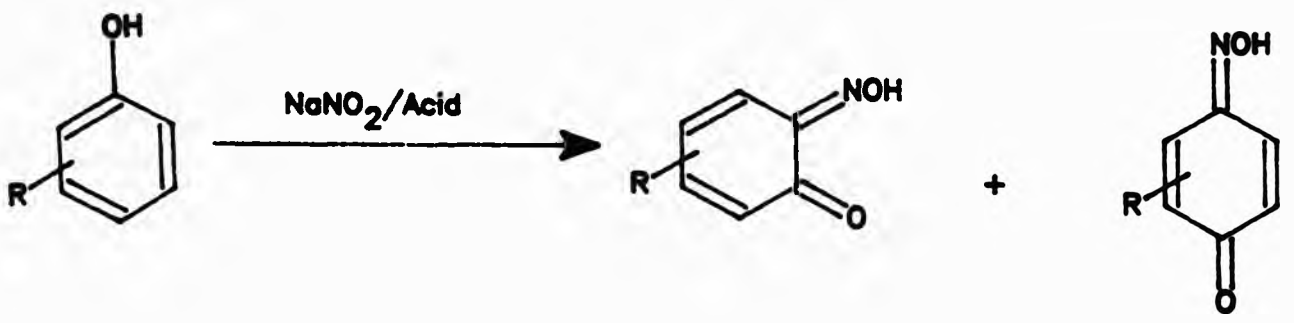
analysis.[6-11] Thus cobalt, nickel, and copper have all been successfully detected in the presence of zinc, chromium and aluminium using 4-hydroxy-5-nitroso-1,2-benzoquinone-2-oxime or 3-hydroxy-5-methyl-6-nitroso-1,2-benzoquinone-2-oxime.[6]

The transition metal complexes have been used in organic synthesis,[12-14] as dyestuffs,[15-19] and as oxidation catalysts.[20-24] For example, bis(1,2-naphthoquinone-2-oximato)manganese(II) has been used to oxidize alkenes to epoxides and subsequently to diols in the presence of air.[24] The redox behaviour of $Cu(4\text{-}Clqo)_2$ and $Ni(4\text{-}Clqo)_2$ both in a chemically suitable medium and when electrochemically induced, have also been recently reported.[25] The oxidizing power of these compounds could have some implications for their extended use in synthesis and in pollution control.

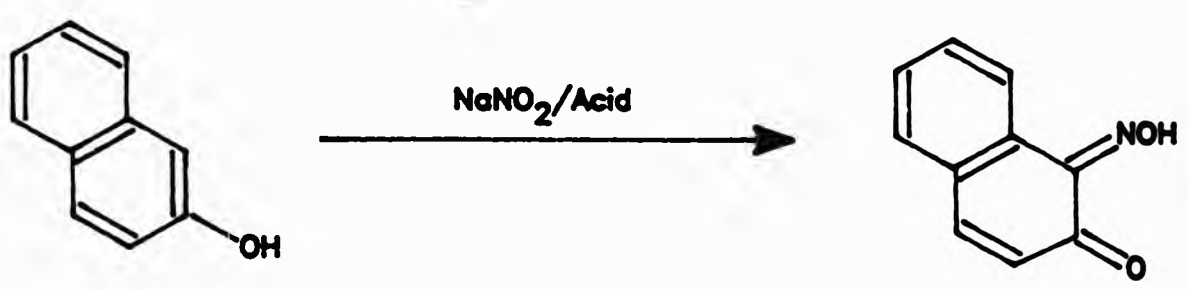
1.2. The Synthesis of 1,2-Quinone Monooximes.

1,2-Quinone monooximes have been prepared by a variety of routes. The most widely reported is the reaction of a phenol with sodium nitrite and an aqueous acid, usually acetic acid.[26,27] As with other aromatic electrophilic substitutions, ring nitrosation occurs easiest when activated aromatics are the substrates. The reaction, which involves the relatively weak electrophile NO^+, occurs readily in the case of phenols because of the activating effect of the phenolic OH group. For most phenols with an unprotected para position, this reaction leads mainly to the formation of the 4-substituted product (eg. Reaction 1.1). However, in a few cases, for example 2-naphthol and 3-alkoxyphenols, the 2-substituted product predominates (eg. Reaction 1.2).[28-30]

Reaction 1.1.

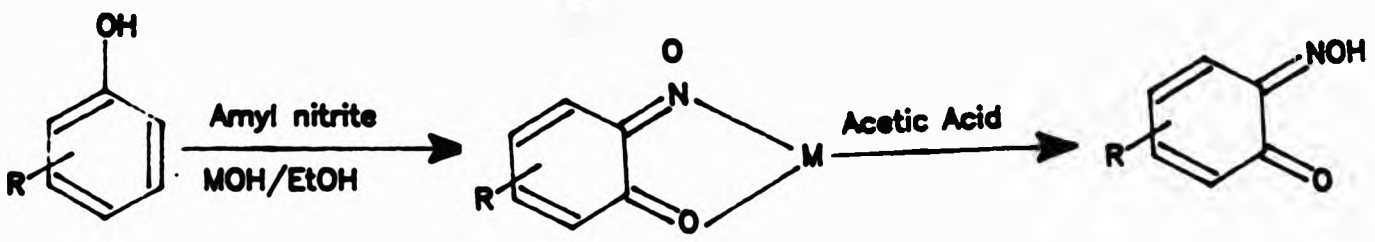


Reaction 1.2.



Among the other methods used to prepare 1,2-quinone monooximes is the reaction of an alkyl nitrite, for example amyl nitrite, with a phenol under various pH conditions ranging from strongly alkaline to weakly acidic (eg. Reaction 1.3).[31,32] This method has been most widely applied to the synthesis of 5-alkoxy-1,2-benzoquinone-2-oximes via their alkali metal complexes.

Reaction 1.3.



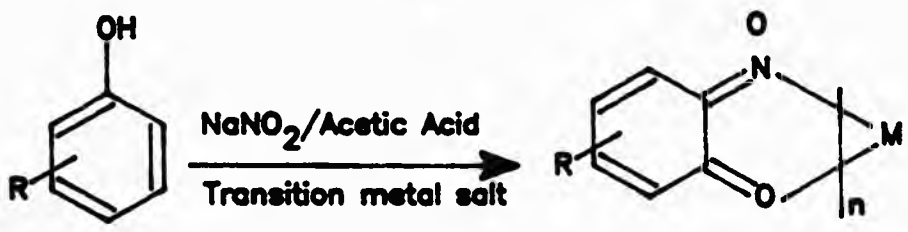
M = Li, Na, K

The action of (i) hydroxylamine on a quinone,[33] (ii) hydroxylamine hydrochloride and hydrogen peroxide on an aromatic compound,[34-36] (iii) sodium hydroxide on some aromatic nitro compounds,[37] (iv) the acidification of quinone monooximic complexes of both main group and transition metals for example sodium, potassium, and nickel,[38,39] (v) the treatment of selected Lewis base adducts of 1,2-quinone monooximato copper(II) complexes with silica,[15] (vi) the light induced reactions of 2-nitrophenoxyacetic acid or 1-naphthol in the presence of N-nitroso-dimethylamine,[40,41] (vii) the boiling of nitrosoaniline in the presence of potassium hydrogen carbonate,[42] and (viii) ion exchange chromatography of selected transition metal complexes,[4] have all been reported as having led to the isolation of 1,2-quinone monooximes. However, the reports of some of these methods for example (ii), (v) and (vii) lack experimental detail or the methods described are not widely applicable.

1.3. The Synthesis of Metal Complexes of 1,2-Quinone Monooximes.

Transition and main group metal complexes of 1,2-quinone monooximes have been widely reported. As for the free ligands, a number of synthetic routes to these complexes have been developed. The nitrosation of a phenol using sodium nitrite/acetic acid in the presence of a transition metal salt (eg. Reaction 1.4) has been the most successful and has been used for the synthesis of several complexes.[27,43,44] This method even affords 1,2-quinone monooximic complexes from phenols which do not afford the uncoordinated compounds by any route.

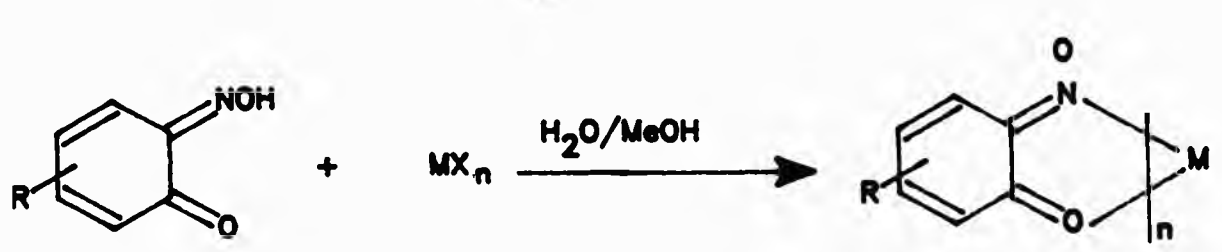
Reaction 1.4.



It has also been claimed that copper(II) complexes of 1,2-quinone monooximes are obtained by the o-nitrosohydroxylation of benzene or substituted benzenes with hydroxylamine hydrochloride, hydrogen peroxide and a copper(II) salt.[33-35] However, the reports of this method, the Baudisch method, lack both experimental details and analytical data for the compounds claimed.

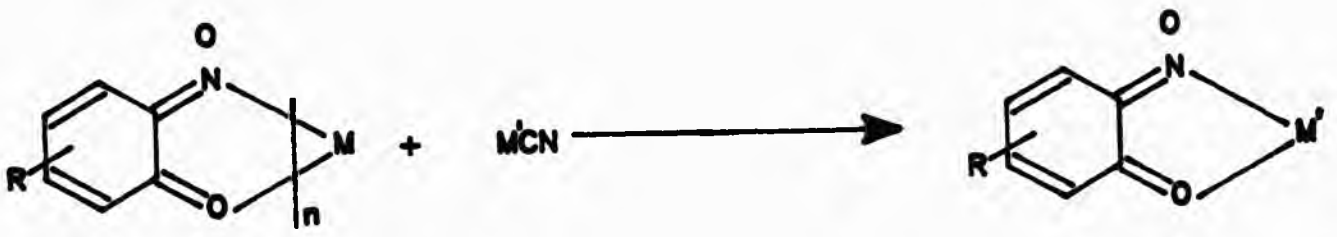
The reaction of aqueous alcoholic solutions of 1,2-quinone monooximes with main group or transition metal salts or metal carbonyls have yielded the corresponding metal complex (eg. Reaction 1.5).[45-47] However, because only a few 1,2-quinone monooximes have been isolated, this method is of limited synthetic utility.

Reaction 1.5.



For main group metals particularly alkali metals, the nitrosation of a suitable phenol with amyl nitrite in the presence of the metal alkoxide has been shown to be most useful for the preparation of their 1,2-quinone monooximic complexes.[31] These complexes may however also be obtained by the reaction of the 1,2-quinone monooximato complexes of transition metals with alkali metal cyanides (eg. Reaction 1.6).[48]

Reaction 1.6.



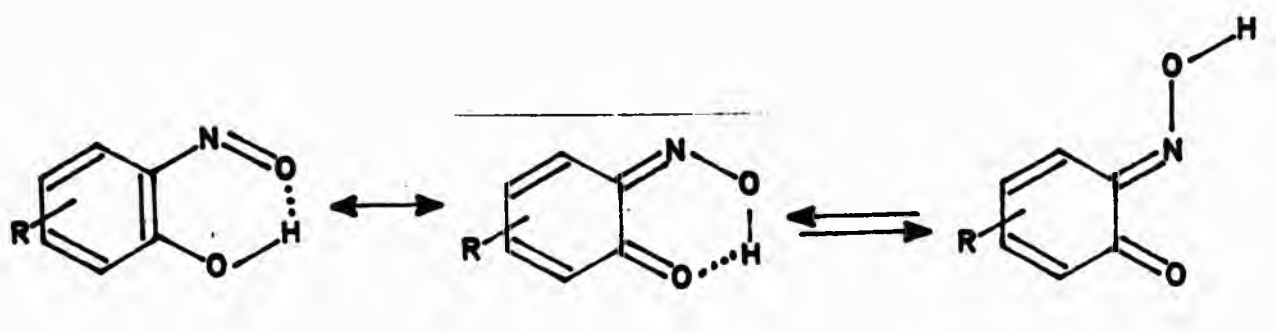
M = Transition metal ion

M' = Alkali metal ion

1.4. The Structure of 1,2-Quinone Monooximes.

1,2-Quinone monooximes can exist in different isomeric forms (Scheme 1.1). The tautomeric relationship of these compounds with 2-nitrosophenols has been the subject of several studies.[49-56]

Scheme 1.1.



A number of spectroscopic investigations of this equilibrium have been reported with the results generally suggesting a predominance of quinone oximic character over nitrosophenolic character both in the solid state and in solution.[57-60] However, only the advent of X-ray techniques provided a means by which the relative importance of the two forms could be irrevocably resolved.

To date, all X-ray crystal structure analysis of ortho nitrosated phenols have shown the compounds to have a predominantly quinone oximic structure, confirming the earlier spectroscopic findings. In fact, in the case of the ortho substituted products of the nitrosation of 3-n-propoxyphenol, 3-(2-bromoethoxy)phenol, and 3-(2-chloroethoxy)-phenol, though two crystalline forms are obtained, both have been shown to be quinone monooximic.[61-63] For example, the two crystalline forms of the 5-n-propoxy analogue were found to differ only in the orientation of the oximic OH group relative to the quinoid carbonyl group. One, α-5-n-PqoH, has the oximic group *anti* to the quinoid carbonyl group (Fig. 1.3) a conformation which is characterised by the absence of any intramolecular hydrogen bonding in the molecule. By contrast the other, β-5-n-PqoH, has the oximic NOH group *syn* to the quinoid CO group (Fig. 1.4) and here, strong intramolecular hydrogen bonds are observed. This is bourne out by a comparison of the O(NOH) - O(CO) bond lengths in this and related compounds. The latter (2.473 Å) in the *syn* isomer compares well with those of ω-salicylic acid (2.590 Å), maleic acid (2.506 Å) and cytosine-5-acetic acid (2.468 Å) all of which are known to contain strong intramolecular hydrogen bonds in the solid state.[64,65] Related studies on substituted naphthoquinone monooximes and other systems have reinforced further the position that most 2-substituted products of the nitrosation of phenols show greater 1,2-quinone monooximic character

than 2-nitrosophenolic character in the solid state.[66-69] The presence of two short and four long C-C bond distances in the carbocyclic ring of the molecules is evidence of this finding. Further, the C-O and C-N bonds in compounds so far characterised by X-ray analysis are found to be shorter (1.247-1.300 Å and 1.319-1.381 Å respectively), and thus show considerably more double bond character than the analogous bonds in salicylaldoximates and related systems.[70-72]

Figure 1.3

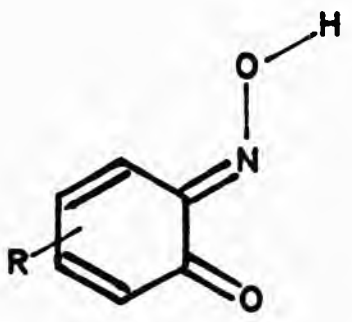
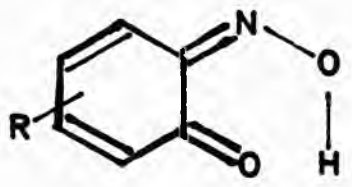


Figure 1.4



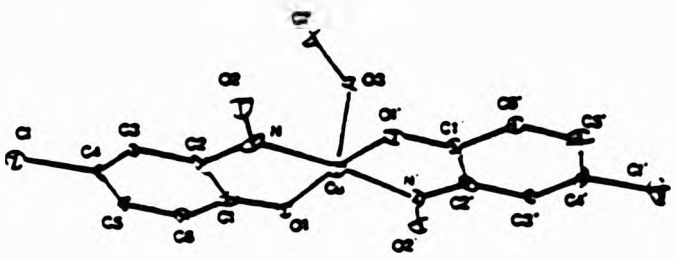
1.5. Types and Structure of Metal Complexes Derived from 1,2-Quinone Monooximes.

Transition metal complexes of these potentially bidentate ligands have been known for some time. However, only since the mid 1960's has any attention been given to the systematic study of these compounds or any attempt made to determine their structure.

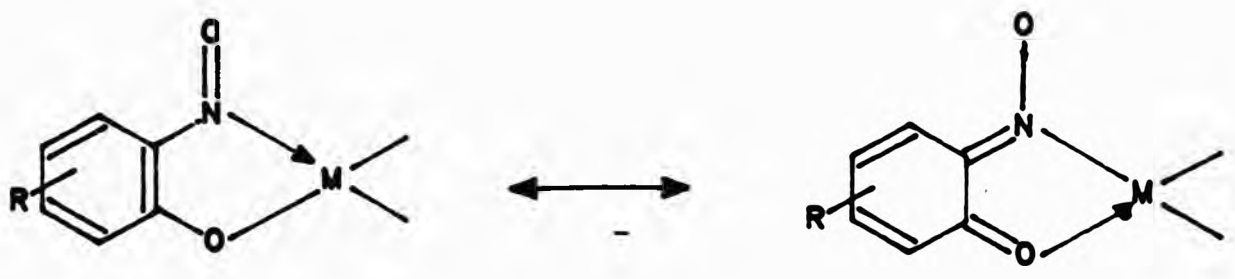
Several types of metal 1,2-quinone monooximates have so far been isolated. The most common type involves the 1,2-quinone monooximato anion coordinated to the metal via the oximic nitrogen and the quinoid oxygen thereby forming a five-membered chelate ring (eg. Fig. 1.5).[27,73-75] The structure of complexes of this type, initially proposed on the basis of IR and other spectroscopic data,[76,77] was

confirmed by X-ray crystal data analysis.[78-83] In all cases, the ligands were found to have predominantly quinone oximic character though the shortening of the N-O and C-C bonds in these chelates compared to the uncoordinated compounds, suggests some nitrosophenolic character as well. Thus, the complexes have been represented as a resonance hybrid of the two cannonical forms I and II shown in Scheme 1.2.

Figure 1.5.



Scheme 1.2.



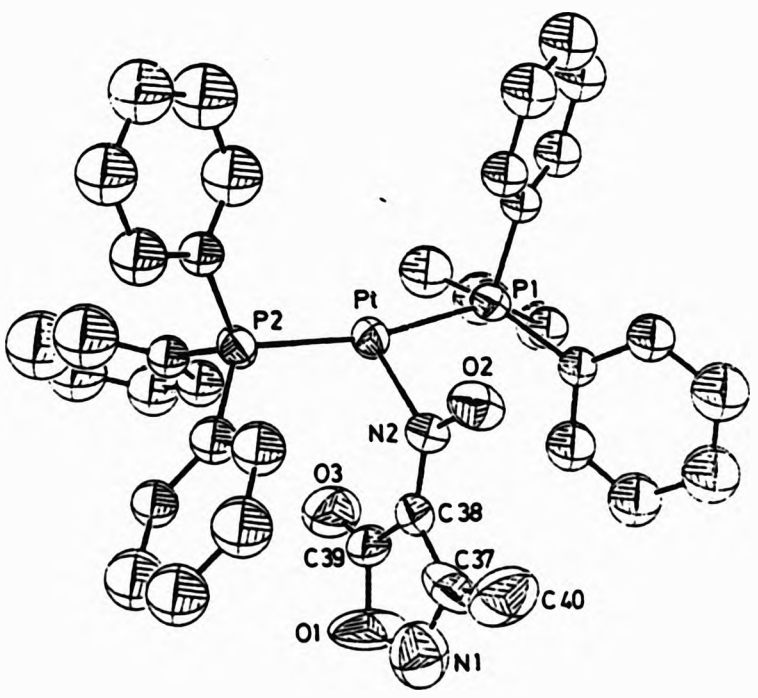
There have been suggestions of the occurrence of 1,2-quinone monooximato complexes in which the metal is coordinated to the ligand via both the quinoid and oximic oxygens to form six membered chelate rings.[84,85] However, to date, this structure has not been demonstrated by X-ray crystallography.

A second class of 1,2-quinone monooximato complex contains the central metal ion coordinated to ligands to form an anionic species. Usually in these cases, an alkali metal is present as the counter ion. The most well known of this type of 1,2-quinone monooximato complexes are the iron based compounds referred to as ferro and ferriverdins, $Na[Fe^{II}(qo)_3]$ and $Fe^{III}(qo)_3$.[86,87]

The type of structure and bonding described above is that usually observed in the complexes of 1,2-quinone monooximes with early (*d*-block) transition metal elements.

In the case of the heavier transition metals, for example platinum and gold, a second mode of bonding is encountered. In these complexes, coordination to the ligand has been shown to involve only the oximic (NOH) group. Thus the complexes of 4-isonitroso-3R-isoxazol-5-one with these metals (eg. Fig. 1.6) contains the metal ion linked only by the nitrogen atom of the oximic group. Here the ligand is therefore acting in monodentate mode.[88]

Figure 1.6



Similarly, the actinide uranium forms complexes with 1,2-quinone monooximes in which coordination involves only the oximic group. The X-ray crystal structure of the uranyl complexes $(UO_2(1\text{-nqo})_2(H_2O)_2).2CHCl_3$ (Fig. 1.8) and $UO_2(1\text{-nqo})_2(Ph_3PO)(H_2O)$ (Fig. 1.7), showed the metal bonded through both the oxygen and nitrogen of the oximic group.[89] Although the resulting linkage is presented as a three-membered chelate ring, the bonding could also be visualized as η^2 coordination involving the interaction of metal *f*-orbitals with the π component of the N=O group or with the delocalized electron cloud of the C-N-O group. This could occur despite the high oxidation state of the metal (U (IV)).[90]

Figure 1.7

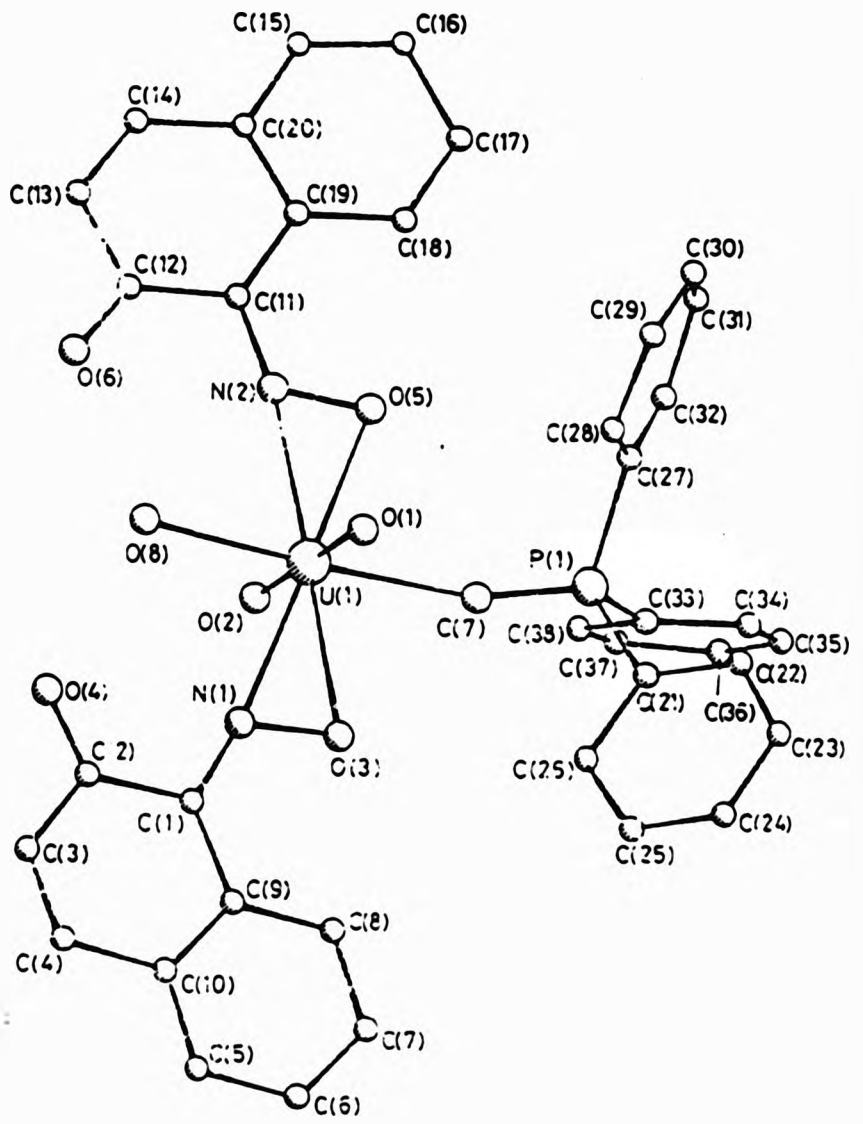
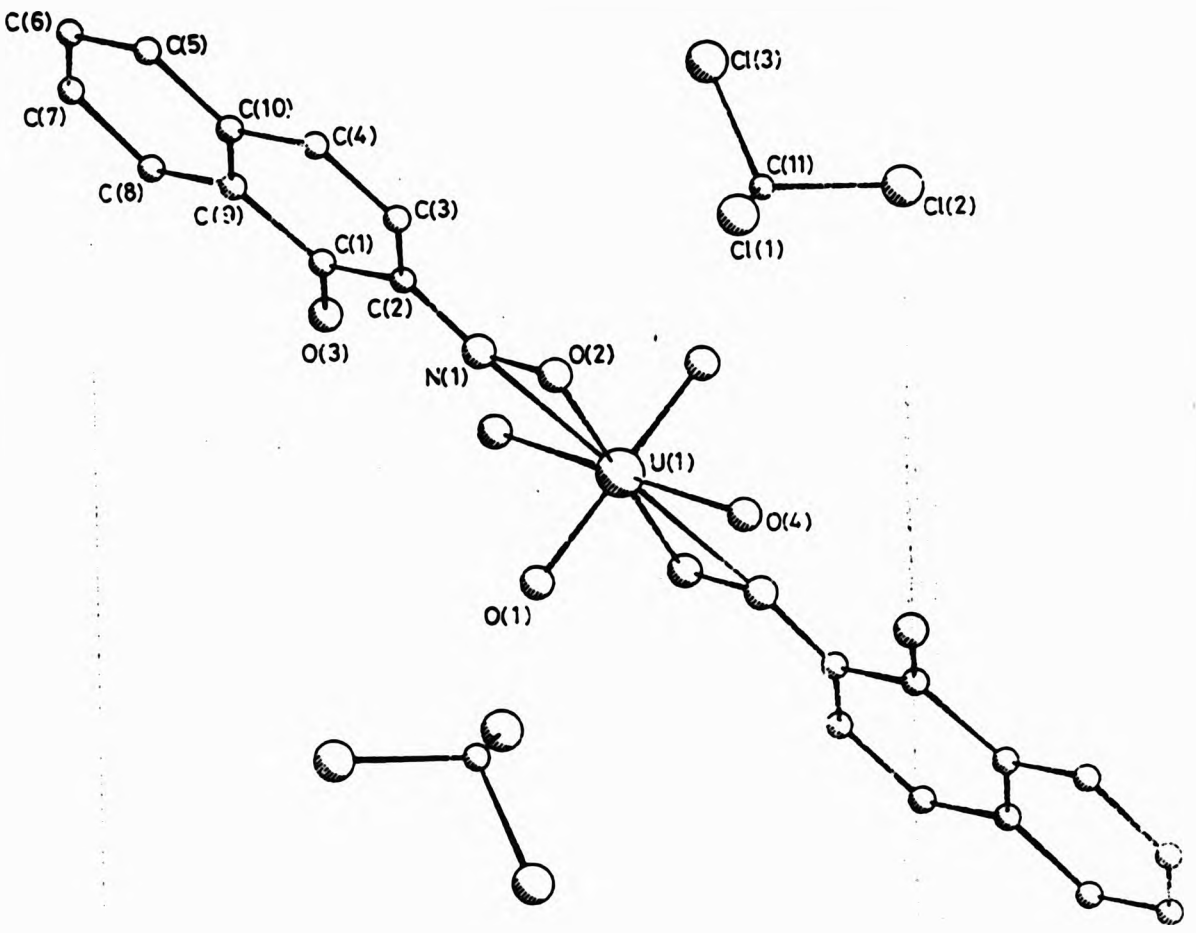
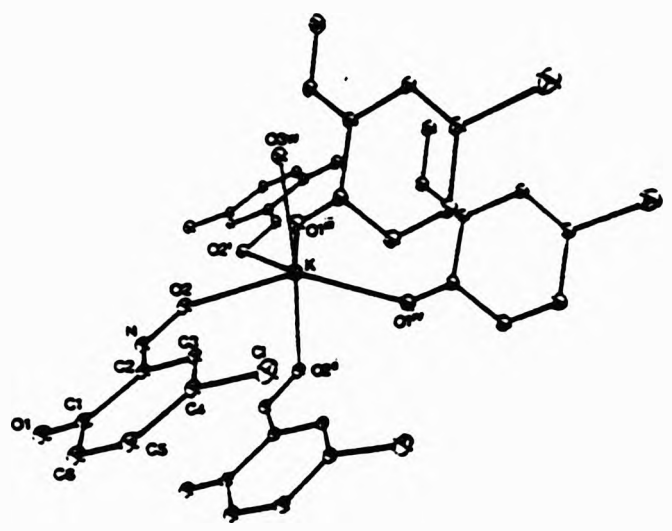


Figure 1.8



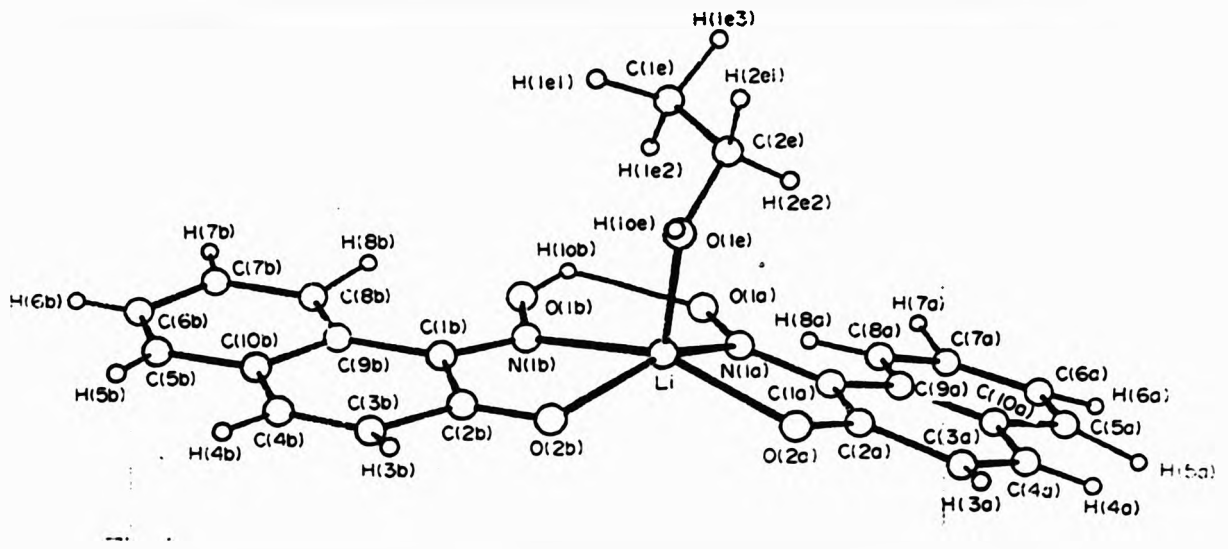
1,2-Quinone monooximato complexes in which the ligand is acting not as a chelating ligand but rather as a bridging ligand have also been reported. Thus in the complex 4-chloro-1,2-benzoquinone-2-oximato-potassium(I) hemihydrate, K(4-Clqo).1/2H_2O, the potassium ion was found to be coordinated to five 4-Clqo$^-$ ions three of which were coordinated via the oximic oxygen atom and the other two via the quinoid oxygen. In this complex, each 4-Clqo$^-$ ligand shares its two oxygen atoms with different potassium ions (Fig. 1.9).[91]

Figure 1.9



Another type of complex derived from 1,2-quinone monooximes is that in which the metal is coordinated to one anionic ligand and one neutral ligand.[92,93] The X-ray crystal structures of two such complexes Li(1-nqo)(1-nqoH) and K(5-Et-4-Meqo)(5-Et-4-MeqoH) have been determined in these laboratories.[94,95] They show the metals coordinated to both ligands via the oximic nitrogen and quinoid oxygen as is the case with most transition metal complexes. In these complexes the oximic proton of the neutral ligand is found to be hydrogen bonded to the oximic oxygen of the anionic ligand (eg. Fig. 1.10). Although other alkali and alkaline earth metal complexes have been reported,[96-99] little details on the bonding in these complexes are currently available and so, it is unclear whether bridging or chelate ring formation is the dominant mode of interaction between 1,2-quinone monooximes and these metals.

Figure 1.10



1.6. Synthetic Applications of 1,2-Quinone Monooximes and their Metal Complexes.

1,2-Quinone monooximes have found applications in metal analysis and extraction because of their chelating ability. Hence, they have been used to prepare complexes of a wide variety of metals. Their direct use in organic synthesis however, has been limited. In contrast, the use of the metal complexes in organic synthesis has been the focus of much of the recent attention.

The multifunctional character of the 1,2-quinone monooximic moiety in the both the free 1,2-quinone monooximes and their complexes presents numerous possibilities for the synthesis of interesting and novel compounds. In fact, several investigations of the synthetic applications of these compounds have been carried out. The action of triphenylphosphine on the copper(II), nickel(II), iron(II), iron(III) and zinc(II) complexes of some 1,2-quinone monooximes, performed in these laboratories, led to the isolation of several interesting products (Scheme 1.3).[80, 100, 101]

In the case of the nickel(II) and zinc(II) complexes, the corresponding bis(triphenylphosphoranylideneaminophenolato)nickel(II) or zinc(II) complexes (eg. Fig.1.11) were the products arising directly from the reactions. In contrast, the copper(II) and iron(III) complexes yielded dihydrophenoxazinones (eg. Fig. 1.12), and adducts of the type $M(qo)_nL_2$ where L=py or PPh_3 (M = Cu, n = 1, M = Fe, n = 2 (eg. Fig. 1.13).

The proposed mechanism by which these reactions proceed is believed to involve the removal of the oximic oxygen by triphenylphosphine with the resultant formation of highly reactive nitrene intermediates. It has also been shown that in the case of the copper(II) and iron(III) complexes, the reactions proceed with the reduction of the metal ion. Thus, the metal nitrene intermediates with copper(II) and iron(III) both of which have stable lower oxidation states, dissociate to give the free nitrene and copper(I) and iron(II) adducts. The free nitrene units subsequently couple with other species, possibly another nitrene, to afford products like the dihydrophenoxazinones. For nickel(II), iron(II) and zinc(II) neither of which have any stable lower oxidation states under the reaction conditions, the metal nitrene intermediate reacts with excess triphenyl-phosphine to give the iminophosphorane complexes.

Scheme 1.3.

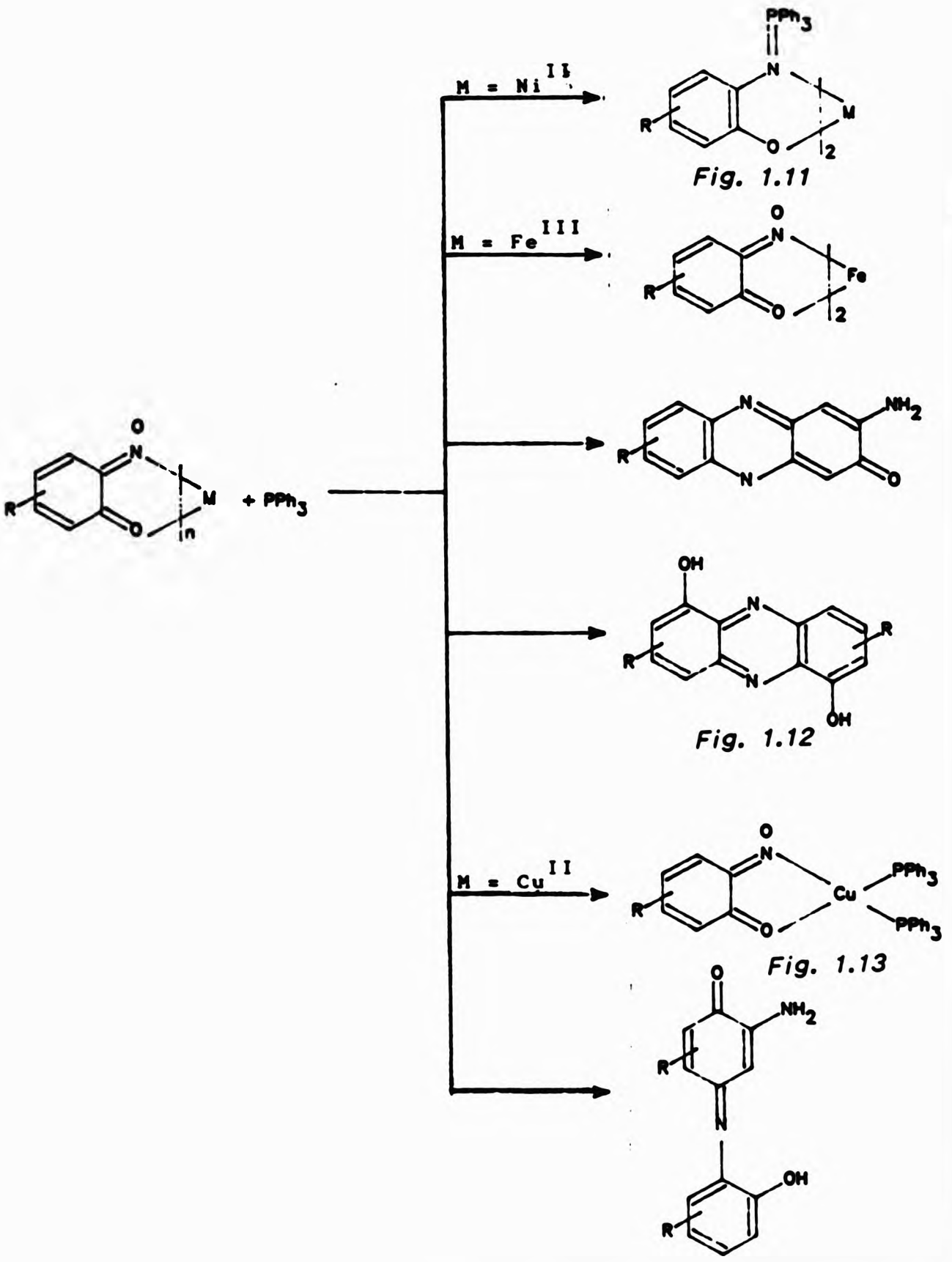


Fig. 1.11

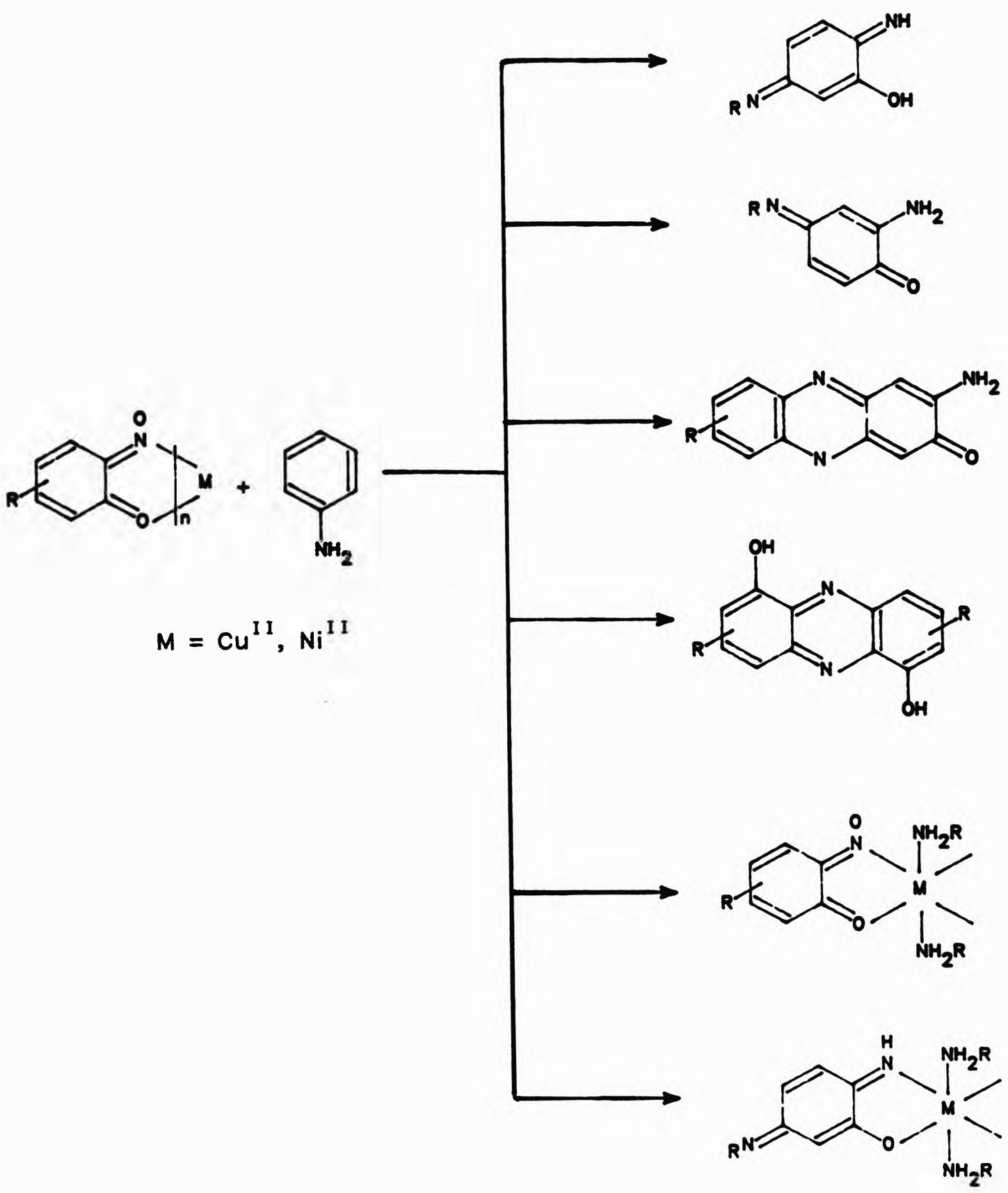
Fig. 1.12

Fig. 1.13

Reaction with nitrogen containing Lewis bases such as pyridine and aniline have also been extensively studied in these laboratories. The outcome of the reaction of pyridine and metal 1,2-quinone monooximates has been shown to be dependent on such factors as; (i) the nature of the metal involved, (ii) the nature of the solvent used, and (iii) the reaction conditions. For nickel(II) and iron(II) complexes, the only reported products are the 1:2 adducts. However, in the case of iron(III), the phenomenon of internal redox behaviour has been observed. Thus, the reaction of $Fe(nqo)_3$ with pyridine yields $Fe(nqo)_2.(py)_2$ and nqoH as products.

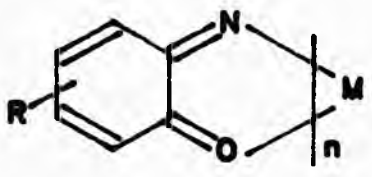
With aniline and other amines, for example ethylenediamine, the reactions are more complex and are said to involve ligand displacement, condensation, coupling, or indeed a combination of these reactions.[102,103] Several organic products, the formation of which has been rationalized in terms of the deoxygenation of the oximic NO group and the involvement of nitrene intermediates, have been isolated from these reactions (Scheme 1.4).

Scheme 1.4.



Reaction of metal 1,2-quinone monooximates with other Lewis bases such as NO and CO have also been studied. Although less is known about the mechanism of these reactions, deoxygenation of the complexes to give the corresponding 1,2-quinone iminato complex (eg. Fig. 1.14) and reduction of the metal ion have been suggested.[104,105] In fact the ready interaction of CO and NO with 1,2-quinone monooximic complexes has been usefully harnessed in the preparation of filters for tobacco smoke. Thus, the iron(III) complexes $Fe(1\text{-nqo})_3$ and $Fe(2\text{-nqo})_3$ adsorbed onto a particulate support and incorporated into cigarette filters were found to be highly effective at reducing the level of CO and NO to which the smoker is exposed. This application of metal 1,2-quinone monooximates has been patented.[106]

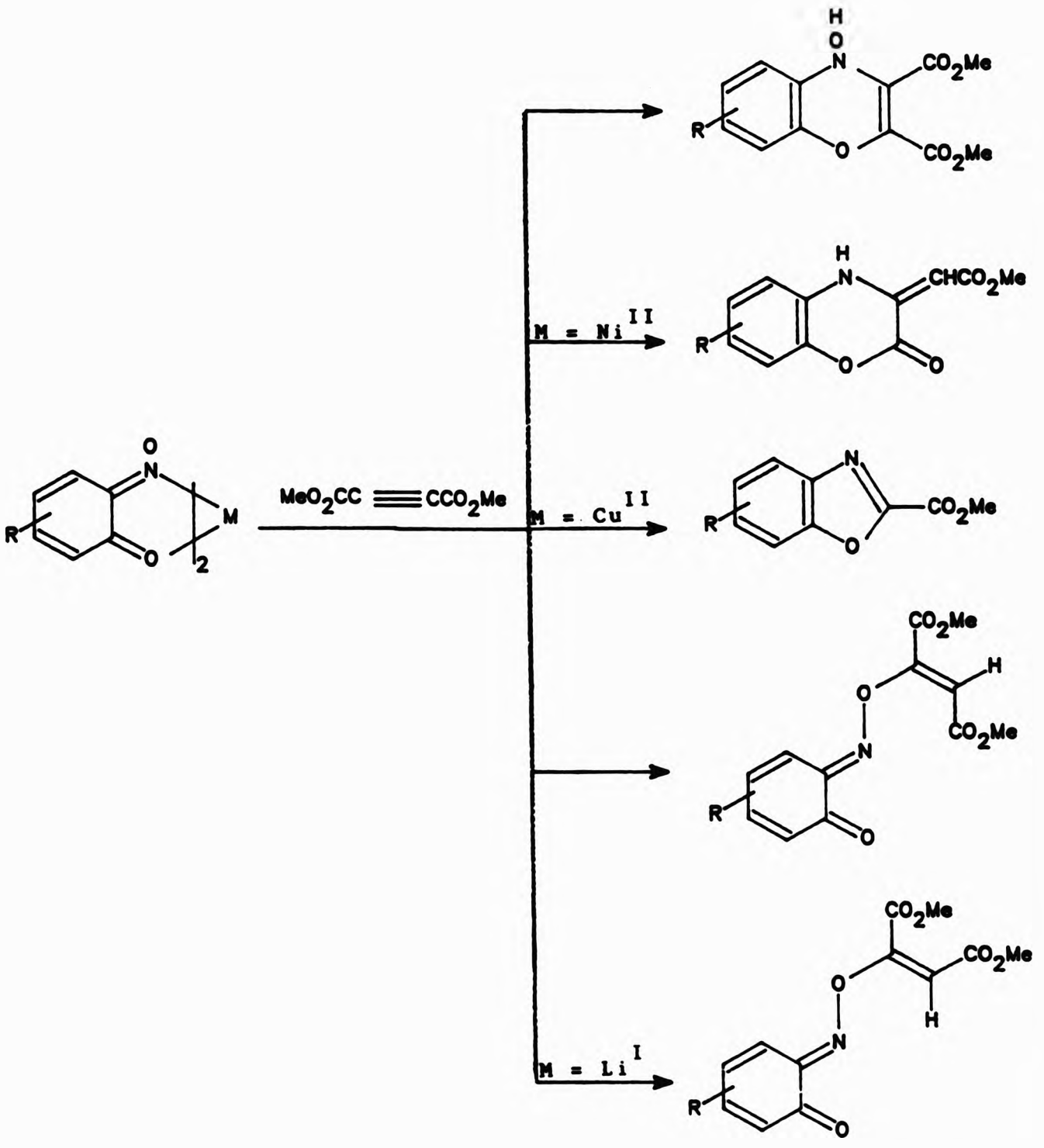
Figure 1.14.



The diene, dienophile, or heterodiene character of these compounds have been studied by a number of different workers. McKillop and Sayer in 1976, reported the isolation of the 1,4-oxazines from the reaction of bis(1,2-benzoquinone-2-oximato)copper(II) complexes with dimethyl acetylenedicarboxylate.[107] Since then, the isolation of several other organic products from similar reactions has been reported (Scheme 1.5).[108,109] The mode of reaction and the factors affecting the formation of products in this system is one of the subjects of the present study. A more detailed description of these reactions is

therefore presented in Chapter 5.

Scheme 1.5.

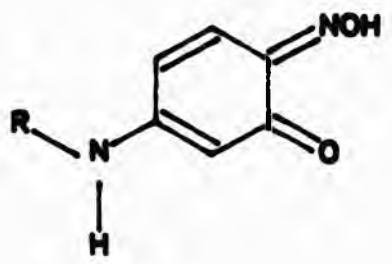


1.7. The Use of 1,2-Quinone Monooximes in Metal Separation.

Apart from their synthetic utility, current interest in 1,2-quinone monooximes extends to other areas. Of particular importance is their application in metal separation/recovery, a subject, which was the focus of a recent study carried out in these laboratories. In this study, the potential of 1-nqoH to separate rhodium and iridium was examined.[110] It was found that these compounds afforded excellent separation of the metals and had several advantages over the traditional methods.[111-112] Industrially, the preferred method of metal separation/recovery is a continuous system involving acidification of metal complexes and recycling of the ligands. The afore mentioned study showed that 1,2-quinone monooximes were potentially of great value in such a system for the separation of rhodium and iridium. However, neither $Rh(1\text{-nqo})_3$ nor $Ir(1\text{-nqo})_2$ afforded the ligand on acidification and the metals were only recoverable by the complete decomposition of the complexes.

Consequently, it was thought that ligands, the chelating power of which could be reversibly altered, might circumvent the problem of ligand recycling. Part of this current study was concerned with the development of quinone monooximic ligands which could achieve separation and allow ligand recycling. To this end, 1,2-quinone monooximic ligands bearing acylamino or alkylamino substituents directly attached to the quinone monooximic ring (eg. Fig. 1.15) were considered potentially useful.

Figure 1.15.

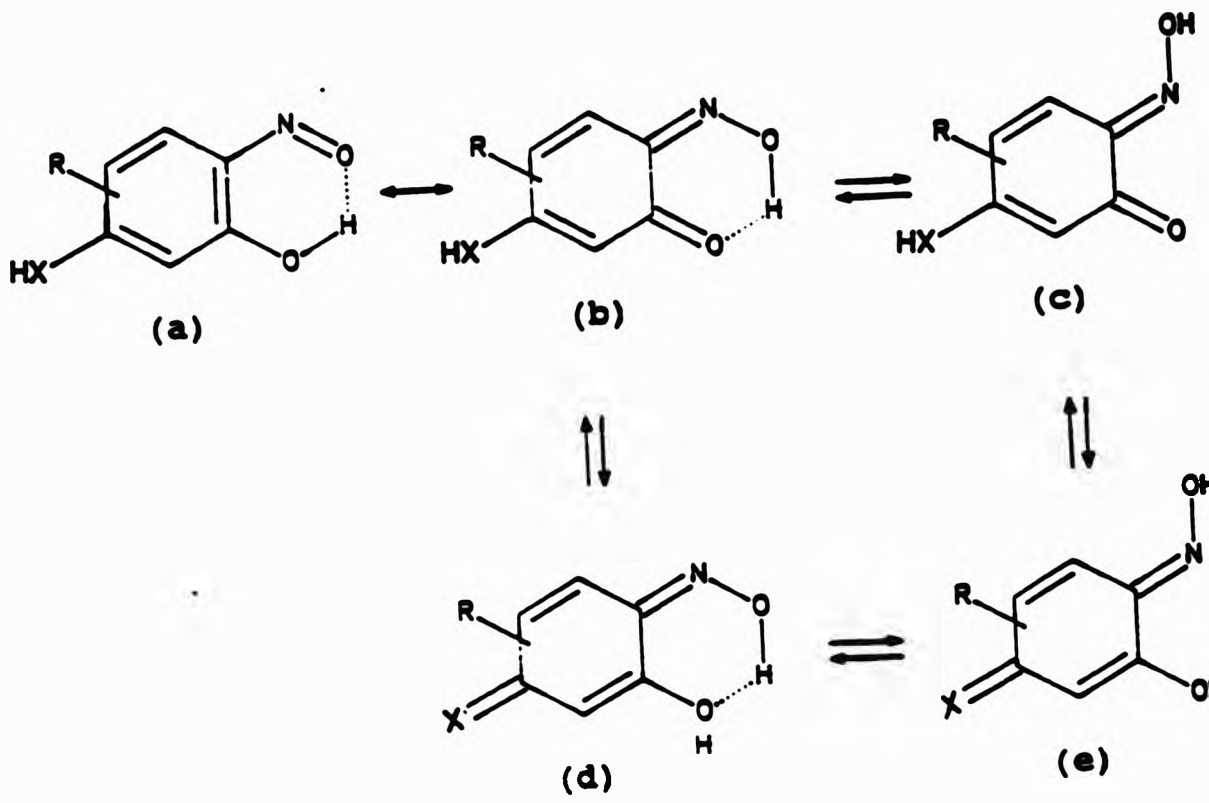


(R = $C_nH_{2n+1}CO$, C_nH_{2n+1})

The basic properties of the amino group and, to a lesser extent the amido group, and the possible lability of the hydrogen atom on both these groups in compounds of the type shown in Figure 1.15, allows for their existence in several prototropic forms (a - e; Scheme 1.6). An analogous equilibrium for hydroxy substituted 1,2-quinone monooximes has been proposed recently.[113] Prototropic equilibria involving the chelated ligand could also occur (Scheme 1.7). These equilibria, induced or otherwise, is thought capable of altering the form of the ligand, and by extension the nature and strength of the metal-ligand bond in the complexes. This could allow for metal/ligand separation by acidolysis.

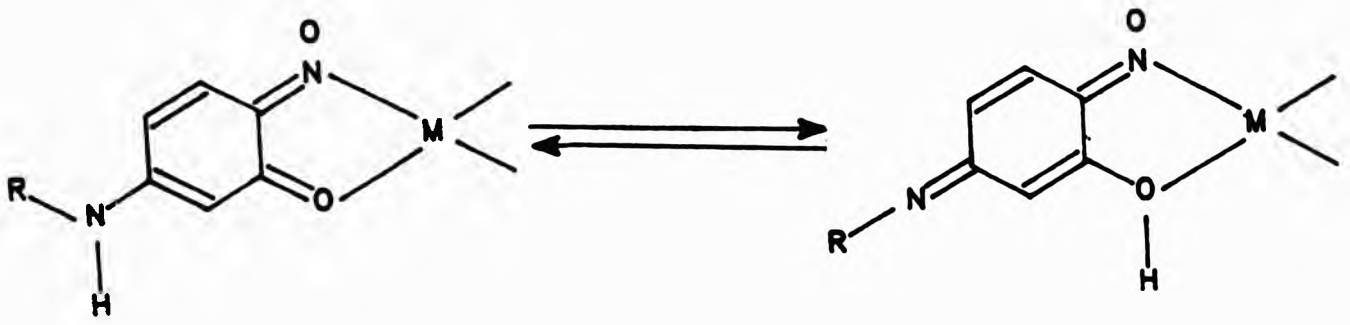
During this study, the stability of the amino substituted 1,2-benzoquinone monooximes to acid decomposition was demonstrated by the synthesis of these compounds in the presence of concentrated hydrochloric acid. In addition, the existence of an equilibrium between the 1,2-quinone monooximic and the 1,4-quinone oximino limiting forms of these compounds was demonstrated by solving the X-ray crystal structure of 5-hexylamino- and 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime. The effect of acid on the structure of the compounds was also demonstrated by the X-ray crystallographic study of the structure of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate.
These studies are described in Chapter 2.

Scheme 1.6



X = NR''

Scheme 1.7



1.8 *References*

1. H . H. Hodgson, F. H. Moore, *J. Chem. Soc.,* 1923, 123, 2499.
2. S. Candoro, D. Grdenic, N. Taylor, B. Thompson, M. Viswamitra, D. C. Hodgkins, *Nature,* 1969, 224, 589.
3. E. B. Chain, A. Tonolo, A. Carilli, *Nature,* 1955, 176, 645.
4. N. D. Pathirana, Ph.D Thesis, 1990, The Polytechnic of North London.
5. N. V. Bataafsche, Petroleum Maatschappij (Nicholas Dost and Gerrit Koustra) Dutch Pat. 87,796, 15 Apr. 1958.
6. S. S. Guha-Sicar, Sasanka Chandra Bhattacharjee, *J. Ind. Chem. Soc.,* 1941, 18, 155-160, 161-63.
7. R. S. Young, 'Cobalt: Its Chemistry Metallurgy And Uses', Rheinhold Publishing Corporation, New York, 1965, pp 57.
8. I. V. Pyathnitski, 'Analytical Chemistry Of Cobalt', Translated from Russian by N. Kanas, D. Slutzkin (Ed), Isreal Program For Scientific Translations Ltd, 1966, pp 39-41.
9. S. Peach, *Analyst,* 1956, 81, 371.
10. G. Cronheim, *Ind. and Eng. Chem.,* 1942, 14, 445.
11. H. El Khadin, S. E. Zayan, *Anal. Chem.,* 1962, 34, 1384.
12. W. M. Shutie, Ph.D Thesis, 1981, The Polytechnic of North London.
13. M. H. Johri, Ph.D Thesis, 1979, The Polytechnic of North London.
14. H. L. Benson jr, Shell Oil Co., US. Pat. 3,527,822 08 Sept. 1970.
15. I. G. Farbenind A-G, French Pat. 701,915, 12 Sept. 1930.
16. W. Federkiel, H. Pfitzer, H. Baumann, US. Pat. 2,726,920. 13 Dec. 1955.
17. W. G. Huey, W. G. Drautz, US. Pat. 2,454,453. 23 Nov. 1948.
18. X. Bilger, P. Muller, French. Pat. 1,122,461. 7 Sept. 1956.

19. K. Venkataraman (Ed.) 'The Chemistry Of Synthetic Dyes: Metal Complex Dyestuff', Vol. 5, Academic Press, New York, 1971.

20. B. L. Feringa, *J. Chem. Soc.*, 1986, 909.

21. M. A. Brook, J. R. Lindsay-Smith, R. Higgins, D. Lester, *J. Chem. Soc. Perkins Trans. 2* 1985, 1049.

22. E. G. Samsel, K. Srinivasa, J. K Kouli, *J. Am. Chem. Soc.*, 1985, 107, 7606.

23. D. Baluch, J. Charalambous, L. I. B. Haines, *J. Chem. Soc. Chem. Comm.*, 1988, 1178.

24. K. W. P. White, Ph.D Thesis, 1988, The Polytechnic of North London.

25. C. B. Castellani, A. Buttafava, O. Carugo, A. Poggi, *J. Chem. Soc. Dalton Trans.*, 1988, 1497.

26. G. Cronheim, *J. Org. Chem.*, 1947, 12, 7.

27. J. Charalambous, M. J. Frazer, F. B. Taylor, *J. Chem. Soc. A.*, 1969, 2787.

28. N. V. Sidgewick, 'The Organic Chemistry Of Nitrogen', 3rd Oxford University Press, Oxford, 1966.

29. I. L. Finar, 'Organic Chemistry', Vol. 1, 6th edn. Longmans, London, 1973.

30. A. I. Vogel, 'Textbook Of Practical Organic Chemistry', Longmans, London, 1977.

31. T. Teshigawara, Jap. Pat. 13,918, 17 Jul. 1964.

32. S. Oh, D. L. H. Williams, *J. Chem. Soc. Perkin Trans. 2,* 1991, 685.

33. H. Goldschmidt, *Ber.*, 1884, 17, 213.

34. O. Baudisch, *Science,* 1940, 92, 336.

35. O. Baudisch, *J. Am. Chem. Soc.*, 1941, 63, 622.

36. K. Maruyama, I. Tanimoto, *J. Org. Chem.*, 1967 32, 2516.

37. R. D. Gillard, R. P. Houghton, J. N. Tucker, *J. Chem. Soc. Dalton Trans.*, 1980, 2102.

38. O. Baudisch, *Naturwissenschaften*, 1939, 27, 768.

39. R. G. Cawthorne, J. Charalambous, W. M. Shuti, F. B. Taylor, A. Betts, *Inorg. Chim. Acta.*, 1979, 37, 245.

40. P. H. McFarlene, D. W. Russel, *J. Chem. Soc. Chem. Comm.*, 1967, 475.

41. Y. L. Chow, Z. Z. Wu, *J. Am. Chem. Soc.*, 1985, 107, 3338.

42. A. V. Bayer, E. Knorr, *Ber.*, 1902, 35, 3034. .

43. J. Charalambous, M. J. Frazer, *J. Chem. Soc. A.*, 1970, 2645.

44. J. Charalambous, M. J. Frazer, F. B. Taylor, *J. Chem. Soc A.*, 1971, 602.

45. J. Charalambous, M. J. Frazer, R. Simms, *Inorg. Chim. Acta.*, 1976, 18, 247.

46. P. Basu, A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1992, 809.

47. D. Baluch, PhD. Thesis, 1987, The Polytechnic of North London.

48. C. B. Castellani, O. Carugo, A. Coda, *Acta. Cryst.* 1988, C44, 265.

49. F. Heinrich, E. Eisenach, *J. Prakt. Chem.*, 1904, 70, 332.

50. H. S. French, D. J. Perkins, *J. Am. Chem. Soc.*, 1937, 59, 1182.

51. E. Baltazzi, *Compt. Rend.* 1951, 232, 986.

52. A. Fischer, R. M. Golding, W. C. Tennant, *J. Chem. Soc.*, 1965, 6032.

53. L. C. Anderson, M. B. Geiger, *J. Am. Chem. Soc.*, 1932, 54, 3064.

54. L. C. Anderson, R. L. Yanke, *J. Am. Chem. Soc.*, 1934, 56, 732.

55. E. Havinga, A. Kraaijeveld, J. Schors, *Rec. Trav. Chim.*, 1955. 74, 1243.

56. E. Fischmann, C. Romers, C. B. Shoemaker, *Rec. Trav. Chim.*, 1957, 76, 490.

57. A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge, A. R. Thompson, *J. Chem. Soc.*, 1955, 3727.

58. D. Hadzi, *J. Chem. Soc.*, 1956, 2725.

59. R. K. Norris, S. Sternell, *Aust. J. Chem.*, 1966, 19, 841.

60. T. Shono, Y. Hayashi, K. Shinra, *Bull. Chem. Soc.*, 1971, 44, 3179.

61. G. W. R. Bartindale, M. M. Crowder, K. A. Morley, *Acta. Cryst.*, 1959, 12, 111.

62. C. Romers, *Acta. Cryst.*, 1964, 17, 1287.

63. C. Romers, E. Fischmann, *Acta. Cryst.*, 1960, 13, 809.

64. C. Romers, E. Fischmann, A. J. H. Umans, *Acta. Cyrst.*, 1960, 13, 885.

65. J. W. L. Van Oijen, C. Romers, *Acta. Cryst.*, 1966, 20, 169.

66. J. C. A. Boyens, *J. Cryst. Mol. Str.*, 1976, 6, 217.

67. H. Saarinen, J. Korvenranta, E. Nasakkala, *Finn. Chem. Lett.*, 1977, 47.

68. H. Saarinen, E. Nasakkala, *Acta. Chem. Scand. Ser. A*, 1977, 31, 213.

69. H. Saarinen, J. Korvenranta, *Finn. Chem. Lett.*, 1977, 31, 213.

70. L. L. Merrit, C. Gaure, A. E. Lesson, *Acta. Cryst.*, 1956, 9, 253.

71. C. K. Prout, T. S. Cameron, R. M. A. Dunn, O. J. R. Hodder, D. Viterbo, *Acta. Cryst.*, 1971, 27, 1310.

72. S. Pal, T. Melton, R. Mukherjee, A. Charavarty, M. Tomas, L. Falvello, A. Chakravorty, *Inorg. Chem.*, 1985, 24, 1250.

73. H. H. Hodgson, W. Batty, *J. Chem. Soc.*, 1935, 1617.

74. E. El Khadem, W. M. Orabi, *Z. Anorg. and Allg. Chem.,* 1969, 365, 315.

75. O. Makitie, M. Helminen Soudmen, *Kimistilehti,* 1969, B42, 480.

76. K. K. Chatterjee, *Anal. Chem. Acta.,* 1959, 20, 423.

77. S. Gurrieri, G. Siracusa, *Inorg. Chem. Acta.,* 1971, 5, 650.

78. P. W. Carrick, J. Charalambous, M. J. Kensett, M. McPartlin, R. Simms, *Inorg. Nucl. Chem. Lett.,* 1974, 10, 749.

79. H. Saarinen, J. Korvenranta, *Acta. Chem. Scand. Ser.A.,* 1975, 29, 409.

80. R. G. Buckley, J. Charalambous, M. J. Kensett, M. McPartlin, D. Mukerjee, E. G. Brain, J. M. Jenkins, *J. Chem. Soc. Perkin Trans. 1,* 1983, 693.

81. J. Korvenranta, H. Saarinen, *Acta. Chem. Scand. Ser.A.,* 1975, 29, 861.

82. M. McPartlin, Inorg. *Nucl. Chem. Lett.,* 1973, 9, 1287.

83. C. B. Castellani, G. Gatti, R. Millini, *Inorg. Chem.,* 1984, 23, 4004.

84. A. Chakravorty, *Coord. Chem. Rev.,* 1974, 13, 1.

85. A. Janowski, J. Cukrowski, *J. Mol. Struct.* 1971, 9, 185.

86. P. Basu, S. Pal, A. Chakravorty, *J. Chem. Soc, Daltons Trans.,* 1990, 9.

87. P. Basu, S. Bhanja, S. Pal, A. Chakravorty, *Inorg. Chem.,* 1989, 28, 2680.

88. E. Leidl, O. Nagel, W. Beck, *Chem. Ber.,* 1983, 116, 1370.

89. G. Graziani, U. Casellato, P.A.Vigato, S. Tamburini, M. Vidali, *J. Chem. Soc. Dalton Trans.,* 1983, 697.

90. J. J. Katz, E. Rabinowitch, 'The Chemistry of Uranium The Element and its Binary Compounds', Dover Publications, New York, 1951.

91. C. B. Castellani, O. Carugo, A. Coda, *Acta. Cryst.*, 1988, C44, 265.

92. R. Simms, Ph.D Thesis, 1974, University of London.

93. P. Gaganatsou, Ph.D, Thesis, 1988, The Polytechnic of North London.

94. A. K. Banerjee, A. J. Cayton, R. S. Nyholm, R. S. Truter, *J. Chem. Soc. A.*, 1969, 2536.

95. O. Carugo, J. Chakrabarty, J. Charalambous, T. A. Thomas, Unpublished data.

96. J. Charalambous, P. G. T. Fogg, P. Gaganatsou, *Polyhedron,* 1993, 12, 879.

97. A. J. Cayton, R. S. Nyholm, A. K. Banerjee, V. E. Renton, C. N. Lestas, M. R. Truter, *J. Chem. Soc.A.*, 1970, 1894.

98. A. K. Banerjee, A. J. Cayton, R. S. Nyholm, M. R. Truter, *J. Chem. Soc.A.*, 1970, 292.

99. A. K. Banerjee, D. Prakash, S. K. Roy, *J. Chem. Soc.*, 1976, 53, 773.

100. J. Charalambous, M. J. Kensett, J. M. Jenkins, *J. Chem. Res.(S),* 1982, 306.

101. J. Charalambous, M. J. Kensett, J. M. Jenkins, *J. Chem. Soc. Chem. Comm.*, 1977, 400.

102. R. G. Buckley, J. Charalambous, E. G. Brain, *J. Chem. Soc. Perkin Trans.1,* 1982, 1075.

103. J. S. Morgan, Ph.D, Thesis, 1986, The Polytechnic of North London.

104. J. Charalambous, L. I. B. Haines, J. S. Morgan, J. Bailey, J. M. J. Campbell, *Polyhedron,* 1987, 5, 1027.

105. Yu E. Belyaev, M. S. Tovbis, T. P. Kononchuk, A. V. El'tsov, *Khim. Geterotsikl. Soedin.*, 1976, 1338. Chem. Abs. 86:72501n

106. J. Charalambous, L. I. B. Haines, J. S. Morgan, U.K. Pat. G.B. 2150,806B, 1983.

107. A. McKillop, T. S. B. Sayer, *J. Org. Chem.*, 1976, 41, 1079.

108. C. B. Castellani, R. Millini, *J. Chem. Soc., Dalton Trans.*,1984, 1461.

109. H. Barjesteh, Ph.D Thesis, 1991, University of North London.

110. Y. Musa, Ph.D Thesis, 1991, The Polytechnic of North London.

111. F. S. Clements, *Ind. Chemist.* 1962, 345.

112. D. C. Morris, M. A. Khan, *Talanta,* 1968, 15, 1301.

113. J. Charalambous, P. C. Christidis, A. Dodd, M. McPartlin, N. D. Pathirana, N. Talee, *Acta. Cryst.*, 1991, C47, 2640.

CHAPTER TWO

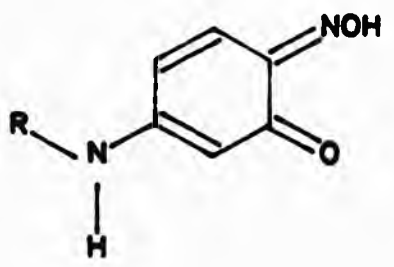
CHAPTER 2

The Synthesis and Characterisation of Acylamino and Alkylamino Substituted 1,2-Benzoquinone Monooximes.

2.1. Introduction

In this chapter, the synthesis and detailed structural characterisation of acyl and alkylamino substituted benzoquinone monooximes of type (1) is described.

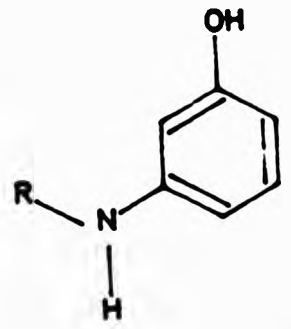
(1)



($R = C_nH_{2n+1}CO$, C_nH_{2n+1}; $n = 1 - 7$)

Several routes to these potentially useful chelating agents, all of which involved the nitrosation of compounds of type (2) were investigated.

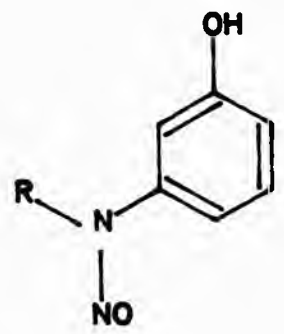
(2)



($R = C_nH_{2n+1}CO$, C_nH_{2n+1}; $n = 1 - 7$)

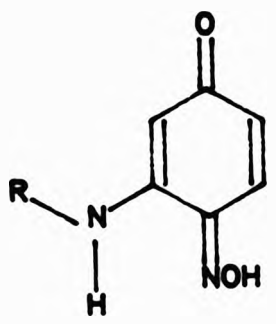
Compounds of type (2) contain strongly activating groups and as a consequence, are ammenable to ring nitrosation. However, the presence of the acylamino and alkylamino groups make the compounds susceptible to N-nitrosation as well. The latter is highly undesirable because of the potential carcinogenicity of N-nitroso derivatives (3).

(3)

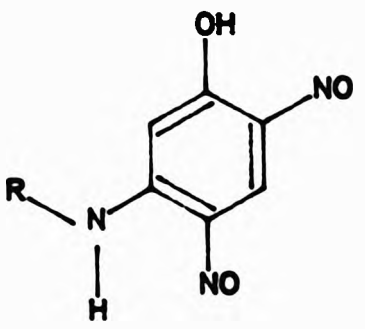


One further complication encountered in the nitrosation of compounds of type (2) is the competition between 1,2- and 1,4- ring nitrosation, as well as the possibility of dinitrosation. These reactions can lead to the formation of 1,4-benzoquinone monooximes (4) or other products (eg. 5).

(4)



(5)



The principal aim of the work described in this chapter has been to examine the behaviour of compounds of type (2) towards various

nitrosation systems. In particular, this study has been aimed at developing routes to acyl and alkylamino substituted 1,2-benzoquinone-2-oximes which suppress the formation of the other likely products particularly the N-nitroso compounds.

Before considering the findings of the current study, it is thought prudent to present a critical assessment of relevant previous results since the latter have influenced the achievement of the aims and, interpretation of the results of this work.

Traditionally, the main techniques used for the nitrosation of aromatic compounds involve the reaction of the aromatic substrate with (i) an alkali metal nitrite and an aqueous acid, usually acetic acid (eg. Equation 2.1),[1]

(ii) dinitrogen tetraoxide in the presence of a mineral acid (Equation 2.2),[2] or

(iii) an alkyl nitrite in the presence of a strong base (Equation 2.3).[3]

Equation 2.1

$$NaNO_2 + Acid \longrightarrow H_2ONO^+ \rightleftharpoons H_2O + NO^+$$

Equation 2.2

$$N_2O_4 + Acid \longrightarrow HNO_3 + NO^+$$

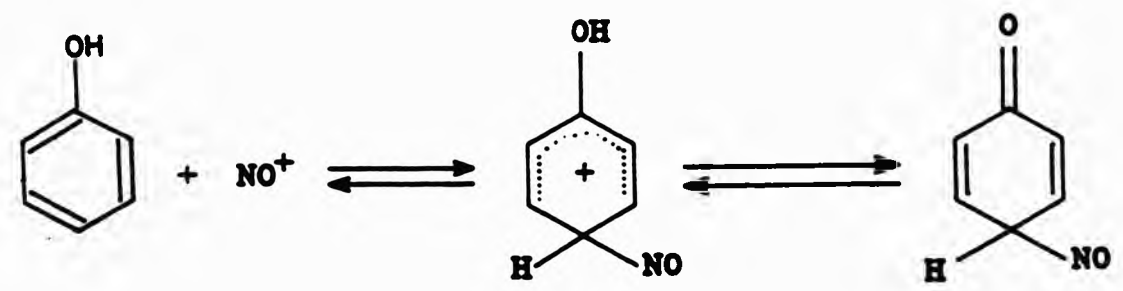
Equation 2.3

$$RONO + Base \longrightarrow RO^- + NO^+$$

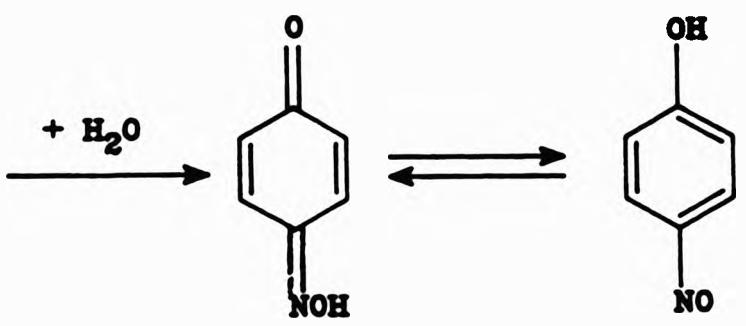
It has been well established that only activated aromatics, that is those bearing such groups as NR_2 or OR (R = H, alkyl or aryl), are susceptible to ring nitrosation.[4] It is generally believed that in all cases, the active species is a weak electrophile such as the nitrosonium ion NO^+.[5]

That NR_2 or OR groups activate aromatic rings towards nitrosation may be bourne out by consideration of the mechanism for these reactions (Scheme 2.1). As with other aromatic electrophilic substitutions, nitrosation proceeds via the formation of a Wheland intermediate (6).[6] This positively charged species is stabilised by electron donating substituents in the aromatic ring, hence the greater susceptibility of amino and hydroxy substituted aromatic compounds towards this kind of reaction.[7]

Scheme 2.1.



6



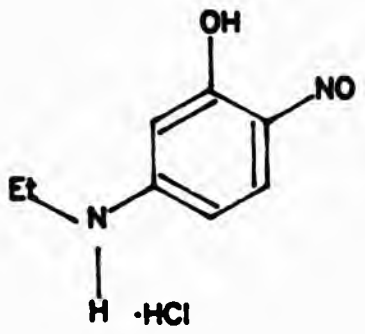
A general consideration with regards the nitrosation of such compounds is the competition between ortho and para substitution. Because the OH group is ortho/para directing, nitrosation of phenolic compounds should in theory yield mixtures of the 1,2- and 1,4-substituted products. In practise however, most phenols give only the 4-isomers with the 2-isomers being isolated only in some cases.[8-11]

Previous results[12,13] have suggested that the isolation of 1,2-quinone monooximes by the nitrosation of a phenol may be enhanced by the presence of metal ions which imparts stability to the 2-isomer by chelate formation. However, even in the presence of metal ions, the 1,4-quinone monooxime may also occur. For example, the nitrosation of 3-acetylaminophenol in the presence of copper(II) and nickel(II) chloride gave the metal complex of the 1,2-isomer as well as the uncomplexed 1,4-isomer.[14]

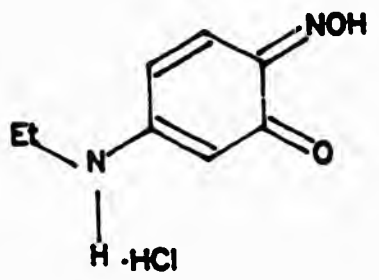
Compared to phenols, the behaviour of aromatic amino compounds towards nitrosation is even more complex. Such compounds, in addition to 1,2- and 1,4- ring substitution, can also undergo N-nitrosation reactions.[7] These reactions are usually enhanced when R is an electron donating group (eg. alkyl), which by its inductive effect, increases the electron density around nitrogen making it more basic. Thus, primary aromatic amines give diazonium compounds via N-nitroso intermediates,[15,16] while secondary aromatic amines readily form N-nitrosamines on nitrosation.[17,18] In both cases, ring nitrosated compounds can be afforded by the acid promoted intramolecular migration of the NO group from the amino nitrogen to carbon in an unsubstituted para position.[19,20] Thus, the reported synthesis of 5-ethylamino-2-nitrosophenol hydrochloride (7),[21] a compound better represented as 5-ethylamino-1,2-benzoquinone-2-oxime hydrochloride (8), was a two step

process involving the isolation and subsequent rearrangement of the corresponding N-nitrosamine by the Fischer-Hepp method (Reaction 2.1).[21,22] This method, discovered in 1886, is a commonly used method of preparation of aromatic C-nitroso compounds. The reaction is usually brought about by hydrogen chloride in diethyl ether or ethanol at room temperature.[23]

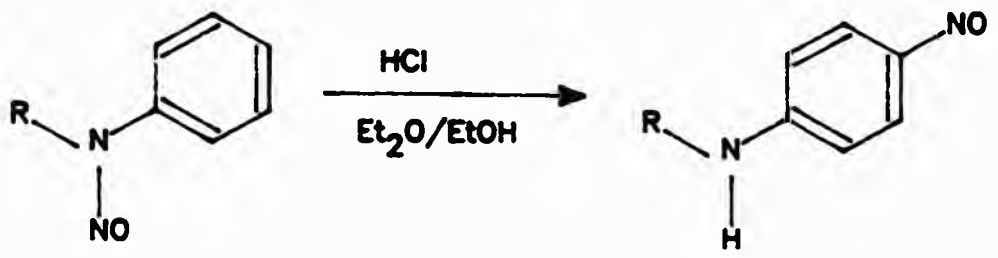
(7)



(8)



Reaction 2.1



It has been found that the conversion of N-nitroso to C-nitroso compounds by the Fischer-Hepp method occurs more efficiently with hydrochloric acid than with any other acid.[24] On this basis, and in view of the protection of the amino group to electrophilic substitution reactions afforded by its protonation at low pH, it was thought during this study that C-nitrosation could be promoted and N-nitrosation

suppressed if the nitrosation of compounds of type (2) (R = C_nH_{2n+1}) was carried out in concentrated hydrochloric acid. This proved to be the case and thus a route to amino substituted benzoquinone monooximes from aminophenols which precluded the formation of N-nitrosamines was developed.

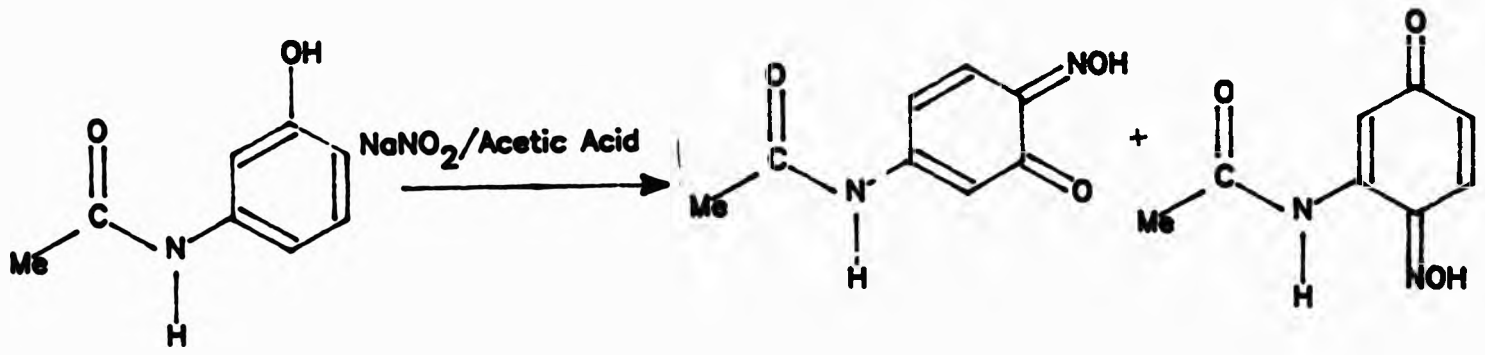
Like for aromatic amines, N-nitrosation of aromatic amides, is also possible. However, since R is now an electron withdrawing substituent, N-nitrosation is hindered because of the lower electron density around, and lower basicity of the nitrogen nucleus. This however does not preclude the formation of N-nitrosamides several of which have been reported.[25,26] They, like their amino analogues are highly carcinogenic.[27]

2.2. The Synthesis of Amino, Acylamino and Alkylamino Substituted Benzoquinone monooximes.

2.2.1. *The action of $NaNO_2$/acid on acyl and alkylaminophenols.*

Recently, 5-acetylamino-1,2-benzoquinone-2-oxime and its isomer, 3-acetylamino-1,4-benzoquinone-4-oxime were prepared in these laboratories by the reaction of 3-acetylaminophenol with sodium nitrite/acetic acid in water (Reaction 2.2).[14] Interestingly, the 1,2-isomer was the major product.

Reaction 2.2



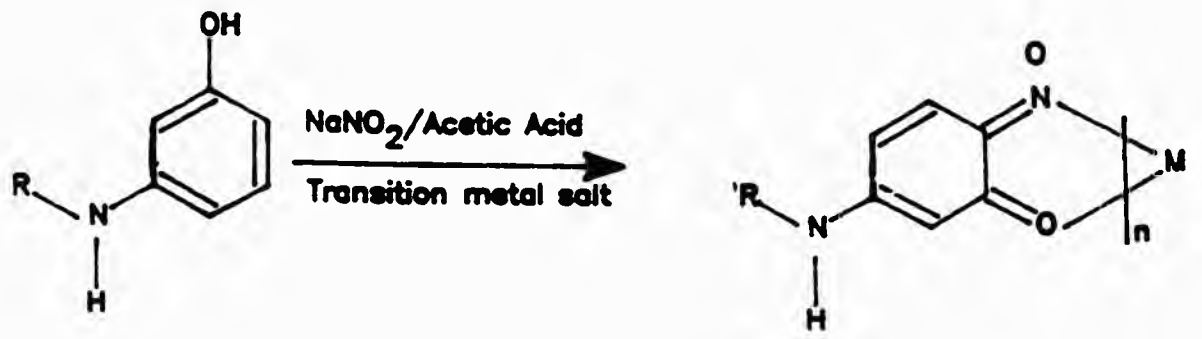
During this study, the procedure was repeated for a series of 3-acylaminophenols ((2); R= MeCO, EtCO, PrCO, BuCO, HxCO). In agreement with the previous report,[14] 3-acetylaminophenol reacted smoothly to afford the orange 5-acetylamino-1,2-benzoquinone-2-oxime in high yield. The yellow 3-acetylamino-1,4-benzoquinone-4-oxime was also obtained though as the minor product.

By contrast, the larger homologues afforded the yellow, powdery 3-acylamino-1,4-benzoquinone-4-oximes in reasonable yields, as well as some unreacted starting material, even when the reaction was carried out in neat glacial acetic acid. The 1,2-isomers were not isolated although qualitative tests with aqueous ferrous ammonium sulphate indicated some formation of these compounds.*

*The close juxtaposition of the oximic and quinoid donor sites in the 1,2-quinone monooximes enables these compounds to form highly coloured chelate complexes with most metal ions. In the case of iron(II), 1,2-quinone monooximes give a characteristic green complex which, in this study provided a convenient qualitative test for the detection of the 1,2-quinone monooximes.

Despite the failure of the phenol/sodium nitrite/acetic acid systems to afford the 5-acylamino-1,2-benzoquinone-2-oximes, the compounds were obtained in high yields as their metal complexes when the 3-acylaminophenols were reacted with sodium nitrite/acetic acid in water in the presence of copper(II), nickel(II) or palladium(II) chloride (eg. Reaction 2.3). The reaction also afforded the corresponding 1,4-isomers though here they were the minor product. The copper(II) and nickel(II) complexes readily afforded the free ligands in good yields on acidification or by using ion exchange chromatography.

Reaction 2.3



(R = C_2H_5CO - $C_6H_{13}CO$)

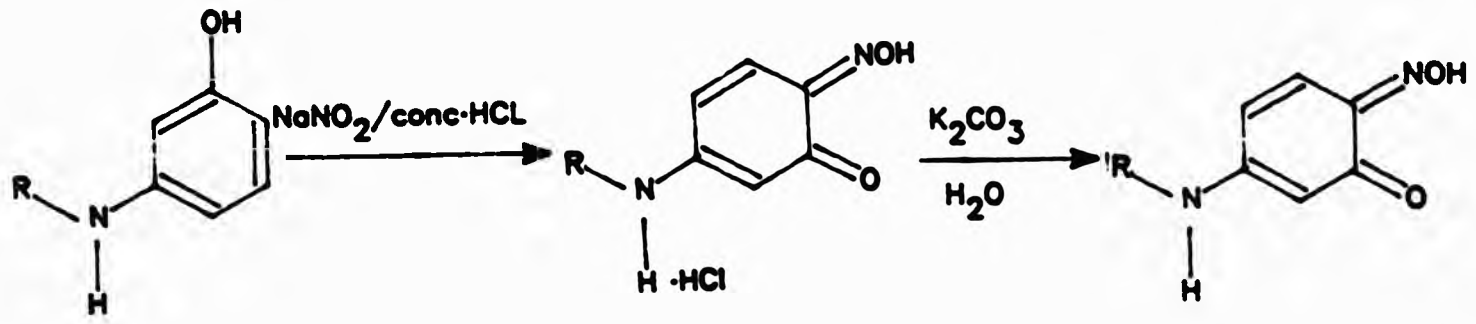
In the case of 3-aminophenol and the 3-alkylaminophenols (2; R = Et, Hx, Hp), the small scale reaction with sodium nitrite/acetic acid and water afforded dark brown solids. Qualitative tests on these solids with aqueous ferrous ammonium sulphate indicated the absence of any 1,2-quinone monooximic species. As a consequence, the products, thought to be N-nitroso compounds were not investigated further.

Like their acylamino analogues, the 5-alkylamino-1,2-benzoquinone-2-oximes were recovered, though in very poor yields, as the metal complexes when the reaction was repeated in the presence of copper(II) or nickel(II) chloride. The 1,4-isomers were not recovered.

In marked contrast to their behaviour with the sodium nitrite/acetic acid systems, the 3-alkylaminophenols afforded the 5-alkylamino-1,2-benzoquinone-2-oximes in high yields as their yellow hydrochloride salts when the phenols were reacted with sodium nitrite in concentrated hydrochloric acid. The free bases were obtained as bright orange solids by neutralization of the hydrochlorides with sodium or potassium carbonate (Scheme 2.2). Importantly, this method failed to give any 1,4-isomers and, no evidence of the formation of N-nitroso derivatives was found.

Because of the possibility of the acid promoted hydrolysis of the amido group, the above method was not attempted with the 3-acylamino-phenols.

Scheme 2.2



The success of the sodium nitrite/concentrated hydrochloric acid system at affording the 5-alkylamino-1,2-benzoquinone-2-oximes, compared to that of the sodium nitrite/acetic acid system can be attributed to the greater protection of the amino group effected by HCl. In order to achieve ring and not N-nitrosation, it is necessary to protect the amino group from attack by the nitrosonium ion. Protonation has previously been shown to be an effective means of protecting amino groups.[28] Thus, the greater acidity of hydrochloric acid over acetic acid makes the

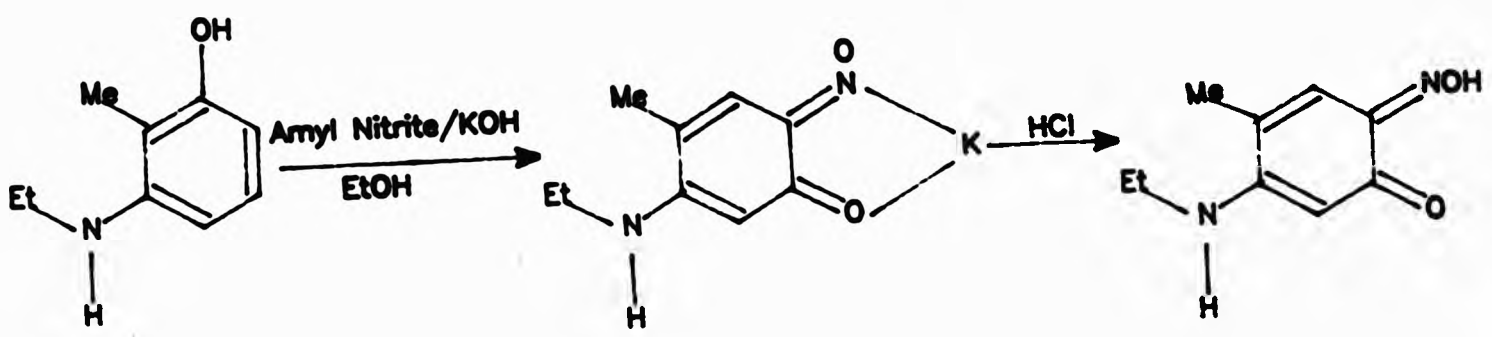
former considerably more efficient at achieving this.

2.2.2. *The action of amyl nitrite/base on acylamino and alkylaminophenols.*

The 3-acylaminophenols (2; R = C_2H_5CO – $C_6H_{13}CO$) failed to afford any quinone monooximic compounds when reacted with amyl nitrite and sodium or potassium ethoxide. In all cases, the starting phenols were recovered unaffected.

By contrast, 3-ethylamino-4-methylphenol reacted with amyl nitrite to afford the orange potassium complex of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime in good yield. The free ligand, also an orange solid was obtained by the acidification of the complex (Scheme 2.3).

Scheme 2.3



The analogous reaction with 3-hexyl and 3-heptylaminophenol also yielded orange solids which failed to chelate any metal ions. These compounds were identified as 3-hexylamino and 3-heptylamino-1,4-benzoquinone-4-oxime.

2.3. Characterisation of the Acylamino, and Alkylamino Substituted Benzoquinone monooximes.

The compounds prepared during this study were all highly coloured solids which melted at temperatures between 70 °C and 200 °C except in the case of the hydrochlorides which decomposed between 150 °C and 180 °C. All the compounds showed appreciable solubility in common organic solvents, but with the exception of the hydrochlorides, did not dissolve in water.

Characterisation of the compounds was afforded by full elemental and spectroscopic analysis. The yellow, powdery solids obtained by the nitrosation of the 3-acylaminophenols were identified as 3-acylamino-1,4-benzoquinone-4-oximes on account of their failure to chelate any metal ion. The quinone monooximic nature of these solids and of their orange 2-isomers which readily form metal chelates, was indicated by the presence in their IR spectra of prominent bands in the carbonyl region, assignable to the amido νCO and the quinoid νCO groups.

Further support for this formulation was afforded by NMR and mass spectral analysis. Thus, the ^{13}C NMR spectra of both sets of compounds contained signals at approximately 160 ppm and 200 ppm characteristic of carbonyl carbons.[29] The EI mass spectra all contained a fragment ion attributable to the loss of OH$^{\cdot}$ from the molecular ion. Both these findings point towards quinone monooximic rather than nitrosophenolic character.

In the case of the products derived from the nitrosation of the 3-alkylaminophenols in hydrochloric acid, they were identified as hydrochlorides on the basis of their high melting points and solubility in water. Importantly, the presence of only three multiplets each

integrating for one proton in the aromatic region of the ^{1}H NMR spectra of these compounds and the free bases derived from them confirmed all eight compounds as being ring nitrosated.

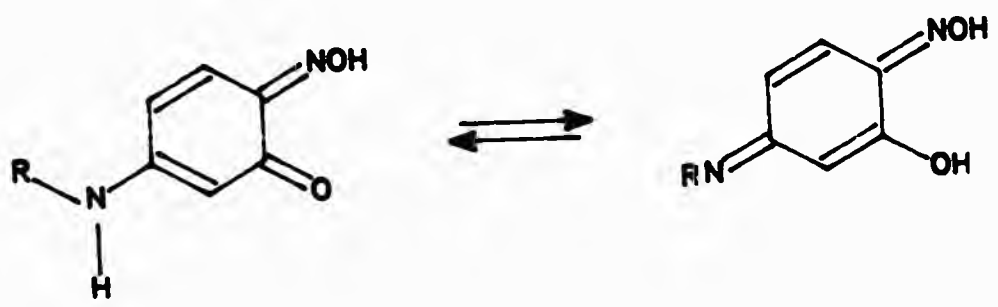
The quinone monooximic nature of both the hydrochlorides and of the free bases derived from them was indicated by the presence in their IR spectra of bands at approximately 1630 cm^{-1} and of a signal at approximately 175 ppm in their ^{13}C NMR spectra assignable to a quinoid carbonyl group. The presence in the mass spectra of these compounds of fragment ions due to the loss of $OH^{\cdot}$, NOH, and CO from the molecular ion was also supportive of the quinone monooximic formulation. The quinone monooximic formulation of the 5-hexylamino- and 5-ethylamino-4-methyl substituted compounds was confirmed by X-ray crystal analysis (see sections 2.5 - 2.7).

2.4. Spectroscopic Studies of Acylamino-, and Alkylamino- Substituted Benzoquinone Monooximes.

As discussed in Chapter 1 of this thesis, quinone monooximes can exist in at least two tautomeric forms.[30,31] In addition, these compounds have been shown to exhibit stereoisomerism based on the orientation of the oximic OH group relative to the quinoid carbonyl group. Thus they can exist as either *syn* or *anti* isomers.[32-36]

For the compounds considered in this study, particularly the alkylamino substituted compounds, there is the additional possibility of a 2,5-oxime imino rather than a 1,2-quinone oxime structure (Scheme 2.4) analogous to that observed in the product obtained by the nitrosation of 3-hydroxy-2-methylphenol (Scheme 2.5).[37]

Scheme 2.4



Scheme 2.5

Traditionally, spectroscopic analyses have been widely used in the study of quinone monooximes.[38-42] Such studies have provided useful information on the existence and importance of the quinone monooximic/ nitrosophenolic tautomerism and the factors which favour either of the two forms. In addition, these studies have been useful in distinguishing between the different isomeric forms of 1,2-quinone monoximes.

The detailed spectroscopic analysis of the compounds prepared during this study was carried out with a view to obtaining structural information as well as determining the effects of the new substituents on the general characteristics of the compounds. Thus the IR, NMR, mass and solution electronic spectra of the compounds were recorded and analysed.

IR spectra.

X-ray crystallographic analysis of the 1,4-substituted product obtained from the nitrosation of 3-acetylaminophenol showed the compound to exist as 3-acetylamino-1,4-benzoquinone-4-oxime.[14] The IR spectrum of this compound consequently contained a band assignable to the quinoid carbonyl group at 1650 cm^{-1}.

Similarly, the IR spectra of the 1,4-substituted compounds prepared during this study (eg. Fig. 2.1) all contained bands at approximately 1650 cm^{-1} and therefore assignable to a quinoid νCO (Table 2.1). This similarity with the spectrum of the crystallographically established structure of 3-acetylamino-1,4-benzoquinone-4-oxime, leads to the conclusion that the 1,4-substituted compounds reported here were also quinone monooximic.

Figure 2.1 *IR spectrum of 3-butyrylamino-1,4-benzoquinone-4-oxime*

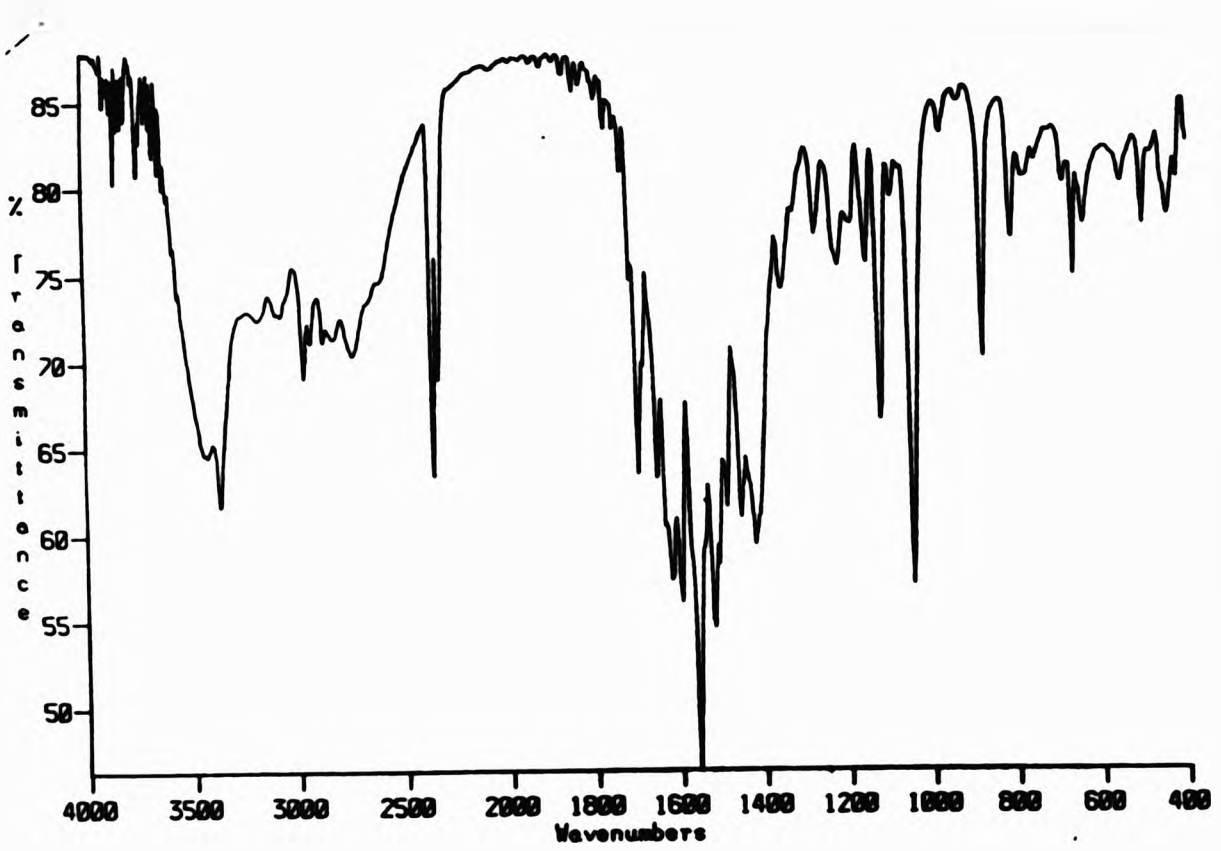


Table 2.1 *Selected IR absorption bands and their assignment for the series of 3-acylamino- and 3-alkylamino- substituted 1,4-benzoquinone-4-oximes.*

R	νOH /cm^{-1}	νNH /cm^{-1}	νCO$_{amido}$ /cm^{-1}	νCO$_{quinoid}$ /cm^{-1}
3-C_2H_5CONH	3448	3369	1695	1650
3-C_3H_7CONH	3444	3367	1697	1653
3-C_4H_9CONH	3442	3364	1692	1631
3-C_6H_{13}CONH	3440	3360	1688	1630
3-C_6H_{13}NH	3429	3231	-	1627
3-C_7H_{15}NH	3425	3212	-	1632

The 1,2-substituted compounds derived from the nitrosation of 3-hexylaminophenol and 3-ethylamino-4-methylphenol were both shown by X-ray crystallography (see later) to be quinone monooximic. Accordingly, the IR spectra of both compounds (eg. Fig. 2.2) as well as their acylamino analogues contained strong absorption bands in the region between 1635 cm^{-1} and 1610 cm^{-1} assignable to the quinoid carbonyl group.

Interestingly, and in contrast to their 1,4-isomers, the quinoid νCO of both acylamino and alkylamino 1,2-benzoquinone monooximes appeared as two bands (Table 2.2). This suggests that the samples were possibly mixtures of the *syn* and *anti* isomers.

It has been shown previously that the νCO of the *anti* isomer appears at higher frequency than for the *syn* isomer because of the

presence of intramolecular hydrogen bonding involving the quinoid carbonyl group[43] in the latter. However, no other spectroscopic evidence for the presence of a mixture of isomers was found for the 1,2-quinone monooximes reported here.

The quinoid νCO stretching frequency of the 1,4-oximes were found to be higher than for the corresponding 1,2-isomer suggesting greater double bond character in the 1,4-quinone monooximes. This finding is not unusual and has previously been attributed to (i) a decrease in the energy of the aromatic conjugation in the phenolic form as a result of the presence of the nitroso group and, (ii) the increase in the energy of enolisation of the carbonyl group which is further stabilised by quinoid conjugation in the 1,4-isomers. In addition, for the 1,2-substituted compounds, νCO is lowered by the presence of an intramolecular hydrogen bond which stabilises the nitroso group and leads to a preference in some of these compounds for the nitrosophenolic form.[44]

Figure 2.2 *IR spectrum of 5-hexylamino-1,2-benzoquinone-2-oxime*

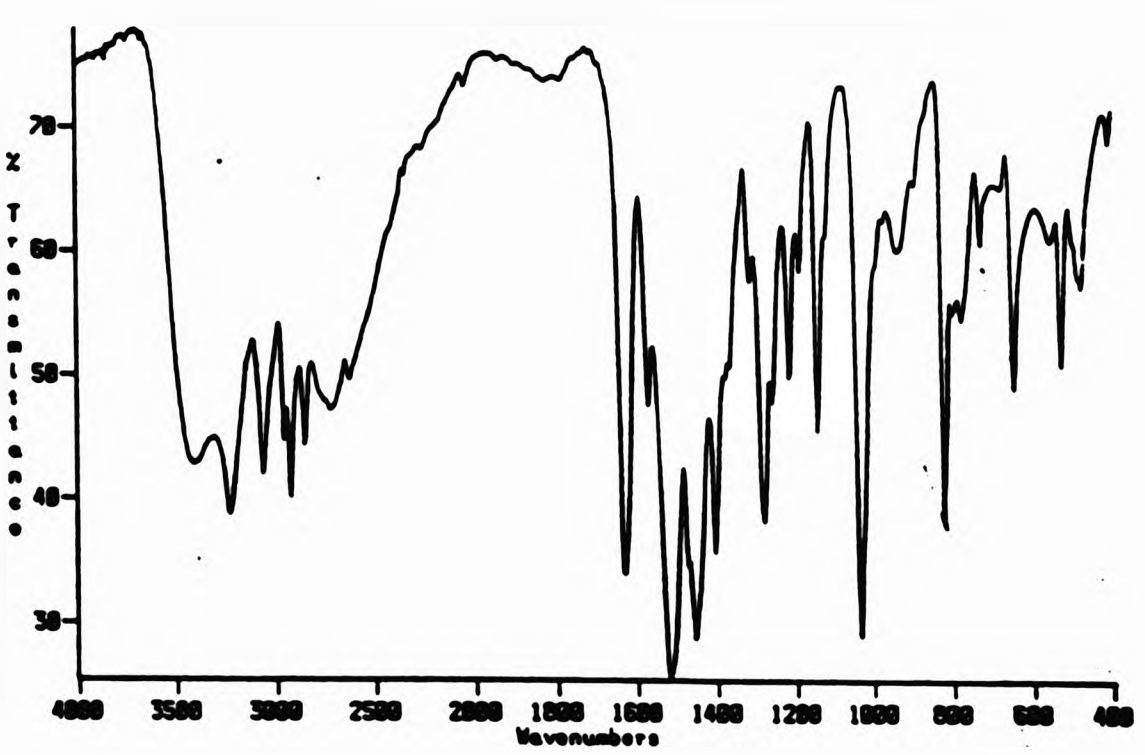


Table 2.2 *Selected IR absorption bands an their assignment for the series of 5-acylamino- and 5-alkylamino- substituted 1,2-benzoquinone-2-oximes.*

R	νOH /cm^{-1}	νNH /cm^{-1}	νCO_{amido} /cm^{-1}	$\nu CO_{quinoid}$ /cm^{-1}
5-C_2H_5CONH	3443	3243	1731	1640 1624
5-C_3H_7CONH	3426	3265	1732	1640 1627
5-C_4H_9CONH	3427	3272	1728	1647 1636
5-$C_6H_{13}CONH$	3475	3277	1717	1642 1638
5-NH_2	3421	3301	-	1685 1639
5-C_2H_5NH	3400	3303	-	1635 1610
5-$C_6H_{13}NH$	3429	3231	-	1633 1612
5-$C_7H_{15}NH$	3425	3212	-	1664 1622

NMR spectra

Previously, NMR spectroscopy was used to study the nitroso–oximino tautomerism in quinone monooximes.[41,42,45] From these studies, a solvent dependent equilibrium between the nitroso and quinone monooximic forms of some compounds was observed. Thus, 1,4-benzoquinone-4-oxime was shown to co-exist with 4-nitrosophenol in DMSO but to occur as the only tautomer in dioxane.[45] Similarly, 1,2-naphthoquinone-2-oxime was shown to co-exist with 2-nitrosonaphthol in DMSO/acetic acid but to exist only in the oximic form in various other solvents.[45]

In the current study, the NMR spectra of all the compounds studied either in methanol or acetone were particularly useful in confirming the compounds as ring and not N-nitrosated. In addition, the spectra were found to be quite useful in demonstrating the quinone monooximic character of the compounds. For example, the ^{1}H NMR spectrum 3-butyrylamino-1,4-benzoquinone-4-oxime (Fig. 2.3) displayed three multiplets (compared to four for its precursor phenol; see Appendix 1) each integrating for a single proton at 6.35 (H-3), 7.40 (H-1) and 7.70 ppm (H-2). The spectrum also contained all the signals expected for the acylamino substituent (Table 2.3).

The spectra of the other 1,4-benzoquinone monooximes were similar to that described above with only minor shifts of the signals to lower field in the case of the alkylamino substituted compounds.

Figure 2.3 ^{1}H *NMR spectrum of 3-pentanoylamino-1,4-benzoquinone-4-oxime*

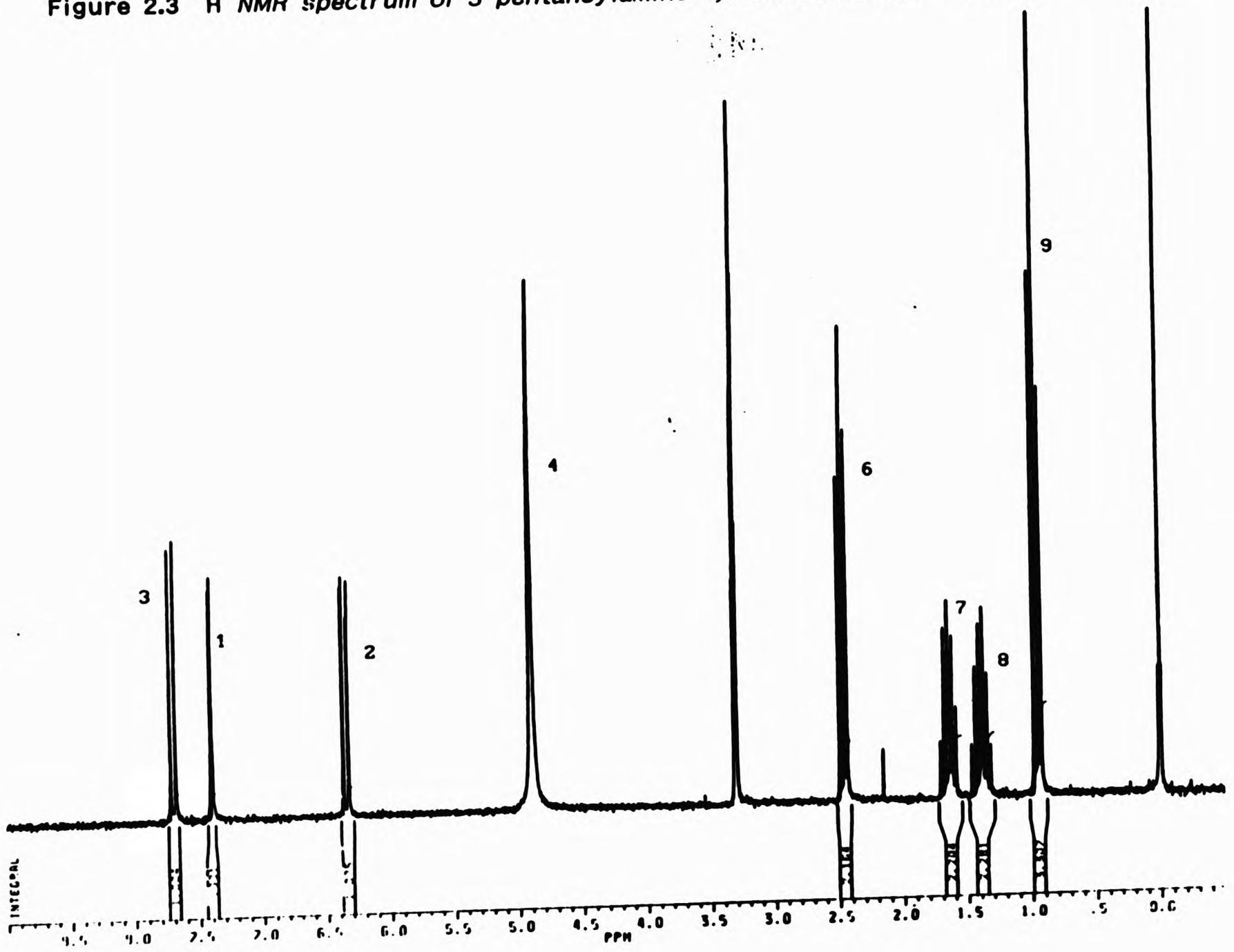
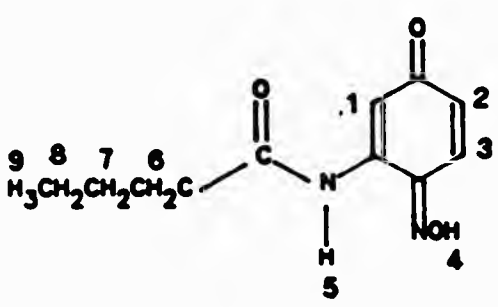


Table 2.3 ^{1}H *NMR spectral assignments for 3-pentanoylamino-1,4-benzoquinone-4-oxime*

	Assignment	Multiplicity J/Hz	δppm
	9	t $^{3}J_{8,9}$ (8.20)	0.95
	8	sxt $^{3}J_{8,7}$ (8.20)	1.40
	7	qn $^{3}J_{7,6}$ (8.25)	1.65
	6	t $^{3}J_{6,7}$ (8.25)	2.45
	5	s	11.93
	4	s	4.90
	2	d,d $^{3}J_{2,3}$ (7.04)	6.35
	3	d $^{3}J_{2,3}$ (7.64)	7.70
	1	d $^{4}J_{3,1}$ (1.25)	7.40

* s, singlet; d, doublet; d,d, doublet of doublets; t, triplet; q, quartet; qt, quintet; sxt, sextet; m, multiplet.

The ^{1}H NMR spectra of the acyl and alkylamino substituted 1,2-quinone monooximes were not too dissimilar from that of the 1,4-isomers. For example, the spectrum of 5-hexylamino-1,2-benzoquinone-2-oxime (Fig. 2.4) displayed three single proton multiplets centred at 5.60 (H-3), 6.50 (H-2), and 7.00 ppm (H-1), together with the expected signals for the alkylamino group (Table 2.4).

The magnitude of the ortho H-H coupling constants in these spectra provided evidence of their quinone monooximic character. Typically, the observed J_{ortho} value was approximately 8.5 Hz. This

value is markedly greater than for the corresponding phenols (7.04 Hz) which are known to have benzenoid structures.

More significantly however, the presence in the ^{13}C NMR spectra of a signal between 175 ppm and 210 ppm assignable to a quinoid carbonyl group supports the formulation of these compounds as quinone monooximes.

Figure 2.4 ^{1}H NMR spectrum of 5-hexylamino-1,2-benzoquinone-2-oxime

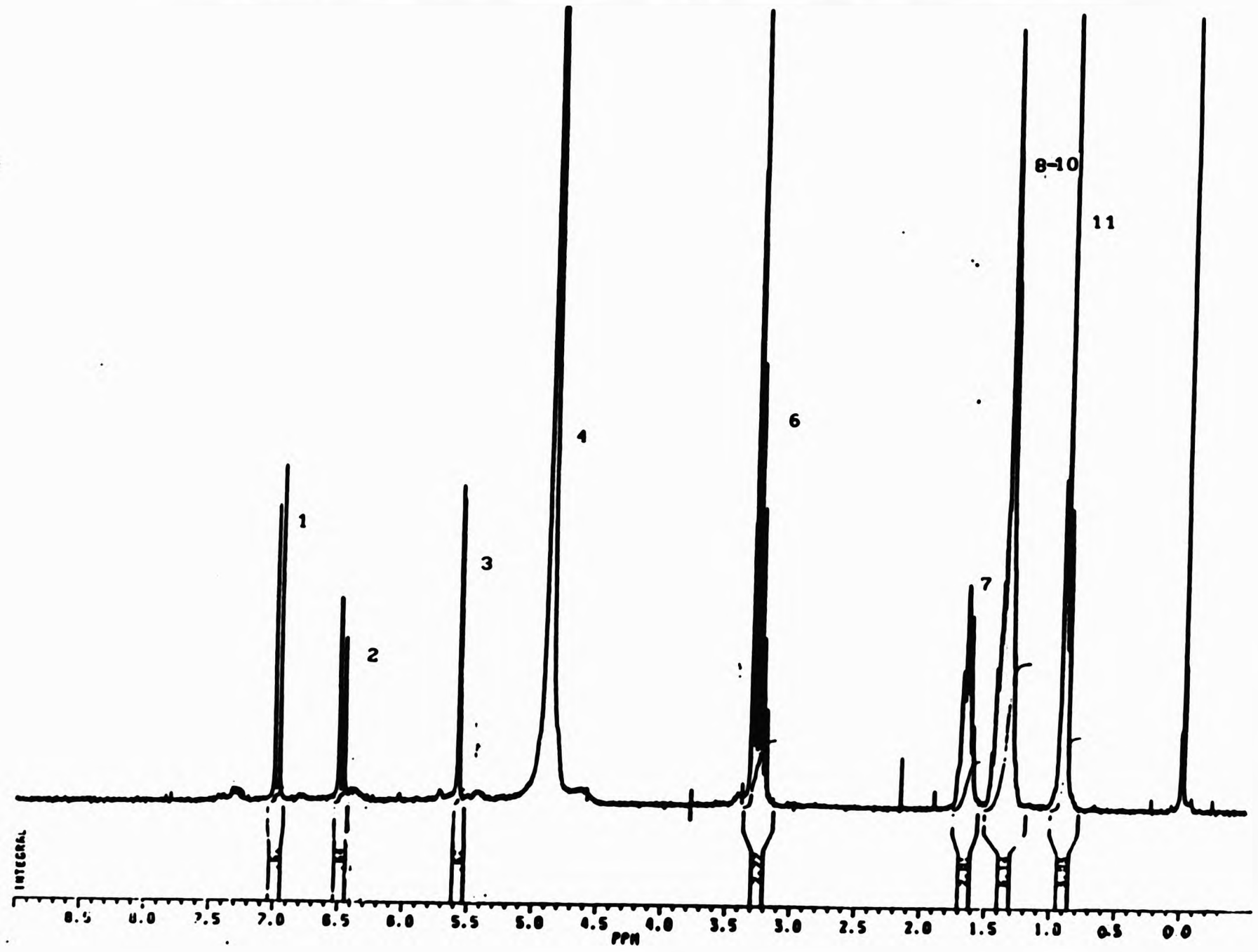
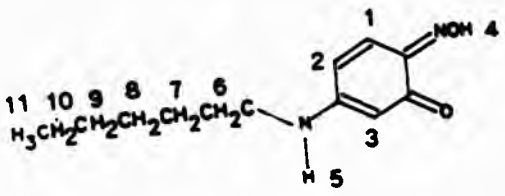


Table 2.4 ^{1}H *NMR spectral assignments for 5-hexylamino-1,2-benzoquinone-2-oxime*

Assignment	Multiplicity J/Hz	δppm
11	m	0.90
8–10	m	1.35
7	m	1.65
6	m	3.25
5	s	10.20
4	s	4.95
3	d $^{3}J_{2,3}$ (1.56)	5.60
2	d,d $^{3}J_{2,1}$ (7.95)	6.50
1	d $^{3}J_{2,1}$ (7.95)	7.00



x s, singlet; d, doublet; d,d, doublet of doublets; t, triplet; q, quartet; qt, quintet; sxt, sextet; m, multiplet.

Mass spectra

Proposed fragmentation patterns for both the 1,4- and 1,2-substituted quinone monooximes prepared during this study are presented in Schemes 2.6 and 2.7.

Unlike that of their precursor phenols, the EI mass spectra of the benzoquinone monooximes reported here were not dominated by the fragmentation of the acyl or alkylamino substituents. Instead, the spectra were characterised by the presence of fragment ions arising from the fission of the oximic and quinoid groups.

Thus, in the EI mass spectra of the 3-acylamino and 3-alkylamino-1,4-benzoquinone-4-oximes (eg. Fig. 2.5), prominent molecular ion peaks were present. In addition, the spectra contained fragment ions arising from the loss of $HO^{\cdot}$, $NO^{\cdot}$, NOH, O and CO. These ions are characteristic of quinone monooximic compounds, although the loss of $NO^{\cdot}$ and CO could also be associated with nitrosophenolic character.[46-48]

In the case of the acylamino substituted compounds, the loss of the acyl group gave rise to the base peak at m/z = 138 (Table 2.5). By contrast, the base peak in the mass spectra of the alkylamino analogues corresponded to the $[M-OH]^{+}$ ion. The greater propensity of the acyl carbonyl oxygen to accomodate an extra electron[49] accounts for the facile loss of this group and the high relative abundance of the $[M-RCO]^{+}$ ion in the spectra of the acylamino substituted compounds.

Figure 2.5 *EI mass spectrum of 3-pentanoylamino-1,4-benzoquinone-4-oxime.*

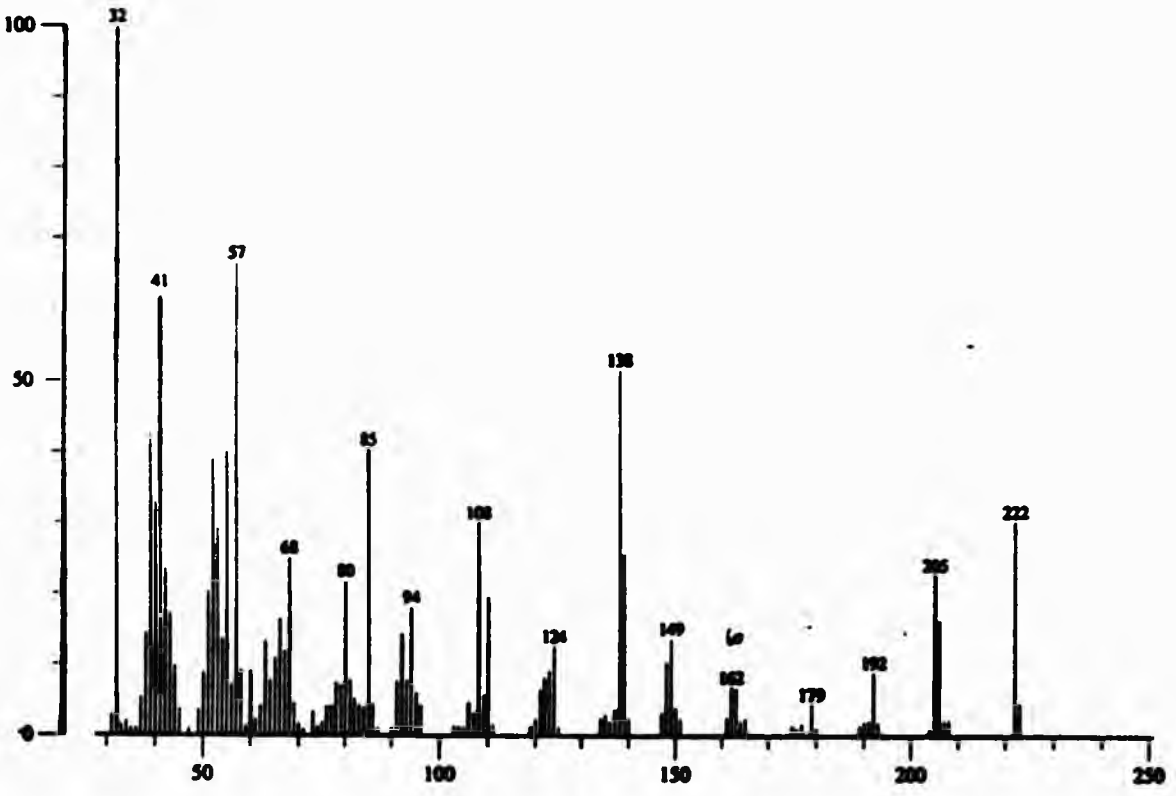


Table 2.5. *M/Z figures for selected ions in the mass spectra of the 3-acylamino- and 3-alkylamino-1,4-benzoquinone-4-oximes (3-XqoH).*

3-XqoH	$[M]^{+\cdot}$	$[M+2H-O]^{+\cdot}$	$[M-O]^{+\cdot}$	$[M-OH]^{+}$	$[M-NO]^{+}$	$[M-NOH]^{+\cdot}$	$[M+H-R]^{+}$	$[M-R/OH]^{+\cdot}$
3-AcqoH	180	166	164	163	150	149	138	121
	(82)	(8)	(4)	(2)	(2)	(4)	(74)	(100)
3-PrqoH	194	180	178	177	164	163	138	121
	(64)	(3)	(17)	(55)	(23)	(5)	(100)	(10)
3-BuqoH	208	194	192	191	178	177	138	121
	(63)	(4)	(14)	(46)	(14)	(4)	(100)	(7)
3-PeqoH	222	208	206	205	192	191	138	121
	(30)	(2)	(16)	(23)	(2)	(3)	(100)	(7)
3-HpqoH	250	236	234	233	220	219	138	121
	(43)	(5)	(12)	(27)	(11)	(3)	(100)	(8)
3-HxqoH	222	208	206	205	192	191	138	121
	(50)	(7)	(20)	(100)	(2)	(3)	(5)	(43)
3-HptqoH	236	222	220	219	206	205	138	121
	(81)	(2)	(21)	(100)	(3)	(2)	(4)	(84)

Numbers in parenthesis are relative abundances.

Like for their 1,4-isomers, the EI mass spectra of the 5-acylamino and 5-alkylamino-1,2-benzoquinone-2-oximes (eg Figs. 2.6 and 2.7) also contained prominent molecular ion peaks as well as ions such as $[M-O]^{+\cdot}$, $[M-OH]^{+}$, $[M-CO]^{+\cdot}$, $[M-NO]^{+}$ and $[M-NOH]^{+\cdot}$. Interestingly though, the $[M-OH]^{+}$ ion was highly prominent in the spectra of the alkylamino compounds whilst being of relatively low abundance (< 10%) in the spectra of the 5-acylamino analogues (Table 2.6).

In both groups of compounds, the loss of the acyl and alkyl substituents gave rise to a relatively abundant ion at m/z = 138. The latter corresponds to the molecular ion in the mass spectrum of 5-amino-1,2-benzoquinone-2-oxime. This compound was isolated during this study and its mass spectrum is shown in Figure 2.8 (Table 2.7).

The most interesting ion in all the spectra was the $[M - 14]^{+}$. This ion which has been observed previously in the mass spectra of other quinone monooximes was attributed to the loss of an oxygen radical from, and the addition of two hydrogen radicals to the molecular ion. This reaction gives an anilinium species.[46] These anomalous reactions are not without precedent however, since N-nitroso compounds are known to give rise to ions of the parent amine by N-N bond cleavage and subsequent proton abstraction.[50] Moreover, anilinium ions found in the mass spectra of both 2-nitrosotoluene and 2-nitrotoluene have been accounted for by the operation of an *'ortho effect'* which results in the loss of CO and the formation of an anilinium ion.[50,51]

Figure 2.6. *EI mass spectrum of 5-butyrylamino-1,2-benzoquinone-2-oxime*

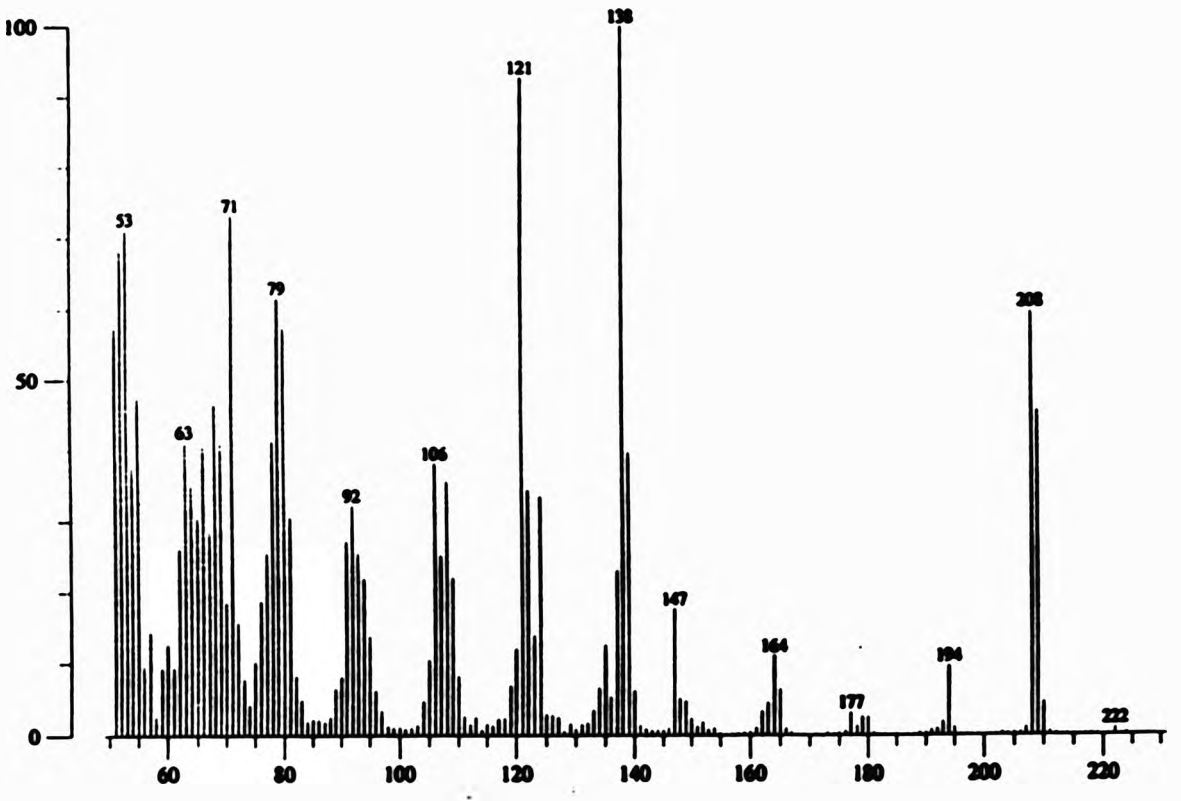


Figure 2.7. *EI mass spectrum of 5-hexylamino-1,2-benzoquinone-2-oxime*

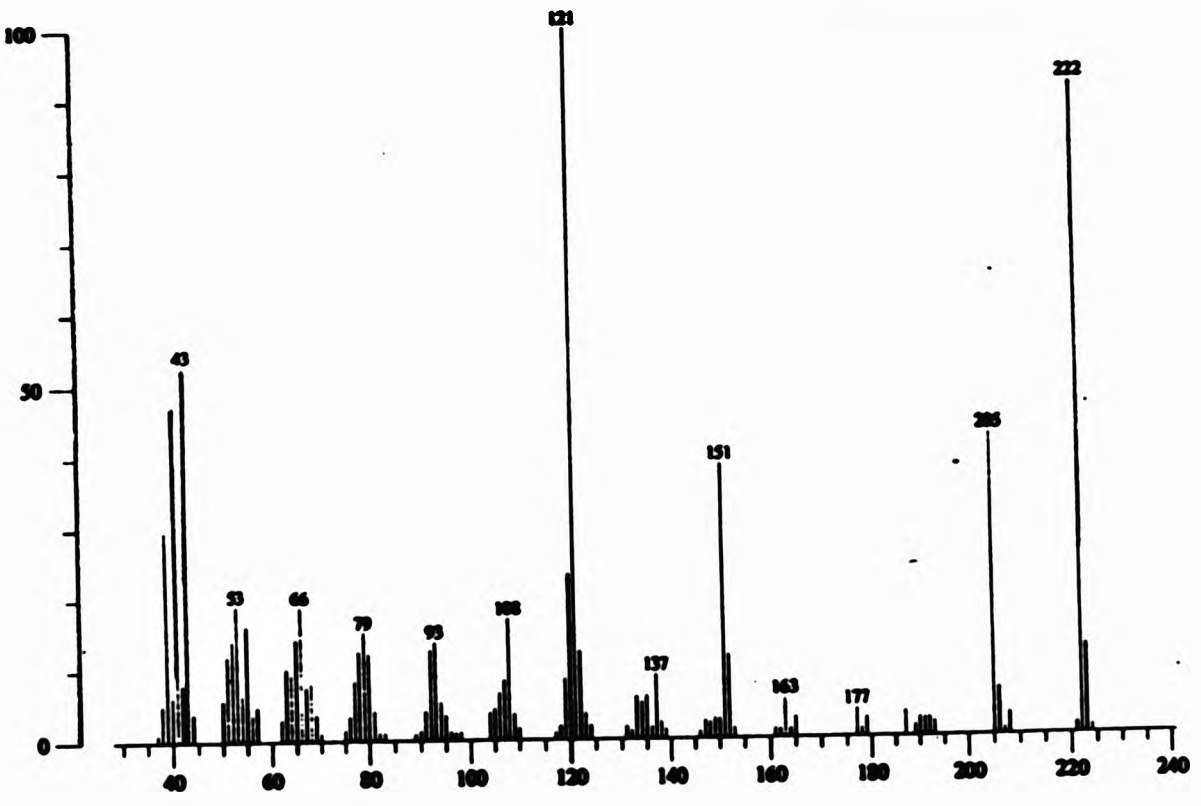


Table 2.6. *M/Z figures for selected ions in the mass spectra of the 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-oximes (5-XqoH).*

5-XqoH	$[M]^{+\cdot}$	$[M+2H-O]^{+\cdot}$	$[M-O]^{+\cdot}$	$[M-OH]^{+}$	$[M-NO]^{+}$	$[M-NOH]^{+\cdot}$	$[M+H-R]^{+\cdot}$	$[M-R/OH]^{+}$
5-AcqoH	180 (82)	166 (8)	164 (4)	163 (2)	150 (2)	149 (4)	138 (74)	121 (100)
5-PrqoH	194 (64)	180 (17)	178 –	177 –	164 (23)	163 (5)	138 (96)	121 (100)
5-BuqoH	208 (60)	194 (10)	192 (2)	191 –	178 (3)	177 (3)	138 (92)	121 (100)
5-PeqoH	222 (67)	208 (22)	206 –	205 (3)	192 (7)	191 (17)	138 (84)	121 (100)
5-HpqoH	250 (65)	236 (23)	234 (4)	233 (10)	220 (9)	219 (5)	138 (72)	121 (100)
5-HxqoH	222 (75)	208 (15)	206 (16)	205 (41)	192 (3)	191 (3)	138 (52)	121 (100)
5-HptqoH	236 (36)	222 (5)	220 (21)	219 (100)	206 (2)	205 (1)	138 (4)	121 (32)

Numbers in parenthesis are relative abundances.

Figure 2.8. *EI mass spectrum of 5-amino-1,2-benzoquinone-2-oxime.*

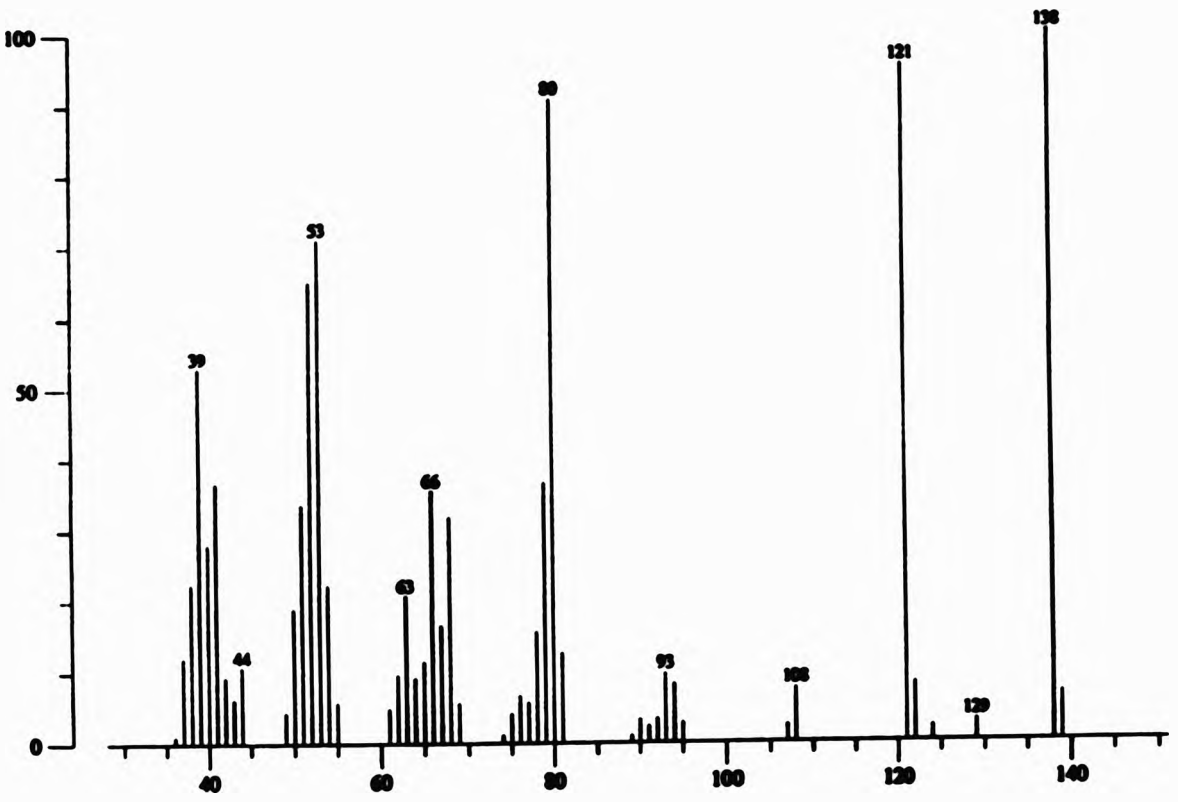
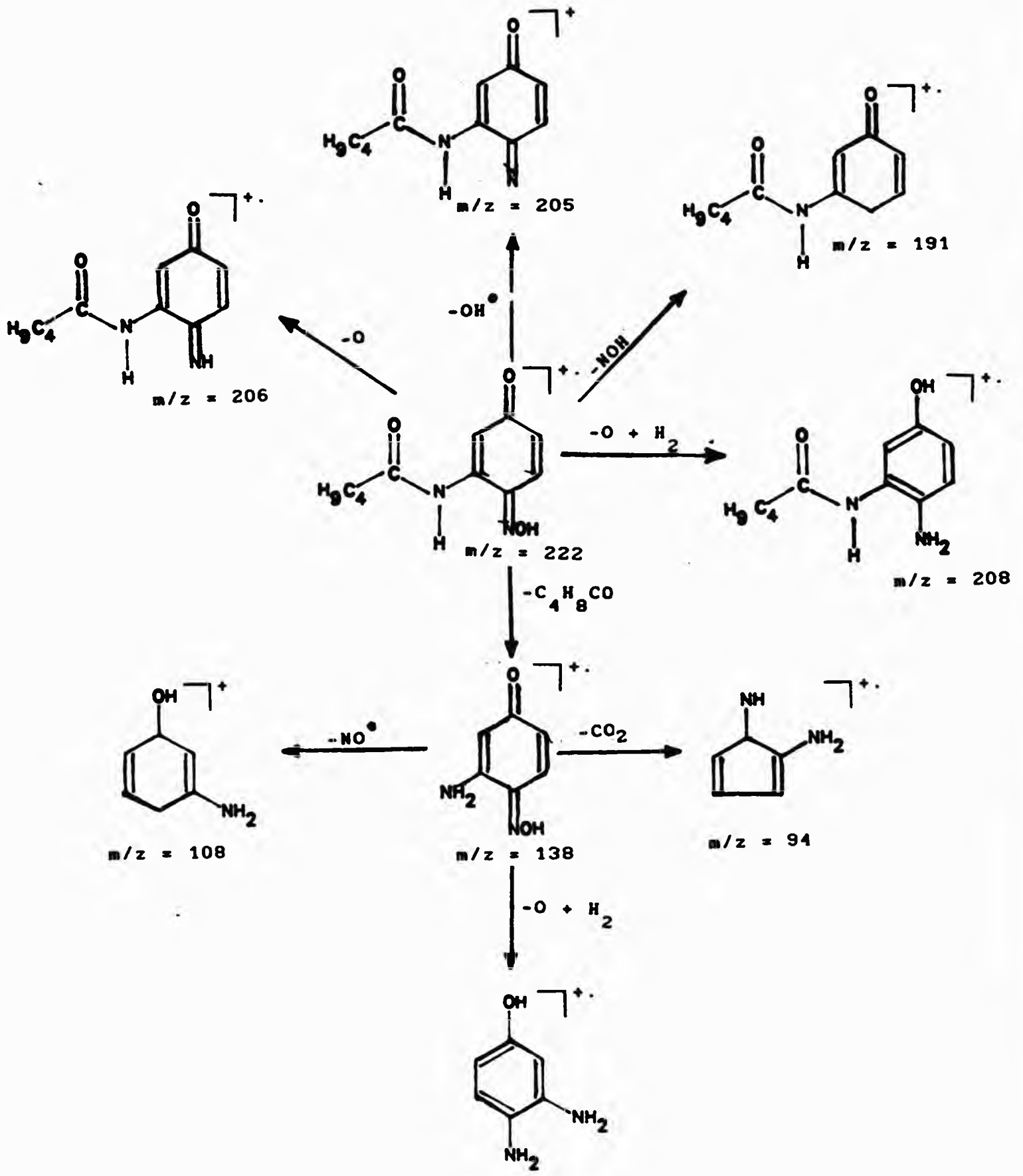


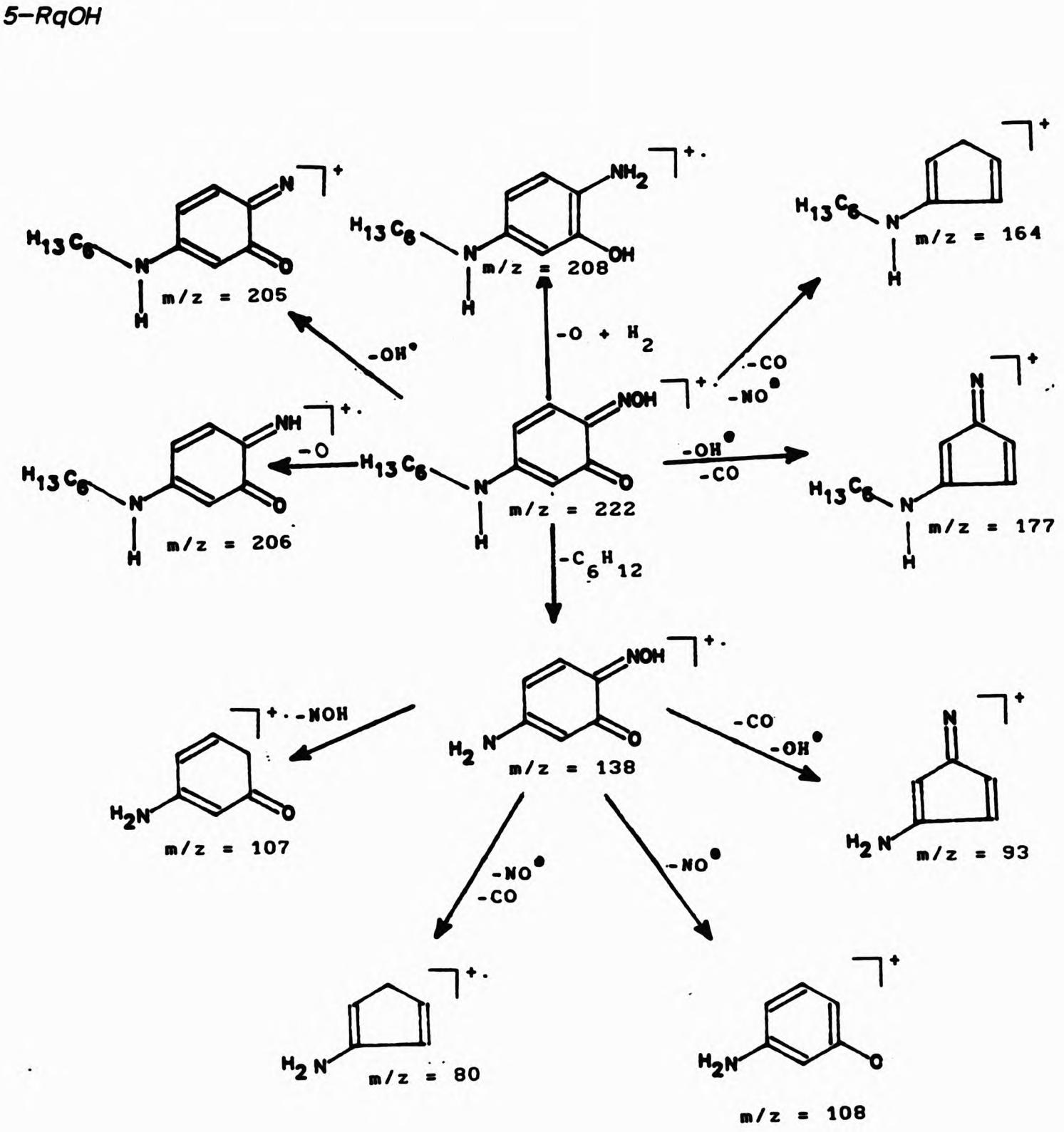
Table 2.7 *Ion abundances and assignment in the mass spectrum of 5-amino-1,2-benzoquinone-2-oxime.*

Ion	Abundances %	m/z
$[M]^{+\cdot}$	100	138
$[M-OH]^{+}$	95	121
$[M-NO]^{+}$	8	108
$[M-CO/OH]^{+}$	10	93
$[M-CO/NO]^{+}$	91	80
$[M-NO/CO/NH]^{+\cdot}$	12	65

Scheme 2.6 *Proposed fragmentation pattern for compounds of the type 3-RqOH*



Scheme 2.7. *Proposed fragmentation pattern for compounds of the type 5-RqOH*



2.5 Single Crystal X-ray Structure of 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

The X-ray crystal structure of several 1,2-quinone monooximes have been determined previously.[52-55] In general, these structures show that the compounds are quinone monooximic and not nitrosophenolic in the solid state. In addition, X-ray crystal structure analysis confirm the presence of *cis* - *trans* isomers centred on the orientation of the oximic OH group relative to the ring carbonyl.

To date, none of the structures reported have included an amino substituent. Hence, it was interesting to see what effect if any, the inclusion of such a group would have on the overall geometry of the 1,2-quinone monooximic moiety. Additionally, the presence of the amino group introduces the possibility of 1,2-quinone oxime/ 2,5-oxime imino tautomerism not dissimilar from that observed recently with 3-hydroxy-2-methyl-1,4-benzoquinone-4-oxime.[37] Thus the single crystal X-ray structure of 5-hexylamino-1,2-benzoquinone-2-oxime monohydrate was determined.

Crystal preparation and data collection.

5-Hexylamino-1,2-benzoquinone-2-oxime mono-hydrate was prepared by the nitrosation of 3-hexylaminophenol with sodium nitrite in concentrated hydrochloric acid, and subsequent neutralization of the yellow hydrochloride salt. The orange powdery solid was recrystallised from water: methanol (1:3) to give orange, octagonal crystals.

The crystal selected for X-ray analysis had dimensions 0.70 x 0.35 x 0.25 mm. Unit cell parameters and intensity data were collected

on an ENRAF-NONIUS CAD-4 diffractometer. All calculations were performed using the SDP software[56] on a MICROVAX-3100 computer. The cell dimensions were determined by least-squares fitting of 25 centred reflections monitored in the range $40 < 0 < 48^0$. Lorentz polarization, empirical absorption and decay corrections[57] were applied to all reflections. The structure was solved by direct methods using the MULTAN 80 computer package.[58] All atoms were refined by full matrix least-squares analysis with the non-hydrogen atoms being positioned anisotropically. All hydrogen atoms were experimentally positioned isotropically. Secondary extinctions[59] were applied in all cases and scattering factors[60] were taken from published tables of X-ray crystallographic data.[61] All relevant experimental details are given in Table 2.8. Atomic coordinates, temperature factors, bond lengths, bond angles, intra and intermolecular contact distances are given in Appendix 2.

Table 2.8 *Crystal data, data collection and processing parameters for 5-hexylamino-1,2-benzoquinone-2-oxime monohydrate.*

Formula	$C_{12}H_{20}N_2O_3$
MW	240.31
System	Orthorombic
Space group	$P2_12_12_1$ (n. 19)
a	8.016(1) Å
b	11.552(1) Å
c	14.409(2) Å
V	1334.22 $Å^3$
Z	4

Table 2.8 *contd...*

D_{calc}	1.186 g cm^{-3}
Radiation	Cu K_α (λ = 1.54184 Å)
	graphite monochromated
μ	0.645 cm^{-1}
F(000)	516
T	293(2) K
$R = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$	0.046
R_w	0.023
Weighing scheme	$w = F_o/P$ for $P<F_o$
	$w = P/F_o$ for $F_o>P$
	$P = F_{o,max}/3$
Crystal size	0.70x0.35x0.25 mm
Scan type	ω–2θ
Scan speed	3.3^0 min^{-1}
Scan width	(1.0 + 0.14 tanθ)
Aperture	(2.5 + 0.5 tanθ) mm
Reflections measured	hkl, hk–l
	0<h<9
	0<k<14
	–17<l<17
Unique reflections	1487
R_{int}	0.026
Observed Reflections ($I>3\sigma(I)$)	1198
Refined parameters	235
Final Fourier Map	max 0.16 e $Å^{-3}$
	min –0.12 e $Å^{-3}$
	$(shift/e.s.d.)_{max}$ 0.03

Results and discussion.

A perspective view of the molecule with the relevant atomic numbering is presented in Figure 2.9. The oximic OH group of 5-hexylamino-1,2-benzoquinone-2-oxime monohydrate was found to be in the *anti (trans)* configuration with respect to the quinoid carbonyl group. Thus, no intramolecular hydrogen bonds were observed in this molecule.

Figure 2.9 *X-ray crystal structure of 5-hexylamino-1,2-benzoquinone-2-oxime monohydrate.*

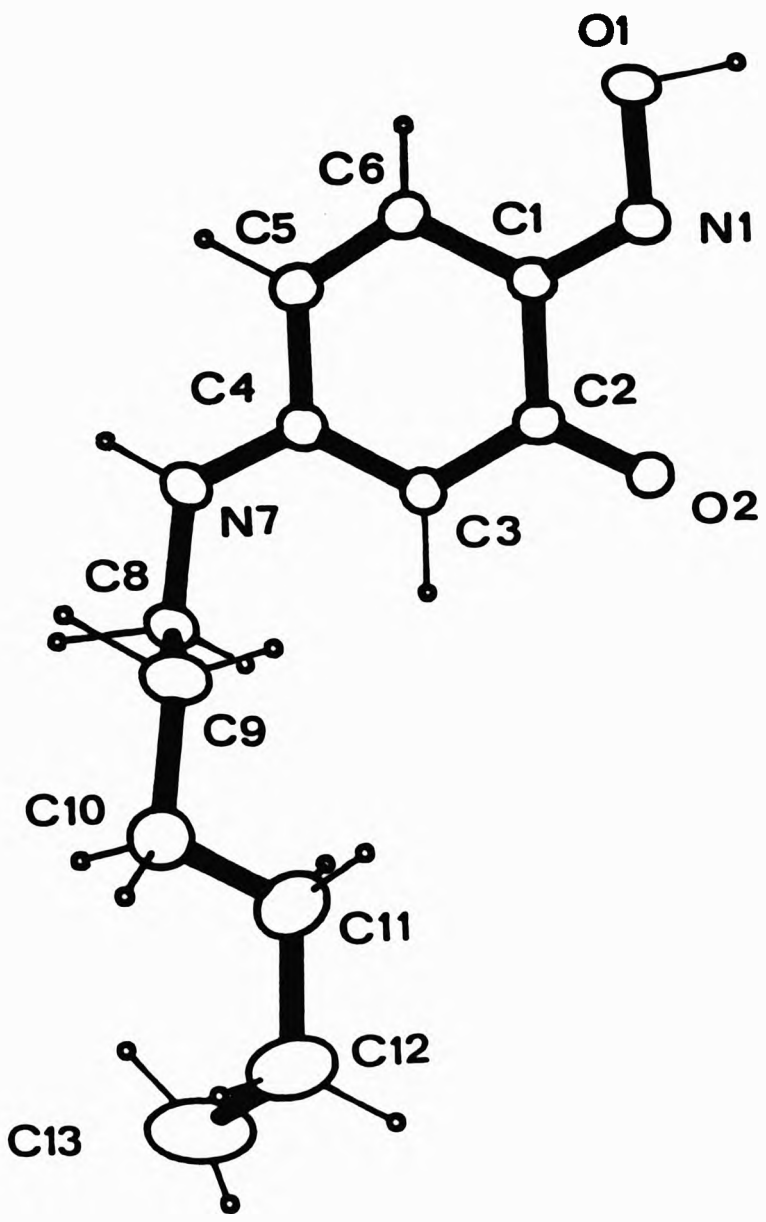
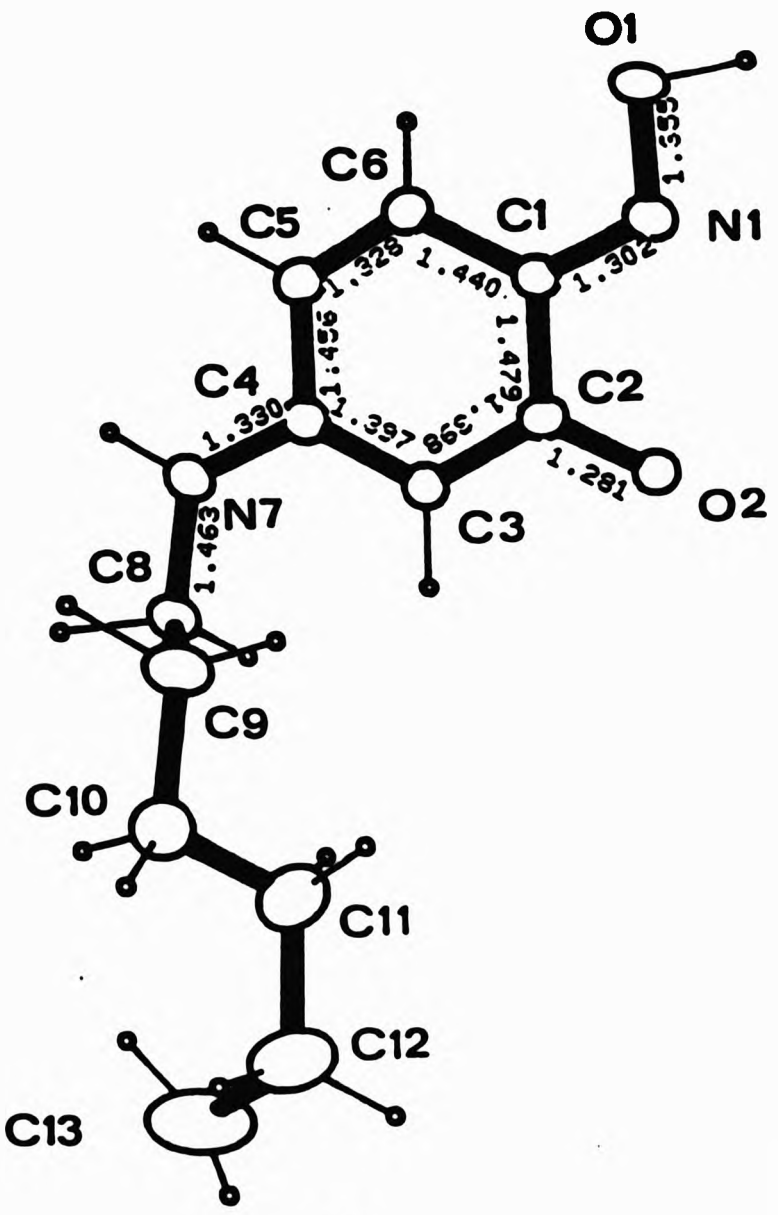
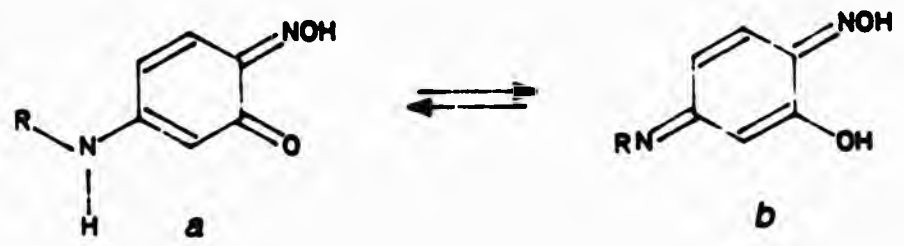


Figure 2.10 shows selected bond lengths in the molecule. The intermediacy of the bond distances in the carbocyclic ring suggest that the molecule could be represented as a resonance hybrid of the two limiting forms *a* and *b* (Scheme 2.8). The bond distances C(2) - C(3) (1.398(5) Å) and C(3) - C(4) (1.397(4) Å) are statistically equivalent, the bond C(2) - O(2) (1.281(4) Å) is longer than the average quinoid carbonyl C=O bond (1.222(4) Å) while the N(7) - C(4) bond (1.330(4) Å) is shorter than the average Csp_2 - NHR bond distance (1.339(1) Å - 1.416(18) Å).[62] All this points towards some contribution from the 2,5-oxime imino structure *b*.

Figure 2.10 *Selected bond lengths in 5-hexylamino-1,2-benzoquinone-2-oxime monohydrate.*



Scheme 2.8 *1,2-quinone monooxime/1,4 quinone monooximino equilibrium.*



Although no intramolecular hydrogen bonding was found in this molecule, extensive intermolecular interactions were found between neighbouring quinone monooximic molecules and with the associated water molecule. The water oxygen atom is a strong hydrogen acceptor and thus interacts with the oximic proton forming a fairly strong hydrogen bond. The water hydrogens were found to be hydrogen bonded to the quinoid carbonyl oxygen (Fig. 2.11). In addition, interaction between the quinoid carbonyl oxygen and the amino proton on neighbouring molecules (Fig. 2.12) were also found to be important in the packing arrangement of the molecules in the unit cell (Fig. 2.13). These extensive intermolecular associations which result in the formation of a quasi polymeric unit are bourne out by the short contact distances O(2)...O(w) (2.77(1) Å), H(O1)...O(w) 1.42(2) Å, O(2)...H(N7) 2.46(1) Å and O(2)..N(7) 2.94(1) Å.

The unusual bond distances and high thermal parameters (Tables 2 and 6, Appendix 2), suggest that the large alkyl chain in the molecule is free to assume any of the equilibrium conformations available to it. This is further supported by the absence of any contacts involving non-hydrogen atoms and which are not associated with the packing interactions already described.

Figure 2.11 *Interactions between 5-hexylamino-1,2-benzoquinone-2-oxime and water in the crystal structure of 5-Hexylamino-1,2-benzoquinone-2-oxime monohydrate.*

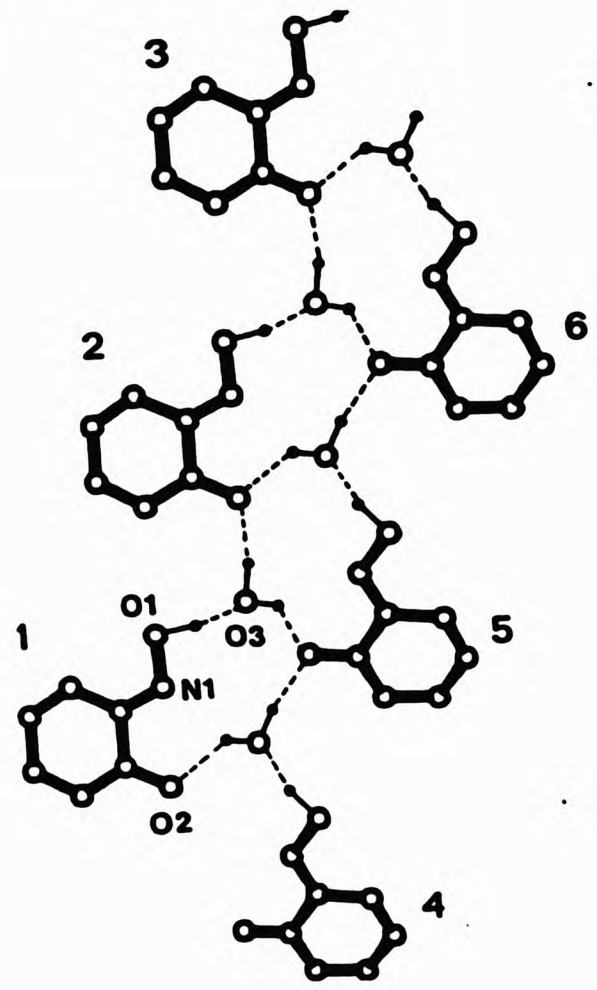


Figure 2.12 *Interactions between neighbouring molecules of 5-hexylamino-1,2-benzoquinone-2-oxime.*

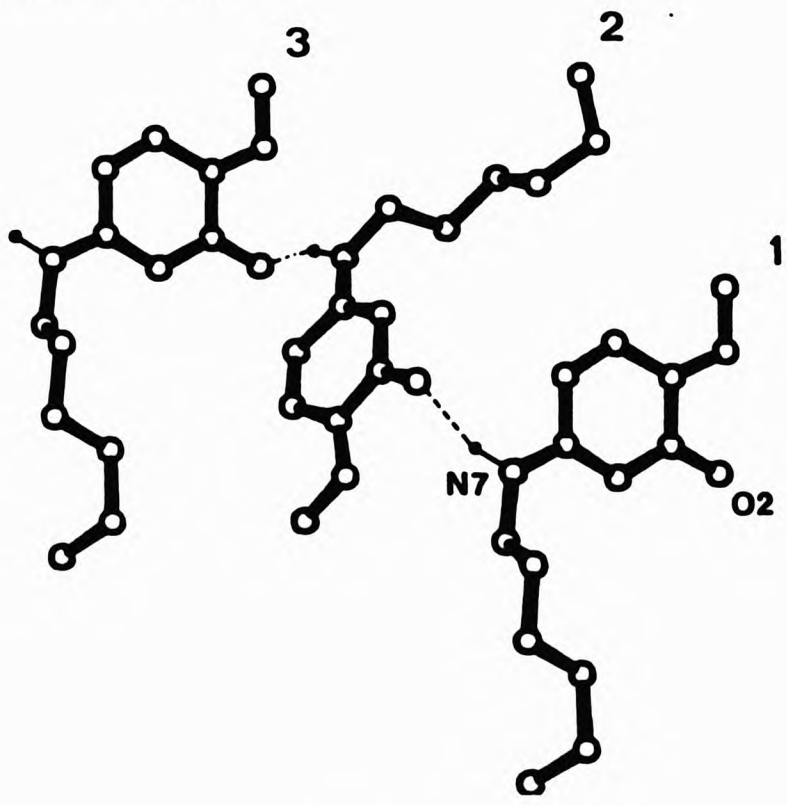
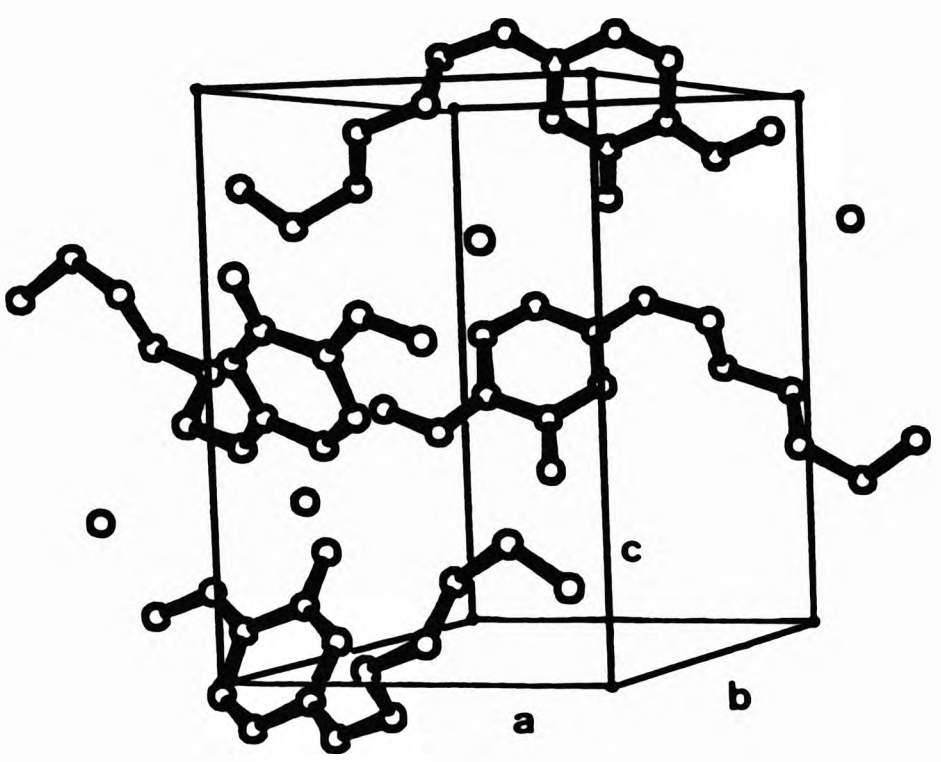


Figure 2.13 *Unit cell for crystals of 5-hexylamino-1,2-benzoquinone-2-oxime monohydrate.*



2.6. Single Crystal X-ray Structure of 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Crystal preparation and data collection.

Orange crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime were prepared by the same method as described for its 5-hexylamino analogue. The crystal selected for X-ray structure analysis had dimensions 0.35 x 0.30 x 0.30 mm which were determined by least-squares fitting of 25 centred reflections monitored in the range $30 < \theta < 40^0$. Other experimental conditions and techniques used to solve this structure were similar to that described in the section 2.5. Relevant crystal data and processing parameters are summarised in Table 2.9. Selected bond lengths, bond angles, and data are given in Appendix 3.

Table 2.9 *Crystal data, data collection and processing parameters for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.*

Formula	$C_9H_{12}N_2O_2$
MW	180.21
System	Monoclinic
Space group	$P2_1/n$ (n. 14)
a	4.086(1) Å
b	17.098(1) Å
c	12.792(1) Å
β	$95.01(1)(1)^0$
D_{calc}	1.344 g cm^{-3}
Radiation	Cu K_α (l = 1.54184 Å) graphite monochromated

Table 2.9 *cont'd...*

μ	7.56 cm^{-1}
F(000)	384
T	293(2) K
$R = \Sigma Fo - Fe / \Sigma Fo$	0.047
R_w	0.042
Weighing scheme	$w = \sigma(Fo)^{-2}$
Crystal size	0.35x0.30x0.30 mm
Scan type	ω–2θ
Scan speed	2.2^0 min^{-1}
Scan width	$(0.8 + 0.14 \tan\theta)^0$
Aperture	$(2.2 + 0.5 \tan\theta)$ mm
Reflections measured	hkl, hk–l
	0<h<4
	0<k<20
	–15<l<15
Unique reflections	1744
Observed Reflections ($I>2\sigma(I)$)	1312
Refined parameters	167
Final Fourier Map	max 0.11 e $Å^{-3}$
	min –0.09 e $Å^{-3}$
	$(shift/e.s.d.)_{max}$ 0.01

Results and discussion.

A perspective view of the molecule with relevant atomic numbering is presented in Figure 2.14. Selected bond lengths and bond angles are shown in Figures 2.15 and 2.16.

Figure 2.14 ***X-ray crystal structure of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.***

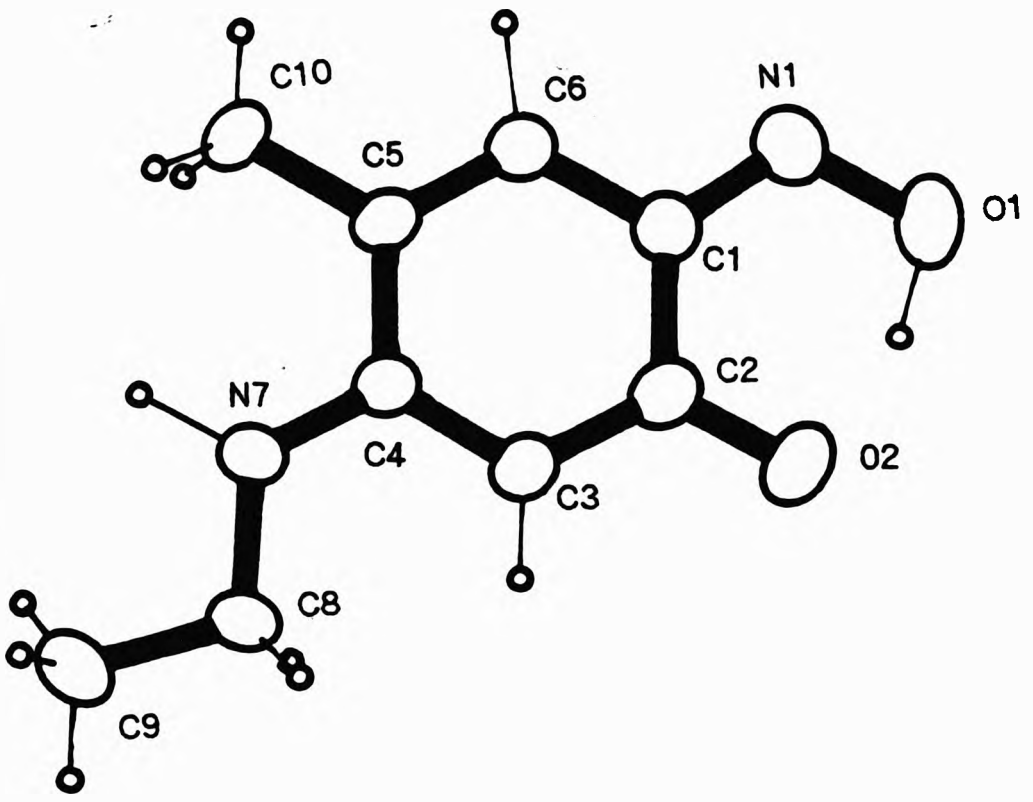


Figure 2.15 ***Selected bond lengths for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.***

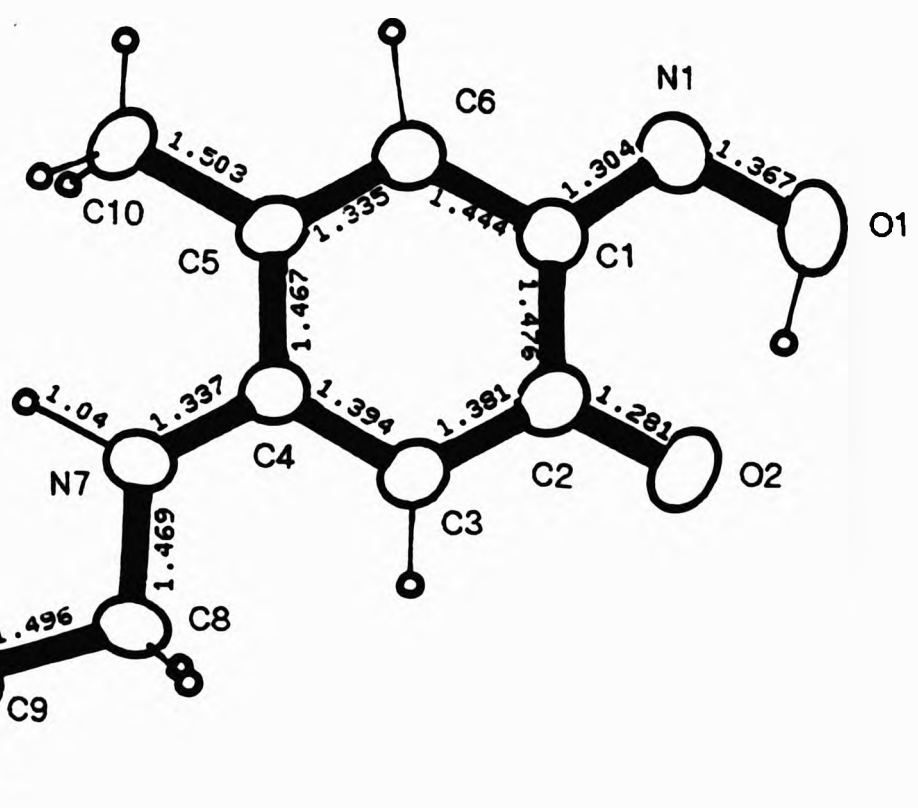
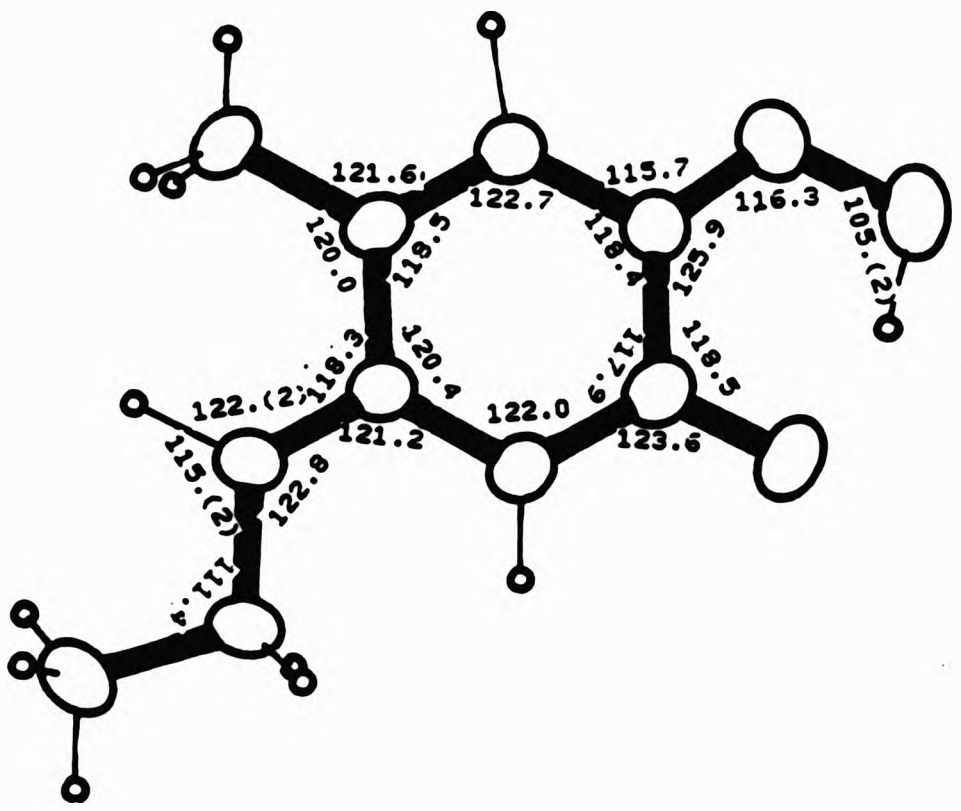


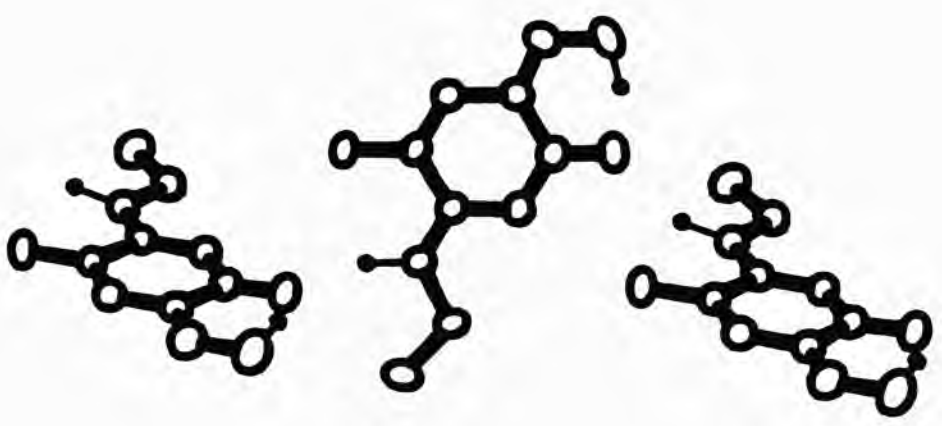
Figure 2.16 ***Selected bond angles for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.***



In contrast to the 5-hexylamino and 5-pentylamino[62] analogues, the oximic OH group in 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime was found to be *syn* (*cis*) to the quinoid carbonyl group. Thus, the molecule contained an intramolecular hydrogen bond between the quinoid carbonyl oxygen and the oximic hydrogen. This was bourne out by the short H(01)-02 contact distance of 1.56(3) Å and N7-H(N7)-02^{1} angle (149(2)^{0}). The bond distances in this molecule were quite similar to that found in both 5-pentylamino and 5-hexylamino analogues. For example, the bond distances C(2) - C(3), C(3) - C(4), C(2) - O(2), and C(4) - N(7) were 1.381(3), 1.394(3), 1.281(3), and 1.337(3) Å respectively. This marked similarity with the two previously decribed structures suggests that, like the pentylamino and hexylamino analogues this molecule also has some 2,5-oxime imino character. The crystal

packing in this molecule is relatively simple. The molecules are arranged in strands through weak hydrogen bonds (Fig. 2.17). The inter-strand interactions are weak Van der Waals interactions. No other stacking arrangements or hydrogen bonds were observed.

Figure 2.17 ***Packing arrangements for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.***



2.7. Single Crystal X-ray Structure of 5-Ethylamino-4-methyl-1,2-benzo-quinone-2-oxime Chloridrate Monohydrate.

As stated earlier, one of the attractions of amino substituted 1,2-quinone monooximes is the possibility of the pH influenced equilibrium between 1,2-quinone monooxime/1,4-oxime-imino structures. The existence of an equilibrium structure as described above is demonstrated here by X-ray crystal data analysis of the compound obtained by dissolving 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime in dilute hydrochloric acid.

Crystal preparation and data collection.

5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate mono-monohydrate was obtained as yellow octahedral cyrstals by dissolving 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime in a mixture of water, methanol and dilute hydrochloric and allowing the mixture to stand for several days.

The crystal selected for X-ray analysis had dimensions 0.70 x 0.35 x 0.25 mm. The cell dimensions were determined by least-squares fitting of 25 centred reflections monitored in the range $35 < 0 < 45^{0}$. The acidic (N-H and O-H) hydrogen atoms were positioned experimentally and refined isotropically. The other hydrogen atoms geometrically positioned (at 0.95 Å from their neighbour atom), were not refined, but their thermal parameters were taken as proportional (x 1.3) to those of their non-hydrogen neighbours. All other experimental conditions and techniques were the same as described previously. The relevant experimental details are given in Table 2.10. Atomic coordinates, temperature factors, bond lengths, bond angles, intra and intermolecular

contact distances are given in Appendix 4.

Table 2.10 *Crystal data, data collection and processing parameters for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate.*

Formula	$C_9ClH_{15}N_2O_3$
MW	234.68
System	Triclinic
Space group	$P\bar{1}$ (n. 2)
a	7.548(1) Å
b	8.171(1) Å
c	10.010(1) Å
α	$102.47(6)^0$
β	$104.35(1)^0$
γ	$94.97(5)^0$
D_{calc}	1.349 g cm^{-3}
Radiation	Cu K_α (λ = 1.54184 Å) graphite monochromated
μ	21.92 cm^{-1}
F(000)	248
T	293(2) K
$R = \Sigma \lvert Fo - Fe \rvert / \Sigma Fo$	0.057
R_w	0.055
Weighing scheme	$w = \sigma(Fo)^{-2}$
Crystal size	0.35x0.30x0.25 mm
Scan type	ω–2θ
Scan speed	2.2^0 min^{-1}
Scan width	$(0.8 + 0.14 \tan\theta)^0$

Table 2.10 *cont'd...*

Aperture	(2.2 + 0.5 tanθ) mm
Reflections measured	hkl, h-kl, hk-l, h-k-l
	0<h<9
	-9<k<9
	-12<l<12
Unique reflections	2068
Observed Reflections (I>2σ(I))	1871
Refined parameters	157
Final Fourier Map	max 0.12 e $\dot{A}^{-3}$
	min -0.12 e $\dot{A}^{-3}$
	$(shift/e.s.d.)_{max}$ 0.01

Results and discussion.

A perspective view of the molecule including selected bond lengths is shown in Figure 2.18. Selected bond angles are shown in Figure 2.19.

Figure 2.18 *Selected bond lengths in 5-ethylamino-1,2-benzoquinone-2-oxime chloridrate monohydrate.*

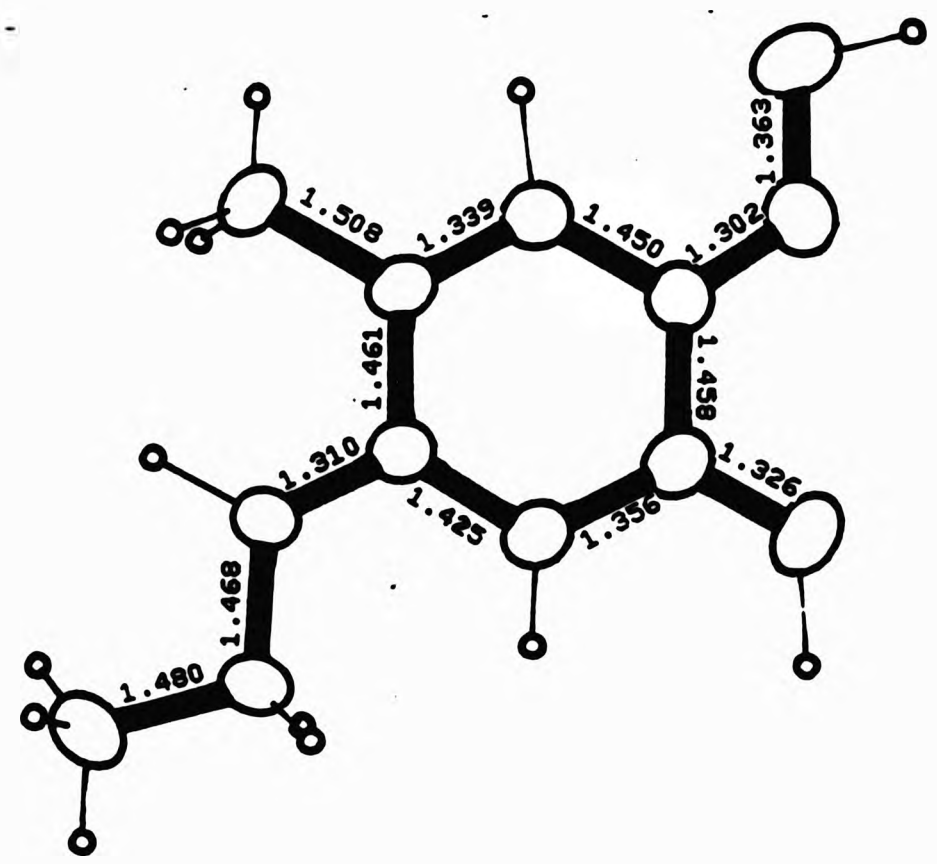
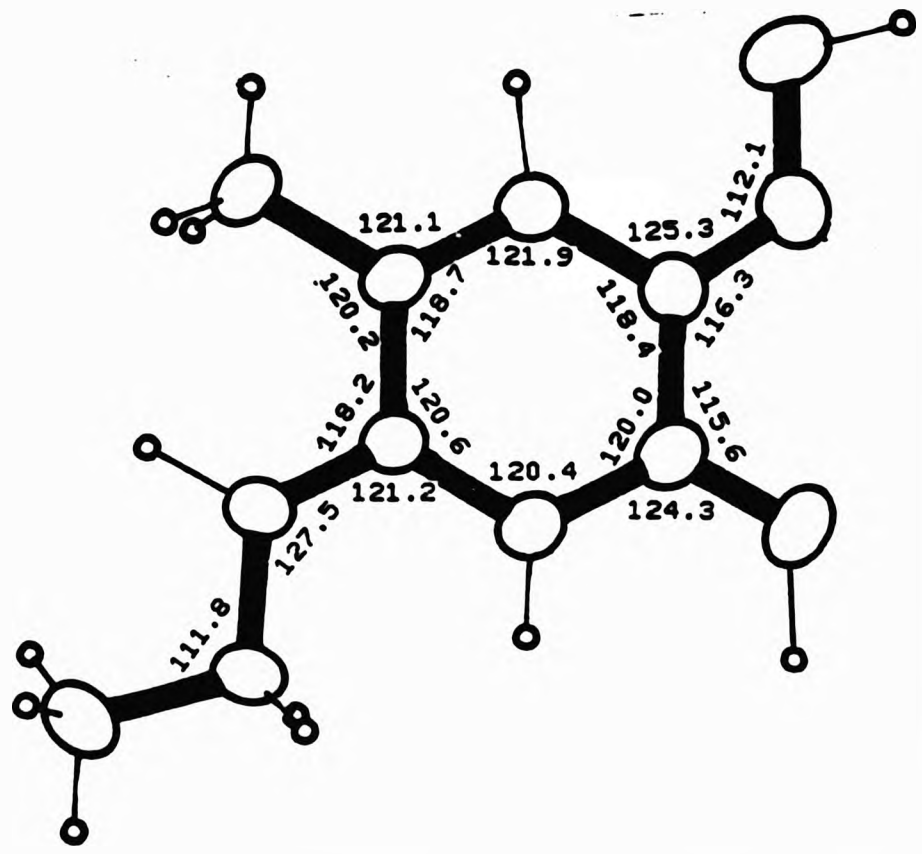


Figure 2.19 *Selected bond angles in 5-ethylamino-1,2-benzoquinone-2-oxime chloridrate monohydrate.*

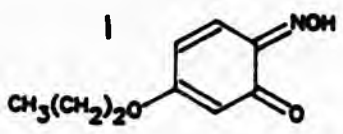
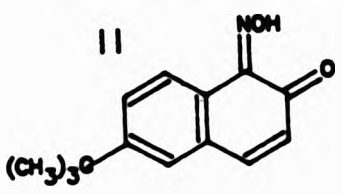
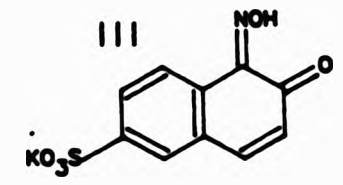
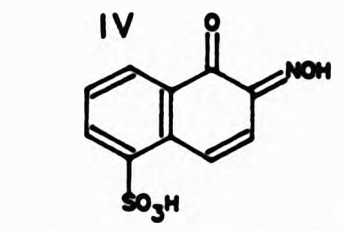
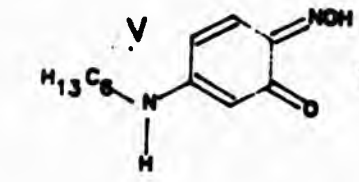
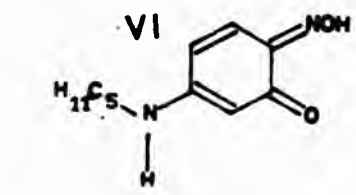
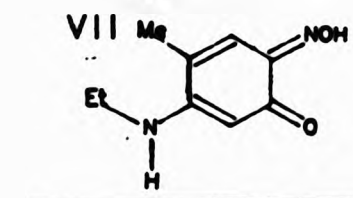


Comparison of the bond length of the CO group in the structure of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate (Fig. 2.18) to those reported (Table 2.11) for compounds of confirmed quinone monooximic structure show that C(2) - O(2) (1.326(1) Å) is longer than the average length of compounds I - VII. Significantly, this bond is longer than the corresponding bond in the free bases 5-ethylamino-4-methyl- 5-pentyl- and 5-hexylamino-1,2-benzoquinone-2-oximes (1.281(1), 1.25(2) Å and 1.281(1) Å respectively). This increased bond length is consistent with more single bond character. The C(1) - N(1) bond length (1.302(3) Å) is within the range observed for oximic C - N bonds. The C(4) - N(7) bond (1.310(1) Å) is considerably shorter than the typical C_{sp}^{2} - NRH bond and thus show that the latter has much double bond character.

On the basis of these results, the molecule could therefore be represented as a hybrid of the two structures *c* and *d* (Scheme 2.9). Further supporting evidence for this conclusion is provided by consideration of the bond distances of the C - C bonds in the hexa-atomic ring. Thus a pattern of four long and two short bonds were found. The short bonds were C(2) - C(3) (1.356(4) Å) and C(5) - C(6) (1.339(2) Å) confirming the 2,5-oxime imino structure of the molecule.

The molecular packing arrangements of the crystal are shown in Figure 2.20. One of the most interesting features of the structure is the extensive H-bonding observed. The three acidic protons of each molecule is H-bonded, two with two different chloride anions and the other with a water molecule. The water molecule forms H-bonds with a chloride anion and an adjacent oximic nitrogen atom. The chloride ion is thus surrounded by three hydrogen atoms. Stacking interactions between the hexa-atomic rings are also present (Fig. 2.21).

Table 2.11 *Selected bond lengths of some previously reported 1,2-quinone monooximes*

Compound	Bond lengths (Å) C – O	C – N	C – C[a]	C – C[b]	Refs
I 	1.27	1.32	1.35	1.45	36
II 	1.24	1.30	1.37	1.47	52
III 	1.22	1.31	1.31	1.47	53
IV 	1.24	1.30	1.33	1.46	54
V 	1.28	1.30	1.37	1.45	*
VI 	1.25	1.29	1.36	1.46	62
VII 	1.28	1.30	1.36	1.46	*

a, Average length of the two short bonds; b, Average length of the four long bonds

* Results obtained during this study.

Scheme 2.9.

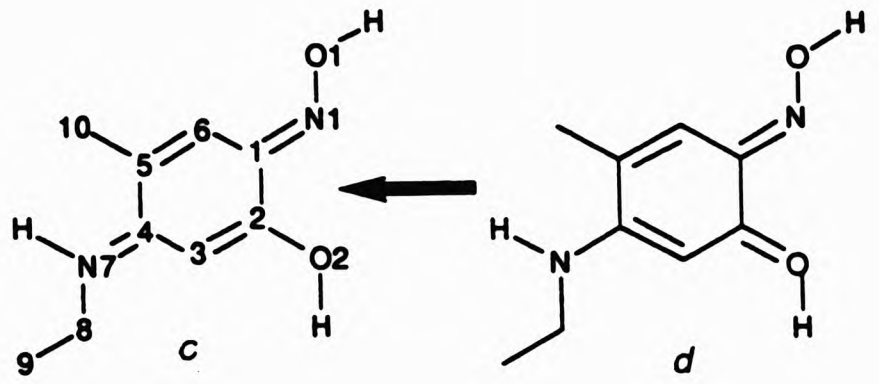


Figure 2.20 *Molecular packing in the crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate.*

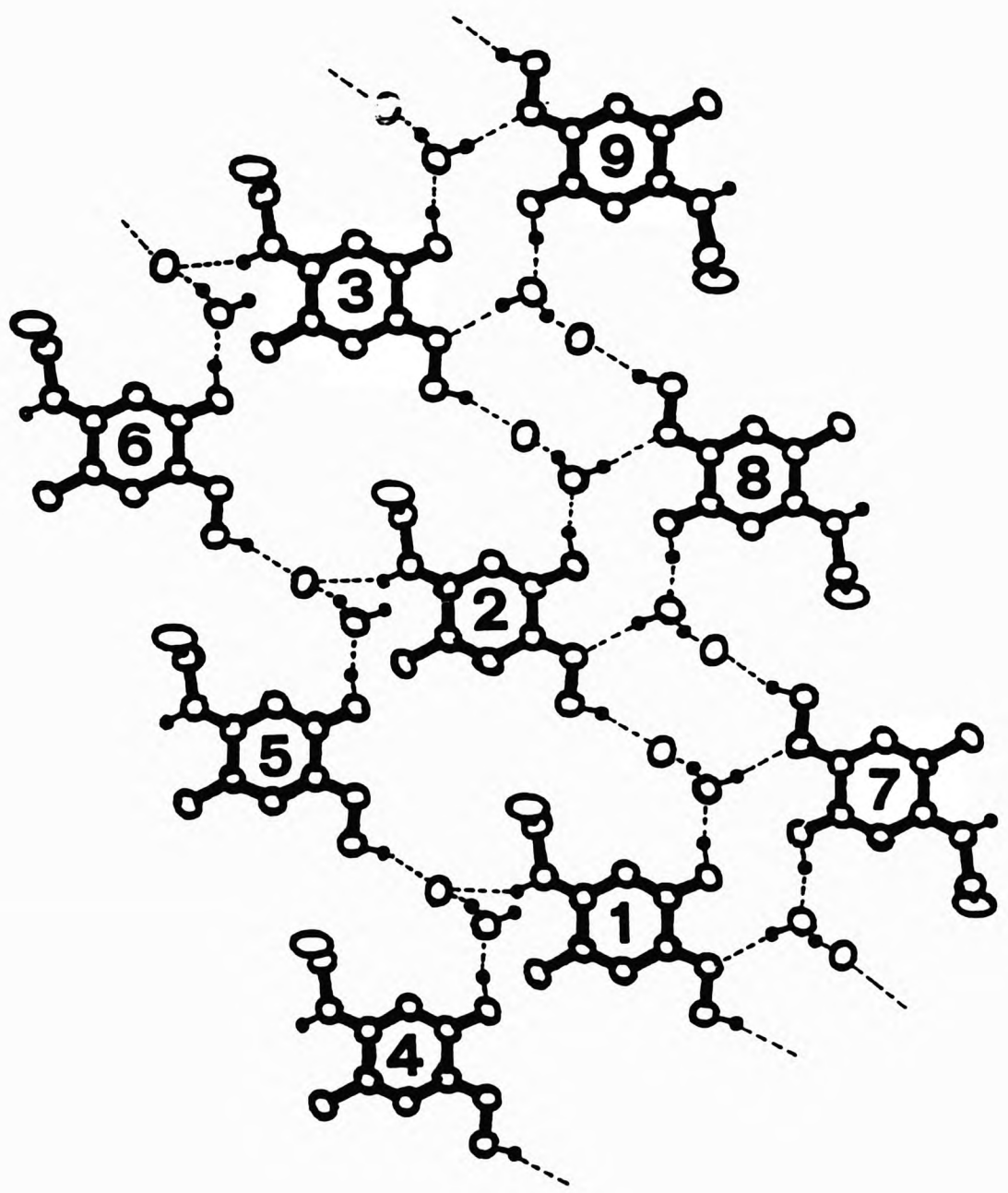
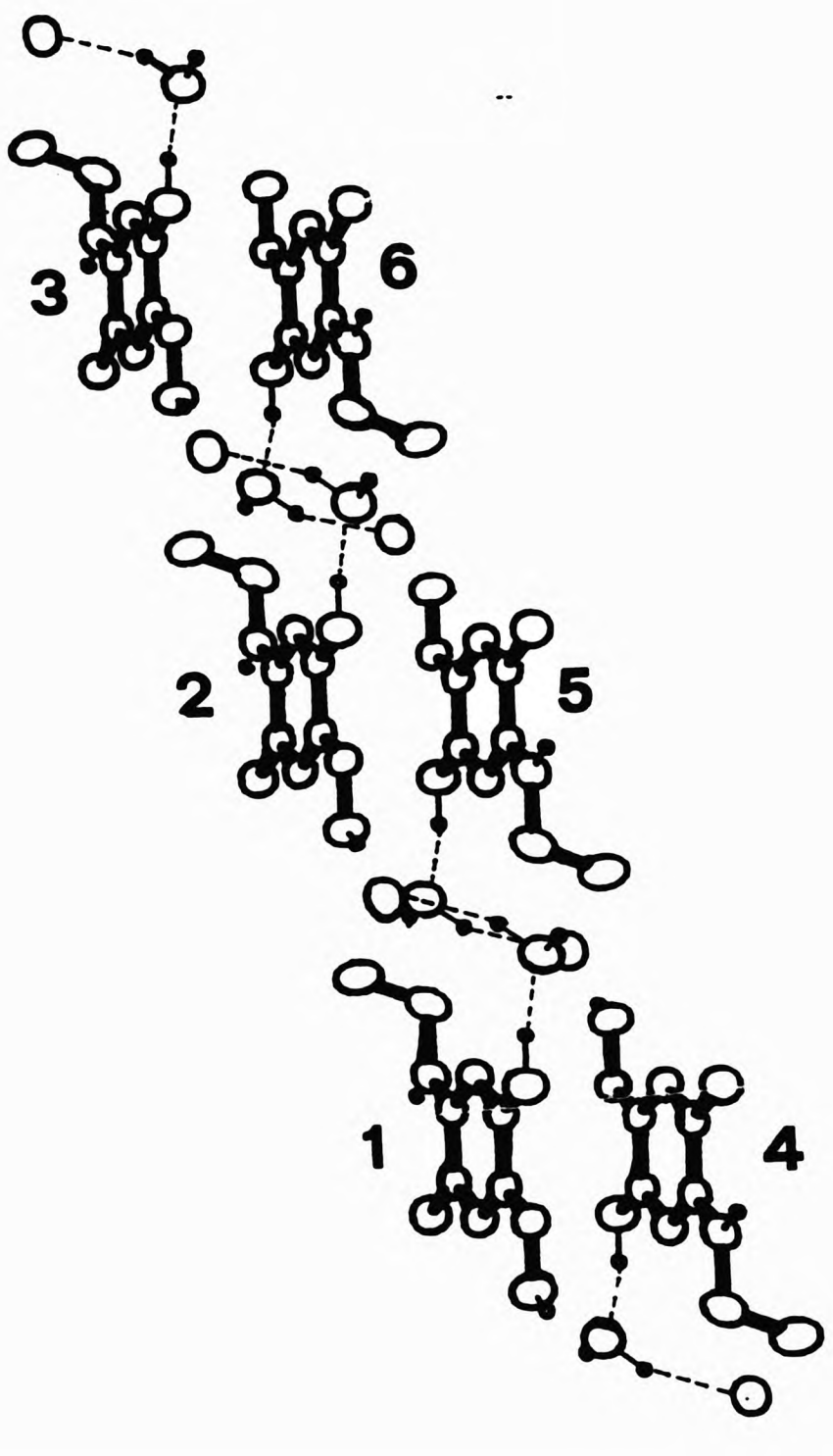


Figure 2.21 *Stacking interactions between the hexa-atomic rings in the crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate.*



2.8. *References.*

1. J. H. Ridd, *Quart. Rev.,* 1961, 15, 418.
2. B. C. Challis, S. A. Kyrtopoulos, *J. Chem. Soc. Perkin Trans.1,* 1979, 299.
3. T. Teshigawara, Jap. Pat. 13,918, 17 Jul. 1964.
   S. Oh, D. L. H. Williams, *J. Chem. Soc. Perkin Trans. 2,* 1991, 685.
4. D. L. H. Williams, 'Nitrosations', Cambridge University Press, Cambridge, UK, 1988.
5. N. S. Bayliss, R. Dingle, D. W. Watts, R. J. Wilkie, *Aust. J. Chem.,* 1963, 16, 933.
6. B. C. Challis, A. J. Lawson, *J. Chem. Soc. (B).,* 1971, 770.
7. R. T. Morrison, R. N. Boyd, 'Organic Chemistry', 3rd edn. Allyn and Bacon, Boston, 1973.
8. H. H. Hodgson, *J. Chem. Soc.,* 1931, 1494.
9. H. H. Hodgson, F. H. Moore, *J. Chem. Soc.,* 1923, 2499.
10. H. H. Hodgson, A. Kershaw, *J. Chem. Soc.,* 1929, 1553.
11. S. Veidel, *Ber.,* 1930, 63(B), 1577.
12. J. Charalambous, M. J. Fraser, F. B. Taylor, *J. Chem. Soc. A,* 1969, 2787.
13. G. Cronheim, *J. Org. Chem.,* 1947, 12, 1, 7, 20.
14. H. Barjesteh, Ph.D Thesis, 1991, University of North London.
15. H. Schmid, *Monatsh,* 85, 1950, 424.
16. J. C. Earl, N. G. Hills, *J. Chem. Soc.,* 1938, 1954.
17. L. Blangey, *Helv. Chim. Acta.,* 1938, 21, 1579, 60.
18. J. C. Earl, C. S. Ralph, *J. Chem. Soc.,* 1939, 1089.
19. D. L. H. Williams, *J. Chem. Soc. Perkin Trans. 2,* 1975, 655.
20. S. Patai, (ed) 'The Chemistry of Amino, Nitroso, and Nitro Compounds and Their Derivatives', J. Wiley & Sons, New York, 1982.

21. E. F. Elsager, D. F. Worth, *J. Med. Chem.*, 1970, 13, 3, 370.

22. M. L. Crossley, P. F. Driesbach, C. M. Hoffmann, R. P. Parker, *J. Am. Chem. Soc.*, 1952, 74, 573.

23. O. Fischer, E. Hepp, *Ber.*, 19, 2991.

24. I. Houben, *Ber.*, 1913, 46, 3984.

25. E. H. White, *J. Am. Chem. Soc.*, 1955, 77, 6008.

26. E. H. White, *J. Am. Chem. Soc.*, 1955, 77, 6011.

27. P. N. Magee, R. Montesano, R. Preussman, 'Chemical Carcinogens', (Edited by C. E. Searle), ACS Monograph 173, American Chemical Society, Washington D.C., 1976, pp. 491.

28. J. F. W. McOmie, 'Protective Groups in Organic Chemistry', Plenum Press, London, 1973.

29. D. H. Williams, I. Flemming, 'Spectroscopic Methods In Organic Chemistry', 4th edn., McGraw and Hill, London, 1987.

30. H. Hodgson, *J. Chem. Soc.*, 1937, 520.

31. H. Hodgson, *J. Chem. Soc.*, 1943, 84.

32. C. Romers, E. Fischmann, *Acta. Cryst.*, 1960, 13, 809.

33. E. Fischmann, C. Romers, A. J. H. Uman, *Acta. Cryst.*, 1960, 13, 885.

34. F. Heinrich, H. Eisenach, *J. Prakt. Chem.*, 1904, 70, 332.

35. G. W. R. Bartindale, M. M. Crowder, K. A. Morley, *Acta. Cryst.*, 1959, 12, 111.

36. C. Romers, *Acta. Cryst.*, 1964, 17, 1287.

37. P. C. Christidis, A. Dodd, N. D. Pathirana, J. Charalambous, M. Mcpartlin, N. Talee, *Acta. Cryst.*, 1991, C47, 2640.

38. A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge, A. R. Thompson, *J. Chem. Soc.*, 1955, 3727.

39. H. S. French, J. D. Perkin, *J. Am. Chem. Soc.*, 1937, 59, 1182.

40. D. Hadzi, *J. Chem. Soc.,* 1956, 2725.

41. R. K. Norris, S. Sternell, *Aust. J. Chem.,* 1966, 19, 841.

42. T. Shono, Y. Hayashi, K. Shinra, *Bull. Chem. Soc. Jpn.,* 1971, 44, 3179.

43. H. Jaffe, *J. Am. Chem. Soc.,* 1955, 77, 4440.

44. V. V. Ershov, G. A. Nikiforov, *Russian Chem. Rev.,* 1966, 35, 11, 823.

45. A. Fischer, R. M. Golding, W. C. Tennant, *J. Chem. Soc.,* 1965, 6032.

46. M. E. Knowles, J. Gilbert, D. J. McWeeny, *Biomed. Mass Spec.,* 1974, 286.

47. J. Charalambous, R. R. Fysh, C. G. Herbert, M. H. Johri, W. M. Shutie, *Org. Mass Spec.,* 15, 1980, 221.

48. I. Bolker, F. L. Kung, *Can. J. Chem.,* 1969, 47, 2109.

49. D. H. Williams, 'Principles of Organic Mass Spectra', McGraw & Hill, 1972.

50. G. Schroll, R. G. Cooks, P. Klemmensen, S. O. Lawesson, *Akriv. Kemi.,* 1967, 28, 413.

51. S. Meyerson, I. Puskas, E. K. Fields, *J. Am. Chem., Soc.,* 1966, 88, 4974.

52. J. C. A. Boyens, *J. Cryst. Mol. Struct.,* 1976, 6, 217.

53. H. Saarinen, J. Korvenranta, E. Naasakala, *Acta. Chem. Scand., Ser. A,* 1977, 31, 213.

54. H. Saarinen, J. Korvenranta, E. Naasakala, *Finn. Chem. Lett.,* 1977, 47.

55. J. W. L. Oijen, C. Romers, *Acta. Cryst.,* 1966, 20, 169.

56. B. A. Frenz and Associates Inc., *SDP Structure Determination Package,* College Station, Texas, USA, and Enraf-Nonius, Delft The

Netherlands, 1985.

57. A. C. T. North, D. C. Phillips, F. S. Matthews, *Acta. Cryst.*, A24, 1968, 351.

58. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq, M. M. Wolfson, MULTAN 80, *A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data,* Universities of York, England, and Louvain, Belgium, 1980.

59. W. H. Zachariasen, *Acta. Cryst.*, 1963, 16, 1139

60. *International Tables For X-ray crystallography,* Kynochn, Birmingham, England, 1974, vol.4, pp 99–101, and 149–150.

61. H. M. J. Bowers et. al. 'Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 11, Chemical Society.

62. O. Carugo, J. Charalambous, I. Ekcan, Unpublished results.

CHAPTER THREE

CHAPTER 3

Copper (II) and Nickel(II) Complexes of 5-Acylamino and 5-Alkylamino-1,2-benzoquinone-2-oximes.

3.1. Introduction

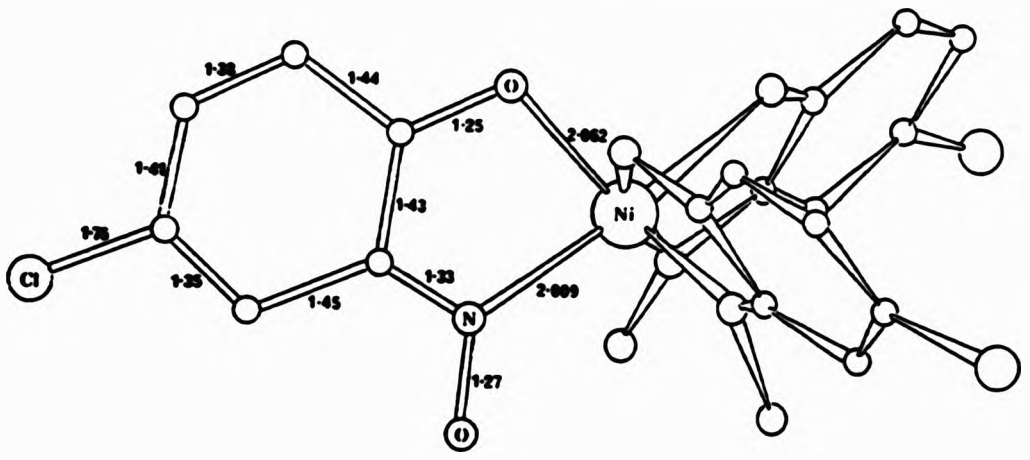
The coordination chemistries of copper and nickel are extensive and are dominated by the divalent ions Cu(II) and Ni(II) though compounds of monovalent copper are widely encountered. Both Cu(II) and Ni(II) form complexes with N and O donor ligands giving either 4, 5, or 6 coordinate complexes. In the case of nickel(II), these complexes generally have square-planar, tetrahedral, square pyramidal or octahedral geometries. For copper(II) however, such regular geometries are not often encountered because of the operation of the Jahn-Teller effect. The latter generally distorts these geometries, particularly the octahedral.[1,2]

Both Cu(II) and Ni(II) readily form thermodynamically and kinetically stable chelate complexes. To date several such compounds formed with the bidentate 1,2-quinone monooximes have been reported.[3-7] These compounds all of which are usually stable, highly coloured materials, have been of much interest because of their usefulness in analysis[8] and organic synthesis.[9]

As discussed in Chapter 1 of this thesis, most transition metal 1,2-quinone monooximates are of the type $M(qo)_n$. X-ray crystal structure analysis reported thus far[10] have shown all copper(II) and nickel(II) complexes of this type to involve 5-membered chelate rings in which the metal is coordinated to the ligand via the oximic nitrogen and quinoid

oxygen (eg. Fig. 3.1).

Figure 3.1.



Despite the wide interest in copper(II) and nickel(II) complexes of various 1,2-quinone monooximes, none of the complexes reported to date involved acylamino or alkylamino substituted ligands except for the bis(5-dimethylamino-1,2-benzoquinone-2-oximato)metal(II) complexes[11], and the recently reported bis(5-acetylamino-1,2-benzoquinone-2-oximato)-copper(II) and nickel(II).[12]

Since the introduction of a new substituent into an organic ligand is known to sometimes markedly affect its behaviour,[13-16] this study sought to ascertain the influence of acylamino and alkylamino groups on the chemistry of 1,2-quinone monooximes and their metal complexes. The interest in the metal complexes surrounds the basicity of the amino NH group which raises the possibility of (i) variation in the mode of attachment of the ligand to the metal through resonance (Fig.

3.2), and (ii) chelate formation by the usually unreactive 1,4-isomers through donation of the lone pair on the acylamino or alkylamino nitrogen (Fig. 3.3).

Additionally, the presence of the basic alkylamino substitutents in some of the ligands was thought capable of determining the sensitivity of the complexes to pH changes. Specifically, the protonation of the amino group in acid solution or its deprotonation in alkaline solution were thought capable of altering the strength and/or nature of the metal-ligand bond.

Already, the possible contribution of a 2,5-oxime imino structure to the chemistry of the alkylamino substituted 1,2-quinone monooximes has been supported by X-ray crystal data analysis (see Chapter 2, Section 2.7), and their stabilty in acid media is implied by their synthesis in the presence of concentrated mineral acids.

Figure 3.2.

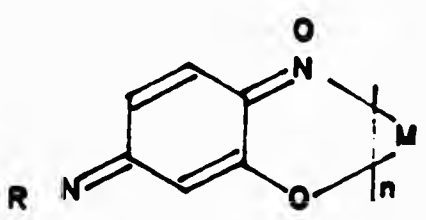
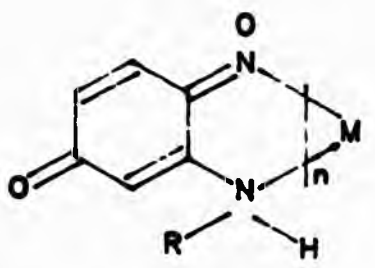


Figure 3.3.

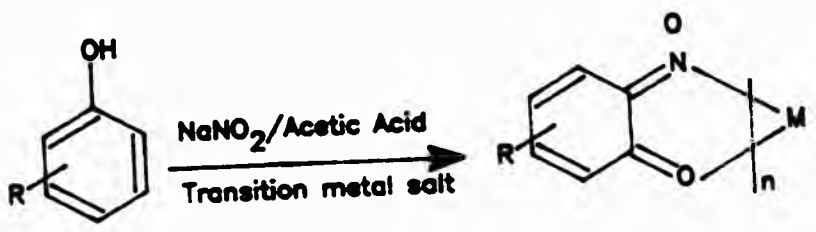


Another attraction of acylamino and alkylamino substituted 1,2-quinone monooximates is the synthetic possibilities presented by the presence of the relatively labile NH proton in these molecules.

In this work therefore, the synthesis and characterisation of a series of copper(II) and nickel(II) complexes of 5-acylamino and 5-alkylamino substituted 1,2-benzoquinone-2-oximes has been studied and

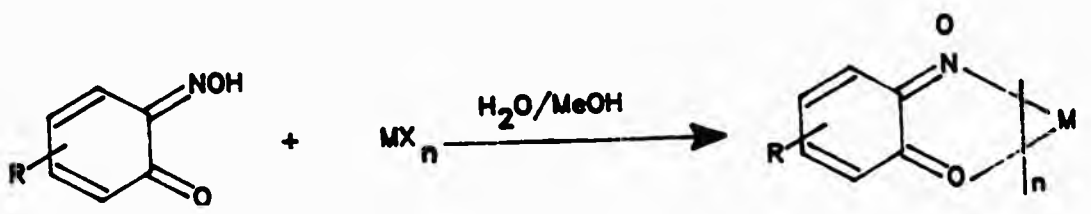
the results are presented in this chapter. Two synthetic routes, both of which have been widely used in the synthesis of related compounds were investigated. The first involved the nitrosation of an appropriate phenol in the presence of hydrated copper(II) or nickel(II) chloride (Reaction 3.1).[17-19]

Reaction 3.1



The second route was the reaction of methanolic solutions of the relevant 1,2-quinone monooxime with the aqueous metal salt (Reaction 3.2).[20-24]

Reaction 3.2.



3.2 Synthesis and Characterisation of Copper(II) and Nickel(II) Complexes of 5-Acylamino and 5-Alkylamino-1,2-benzoquinone-2-oximes.

Nitrosation of the 3-acylaminophenols with sodium nitrite/acetic acid in the presence of copper(II) chloride dihydrate gave brown multicomponent solids. Separation of these mixtures by Soxhlet extraction with ethylacetate or dichloromethane gave the dark brown bis(5-acylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrates as the residues and in high yields. Concentration of the extracts gave the corresponding yellow 3-acylamino-1,4-benzoquinone-4-oxime.

Similarly, nitrosation of the 3-acylaminophenols in the presence of nickel(II) chloride hexahydrate gave orange solids. Soxhlet extraction of the latter with ethylacetate or dichloromethane afforded pure orange bis(5-acylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrates in good yields as well as small amounts of the 3-acylamino-1,4-benzoquinone-4-oximes.

By contrast to their acylamino analogues, the nitrosation of the 3-alkylaminophenols with sodium nitrite/acetic acid in the presence of copper(II) or nickel(II) chloride afforded orange-brown multicomponent solids from which the bis(5-alkylamino-1,2-benzoquinone-2-oximato)-copper(II) monohydrates or bis(5-alkylamino-1,2-benzoquinone-2-oximato)-nickel(II) dihydrates were recovered in poor yields again by Soxhlet extraction. For reasons discussed in Chapter 2, the diethyl ether and dichloromethane extracts were thought to contain N-nitroso compounds and therefore were not investigated further.

Both the hydrated acylamino and alkylamino complexes were recovered in almost quantitative yield when methanolic solutions of the free substituted 1,2-quinone monooximes were reacted with aqueous

copper(II) or nickel(II) chloride.

The anhydrous complexes were obtained from the corresponding hydrates by macroscale pyrolysis at temperatures between 90 and 140 ^{0}C and at a pressure of 0.1 mmHg.

Although transition metal 1,2-quinone monooximates are known to undergo several kinds of reactions with Lewis bases,[25-27] the complexes prepared during this study only gave adducts of the type $Cu(qo)_2.py$, $Ni(qo)_2.py_2$ and $M(qo)_2.dipy$ on reaction with pyridine and 2,2-dipyridyl respectively.

The isolation of only 1:1 adducts of the acylamino substituted copper(II) complexes with pyridine, agrees with previous results for related compounds.[3-5,28] Interestingly however, this is in direct contrast to the results obtained with the 5-acetylamino analogue for which a bis-pyridine adduct has been reported.[12]

Usually the formation of 2:1 adducts of the type $CuL_2(py)_2$ (where L is a bidentate ligand) which requires the copper(II) ion to be six coordinate and octahedral, is only observed in the presence of strongly electron withdrawing ligands like hexafluoroacetylacetonate.[29,30] The isolation therefore, of a bis-pyridine adduct of bis(5-acetylamino-1,2-benzoquinone-2-oximato)copper(II) may be accounted for in terms of the electron withdrawing effects of the acetylamino group in the ligand. The failure of the heavier homologues to form bis-pyridine adducts could arguably be due to their relatively lower electron withdrawing potential.

Both the complexes and Lewis base adducts reported here decomposed on heating at temperatures between 190 ^{0}C and 300 ^{0}C. As might be expected, the compounds showed varying degrees of solubility in common organic solvents as the size and nature of the substituent

changes. Thus, bis(5-propionylamino-1,2-benzoquinone-2-oximato)-nickel(II) hexahydrate was found to be soluble in methanol, acetone and tetrahydrofuran but insoluble in diethyl ether and dichloromethane. By comparison, bis(5-heptanoylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrate was very soluble in acetone, methanol and tetrahydrofuran, and sparingly soluble in diethyl ether and dichloromethane. All the complexes are readily soluble in dimethyl sulphoxide.

3.3 Structural Studies of Bis(5-acylamino)- and Bis(5-alkylamino-1,2-benzoquinone-2-oximato)metal(II) Complexes and their Lewis Base Adducts.

The complexes and 3-acylamino-1,4-benzoquinone-4-oximes isolated from the nitrosation of the 3-acylaminophenols in the presence of copper(II) and nickel(II) chloride were characterised by elemental analysis, IR and NMR spectroscopy (where applicable) as well as mass spectrometry and magnetic measurements. On the basis of elemental analysis, the complexes were formulated as $M(qo)_2.nL$ (n = 0 - 6; L = H_2O). Similarly, the pyridine and 2,2-dipyridyl adducts were formulated as $M(qo)_2.(py)_n$ and $M(qo)_2.(dipy)$ (M = Ni, n = 2; M = Cu, n = 1).

Thermal gravimetric analysis of $M(qo)_2.nH_2O$ (Table 3.1), showed gradual and quantative loss of water at temperatures between 90 and 140 ^0C, followed by decomposition of the parent complexes $M(qo)_2$. Similarly, t.g.a. of $Cu(qo)_2.py$ (Table 3.2) showed quantitative loss of one mole of pyridine per mole of complex at temperatures below 200 ^0C again followed by decomposition of the parent complexes. By contrast, t.g.a. of $Niqo)_2.py_2$ and $M(qo)_2.dipy$ (Table 3.2) showed no loss of ligands, the compounds decomposing in a single step at temperatures between 190 and

300 ^{0}C.

Table 3.1 *Thermal gravimetric analytical data for $M(qo)_2.xH_2O$ (M = Cu, Ni; x = 1 - 6).*

Compound	*Weight of sample (mg)*	$T^{a,b}$ *(^{0}C)*	*Weight loss (mg)*		*Decomposition temperature (^{0}C) of $M(qo)_2$*
			Found	*Calc^{c}*	
$Cu(5\text{-}Buqo)_2.2H_2O$	119	90 - 120	8	8	230 - 235
$Cu(5\text{-}Hpqo)_2.2H_2O$	114	100 - 110	7	7	230 - 238
$Cu(5\text{-}Hxqo)_2.H_2O$	120	120 - 130	4	4	215 - 220
$Cu(5\text{-}Hptqo)_2.H_2O$	112	110 - 120	4	4	200 - 205
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2.H_2O$	116	115 - 130	5	5	220 - 225
$Ni(5\text{-}Prqo)_2.6H_2O$	128	100 - 120	25	23	240 - 245
$Ni(5\text{-}Buqo)_2.6H_2O$	106	105 - 130	20	18	250 - 253
$Ni(5\text{-}Peqo)_2.4H_2O$	86	110 - 140	11	11	232 - 240
$Ni(5\text{-}Hpqo)_2.4H_2O$	105	110 - 130	9	8	240 - 245
$Ni(5\text{-}Hxqo)_2.2H_2O$	120	110 - 130	12	12	250 - 253
$Ni(5\text{-}Hptqo)_2.2H_2O$	117	115 - 120	9	9	250 - 253
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2.2H_2O$	123	90 - 120	27	25	230 - 235

a = Temperature of the loss of water

b = Maxima on the rate of weight loss against temperature curve

c = Calculated for the loss of water

Table 3.2. *Thermal gravimetric analytical data for $M(qo)_2.(py)_n$, and $M(qo)_2.(dipy)$ (M = Cu, Ni; n = 1, 2).*

Compound	Weight of sample (mg)	$T^{a,b}$ (°C)	Weight loss (mg) Found	Weight loss (mg) Calc[c]	Decomposition temperature (°C) of $M(qo)_2$
$Cu(5\text{-}Buqo)_2(py)$	109	130 - 150	15	15	240 - 243
$Cu(5\text{-}Hpqo)_2(py)$	113	120 - 140	14	14	220 - 225
$Cu(5\text{-}Hxqo)_2(py)$	121	130 - 140	17	16	240 - 245
$Cu(5\text{-}Hptqo)_2(py)$	99	120 - 150	13	13	250 - 255
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2(py)$	114	130 - 160	18	18	250 - 258
$Cu(5\text{-}Buqo)_2(dipy)$	120	-	-	-	250 - 255
$Ni(5\text{-}Prqo)_2(py)_2$	109	-	-	-	240 - 245
$Ni(5\text{-}Buqo)_2(py)_2$	122	-	-	-	240 - 243
$Ni(5\text{-}Peqo)_2(py)_2$	107	-	-	-	235 - 240
$Ni(5\text{-}Hpqo)_2(py)_2$	111	-	-	-	230 - 236
$Ni(5\text{-}Hxqo)_2(py)_2$	122	-	-	-	240 - 245
$Ni(5\text{-}Hptqo)_2(py)_2$	110	-	-	-	250 - 255
$Ni(5\text{-}Et\text{-}4Meqo)_2(py)_2$	121	-	-	-	250 - 255
$Ni(5\text{-}Buqo)_2(dipy)$	110	-	-	-	230 - 240
$Ni(5\text{-}Hptqo)_2(dipy)$	113	-	-	-	250 - 260
$Ni(5\text{-}Et\text{-}4Meqo)_2(dipy)$	122	-	-	-	250 - 260

a = Temperature of the loss of pyridine

b = Maxima on the rate of weight loss against temperature curve

c = Calculated for the loss of pyridine

The IR spectra of the hydrated complexes (eg. Fig. 3.4) contained prominent bands between 3500 cm^{-1} and 3400 cm^{-1} assignable to νOH of the associated water molecules and νNH of the acylamino or alkylamino groups respectively.

The formulation of the ligands in these complexes as quinone monooximic was supported by the presence of strong bands in the carbonyl region of the spectra (Table 3.3). In the case of the acylamino substituted complexes, two strong bands between 1715 cm^{-1} and 1620 cm^{-1} assignable to the amido νCO and to the quinoid νCO respectively, were present. The quinoid νCO of the alkylamino substituted complexes occurred at about 1623 cm^{-1}. The position of these bands is typical of 1,2-quinone monooximic complexes in which the quinoid carbonyl is involved in binding the metal. The IR spectra of the pyridine and 2,2-dipyridyl adducts had the same general characteristics as that of the hydrated complexes.

By comparison with the hydrated complexes and Lewis base adducts, the quinoid νCO of the anhydrous complexes occurred at considerably lower frequency in the IR spectra (eg. Fig. 3.5). The quinoid νCO bands occurred at between 1605 cm^{-1} and 1602 cm^{-1} for the acylamino substituted complexes, and between 1610 cm^{-1} and 1605 cm^{-1} for their alkylamino analogues (Table 3.4).

This marked lowering of the quinoid νCO stretching frequency in the anhydrous complexes relative to both the free ligands (see Chapter 2) the hydrates and Lewis base adducts, is indicative of decreased double bond character of this group. The latter may be attributed to the greater interaction of the quinoid carbonyl moiety with the metal on dehydration, and to its possible involvement in intermolecular bonding.

Figure 3.4. *IR spectrum of* $Ni(5\text{-}Peqo)_2.6H_2O$.

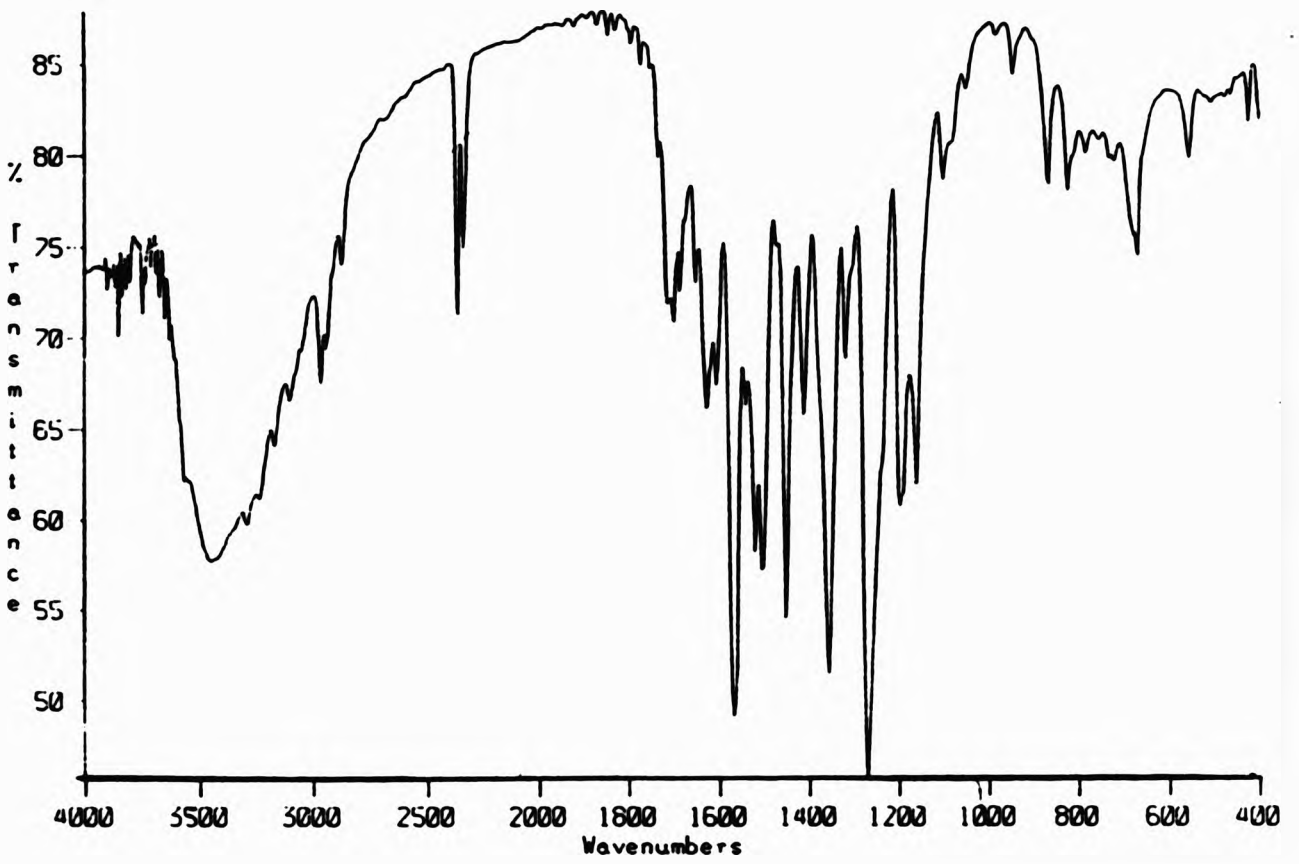


Figure 3.5 *IR spectrum of* $Cu(5\text{-}Hxqo)_2$

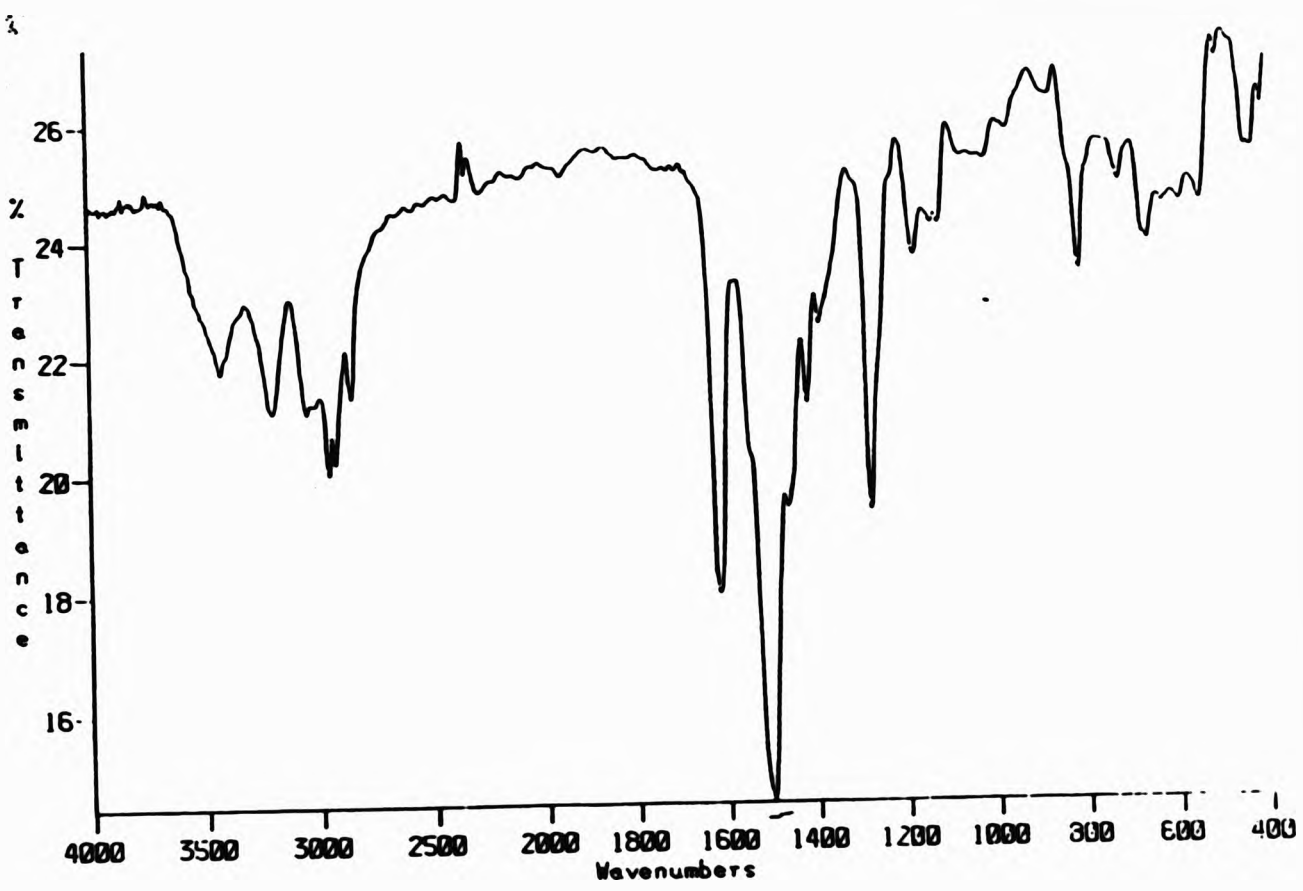


Table 3.3 *Selected IR bands and their assignment for* $M(qo)_2.nH_2O$ *(M = Cu and Ni; n = 1 – 6).*

Complex	νOH /cm^{-1}	νNH /cm^{-1}	νCO_{amido} /cm^{-1}	$\nu CO_{quinoid}$ /cm^{-1}
$Cu(5\text{-}Buqo)_2.2H_2O$	3413	3280	1710	1623
$Cu(5\text{-}Hpqo)_2.2H_2O$	3428	3249	1708	1621
$Cu(5\text{-}Hxqo)_2.H_2O$	3418	3256	–	1622
$Cu(5\text{-}Hptqo)_2.H_2O$	3394	3246	–	1623
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2.H_2O$	3411	3217	–	1623
$Ni(5\text{-}Prqo)_2.6H_2O$	3551	3243	1717	1626
$Ni(5\text{-}Buqo)_2.6H_2O$	3556	3200	1711	1626
$Ni(5\text{-}Peqo)_2.4H_2O$	3564	3245	1711	1626
$Ni(5\text{-}Hpqo)_2.4H_2O$	3560	3248	1709	1624
$Ni(5\text{-}Hxqo)_2.2H_2O$	3418	3256	–	1622
$Ni(5\text{-}Hptqo)_2.2H_2O$	3394	3246	–	1623
$Ni(5\text{-}Et\text{-}4Meqo)_2.2H_2O$	3411	3217	–	1623

Table 3.4 *Selected IR bands and their assignment for* $M(qo)_2$ *(M = Cu, Ni).*

Complex	νOH /cm^{-1}	νNH /cm^{-1}	νCO_{amido} /cm^{-1}	$\nu CO_{quinoid}$ /cm^{-1}
$Cu(5\text{-}Buqo)_2$	–	3260	1690	1602
$Cu(5\text{-}Hpqo)_2$	–	3218	1688	1605
$Cu(5\text{-}Hxqo)_2$	–	3209	–	1612
$Cu(5\text{-}Hptqo)_2$	–	3220	–	1609
$Cu(5\text{-}Et\text{-}4Meqo)_2$	–	3227	–	1613
$Ni(5\text{-}Prqo)_2$	–	3218	1696	1602
$Ni(5\text{-}Buqo)_2$	–	3227	1687	1603
$Ni(5\text{-}Peqo)_2$	–	3228	1685	1602
$Ni(5\text{-}Hpqo)_2$	–	3203	1689	1603
$Ni(5\text{-}Hxqo)_2$	–	3209	–	1612
$Ni(5\text{-}Hptqo)_2$	–	3220	–	1609
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2$	–	3227	–	1613

The observed room temperature magnetic moment of the hydrates, pyridine and 2,2-dipyridyl adducts (Table 3.5), ranged from $1.79_{\mu B}$ to $2.03_{\mu B}$ for the copper(II) complexes, and from $2.87_{\mu B}$ to $3.21_{\mu B}$ for the nickel(II) complexes. These values which approximate the spin only magnetic moment for Cu(II) and Ni(II), and which agree with that reported for related complexes,[31-33] suggest that the compounds are all magnetically dilute and therefore monomeric in the solid state.[34]

By contrast, the observed room temperature magnetic moments for

the anhydrous complexes (Table 3.6) ranged from $0.99_{\mu B}$ to $1.21_{\mu B}$ for the copper(II) complexes and from $1.08_{\mu B}$ to $1.38_{\mu B}$ for the nickel(II) analogues. This lowering of the magnetic moment on dehydration suggests that the water molecules were involved in direct coordination to the metal ion in the hydrated complexes.

Subnormal magnetic moments as those found for the anhydrous complexes prepared during this study have been observed previously for related compounds. The phenomenon has been accounted for in terms of association and antiferromagnetic metal-metal interaction.[35] Thus, it has been suggested that this association is brought about by the sharing of the donor pair on the quinoid oxygen of one ligand between two neighbouring metal ions.[36] In the anhydrous complexes therefore, the quinone monooximic moiety is behaving both as a chelating and a bridging ligand resulting in the formation of an oligomeric species (Fig. 3.6).

A similar kind of interaction has been observed in Schiff base complexes of copper(II) and nickel(II), as well as bis(dimethyl-glyoximato)copper(II). In these cases, dimeric species formed by the sharing of oxygen atoms were found.[37,38]

Support for the involvement of the quinoid carbonyl group in intermolecular association was evident from the marked lowering of the quinoid νCO band in the IR spectra of the anhydrous complexes compared to both the free ligands and the hydrated complexes. Confirmation of association in the anhydrous complexes was afforded by the presence of species corresponding to $[M_2L_2]^{+\cdot}$ and $[M_2L_3]^{+}$ in their LSIMS mass spectra (see Section 3.4).

Figure 3.6

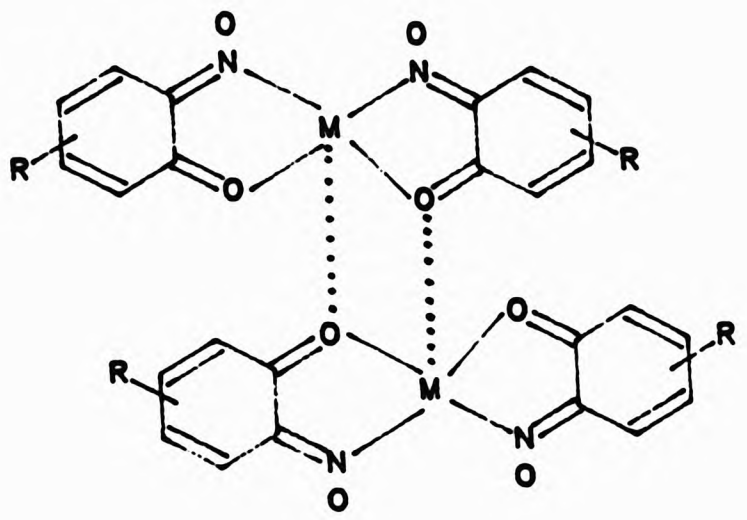


Table 3.5 *Room temperature magnetic moments of* $M(qo)_2.xH_2O$, $M(qO)_2.py_n$ *and* $M(qo)_2.dipy$

Complex	μ_{eff}
$Cu(5\text{-}Buqo)_2.2H_2O$	1.79
$Cu(5\text{-}Hpqo)_2.2H_2O$	1.86
$Cu(5\text{-}Hxqo)_2.H_2O$	1.93
$Cu(5\text{-}Hptqo)_2.H_2O$	2.01
$Cu(5\text{-}Et\text{-}4Meqo)_2.H_2O$	1.88
$Ni(5\text{-}Prqo)_2.6H_2O$	3.03
$Ni(5\text{-}Buqo)_2.6H_2O$	3.06
$Ni(5\text{-}Peqo)_2.4H_2O$	2.97
$Ni(5\text{-}Hpqo)_2.4H_2O$	2.92
$Ni(5\text{-}Hxqo)_2.2H_2O$	3.21
$Ni(5\text{-}Hptqo)_2.2H_2O$	2.87
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2.2H_2O$	3.08
$Cu(5\text{-}Buqo)_2(py)$	1.84
$Cu(5\text{-}Hpqo)_2(py)$	2.08
$Cu(5\text{-}Hxqo)_2(py)$	2.03
$Cu(5\text{-}Hptqo)_2(py)$	1.93
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2(py)$	1.86
$Cu(5\text{-}Buqo)_2(dipy)$	1.95
$Ni(5\text{-}Prqo)_2(py)_2$	3.03
$Ni(5\text{-}Buqo)_2(py)_2$	3.11
$Ni(5\text{-}Peqo)_2(py)_2$	2.97
$Ni(5\text{-}Hpqo)_2(py)_2$	3.05
$Ni(5\text{-}Hxqo)_2(py)_2$	3.13

Table 3.5 *cont'd...*

$Ni(5\text{-}Hptqo)_2(py)_2$	2.88
$Ni(5\text{-}Et\text{-}4Meqo)_2(py)_2$	3.15
$Ni(5\text{-}Buqo)_2(dipy)$	3.10
$Ni(5\text{-}Hptqo)_2(dipy)$	3.18
$Ni(5\text{-}Et\text{-}4Meqo)_2(dipy)$	3.08

Table 3.6 *Room temperature magnetic moments of* $M(qo)_2$

Complex	μ_{eff}
$Cu(5\text{-}Buqo)_2$	1.01
$Cu(5\text{-}Hpqo)_2$	1.01
$Cu(5\text{-}Hxqo)_2$	0.99
$Cu(5\text{-}Hptqo)_2$	1.21
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2$	1.08
$Ni(5\text{-}Prqo)_2$	1.38
$Ni(5\text{-}Buqo)_2$	1.29
$Ni(5\text{-}Peqo)_2$	1.11
$Ni(5\text{-}Hpqo)_2$	1.15
$Ni(5\text{-}Hxqo)_2$	1.08
$Ni(5\text{-}Hptqo)_2$	1.10
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2$	1.21

The intense colour of transition metal 1,2-quinone monooximates has made them amenable to solution electronic spectral studies. However, in most cases, particularly those involving first row transition metal ions, little structural information can be derived from the spectra. The latter are usually characterised by intense ligand charge-transfer absorption bands which originate in the UV region and tail into the visible. These bands tend to mask any d-d transition making their unambiguous assignment difficult.[39]

Because of the great difficulty of isolating free 1,2-quinone monooximes, (except the naphthoquinone monooximes), it has not been found possible until now, to compare the solution electronic spectra of many free ligands and their metal complexes. In this work however, the successful isolation of the free ligands has made such a comparison possible.

Thus, the solution electronic spectra in methanol of the hydrated complexes, the Lewis base adducts, and the free ligands were recorded. As for previously reported complexes of this type, the UV spectra of the complexes and adducts were largely dominated by ligand charge transfer absorption bands, though in the case of the nickel(II) complexes, (eg. Fig. 3.7) they also contained absorption bands expected for an octahedrally coordinated nickel(II) ion.[40,41] At low concentrations, only two of the three bands are apparent and they were assigned as follows;

ν_3 = 464 nm = 26596 cm^{-1} $\quad {}^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$

ν_2 = 376 nm = 20619 cm^{-1} $\quad {}^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$

At high concentrations, the third allowed transition for the octahedral Ni(II) ion and which corresponds to 10Dq was observed. This band was assigned to ν_1 = 888 nm = 11111 cm^{-1} $\quad {}^3T_{2g}(F) \longleftarrow {}^3A_{2g}(F)$. All

the bands had high extinction coefficients (Table 3.7).

For the copper(II) complexes, no unambiguous assignment of the observed bands was possible since, as is commonly the case, the allowed d-d transitions were masked by intense ligand charge transfer bands. (eg. Fig 3.8). The observed band were relatively broad and had high extinction coefficients (Table 3.7).

Considerable blue or hypsochromic shifts in the ligand field of the complexes, relative to that of the free ligands were observed (Fig. 3.9). These shifts are consistent with the presence of strong metal-ligand interactions and the involvement of the quinoid carbonyl group in binding the metal.[43]

Figure 3.7. *UV/Vis spectrum of* $Ni(5\text{-}Peqo)_2.6H_2O$.

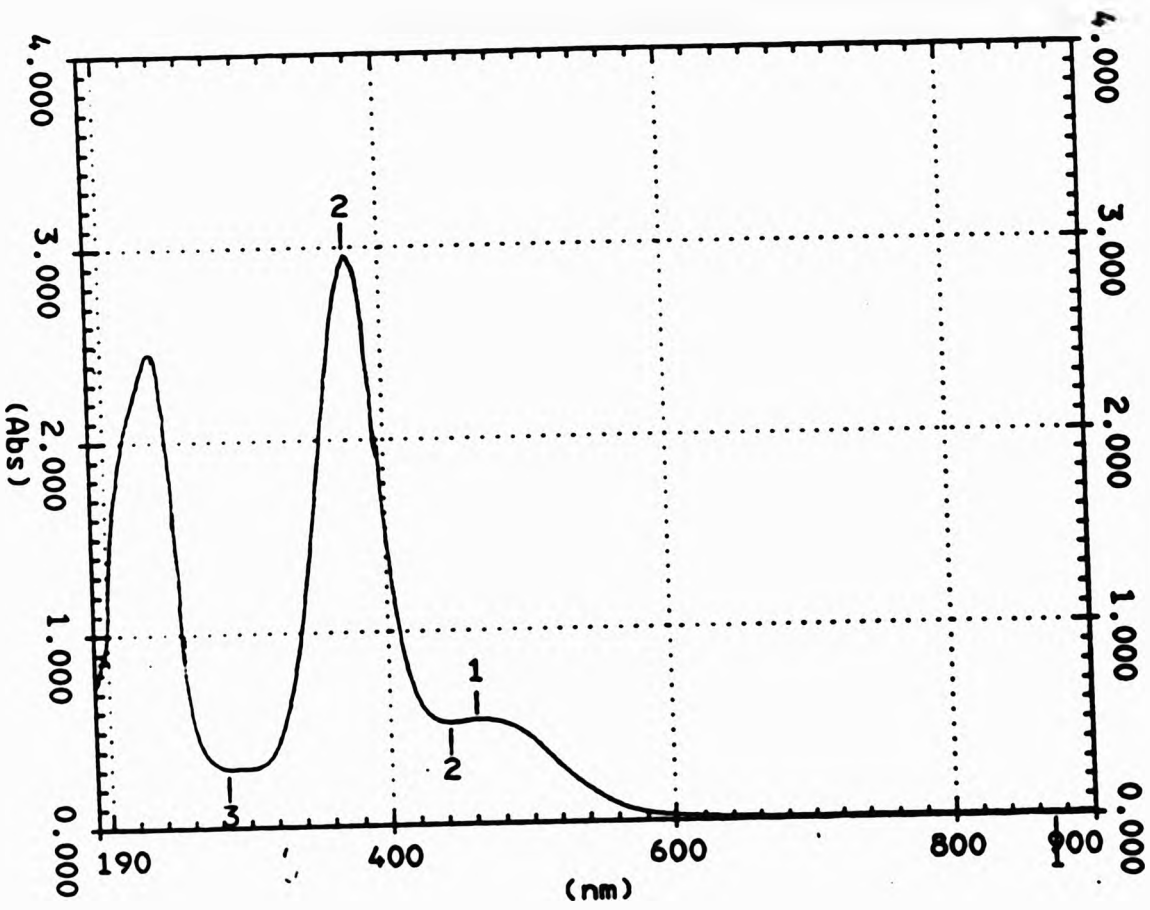


Figure 3.8 *UV/Vis spectrum of* $Cu(5\text{-}Buqo)_2.2H_2O$.

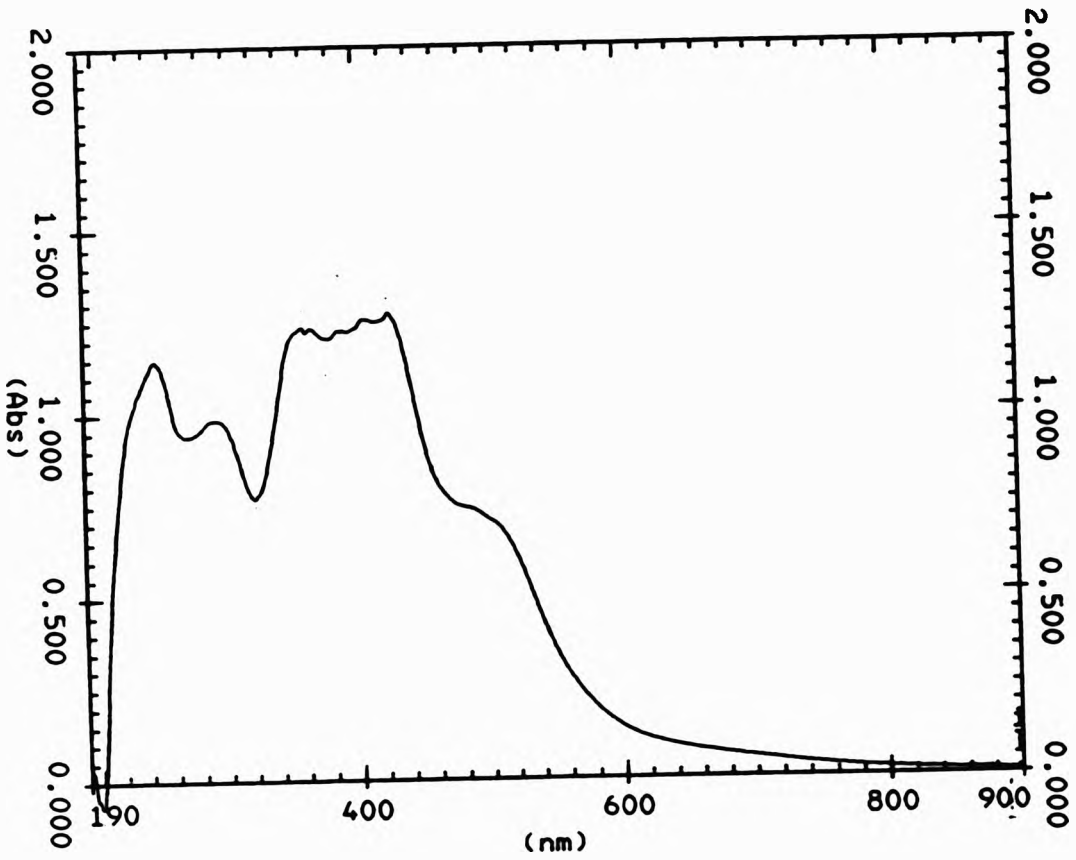


Figure 3.9 *UV/Vis spectra of* $Ni(5\text{-}Hxqo)_2.2H_2O$ *and 5-HxqoH.*

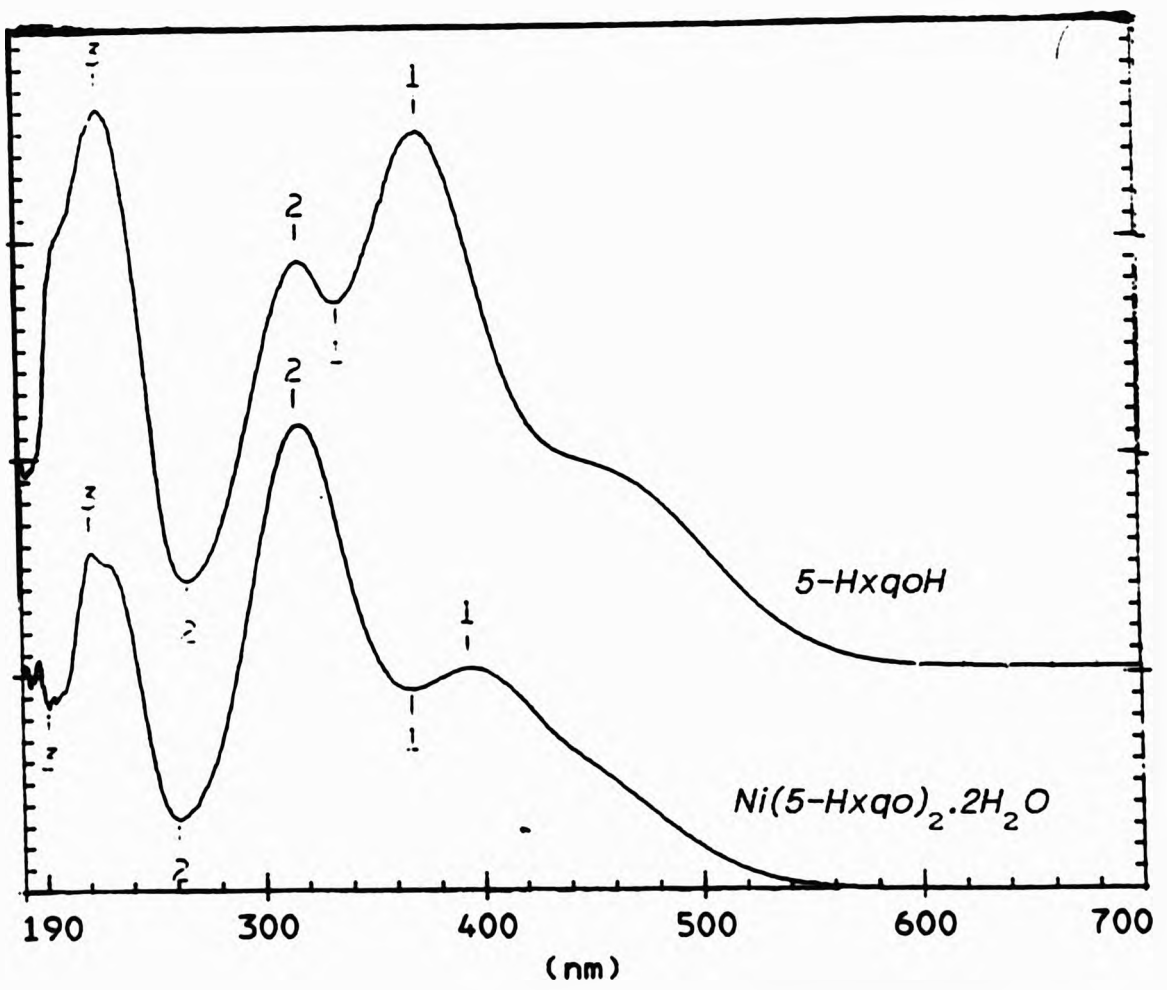


Table 3.7. *Solution electronic spectral data for 5-Rqoh, $M(5\text{-}Rqo)_2$, and $M(5\text{-}Rqo)_2.nH_2O$.*

Compound (concentration /mol dm^{-3})	λ_{max} /nm	ε /mol^{-1} m^2
5-PeqoH	358	1169
(3.082 mol dm^{-3})	248	567
	216	1057
$Ni(5\text{-}Peqo)_2.4H_2O$	464	4377
(9.808 mol dm^{-3})	376	2170
	235	1160
	196	598
(8.010 mol dm^{-3})	888	11
$Ni(5\text{-}Hxqo)_2$	470	390
(5.053 mol dm^{-3})	374	2486
	319	2108
	228	1205
(8.91 mol dm^{-3})	890	12
$Cu(5\text{-}Buqo)_2$	490	375
(9.530 mol dm^{-3})	391	2011
	276	533
	235	1614

3.4. Mass Spectral Studies of Copper(II) and Nickel(II) 1,2–Quinone Monooximates.

IR and magnetic moment data for the complexes and adducts prepared during this study point towards monomeric structures for the compounds $M(qo)_2.nH_2O$, and $M(qo)_2.nL$. By contrast, these studies suggest that for the anhydrous complexes $M(qo)_2$, there is association in the solid state leading to the formation of oligomeric species.

In order to confirm these proposals, mass spectral analysis of the complexes and adducts was undertaken. Primarily, the identification and assignment of metal containing ions which is facilitated by the characteristic isotopic pattern of the metal, was the parameter used. This study was also extended to related compounds with a view to assessing the generality of the observations made regarding the association of metal 1,2–quinone monooximates in the solid state.

The mass spectra of some metal 1,2–quinone monooximates have been reported previously.[5] These spectra were obtained by electron impact using an ionizing voltage of 70 eV. At such high voltages extensive fragmentation of the complexes resulted. Interestingly, the spectra so obtained, showed the complexes to exist at least in part as dimers in the vapour state. However, the high operating temperatures at which EI experiments are conducted and which allow for many thermal reactions meant the dimeric species were of very low abundance.

In this study, a less energetic means of sample ionization was used to obtain the spectra of the subject complexes. Liquid secondary ion mass spectrometry or LSIMS is a relatively new technique which is reputed to be best suited for recording the mass spectra of compounds which are difficult to vapourize or which may decompose on

vapourization.[44,45] In this technique, an ion beam (primary ion source) is used to bombard the sample in solution (viscous liquid matrix). This bombardment results in the sputtering of or ejection of such secondary species as ions, atoms, molecules, electrons and photons from the surface of the bulk sample. Some of these ejected species are ammenable to detection by a mass spectrometer and it is the analysis of these species which forms the basis of SIMS.

Usually, but not always, the use of an organic liquid solvent for example glycerol, as a matrix, is necessary to enhance spectra recording.[46] Therefore, the solubility of the sample in the chosen matrix and the conductivity of the latter are important. During this study, glycerol or 2-nitrobenzylalcohol were used as the matrix and the primary ion source was a cesium ion gun.

Because LSIMS involves the use of less a energetic means of ionization, (< 20 eV), the extensive fragmentation observed in electron impact experiments is not usually a problem. Typically in LSIMS spectra therefore, molecular weight information is retained and the molecular ion $[P]^{+\cdot}$ or an ion corresponding to $[P + 1]^{+}$ is the base peak.*

* [P] is used here in place of [M] to represent the molecular ion so as not to be confused with the use of M for the metal ion.

Except in the case bis(5-propionylamino-1,2-benzoquinone-2-oximato)nickel(II) for which the base peak corresponded to a species $[ML_2 + 23]^{+}$, the most prominent ion in the LSIMS spectra of the $M(qo)_2$, (M = Cu and Ni) (eg. Figs. 3.10 and 3.11, Table 3.8) corresponded to a species $[M_2L_3]^{+}$. The presence of such fragment ions and their high relative abundances suggests that the complexes prepared during this study were associated even in solution. This observation thus confirms the proposal for association in the solid state initially made on the

basis of the low room temperature magnetic moment obtained for the anhydrous complexes.

It has been suggested that the distribution of ions measured by LSIMS reflects the composition of the species in the matrix as well as the species arising from the primary ion source employed.[47] Evidence of such a relationship was observed during this study. For example, in some of the spectra, species 23 and 136 mass units greater than the expected value were found. These fragment ions were assigned to $[P + Na]^+$ and $[P + Cs]^+$, the alkali metal 'residues' arising from the caesium ion gun used as the principal ion source. Additionally species associated with the matrix itself (glycerol and 3-nitrobenzylalcohol) were observed.

Figure 3.10 *LSIMS mass spectrum of* $Ni(5\text{-}Hpqo)_2$

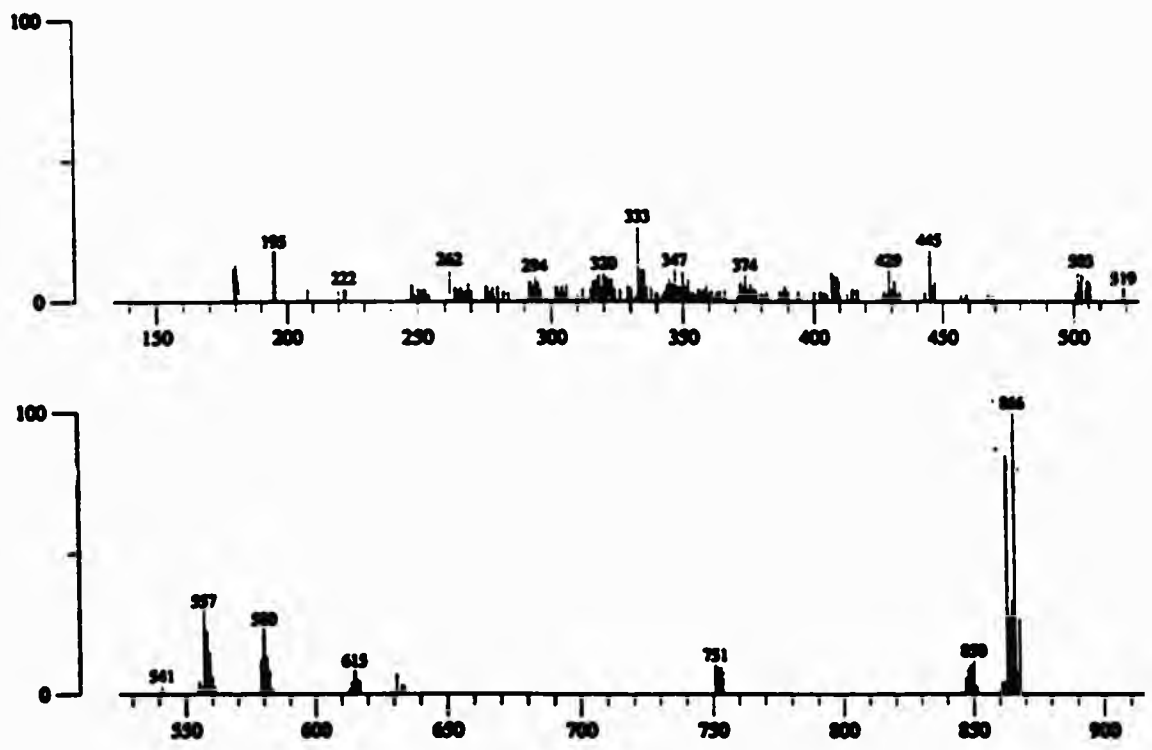


Figure 3.11 *LSIMS mass spectrum of* $Cu(5\text{-}Hxqo)_2$

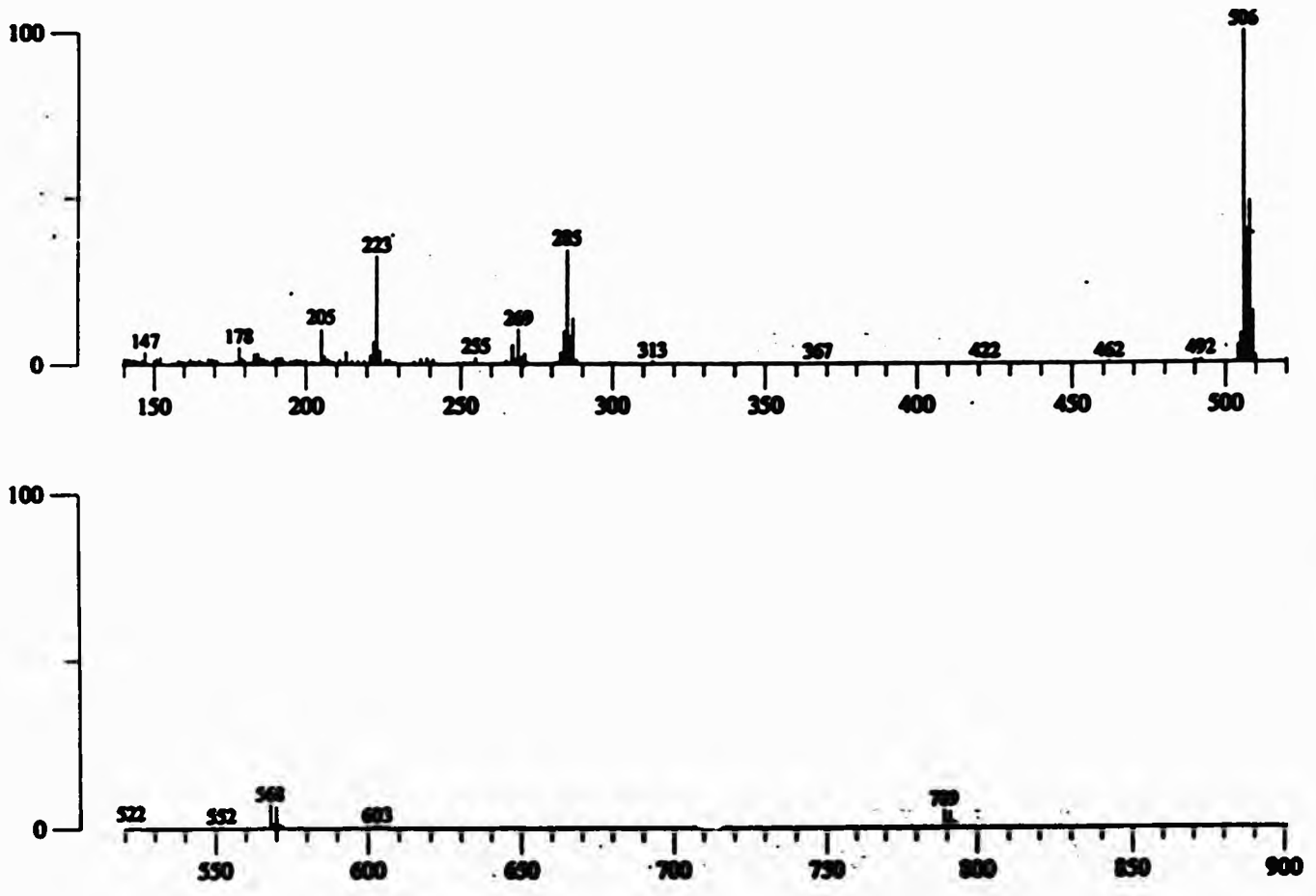


Table 3.8 *M/Z figures for selected ions in the LSIMS mass spectra of copper(II) and nickel(II) 1,2-quinone monooximates.*

Complex	*Ion Assignment and Relative Abundance*					
	$[ML+H]^+$	$[ML_2+H]^+$	$[ML_2+Na]^+$	$[M_2L_2+H]^+$	$[M_2L_3+H]^{+\cdot}$	$[M_3L_3+H]^+$
$Cu(5\text{-}Buqo)_2$	271	478	501	541	748	–
	(18)	(100)	(8)	(18)	(8)	–
$Cu(5\text{-}Hxqo)_2$	285	507	–	569	790	–
	(35)	(100)	–	(7)	(5)	–
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2$	243	422	–	–	–	–
	(23)	(100)	–	–	–	–
$Cu(1\text{-}nqo)_2$	236	408	–	471	643	–
	(7)	(100)	–	(8)	(4)	–
$Cu(2\text{-}nqo)_2$	236	408	–	471	643	708
	(88)	(100)	–	(91)	(43)	(15)
$Ni(5\text{-}Prqo)_2$	252	445	468	–	696	–
	(1)	(10)	(100)	–	(17)	–
$Ni(5\text{-}Buqo)_2$	266	473	497	531	738	796
	(13)	(35)	(9)	(6)	(100)	(10)
$Ni(5\text{-}Peqo)_2$	280	501	524	559	780	838
	(6)	(2)	(5)	(7)	(100)	(13)
$Ni(5\text{-}Hpqo)_2$	308	557	581	615	866	–
	(6)	(30)	(23)	(8)	(100)	–
$Ni(4\text{-}^tBuqo)_2$	237	415	438	473	651	709
	(1)	(9)	(100)	(1)	(26)	(1)
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2$	238	418	–	475	654	–
	(10)	(100)	–	(5)	(28)	–

Numbers in parenthesis are the relative abundances.

Interestingly, the LSIMS mass spectra of the pyridine adducts (eg. Fig. 3.12) contained no ions corresponding to $M(qo)_2.n(py)$. However, ions assignable to $[ML(py)]^{+\cdot}$, and $[M_2L_3(py)]^{+\cdot}$ were observed (Table 3.9). In addition, the spectra also contained prominent $[ML_2]^{+\cdot}$, $[M_2L_2]^{+\cdot}$ and $[M_2L_3]^{+\cdot}$ ions. The presence of both sets of ions suggests that fragmentation of the adducts involves either initial loss of ligand radicals or of pyridine. A decomposition pathway involving the initial loss of pyridine was supported by the presence of the bimetallic ions $[M_2L_2]^{+\cdot}$ and $[M_2L_3]^{+}$ in the mass spectra of the adducts. The occurrence of such ions could probably be explained by ion/molecule interactions and subsequent loss of a ligand radical and pyridine (Scheme 3.1).

Like for the pyridine adducts, the LSIMS mass spectra of the 2,2-dipyridyl adducts (eg. Fig. 3.13) contained no molecular ion. These spectra displayed highly prominent ions $[M(dipy)]^{+}$ and $[M(qo)dipy]^{+\cdot}$. The presence of ions such as $[M(dipy)]^{+}$ in the mass spectra of the copper(II) complexes is not surprising since copper(II) is known to undergo facile, single electron reductions to the relatively stable copper(I). However, with nickel, such reactions are not widely encountered and their occurrence here could only be due to some stabilisation of monovalent nickel afforded by π electron donation by the bidentate Lewis base.

Reactions of the type mentioned above are not novel and some explanation based on the redox potential of the metal ions have been proferred previously in the form of the valence-charge concept.[48,49] This principle suggest that the odd or even electron character of the metal containing ion is determined by the the capacity of the metal to accept ligand electrons or to donate electrons to the ligands. Thus, the presence of certain ions in the mass spectra of metal complexes and

their relative abundances is influenced by the metal ion structure and the relative stabilities of the oxidation states under experimental conditions.

In addition to the ions mentioned above, the mass spectra of the $M(qo)_2(dipy)$ contained bimetallic ions $[M_2L_3]^{+\cdot}$. The formation of such ions can be rationalised in the same way as for their pyridine analogues.

Scheme 3.1

$$ML_2(py) \xrightarrow{-py} ML_2 \longrightarrow [ML_2]^{+\cdot}$$

$$ML_2 + [ML_2]^{+\cdot} \xrightarrow{-L^{\cdot}} [M_2L_3]^{+}$$

$$ML_2(py) + [ML_2]^{+\cdot} \xrightarrow{-L^{\cdot}} [M_2L_3(py)]^{+}$$

Figure 3.12 *LSIMS mass spectrum of $Ni(5\text{-}Hpqo)_2(py)_2$.*

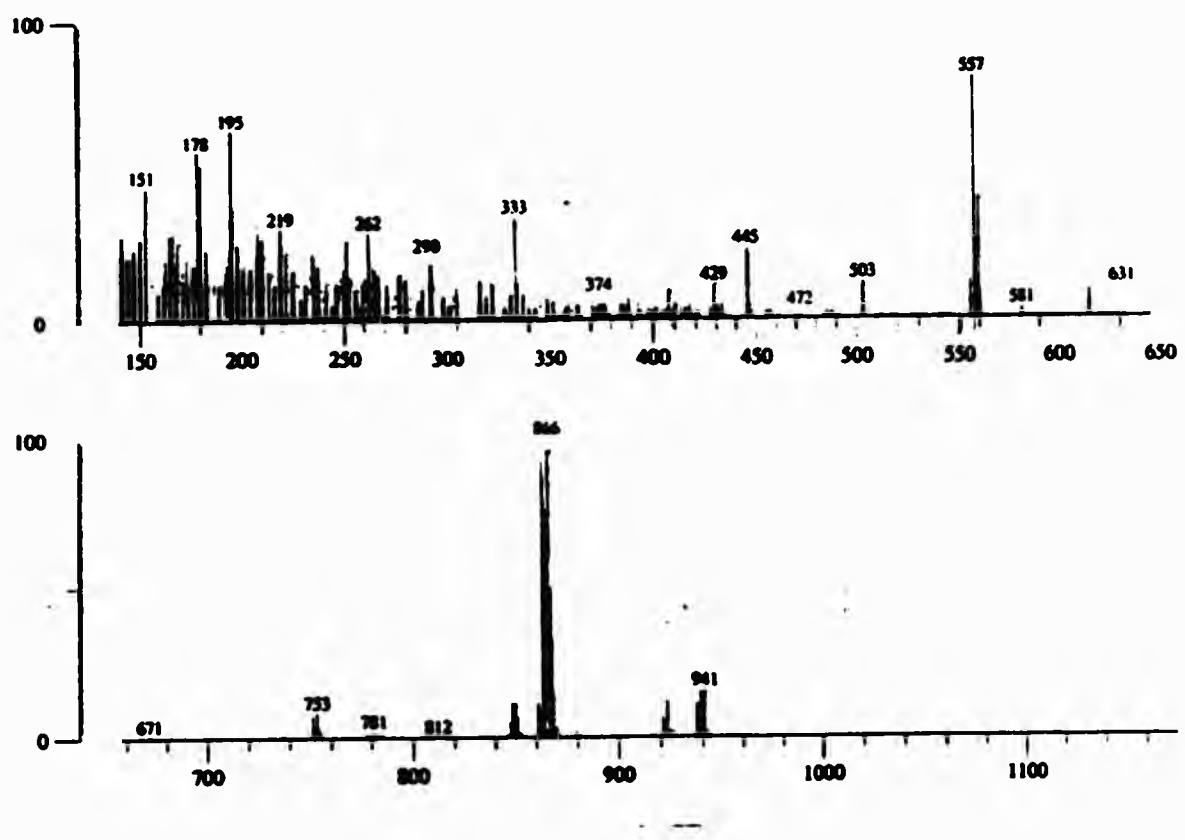


Figure 3.13 *LSIMS mass spectrum of Ni(5-Hxqo)$_2$(dipy).*

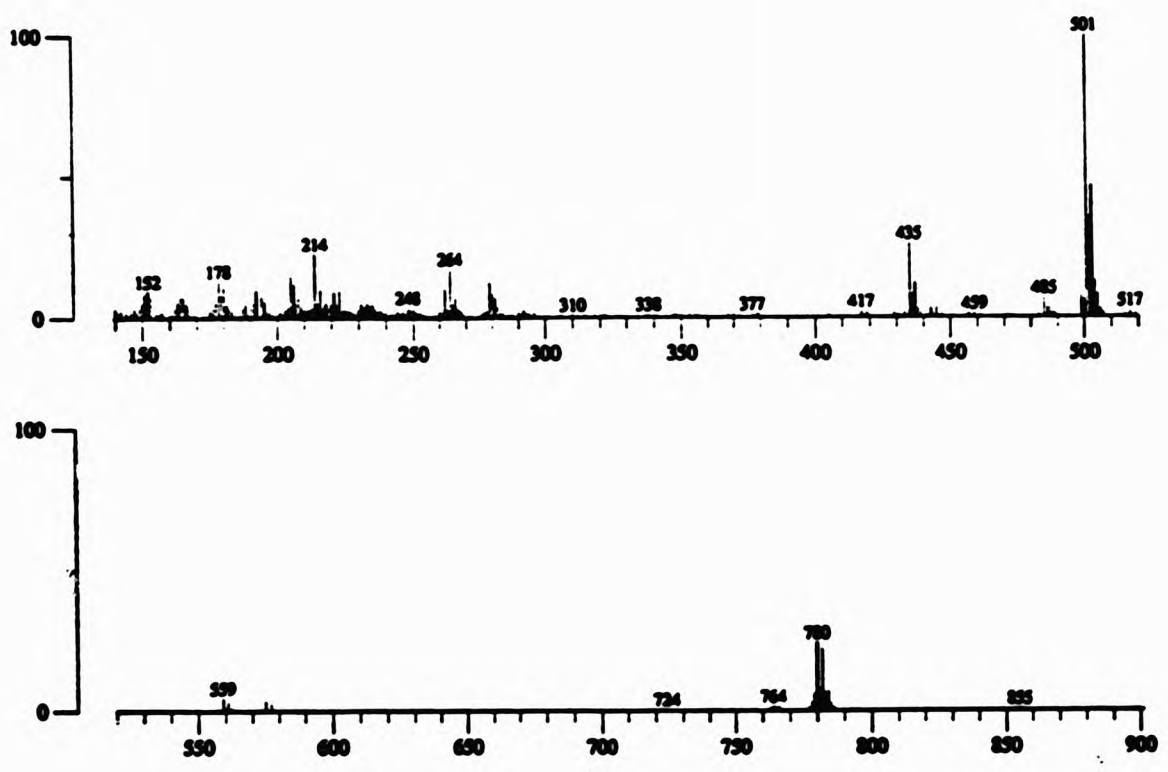


Table 3.9 *M/Z figures for selected ions in the LSIMS mass spectra of* $M(qo)_2(py)_n$ *(M = Cu(II), Ni(II); n = 1, 2).*

Complex	*Ion Assignment and Relative Abundance*					
	$[ML+H]^+$	$[MLB+H]^+$	$[ML_2+H]^+$	$[M_2L_2+H]^+$	$[M_2L_3+H]^+$	$[M_2L_3B+H]^+$
$Cu(5\text{-}Buqo)_2(py)$	271	350	501	564	771	850
	(8)	(3)	(100)	(10)	(6)	(12)
$Cu(5\text{-}Hxqo)_2(py)$	285	363	506	569	790	869
	(3)	(10)	(100)	(5)	(12)	(8)
$Ni(5\text{-}Prqo)_2(py)_2$	252	445	468	696	–	–
	(1)	(10)	(100)	(17)	–	–
$Ni(5\text{-}Buqo)_2(py)_2$	–	344	473	531	739	–
	–	(4)	(9)	(5)	(8)	–
$Ni(5\text{-}Hxqo)_2(py)_2$	280	–	501	559	780	858
	(11)	–	(100)	(8)	(49)	(3)
$Ni(5\text{-}Hpqo)_2(py)_2$	–	387	557	615	864	942
	–	(6)	(81)	(10)	(100)	(3)

B = pyridine

3.5. *Reference*

1. F. A. Cotton, G. Wilkinson, 'Advanced Inorganic Chemistry' 5th Edn., J. Wiley and Sons, USA, 1988.
2. N. N. Greenwood, A. Earnshaw, 'Chemistry of the Elements', Pergamon Press, London, 1984.
3. J. Charalambous, M. J. Frazer, F. B. Taylor, *J. Chem. Soc. (A),* 1967, 2787.
4. J. Charalambous, M. Fraser, F. B. Taylor, *J. Chem. Soc. (A),* 1970, 2645.
5. J. Charalambous, M. J. Fraser, F. B. Taylor, *J. Chem. Soc.(A),* 1971, 602.
6. H. H. Hodgson, W. Batty, *J. Chem. Soc.,* 1935, 1617.
7. D. Ray, A. Chakravorty, *Inorg. Chem.,* 1988, 27, 3292.
8. S. S. Guha-Sicar, Sasanka Chandra Bhattacharjee, *J. Ind. Chem. Soc.,* 1941, 18, 155-160, 161-163.
9. C. B. Castellani, R. Millini, *J. Chem. Soc., Dalton Trans.,* 1984, 1461 and references therein.
10. C. B. Castellani, G. Gatti, R. Millini, *Inorg. Chem.,* 1984, 23, 4004 and references therein.
11. A. McKillop, T. S. B. Sayer, *J. Org. Chem.,* 1976, 41, 1079 and references therein.
12. H. Barjesteh, J. Charalambous, N. D. Pathirana, *Polyhedron,* 1993, 12, 883.
13. L. P. Hammett, *Chem. Rev.,* 1935, 17, 123.
14. H. H. Jaffe, *Chem. Rev.,* 1953, 53, 191.
15. Y. K. Agrawal, *Ann. Chem.,* 1977, 2, 5
16. Y. K. Agrawal, J. P. Shukla, *Aust. J. Chem.,* 1973, 26, 913.

17. J. Charalambous, L. I. B. Haines, J. S. Morgan, D. S. Peat, M. J. Campbell, J. Bailey, *Polyhedron,* 1987, 6, 1027.

18. G. Chronheim, *J. Org. Chem.,* 1947, 12, 7.

19. J. Charalambous, G. R. Soobramanien, A. Betts, J. Bailey, *Inorg. Chem. Acta.,* 1982, 60, 151.

20. J. Charalambous, M. J. Fraser, R. Sims, *Inorg. Chem. Acta.,* 1976, 18, 247.

21. J. Charalambous, W. C. Stoten, K. Henrick, *Polyhedron,* 1989, 8, 103.

22. J. Charalambous, K. Henrick, Y. Musa, R. G. Rees, R. N. Whiteley, *Polyhedron,* 1987, 6, 1509.

23. O. Baudisch, *Science,* 1940, 92, 336.

24. K. Sone, *Bull. Chem. Soc. Jpn.,* 1952, 25.

25. J. F. White, M. F. Farona, *Inorg. Chem.,* 1971, 10, 1080.

26. C. Kowala, J. M. Swan, *Aust. J. Chem.,* 1966, 19, 555.

27. T. N. Lockyer, R. L. Martin, *Prog. Inorg. Chem.,* 1980, 27, 223.

28. W. Partenheimer, R. S. Drago, *Inorg. Chem.,* 1970, 9, 47.

29. L. L. Funk, T. R. Ortolano, *Inorg. Chem.,* 1968, 7, 567.

30. R. G. Gillard, G. Wilkinson, *J. Chem. Soc.,* 1963, 5885.

31. H. El Khaden, W. M. Orabi, *Z. Anorg. Chem.,* 1969, 365, 315.

32. J. Charalambous, M. J. Fraser, F. B. Taylor, *J. Chem. Soc. Chem. Commun.,* 1969, 921.

33. P. W. Ball, A. B. Blake, *J. Chem. Soc. A,* 1959, 1415.

34. A. Earnshaw, 'Introduction to Magnetochemistry', Academic Press, London, 1968.

35. J. Charalambous, P. Maple, N. A. Nassef, F. B. Taylor, *Inorg. Chem. Acta.,* 1978, 26, 107.

36. D. K. Allen, J. Charalambous, M. H. Johri, R. Sims, J. Bailey, H. D. Matthewson, D. Cunningham, *Inorg. Chim. Acta.*, 1978, 29, C235-6.

37. H. S. Maslen, T. N. Waters, *Coord. Chem. Revs.*, 1975, 17, 137.

38. B.Bezzi, A. Bua, D. Schiavinato, *Gazetta*, 1951, 81, 856.

39. R. Simms PhD. Thesis, University of London, 1976.

40. C. J. Ballhausen, 'Introduction To Ligand Field Theory', McGraw and Hill, New York, 1962.

41. C. K. Jorgensen, *Acta. Chem. Scand.*, 1956, 10, 887.

42. K. Nakamoto, P. J. McCarthy, 'Spectroscopy and Structure of Metal Chelate Compounds' J. Wliey & Sons Inc., USA, 1968.

43. O. Makitie, H. Helminen, *Suomen Kemistilehti*, 1969, B42, 480.

44. R, G. Honig, *Int. J. Mass Spectrom. Ion Phys.*, 1985, 66, 31.

45. R. G. Cooks, K. L. Busch, G. L. Glish, *Science*, 1983, 222, 273.

46. A. Benninghoven, F. G. Rudenauer, H. Werner, 'Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends', Vol. 86, J. Wiley & Sons, USA, 1987.

47. E. DePauw, *Mass Spectrom Review*, 1986, 5, 191.

48. M. J. Lacey, J. S. Shannon, *Org. Mass Spectrom.*, 1972, 6, 93.

49. J. Charalambous, 'Mass Spectrometry of Metal Compounds', Butterworths, London, 1975.

CHAPTER FOUR

CHAPTER 4

Palladium(II) and Platinum(II) Complexes of Acylamino and Alkylamino Substituted 1,2-Benzoquinone Monooximes.

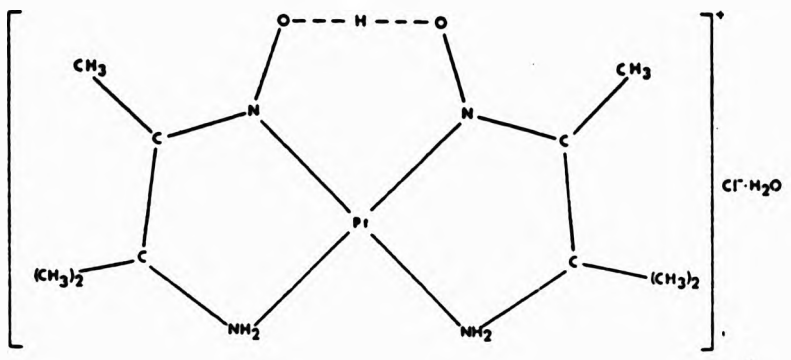
4.1 Introduction

Complexes of both palladium and platinum have been widely reported. In fact, the study of platinum complexes by Alfred Werner and his contemporaries has played a most important role in the development of current theories on coordination chemistry isomerism and inorganic reaction mechanisms.[1-4]

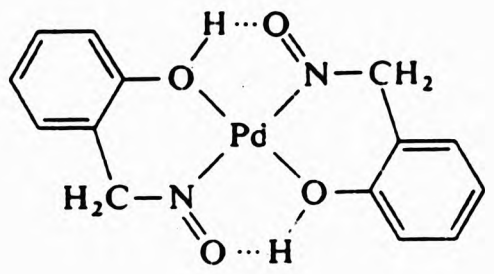
As is typical of transition metal elements, both palladium and platinum can exhibit a wide range of oxidation states. To date, compounds in which these metals are present in oxidation states from 0 to +6 have been reported.[1] However, the chemistry of both elements is dominated by the the +2 and +4 oxidation states. For platinum, the coordination chemistry of both the +2 and +4 states is extensive despite the tendency for the latter to be reduced to +2 by S, Se, P, and As donors.[5] By contrast, palladium, because of its higher ionization potential, is found largely as Pd^{2+}. This study is concerned only with the divalent metals.

Palladium(II) and platinum(II) interact with a wide variety of ligands forming either ionic (1) or neutral complexes (2). Being class b acids, both ions prefer N donor ligands to O donor ligands, though complexes in which the metal is coordinated exclusively to oxygen, for example the anhydrous acetates (eg. 3), are well known.[6]

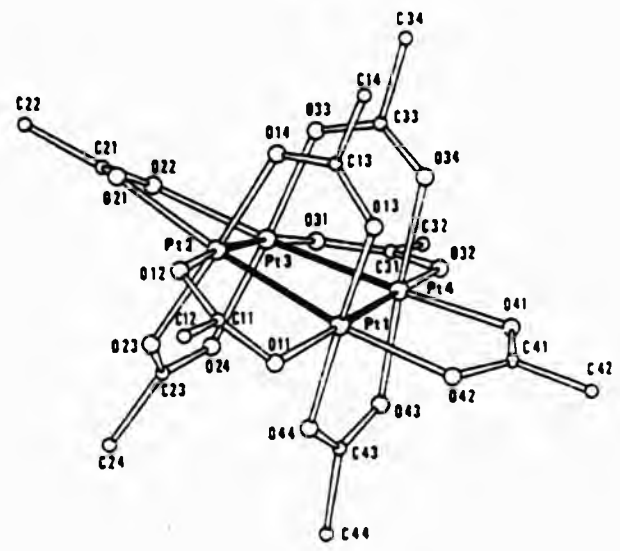
1



2



3

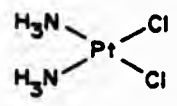
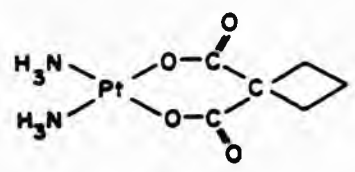
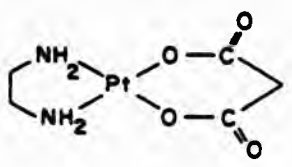
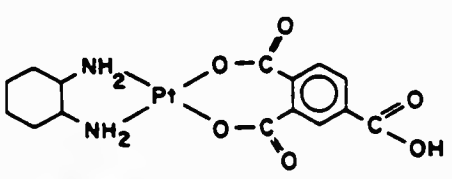
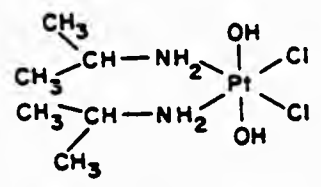
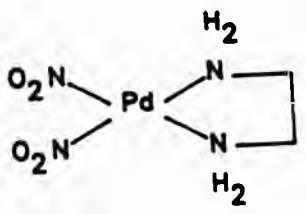
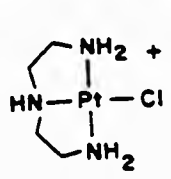


Because of the greater splitting of metal d-orbitals in the ligand field for 2nd and 3rd row transition metal complexes, both Pd(II) and Pt(II) complexes tend to be high spin, diamagnetic, and generally square planar. However, five coordinate, square pyramidal complexes of both palladium and platinum are known.[7]

Traditionally, palladium and platinum complexes have found much use as catalyst,[8] and in organic synthesis.[9] However, much of the recent interest in complexes of both metals have focussed on their medicinal application. This surge in interest which began in 1969 with the discovery of the anti-tumor activity of *cis*-diamminedichloroplatinum(II) or *cisplatin* (4)[10] has led to a proliferation in the number of palladium

and platinum complexes being synthesised and screened for biological activity.[11-14] Table 4.1 shows a few examples of the type of compounds for which clinical activity has been found.

Table 4.1 *Some palladium and platinum containing anti-tumor agents*

Compound	Common Name	Reference
	Cisplatin	13
	Carboplatin	13
	Malonatoplatin	13
Carboplatin 	DCCAP	13
	Iproplatin	11
	cis-diaminoethanenitratopalladium(II)	12
	$[PtdienCl]^+$	13

Numerous complexes of both palladium(II) and platinum(II) with oximic type ligands have been reported.[15-17] In the case of the complexes formed with dioximic ligands, it has been shown that the metal is bound via strong metal-nitrogen bonds (eg. Fig. 4.1). Similarly, in the complexes of mixed N, O donor ligands such as salicylaldoxime and 8-hydroxyquinoline, the metal is bound via nitrogen and a neighbouring oxygen atom forming 5-membered chelate rings (eg. Fig. 4.2) not dissimilar from that observed in the complexes of 1,2-quinone monooximes. The tendency for these metals to form stable chelate complexes with oximic type ligands is further demonstrated by the formation of bis-monooximato complexes with aromatic monooximes. In these complexes (eg 5), the metal is bound via the oximic nitrogen and a ring carbon.

Figure 4.1

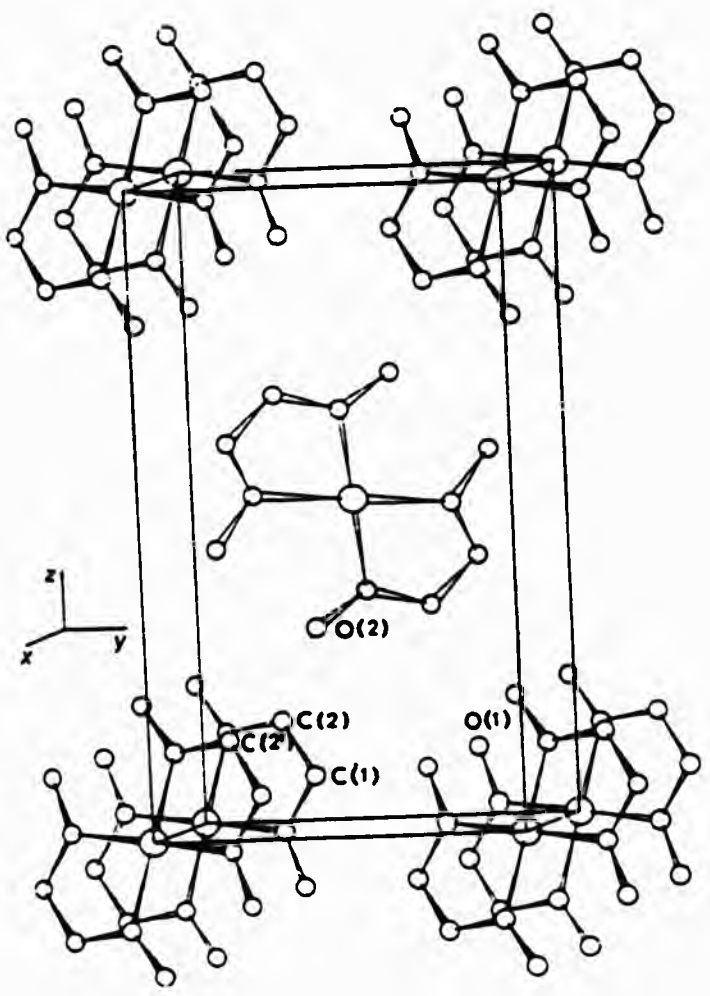
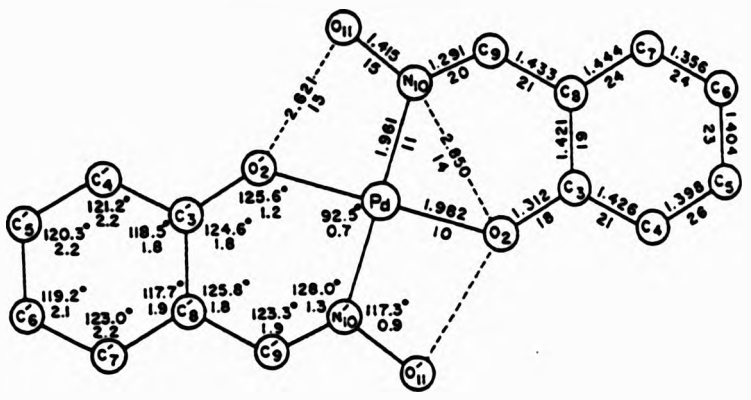
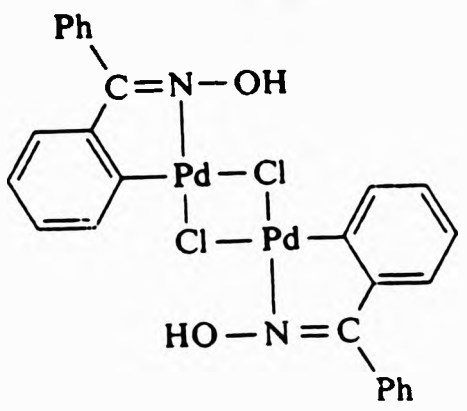


Figure 4.2



5



Despite the wealth of interest in palladium and platinum complexes, the immense synthetic and biological potential of 1,2-quinone monooximic ligands, and the proven stability of palladium and platinum complexes with other oximes, few studies of complexes of these metals with 1,2-quinone monooximes have been reported. In fact, the only report available to date deals with the analytical application of the compounds and thus, few details on their synthesis, characterisation or properties were given.[18]

In this work therefore, the synthesis and detailed structural characterisation of palladium(II) and platinum(II) complexes of selected 1,2-quinone monooximes are described. Two synthetic routes were investigated. These were (i) the nitrosation of an appropriate phenol in the presence of the metal salt, and (ii) the direct reaction of a methanolic solution of the free ligand with aqueous palladium dichloride or potassium tetrachloroplatinate(II).

4.2. Synthesis of Pd(II) and Pt(II) Complexes of 5-Acylamino and 5-Alkylamino-1,2-benzoquinone-2-oxime.

Nitrosation of 3-acetylaminophenol and 3-butyrylaminophenol with sodium nitrite/acetic acid in the presence of palladium(II) chloride gave dark brown solid mixtures. Separation of the latter by Soxhlet extraction with dichloromethane afforded bis(5-acylamino-1,2-benzoquinone-2-oximato)palladium(II) in high yields. Such complexes were also obtained by the direct reaction of aqueous palladium(II) chloride with methanolic solutions of selected 1,2-benzoquinone-2-oximes.

In contrast, the reaction of the 3-acylaminophenols with sodium nitrite/acetic acid in the presence of potassium tetrachloroplatinate(II) failed to give the platinum complexes. Instead these reactions afforded black, multicomponent solids which could not be satisfactorily separated. However, elemental analysis of these solids showed them to have high nitrogen:metal ratio.

The failure to isolate $Pt(qo)_2$ complexes by the nitrosation method was not surprising because of the well known propensity of platinum to form nitrosyl complexes. The facile reaction of platinum

with nitrous oxide, the nitrosating agent in these experiments, has been demonstrated previously by the formation of complexes such as $K[Pt(NO)Cl_3]$ and $K[Pt(NO)pyRCl_2]$ by reaction of a platinum salt with nitrosyl chloride.[19,20] The high metal:nitrogen ratio in the solids recovered by the nitrosation of the phenols in the presence of potassium tetrachloroplatinate(II) point towards the formation of analogous species though this was not confirmed. Similar reactions of palladium are less well known.

Inspite of the limitations of the nitrosation method, a number of platinum(II) complexes of the type $Pt(qo)_2$ were prepared by the reaction of aqueous solutions of potassium tetrachloroplatinate(II) with methanolic solutions of selected free 1,2-benzoquinone monooximes (Table 4.2). These reactions afforded dark brown, neutral complexes in high yields even at low pH.

All the complexes were stable at room temperature but decomposed on heating at temperatures between 250 ^{0}C and 350 ^{0}C. They were sparingly soluble in common organic solvents like methanol, but were all highly soluble in dimethyl sulphoxide.

Table 4.2 *Palladium(II) and Platinum(II) complexes reported in this thesis*

Ligand	Complex	Method
5-AcqoH	$Pt(5\text{-}Acqo)_2$	a
	$Pd(5\text{-}Acqo)_2$	a, b
5-BuqoH	$Pt(5\text{-}Buqo)_2$	a
	$Pd(5\text{-}Buqo)_2$	a, b
5-PeqoH	$Pt(5\text{-}Peqo)_2$	a
5-HxqoH	$Pd(5\text{-}Hxqo)_2$	a
	$Pt(5\text{-}Hxqo)_2$	a
5-Et-4-MeqoH	$Pt(5\text{-}Et\text{-}4\text{-}Meqo)_2$	a
	$Pd(5\text{-}Et\text{-}4\text{-}Meqo)_2$	a

a, direct method; b, nitrosation method

4.3. Characterisation and Structural Studies.

Elemental analysis of the palladium(II) and platinum(II) complexes prepared during this study showed them to have formulations $Pd(qo)_2$ and $Pt(qo)_2$. Thermal gravimetric analysis showed all the complexes to decompose in a single step at temperatures between 250 and 350 ^{0}C.

It has been shown previously that in their complexes, 1,2-quinone monooximes can bind to metals in several ways.[21-27] Thus, in main group and early transition metal complexes, the metal is bound to the ligand

via the oximic nitrogen and quinoid carbonyl oxygen.[20-24] In contrast, the actinide uranium, forms complexes in which the metal is bound to the ligand only through the oximic group.[25]

Studies of palladium and platinum complexes with structurally related ligands have revealed two possible modes of bonding. Thus, in the palladium and platinum complexes of violuric acids (6), spectroscopic evidence suggest that the metal is bound via the oximic nitrogen and an adjacent quinoid carbonyl oxygen. Though this structure has not been confirmed crystallographically, the spectroscopic similarities between these compounds and their ruthenium analogue, the structure of which has been established by X-ray crystallography, (Fig. 4.3)[26] was taken as evidence of 5-membered chelate ring formation.

By contrast, the X-ray crystal structure of the platinum(II) complex of 4-isonitroso-3-(R)-isoxazol-5-one (Fig. 4.4) show the metal to be bound via the oximic group only.[27]

6

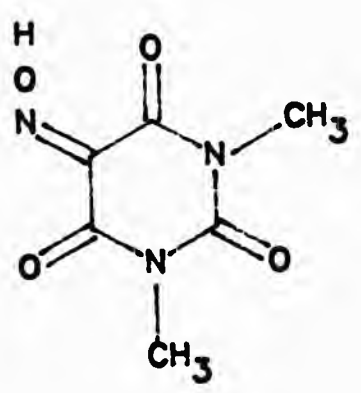


Figure 4.3

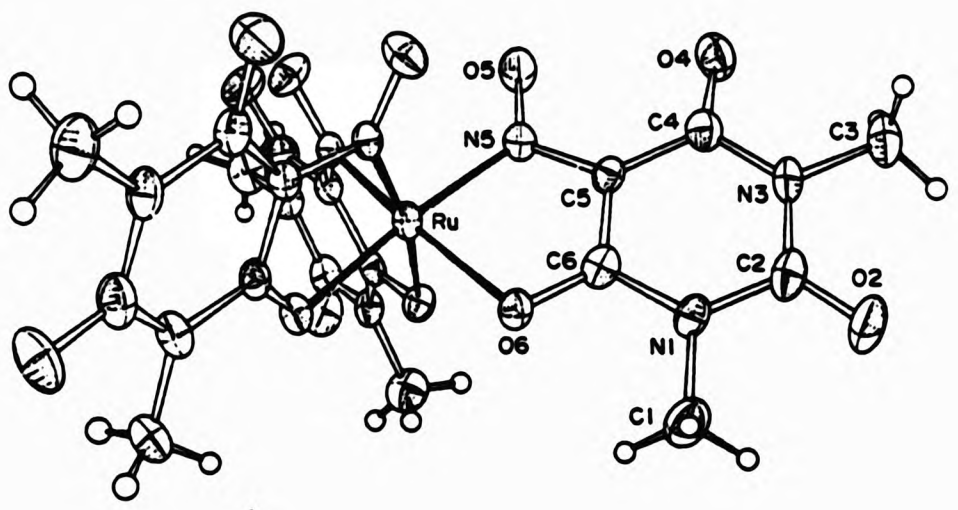
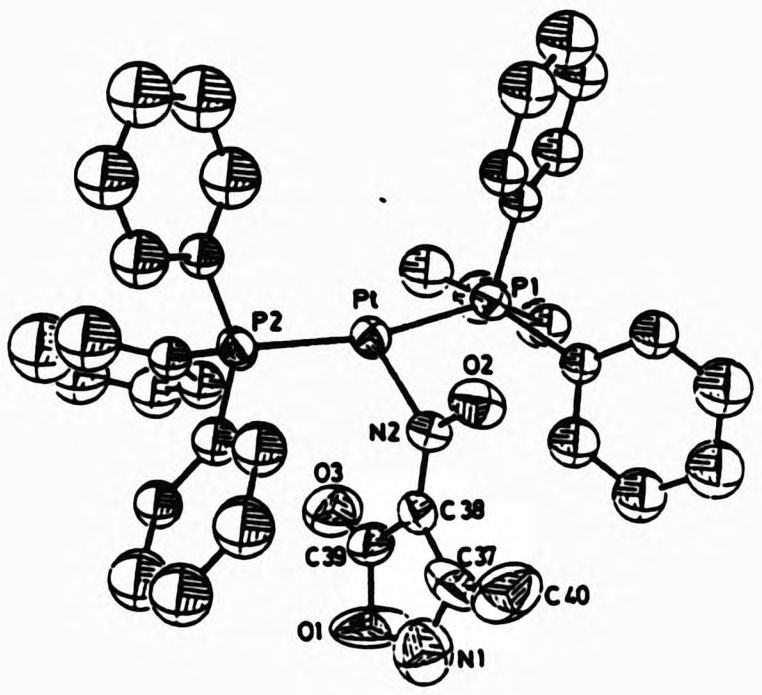


Figure 4.4



The IR spectra of the complexes prepared during this study, (eg. Fig. 4.5) contained bands assignable to the quinoid νCO at between 1620 and 1600 cm^{-1} (Table 4.3). In all cases, these bands occurred at lower frequency than for the corresponding band in the IR spectrum of the free ligand (see Chapter 2). This finding is consistent with the formulation

of the complexes as bis-chelates in which the quinoid carbonyl group is involved in binding the metal (Fig. 4.6).

Figure 4.5. *IR spectrum of Pd(5-Hxqo)$_2$*

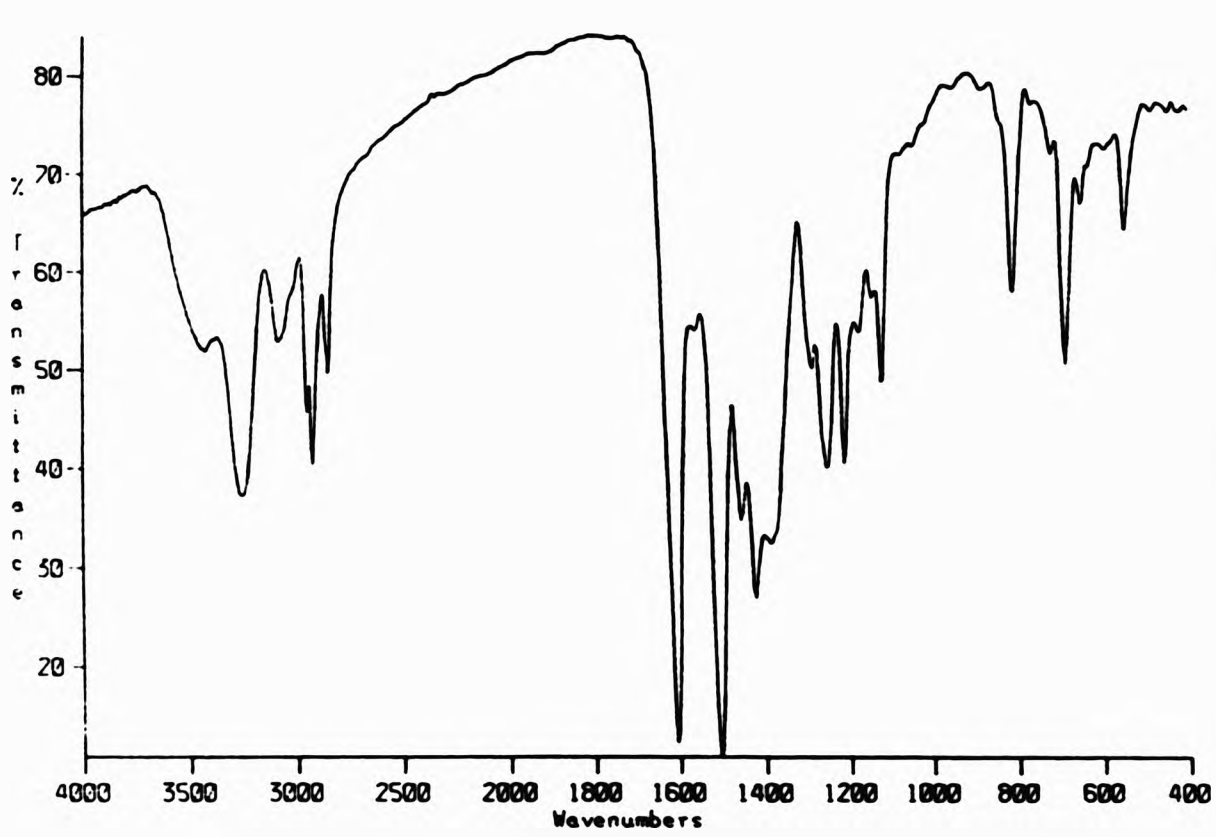
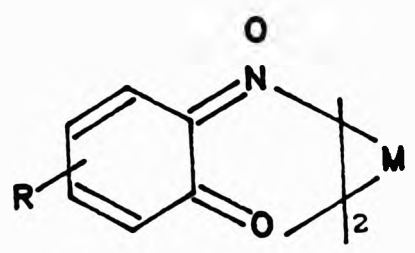


Table 4.3. *IR spectral bands and their assignment for the spectra of Pd(II) and Pt(II) complexes.*

Complex	νNH /cm^{-1}	νCO$_{quinoid}$ /cm^{-1}
Pt(5-Acqo)$_2$	3278	1617
Pt(5-Buqo)$_2$	3288	1619
Pt(5-Peqo)$_2$	3256	1611
Pt(5-Et-4-Meqo)$_2$	3332	1614
Pt(5-Hxqo)$_2$	3253	1607
Pd(5-Acqo)$_2$	3280	1600
Pd(5-Buqo)$_2$	3320	1600
Pd(5-Hxqo)$_2$	3253	1607
Pd(5-Et-4-Meqo)$_2$	3253	1619

Figure 4.6



M = Pt(II), Pd(II)

The room temperature magnetic moments of all the complexes showed them to be diamagnetic as expected for four coordinate, d^8 systems.

Like other transition metal ions, palladium(II) and platinum(II) have excited states which allow for spectroscopic analysis of their compounds. The d^8 configuration of these square planar complexes gives rise to a triplet ($^3A_{2g}$) ground state.[28] Thus, several spin-allowed transitions are possible for such complexes. However, many of the transition are obscured by the broad bands from more intense neighbouring transitions so that only a few can be be unambiguously assigned.[28-30]

The solution electronic spectra of both the palladium(II) and platinum(II) complexes in DMSO (eg. Fig. 4.7 and 4.8) showed d-d bands at approximately 890 and 450 nm. The complexes also showed absorptions in the same region as the free ligands as well as a strong ligand bands at 260 nm. The latter was blue shifted with respect to the free ligand (320-310 nm), and is consistent with strong metal ligand interaction. Similar shifts have been observed in the electronic spectra of related copper(II) and nickel(II) complexes.[31] The unambiguous assignment of the bands in the solution electronic spectra of the metal complexes was not possible though the bands at approximately 450 and 890 nm are believed to be due to d-d transitions. Molar absorptivities for the bands in the spectra of $Pd(5\text{-}Buqo)_2$ and $Pt(5\text{-}Et\text{-}4\text{-}Meqo)_2$ are given in Table 4.4.

Palladium(II), and especially platinum(II) complexes usually show extensive mixing of metal and ligand orbitals through a transfer of electron density from occupied metal d orbitals to suitable, vacant ligand orbitals.[30] This is usually enhanced by the π acceptor character in the ligands and gives rise to backbonding. Little direct experimental

evidence of efficient mixing of metal and ligand orbital was found for the $M(qo)_2$ complexes (M = Pd(II) and Pt(II).

Figure 4.7 *UV/Vis spectrum of (5-Et-4-Meqo)$_2$Pt*

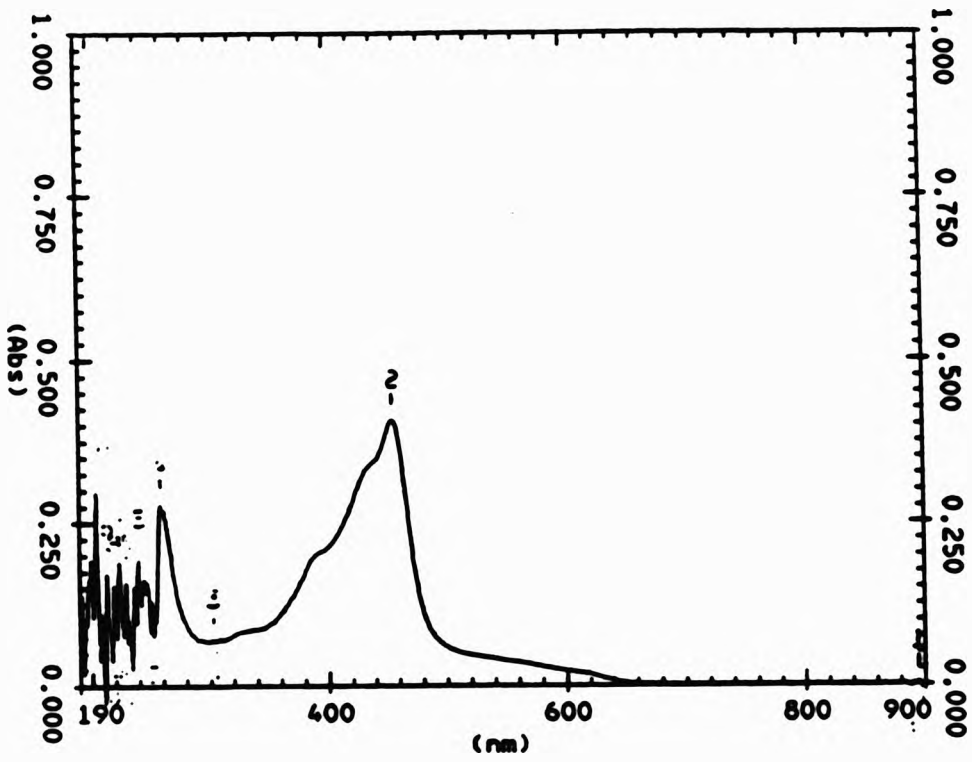


Figure 4.8 *UV/Vis spectrum of (5-Buqo)$_2$Pd*

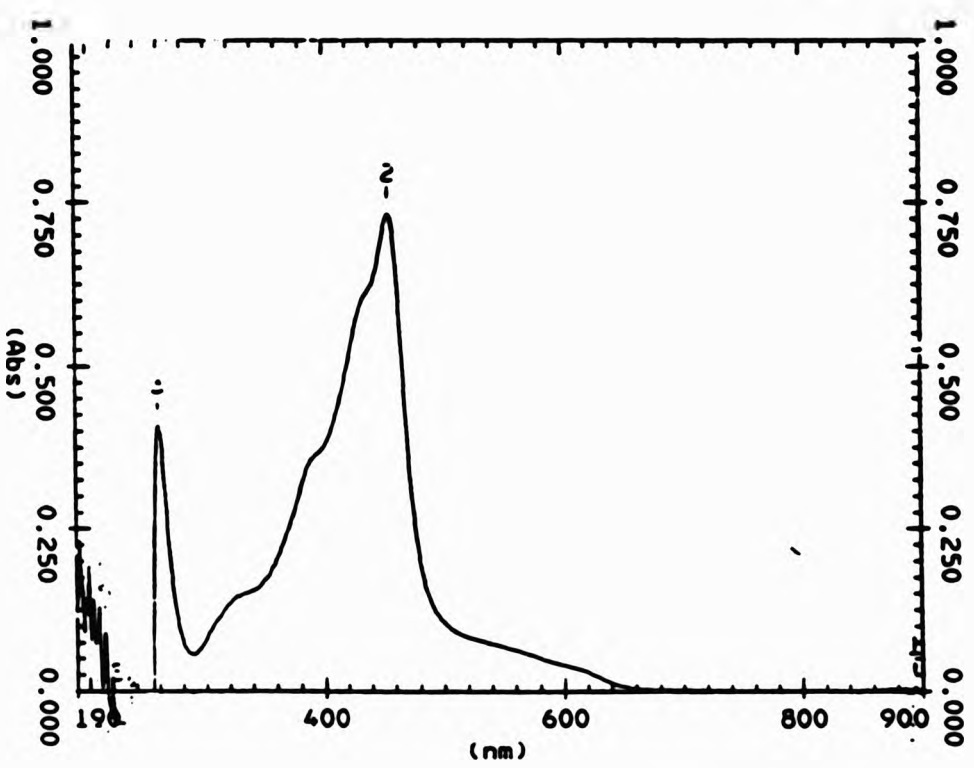


Table 4.4 *UV/Vis data for palladium and platinum complexes*

Complex (concentration/mol dm^{-3})	λ_{max} /nm	ε /mol m^{-2}
$Pt(5\text{-}Et\text{-}4\text{-}Meqo)_2$	883 (11325 cm^{-1})	1
(3.28×10^{-5})	423 (23640 cm^{-1})	192
	260 (38462 cm^{-1})	161
$Pd(5\text{-}Buqo)_2$	894 (11186 cm^{-1})	4
(8.00×10^{-6})	455 (21978 cm^{-1})	588
	258 (38760 cm^{-1})	345

In recent years, both transition metal and multinuclear NMR have been widely used to ascertain the structure and follow the reactions of transition metals complexes.[32] ^{106}Pd and ^{195}Pt are both relatively abundant (27.3 and 33.8% respectively), have I = 1/2 and as such, are amenable to NMR detection. In fact the literature on ^{195}Pt NMR is vast and includes several detailed reviews.[33,34] The chemical shift range for ^{195}Pt is large, 15000 ppm, and it is well established that the chemical shift for the ^{195}Pt and by extension the ^{106}Pd nuclei are determined by the element coordinated to the metal as well as their chemical form. Moreover, δ ^{195}Pt is additive and can be predicted for a given set of donors. This sensitivity of δ ^{195}Pt and δ ^{106}Pd to coordination environment makes NMR a useful technique for indicating the geometry and symmetry of palladium(II) and platinum(II) complexes though this

empiricism sometimes fail because of the differing effects of ligand substituents.[33] A table of reported δ ^{195}Pt for complexes with a PtN_2O_2 nucleus is given below (Table 4.5).

Table 4.5 *Some reported chemical shifts for* ^{195}*Pt.*

Compound	-δ/ppm	Reference
$(NH_3)_2Pt(Amal)$	2160	36
(en)Pt(Amal)	2426	36
$(NO_2)_2Pt(H_2O)_2$	1365	37
$[(NO_2)_2Pt(OH)_2]^{2-}$	1340	37
$[(NO_2)_2Pt(CH_3CO_2)]^{2-}$	1394	37
$[(NH_3)_2Pt(H_2O)_2]^{2+}$	3147	38

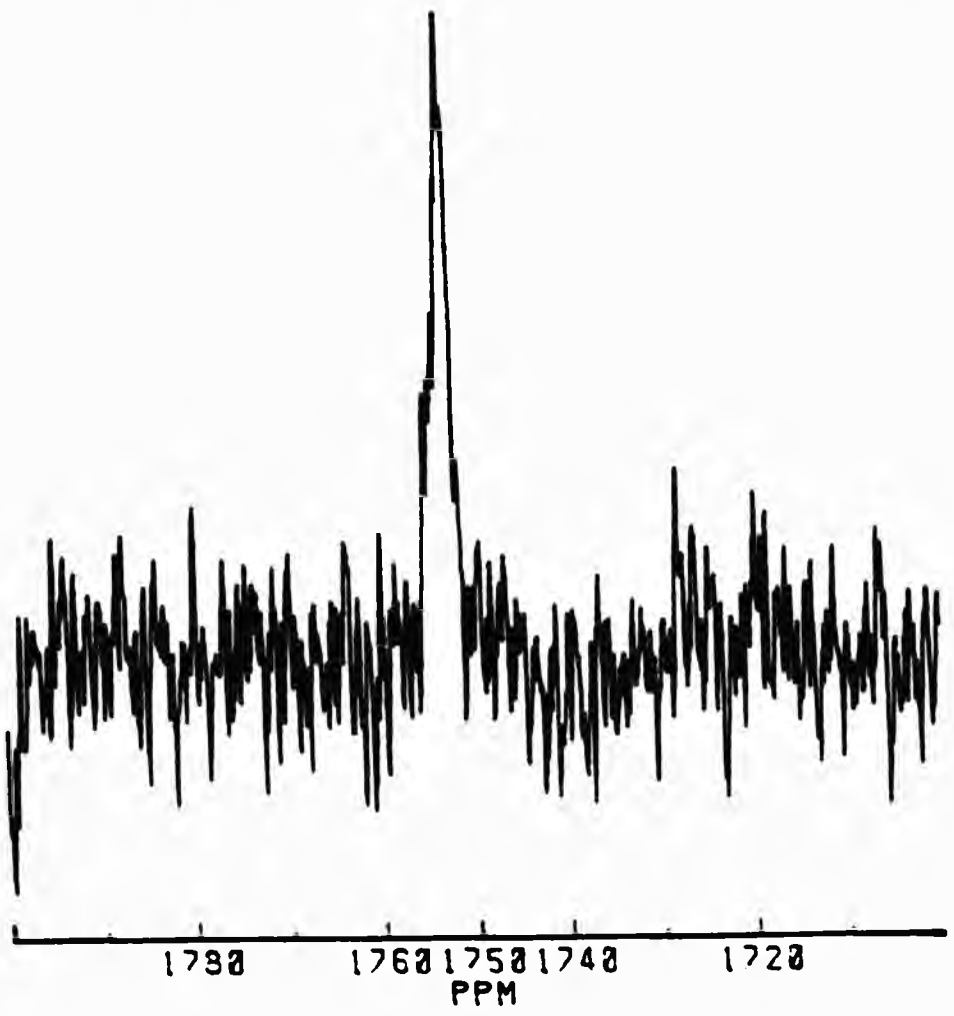
The ^{1}H, ^{106}Pd, and ^{195}Pt NMR spectra of the complexes prepared during this study were recorded in DMSO. The very broad nature of the ^{106}Pd signal meant that no significant structural information could be derived from the spectra of the palladium complexes.

In the case of the platinum(II) complexes, the ^{195}Pt NMR spectra (eg. Fig. 4.9) contained a relatively broad, poorly resolved multiplet due to δ ^{195}Pt between -1650 and -1750 ppm. The broadening of this signal and the consequent loss of coupling information has been attributed to the quadrupolar effect of the neighbouring ^{14}N (I = 1) atoms.[35] The downfield shift of the platinum nucleus compared to that reported for the starting material $[PtCl_4]^{2-}$ (-1764 ppm) confirms the

change in the coordination environment of the metal. The presence of only one signal due to δPt in these spectra demonstrates the symmetry and isomeric purity of the complexes.

The ^{1}H NMR spectra of the complexes displayed resonances for all relevant ligand hydrogens. Importantly, these spectra provided no evidence of the coupling of ^{195}Pt to ^{1}H of the amino or amido groups, confirming that the metal in these complexes is bound via the oximic and quinoid groups. Platinum satellites for the interaction of ^{195}Pt with the hydrogens of the quinoid ring were observed in the spectra. However, there was no evidence of coupling of these nuclei since the latter requires a four bond pathway, not generally significant for ^{195}Pt–^{1}H interactions.[33]

Figure 4.9 *^{195}Pt NMR spectrum of $Pt(5\text{-}Et\text{-}4\text{-}Meqo)_2$*



The LSIMS mass spectra of both the palladium(II) and platinum(II) complexes (eg. Fig 4.10 and 4.11) contained prominent molecular ion peaks. In contrast to that of their copper(II) and nickel(II) analogues discussed in Chapter 3, the spectra contained no bimetallic species. This confirmed the complexes as being monomeric in solution, a result not unexpected since association would require the palladium(II) and platinum(II) ions to be five or six-coordinate, both unfavourable geometries with ligands of this type. The mass spectra of these complexes also show extensive fragmentation of the ligand. Thus, fragments ions attributed to the loss of such fragments as O, NO$^{\bullet}$, and CO were relatively prominent for both the palladium and platinum complexes. This is exemplified by the assignment of the mass spectrum of $Pt(5\text{-}Et\text{-}4\text{-}Meqo)_2$ (Table 4.6).

Figure 4.10 *LSIMS mass spectrum of* $Pt(5\text{-}Buqo)_2$

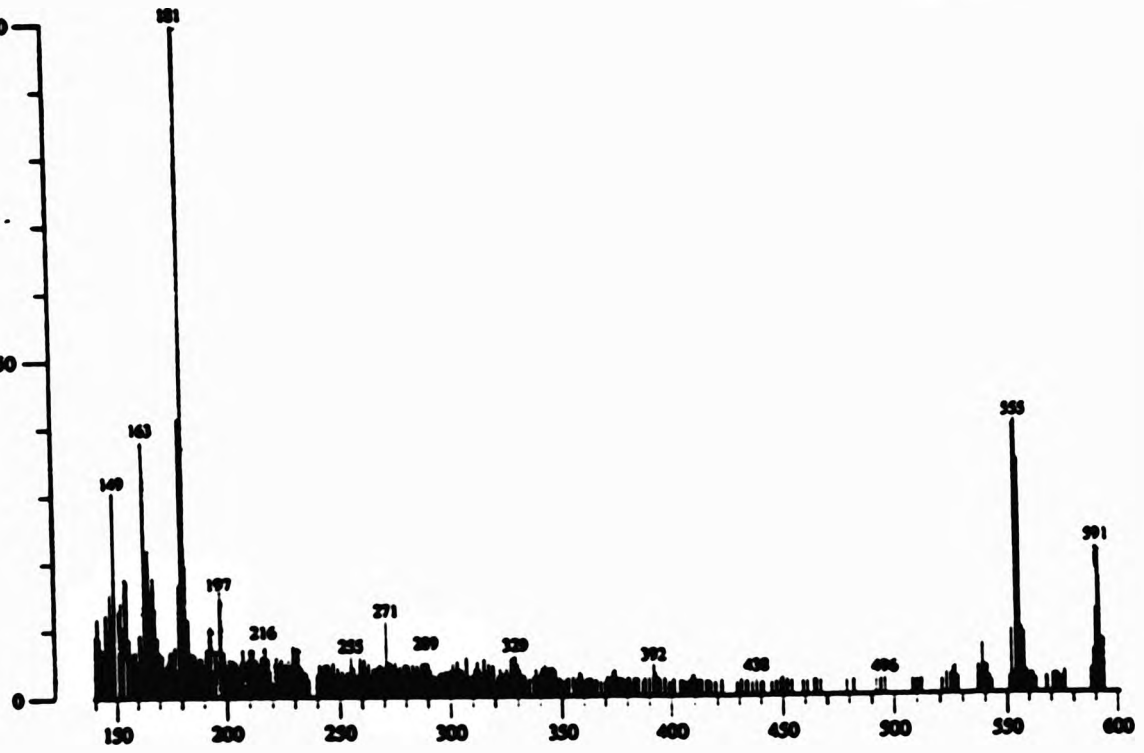


Figure 4.11 *LSIMS mass spectrum of Pd(5-Acqo)$_2$*

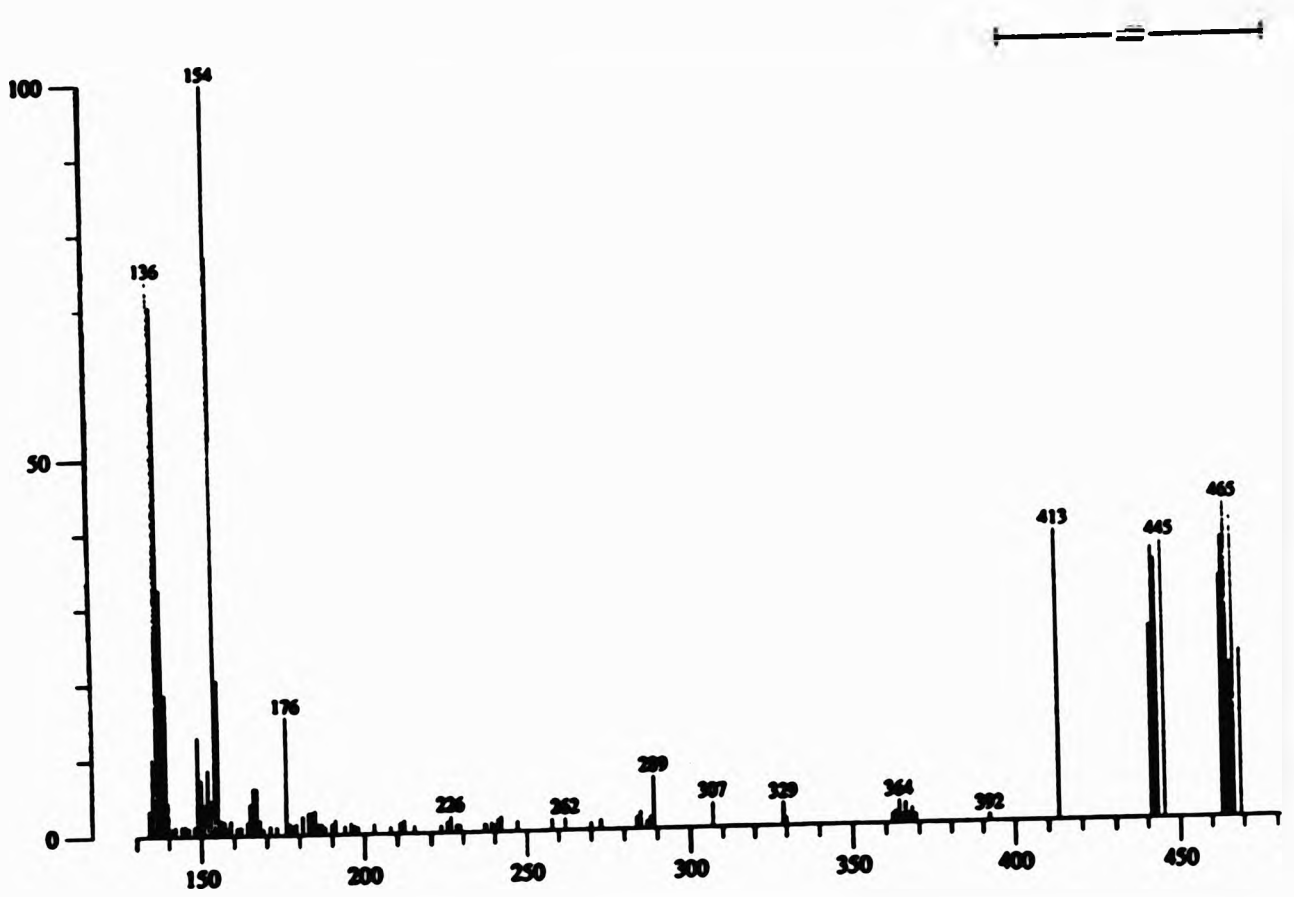


Table 4.7 *Ion abundances and assignment in the mass spectrum of Pt(5-Et-4-Meqo)$_2$*

Ion	Abundance %	m/z
$[ML_2 + H]^+$	40	554
$[ML_2 - O]^{+\cdot}$	7	539
$[ML_2 - CO]^{+\cdot}$	4	526
$[ML - L]^+$	4	374
$[LH + H]^+$	100	181

4.4. Interaction of $Pd(qo)_2$ and $Pt(qo)_2$ with Pyridine.

Usually Pd(II) and Pt(II) complexes are four-coordinate and have square planar geometry. Five and six-coordinate complexes of both ions are however well known particularly with bulky or π-donor ligands.[1]

During this study, the interaction of $Pd(qo)_2$ and $Pt(qo)_2$ with pyridine under mild conditions and under reflux were investigated. In all cases, the complexes were recovered unchanged. This was in marked contrast to other transition metal 1,2-quinone monooximates which, as indicated earlier either afforded adducts, ligand substituted products or products arising from internal redox reactions (IRR).

The failure of the palladium and platinum complexes to react with pyridine was not surprising since four coordination is the prevalent geometry of their complexes. Additionally, the inactivity of these complexes shows the relatively inert nature of palladium and platinum towards facile oxidation or reduction.

4.5 References

1. F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science Publishers, London, 1973.
2. U. Belluco, 'Organometallic and Coordination Chemistry of Platinum', Academic Press, London, 1974.
3. G. B. Kaufmann, 'Classics in Coordination Chemistry', Dover Publ. Inc., New York, 1968.
4. G. B. Kaufmann, *Coord. Chem. Rev.,* 1974, 12, 105.
5. N. G. Greenwood, A. Earnshaw, 'Chemistry of the Elements', Pergammon Press, Oxford, 1984, pp 1340.
6. M. A. A. de Carrondo, A. C. Skapski, *Acta. Cryst.,* 1978, B34, 1357.
7. F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tripicchio, G. Pacchioni, *J. Chem. Soc. Chem. Commun.,* 1992, 333.
8. S. R. Storbat, *J. Am. Chem. Soc.,* 1984, 106, 1314.
9. O. Voshinbu, *Shokabai,* 1964, 6(2), 102. *Chem Abs.* 65:10545c.
10. B. Rosenberg, L. Vancamp, T. Trigas, *Nature,* 1965, 205, 698.
11. S. J. Lippard, 'Platinum, Gold and other Chemotherapeutic Agents' ACS Symposium Series 209; American Chemical Society, Washington DC, 1982.
12. H. Sigel, 'Metal Ions In Biological Systems II', Marcel Dekker Inc., New York, 1980.
13. K. Kofp-Maier, H. Kofp, *Chem. Rev.,* 1987, 87, 1137.
14. S. E. Sherman, S. J. Lippard, *Chem. Rev.,* 1987, 87, 1153.

15. M. Calleri, G. Ferraris, D. Viterbo, *Inorg. Chim. Acta.,* 1967, 1, 297.

16. G. Ferraris, D. Viterbo, *Acta. Cryst.,* 1969, B25, 2066.

17. C. E. Pfluger, R. L. Harlow, H. Simonsen, *Acta. Cryst.,* 1970, B26, 1631.

18. K. Kodama, *Nagoya-ski, Kogyo Kenkyujo Kenkyu Hokoku,* 1959, 20, 1; *Chem. Abs.* 53:19056b.

19. A. D. Helman, Z. P. Maksimova, *Compt. Rend. Acad. Sci. USSR.,* 1939, 24, 748.

20. W. P. Griffith, J. Lewis, G. Wilkson, *J. Chem. Soc.,* 1961, 775.

21. J. Charalambous, W. Stoten, K. Henrick, *Polyhedron,* 1989, 8, 103.

22. J. Charalambous, K. Henrick, Y. Musa, R. G. Rees, R. N. Whitely, *Polyhedron,* 1987, 6, 1509.

23. J. Charalambous, P. G. T. Fogg, P. Gaganatsou, *Polyhedron,* 1993, 12, 8, 879.

24. C. B. Castellani, O. Carugo, A. Coda, *Acta. Cryst.,* 1988, C44, 265.

25. R. Graziani, U. Casellato, P. A. Vigato, S. Tamburini, M. Vidali, *J. Chem. Soc.,* 1983, 697.

26. M. A. Romero, J. M. Salas et al., *Polyhedron,* 1990, 22, 2733.

27. E. Leidl, U. Nagel, W. Beck, *Chem. Ber.,* 1983, 116, 1370

28. U.V. Rao, 'Platinum Group Metal Compounds', Advances in Chemistry Series 98, American Chemical Society, 1969.

29. C. A. Tsipis, *Coord. Chem. Rev.,* 1991, 108, 163

30. P. L. Goggin, R. J. Goodfellow, F. J. S. Red, *J. Chem. Soc. Dalton Trans.,* 1972, 1298.

31. O. Makitie, H. Helminen, *Soumen Kemistilehti,* 1969, B42, 480.

32. P. Laszlo, 'NMR of Newly Accessible Nuclei', Vol.1 and 2, Academic Press, New York, 1983.

33. P. S. Pregosin, *Coord. Chem. Rev.,* 1982, 44, 247.

34. S. J. S. Kerrison, P. J. Sadler, *Magn. Reson.,* 1978, 31, 321.

35. P. S. Pregosin, *Chimia,* 1981, 35, 43.

36. D. Gibson, A. Rosenfeld, F. Apfelbaum, J. Blum, *Inorg. Chem.,* 1990, 29, 5125.

37. T. G. Appeleton, K. J. Barnham, J. R. Hall, M. T. Mathieson, *Inorg. Chem.,* 1991, 30, 2751.

38. R. E. Norman, J. D. Ranford, P. J. Sadler, *Inorg. Chem.,* 1992, 31, 877.

CHAPTER FIVE

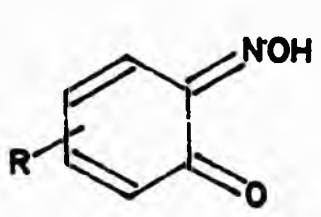
CHAPTER 5

Reaction of 1,2-Quinone Monooximes, 1,2-Dioximes, and Their Metal Complexes With Dimethyl Acetylenedicarboxylate.

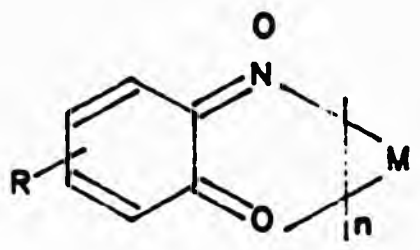
5.1. Introduction

As a result of their multifunctional character, one potential application of 1,2-quinone monooximes (1) and of their metal complexes (2) is their use as substrates in the synthesis of novel and otherwise difficult to prepare organic compounds. For example, the lability of the oximic oxygen in (2) was exploited in the preparation of phosphoranylideneaminophenols (3), their metal complexes (4), and phenoxazin-3-ones (5) by reaction of the metal complexes with triphenylphosphine.[1,2]

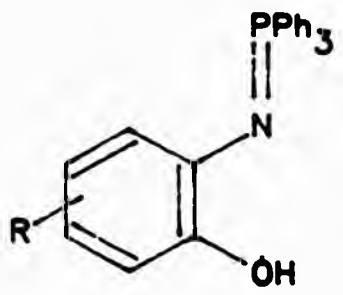
(1)



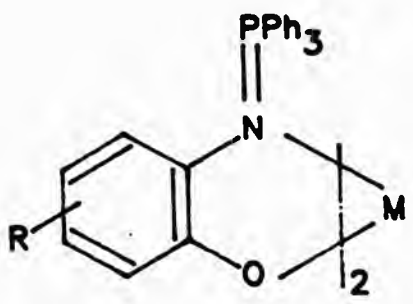
(2)



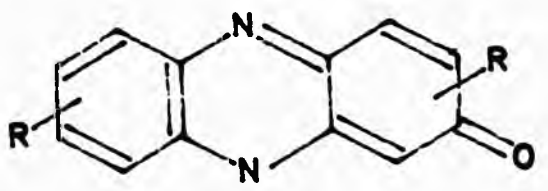
(3)



(4)



(5)

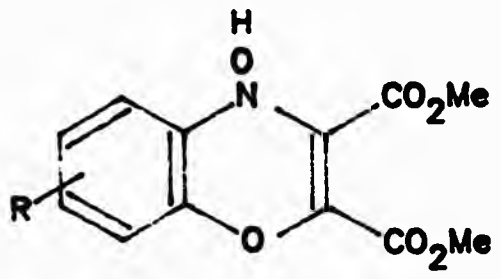


The susceptibility of the cyclic dienyl moiety to nucleophilic attack has been demonstrated by the isolation of interesting amino substituted products from the reaction of amines, for example aniline and ethylene diamine with metal 1,2-quinone monooximates.[3-5] However, much of the recent interest in the synthetic applications of 1,2-quinone monooximes and their metal complexes have focussed on the reactivity of the cis 1,2-heterodienyl moiety in both sets of compounds and in particular, on its interaction with the dienophile dimethyl acetylenedicarboxylate (DMAD).

A common reaction of cis 1,3-dienes and by extension cis 1,2-heterodienes, is facile cycloaddition.[6-8] The latter, which results in ring formation, is well documented and is categorised on the basis of how many π electrons are involved in the reaction and the size of the resultant ring.[9,10] The most common type of cycloaddition is that which leads to six-membered ring formation or the Diels-Alder $4\pi + 2\pi$ cycloaddition.[11-14] This type of reaction has been widely studied and numerous reviews on various aspects of these reactions have been published.[15-18] It is therefore well known that both Lewis acids and Lewis bases catalyse Diels-Alder reactions,[19,20] and that the electronic character of any substituent in either the diene (or heterodiene) or the dienophile, influences the likelihood and rate of these reactions.[21,22]

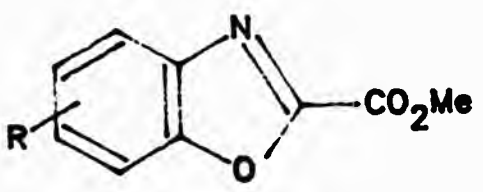
The Diels-Alder reaction was used to rationalize the formation of 1,4-benzoxazines (6) by the reaction of copper(II) 1,2-quinone monooximates with DMAD when the reaction was first reported in 1976.[23] At that stage, the 1,4-oxazines were the only compounds which were identified as the products of these reactions.

(6)



More recently however, several other types of compounds have been isolated from the reaction of metal 1,2-quinone monooximates with DMAD. 1,3-Oxazoles (7) were recovered when copper(II) 1,2-quinone monooximates were refluxed with DMAD in anhydrous methanol.[24] Although thought initally to arise from direct reaction of DMAD with the metal complex, it was later shown that 1,3-oxazoles were the oxidation products of the corresponding 1,4-oxazines, the oxidation being promoted by unreacted metal complex in the reaction system.[25] That this reaction should occur is not surprising since metal 1,2-quinone monooximates are known to be good oxidation catalysts.[26-28]

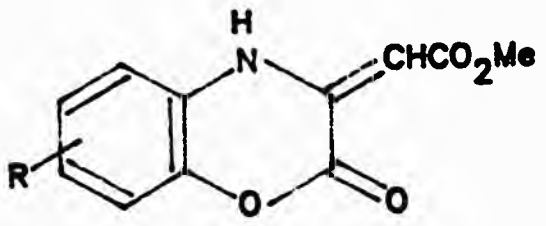
(7)



1,4-Benzoxazinones (8) have also been isolated from the reaction of DMAD with some metal 1,2-quinone monooximates. These compounds, which like the 1,4-oxazines are chemotherapeutically important, were recovered when DMAD was used in considerable excess.[29] Unlike the

1,4-benzooxazines however, the formation of the 1,4-benzoxazinones cannot be rationalized in terms of Diels-Alder cycloaddition, and to date no definite mechanism has been proposed.

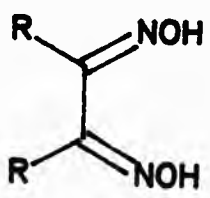
(8)



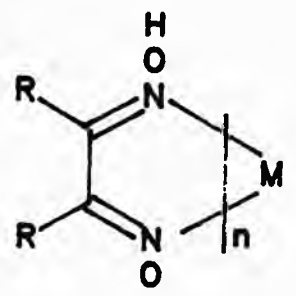
The previous reports of the interaction of DMAD with 1,2-quinone monooximes and their metal complexes suggested that the nature of the products formed depended on such factors as (i) the nature of the quinone monooximic substrate, (ii) the solvent system used and (iii) the nature of the metal ion involved. In fact, one of these reports[23] ascerted that only coordinated 1,2-quinone monooximes, that is, the metal complexes, were capable of giving isolable addition products with DMAD. It was claimed that the free or uncoordinated compounds either failed to react or afforded mixtures which could not be adequately separated.

In contrast to 1,2-quinone monooximes and metal 1,2-quinone monooximates, very little attention has been given to the reaction of the related 1,2-dioximato compounds, (9) and (10), with DMAD. To date, only one such study has been reported and it describes the formation of an adduct (11) by the reaction of 1,2-diaminoethanedione dioxime, its nickel(II) and copper(II) complexes with DMAD.[30]

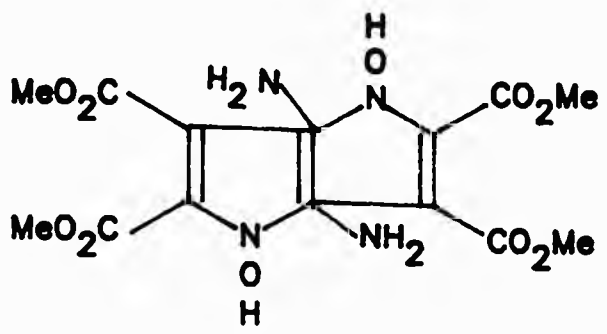
(9)



(10)



(11)



From the above general review, no clear pattern of reactivity of 1,2-quinone monooximes or of their metal complexes has emerged. Additionally, the lack of current literature on the reaction of the related dioximes has meant that no useful comparison of mechanisms or products could be made. Moreover, the formulation of (11) and the proposed mechanism by which it was believed to have been formed were both flawed and as such warranted further investigation.

In this study therefore, a reinvestigation of the reactions of 1,2-quinone monooximes and their metal complexes as well as of related 1,2-dioximato compounds, with DMAD was carried out. The aims of this reinvestigation were to established and account for (i) the supposed inactivity of free 1,2-quinone monooximes towards DMAD, (ii) the role of metal ions in these reactions, and (iii) any similarities or differences between the behaviour of 1,2-quinone monooximic and 1,2-dioximic compounds towards DMAD. In addition, full characterisation of all

products and a mechanistic appraisal of all reactions was to be undertaken.

5.2. The Reaction of Free 1,2-Quinone Monooximes with DMAD.

When the reaction of 1,2-quinone monooximes with DMAD was first reported,[23] it was suggested that the free or uncoordinated compounds did not react and that a metal ion (incooporated in a complexed form, ie. as a metal complex) was essential. The role of the metal ion was considered to be that of (i) polarization of electron density in the 1,2-quinone monooximic moiety towards the heterotermini, making addition across the two heteroatoms possible, and (ii) correctly orientating the 1,2-quinone monooximic moiety and the dienophile (by coordination of the latter) for facile addition. The metal ion thus acted as a template for reaction. It was argued that the latter required the metal to be coordinately unsaturated. However, this proposal has been disproved, in this and other studies, by the successful use of coordinately saturated copper(II) and nickel(II) 1,2-quinone monooximates in cycloadduct synthesis. There is however no doubting the electronic perturbation in the 1,2-quinone monooxime caused by the presence of the metal ion, and thus the validity of suggestion (i) above.

In fact the electron distribution in both free 1,2-quinone monooximes and their metal complexes was the subject of a recent study.[31] The latter which compared the X-ray crystal data for a series of these compounds concluded that in the complexes, there was marked electron polarization from the ligand to the metal.

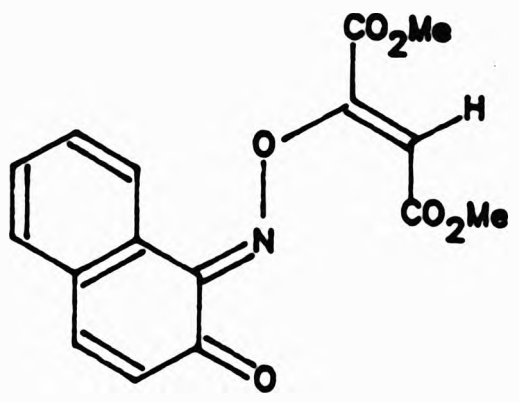
In contrast to the earlier reports however, it was found during this study that free 1,2-quinone monooximes reacted with DMAD either when stirred at 40 - 60 ^{0}C or under gentle reflux in aqueous EGDE. In

most cases these reactions gave, coloured, multicomponent mixtures which could not be satisfactorily separated. However, in the case of 1,2-naphthoquinone-1-oxime, chromatographic separation of the reaction mixture afforded the yellow *trans*-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime (12) and the orange *cis*-(O-1,2-dicarbomethoxy-ethenyl)-1,2-naphthoquinone-1-oxime (13) both in good yields.

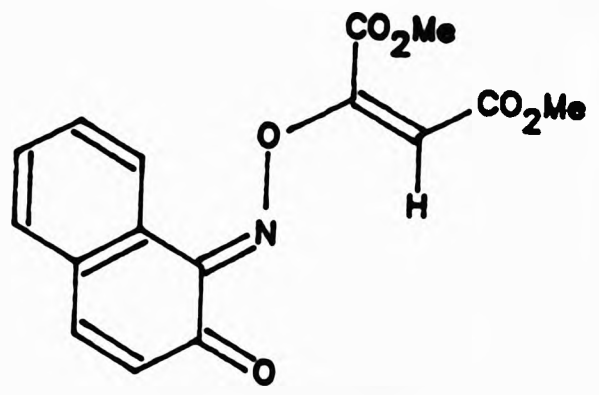
Similarly, the reaction of 5-hydroxy-1,2-benzoquinone-2-oxime with DMAD afforded the yellow-orange *trans*-(O-1,2-dicarbomethoxy-ethenyl)-5-hydroxy-1,2-benzoquinone-2-oxime (14) in moderate yield.

All three compounds were soluble in common organic solvents, stable at room temperature, and were characterised by full elemental and spectroscopic analysis.

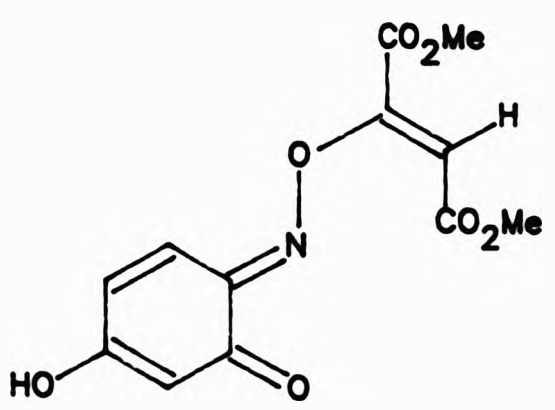
(12)



(13)



(14)



5.3. The Reaction of 1,2-Naphthoquinone-1-oxime with DMAD in the Presence of Metal Ions.

Historically, studies of the reaction of 1,2-quinone monooximes with DMAD have focussed on the reaction of their metal complexes. As stated earlier, this preoccupation with the latter has been due to the finding that transition metal ions promoted addition presumably by polarizing the electron density towards the hetero-termini of the 1,2-quinone monooximic moiety. It was however found in the case of the naphthoquinone monooximates,[25] that when the metal ion involved was main group, no cycloadduct was isolated, but rather, products arising from nucleophilic, Micheal-type addition reactions were recovered.

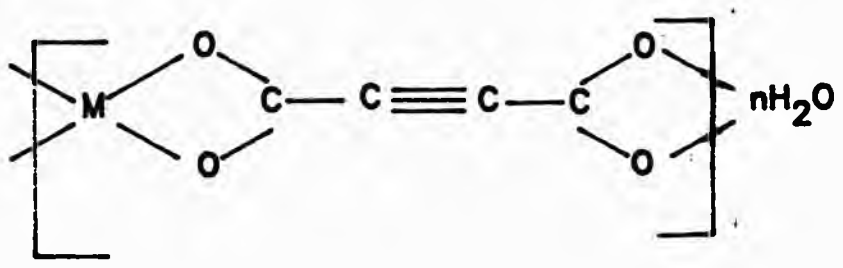
As part of this study, an attempt was made to establish the role of metal ions in these reactions, both by the reaction of the metal complexes and by the addition of catalytic amounts of a given metal salt to the system 1,2-quinone monooxime/DMAD/aqueous EGDE.

Thus, it was found that when 1,2-naphthoquinone-1-oxime was stirred at 40 ^{0}C with DMAD and aqueous EGDE in the presence of catalytic amounts of lithium, sodium, potassium, magnesium or aluminium chloride, yellow-orange mixtures were recovered. Separation of the latter gave the nucleophilic addition products (12) and (13). When the reactions were carried out under reflux complex mixtures of products including the open chain adducts resulted. The cycloadduct 1,4-naphthooxazine was not formed in either case.

In contrast, when 1,2-naphthoquinone-1-oxime was stirred at 40 ^{0}C with DMAD in aqueous EGDE in the presence of catalytic amounts of copper(II) or nickel(II) chloride, the corresponding metal complexes were recovered in high yield. Neither open chain adducts nor cycloadducts were formed. When the reactions were carried out under

reflux however, the 1,4-naphthooxazine was formed in high yield in addition to the hydrated metal butynedioate (15).

(15)



5.4. Reaction of Nickel(II) and Copper(II) 1,2-Quinone Monooximates with DMAD.

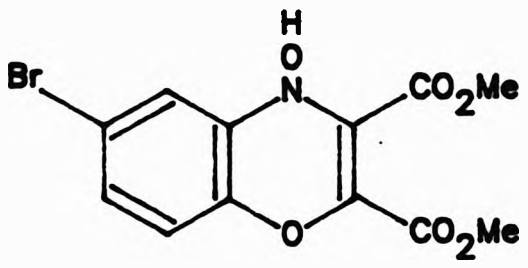
In the earlier sections, the reaction of the uncoordinated 1,2-quinone monooximes with DMAD was discussed. The results of some of the experiments contradicted previous reports. In view of this, and with the new range of complexes prepared during this study, a reinvestigation of the reaction of metal 1,2-quinone monooximates with DMAD was undertaken.

When $Ni(qo)_2$ and $Cu(qo)_2$ (qoH = 1-nqoH and 5-BuqoH) were refluxed with DMAD in aqueous EGDE, the corresponding 1,4-oxazines were recovered in high yield as the only isolable organic products. This was consistent with previous results.[23,25]

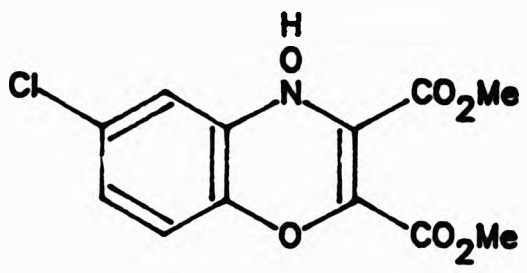
By comparison, reaction of $Ni(4\text{-}Brqo)_2$, $Ni(4\text{-}Clqo)_2$, $Cu(4\text{-}Brqo)_2$ and $Cu(4\text{-}Clqo)_2$ with DMAD in aqueous EGDE afforded mixtures of two sets of organic products. Separation of the reaction mixtures gave yellow-orange 1,4-benzoxazines (16 or 17), the compounds traditionally associated with the reaction of metal 1,2-quinone monooximates with DMAD.[23,24]

The second set of products were identified as 1,4-benzoxazinones (18 or 19). Although related compounds have been previously reported,[32-35] their association with the reaction of metal 1,2-quinone monooximates with DMAD was only made while this study was being conducted.[29]

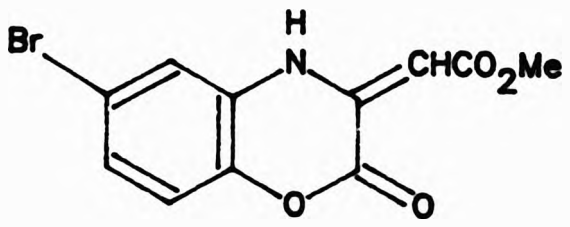
(16)



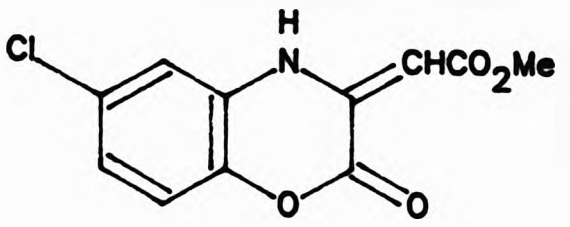
(17)



(18)



(19)



5.5 Reaction of 1,2-Dioximes and Metal 1,2-Dioximates with DMAD.

Like 1,2-quinone monooximes and metal 1,2-quinone monooximates, 1,2-dioximes and their metal complexes also possess a 1,3-heterodiene system and as such, are expected to undergo related addition reactions. However unlike the 1,2-quinone monooximes in which the heterodiene system is frozen in the *cis* conformation, 1,2-dioximes tend to prefer the more thermodynamically stable *trans* conformation. This makes cyclo-adduct formation involving the reaction of 1,2-dioximes difficult since

these reactions require the diene (heterodiene) to be *cis* oriented. Such an orientation is afforded by their metal complexes and hence cyclo-adduct formation becomes possible.

An earlier study of the reaction of 1,2-dioximes and metal 1,2-dioximates with DMAD was carried out in these laboratories.[30] Thus it was found that 1,2-diaminoethanedione dioxime and its complexes reacted with DMAD to afford the same white solid which was formulated as (11).

During this study the reaction of dimethylglyoxime, benzil *anti*monooxime, 1,2-cyclohexanedione dioxime, and 1,2-diaminoethanedione dioxime, their copper(II) and nickel(II) complexes, where available, were refluxed with DMAD in aqueous EGDE. Reaction occurred in all cases though the systems involving dimethylglyoxime, benzil *anti*monooxime and 1,2-cyclohexanedione dioxime, only afforded solids of indefinite composition.

In the case of 1,2-diaminoethanedione dioxime, its copper(II) and nickel(II) complexes however, two white solids A and B which were identified as isomers of bis(O-1,2-dicarbomethoxyethenyl)-1,2-diamino-ethanedione dioxime (20), were formed in reasonable yields. The metal complexes also afforded hydrated metal butynedioates.

Bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedionedioxime can exist in three isomeric forms (Figs. 5.1 - 5.3). The spectroscopic analysis of the two solids A and B (see later) showed marked similarities confirming them as a pair of isomers. The structure of the solid A was determined by X-ray crystallography and is discussed in section 5.8.

(20)

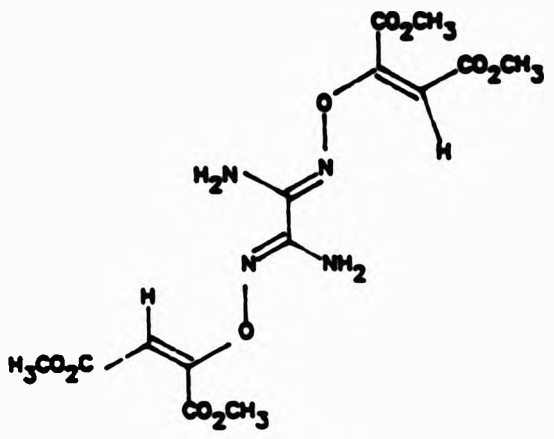


Figure 5.1

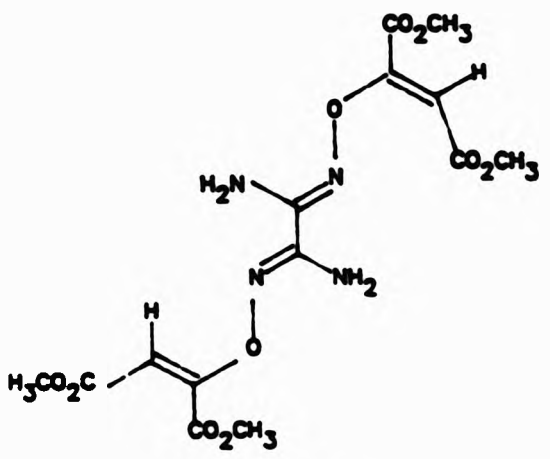


Figure 5.2

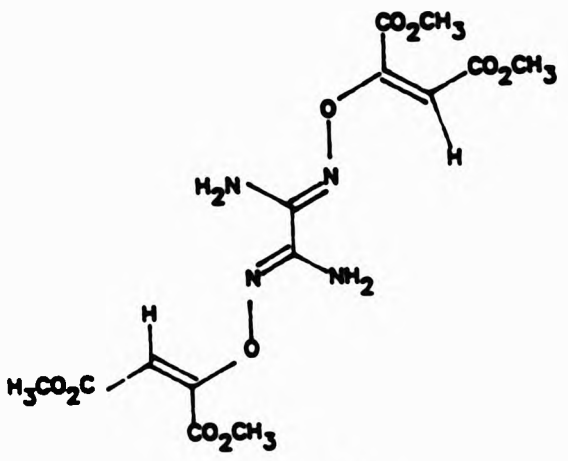
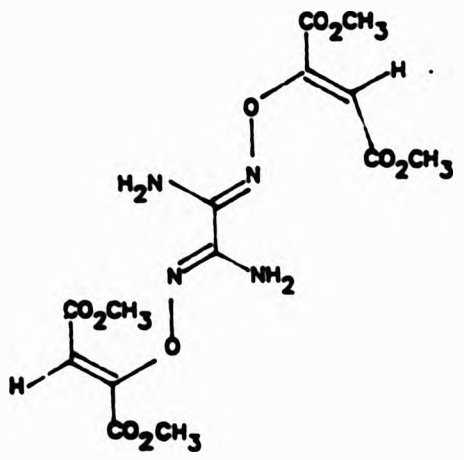


Figure 5.3



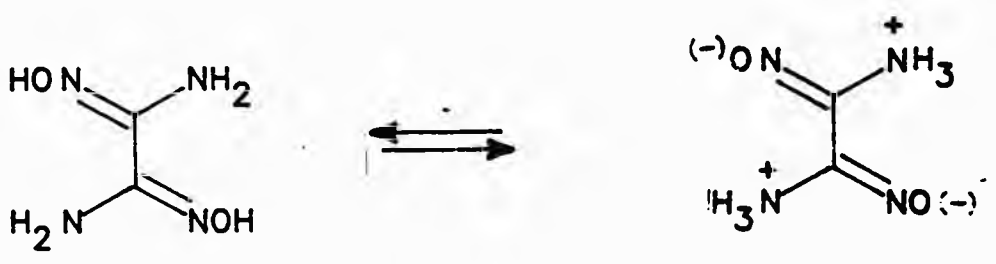
5.6 Mechanistic Appraisal of the Reaction of DMAD with 1,2-Quinone Monooximes, Metal 1,2-Quinone Monooximates and their 1,2-Dioximic Analogues.

The formation of open chain adducts (12, 13 and 14) from the reaction of 1,2-quinone monooximes with DMAD and adducts (20A and 20B) from the reaction of 1,2-dioximes with DMAD, can be rationalized in terms of the nucleophilicity of 1,2-quinone monooximes and 1,2-dioximes. This property which is related to the presence of lone pairs of electrons on both the quinoid and oximic groups, enables such compounds to participate in facile addition and/or substitution reactions.

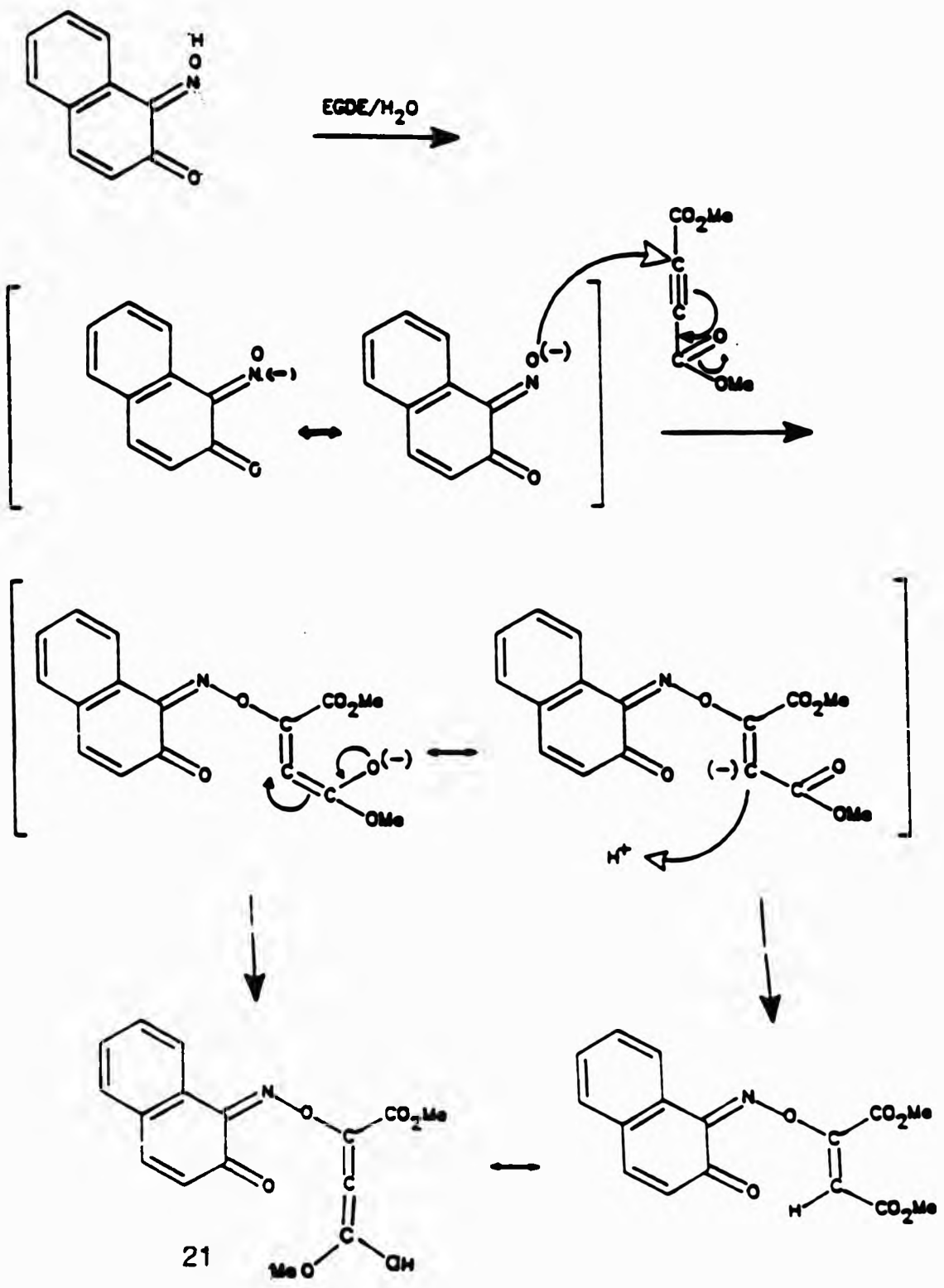
In the case of 1,2-diaminoethanedione dioxime, the nucleophilicity of the oximic group is further enhanced by the presence of the electron donating amino group. The latter confers a high degree of electron density into the oximic group such that the molecule could be represented as shown in Scheme 5.1. Proposed mechanisms for the reactions of 1,2-quinone monooximes and 1,2-diaminoethanedione dioxime with DMAD are given below (Scheme 5.2 and 5.3).

In both cases, the reactions are believed to involve nucleophilic attack of the oximic oxygen on one of the acetylenic carbons of DMAD to give a carbanion which is subsequently protonated by protons from either water or the oxime. The result is therefore an overall nucleophilic 1,2-addition to a triple bond via a pathway not dissimilar from the Micheal-type addition described in the literature.[36-40]

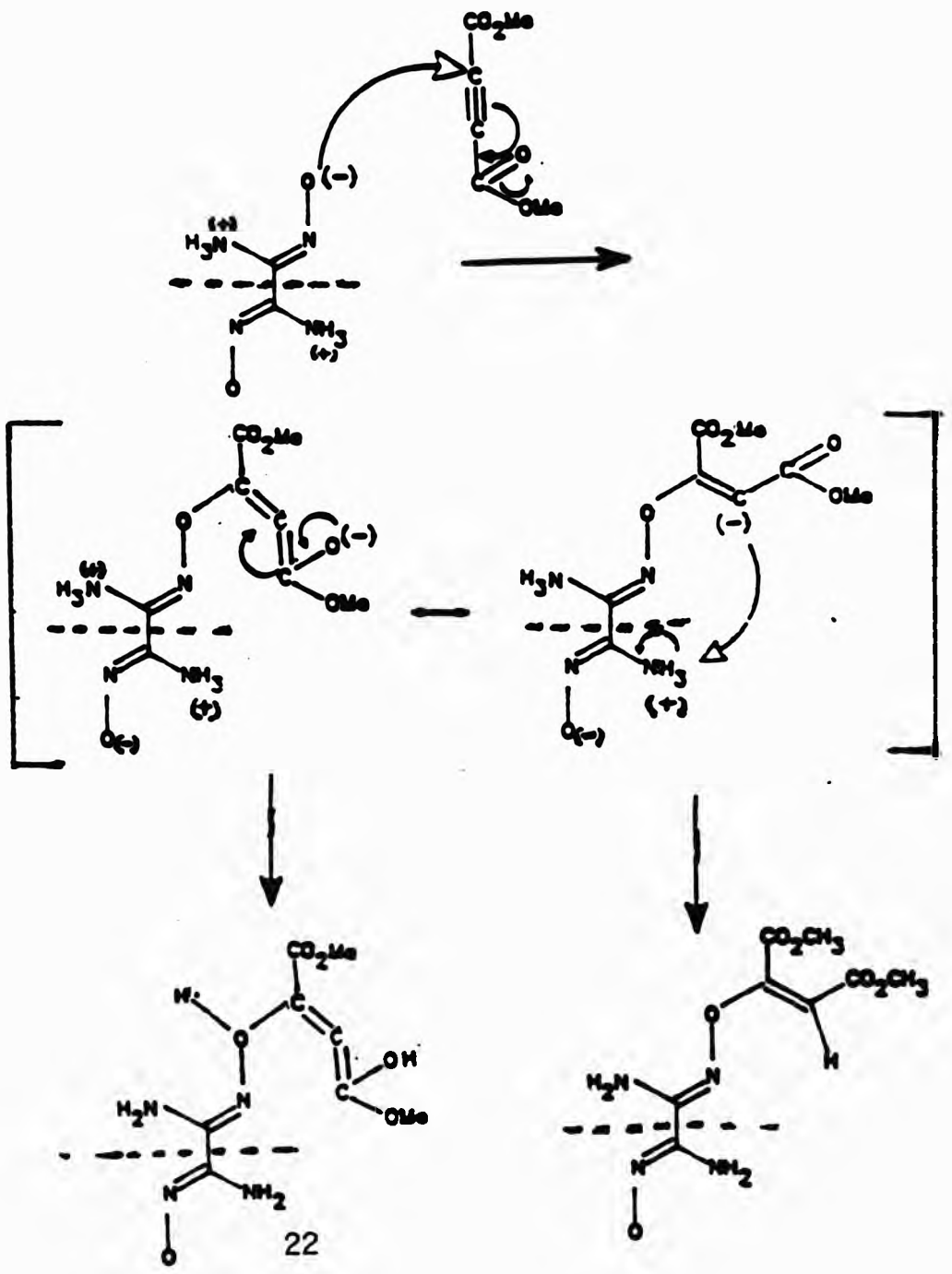
Scheme 5.1



Scheme 5.2



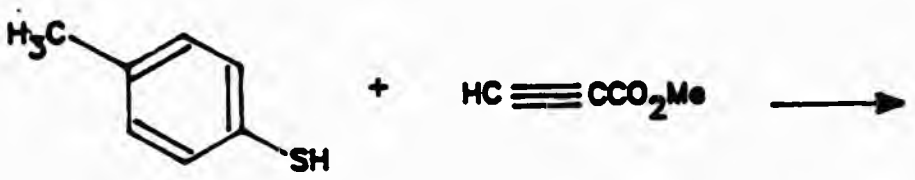
Scheme 5.3

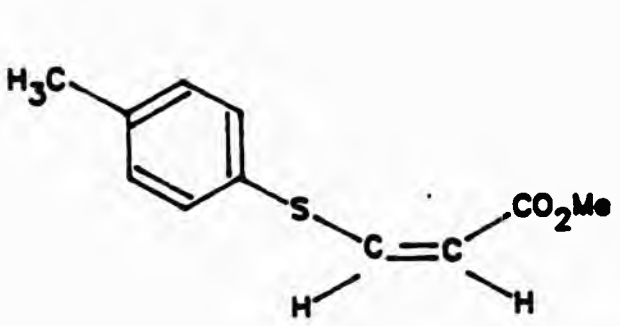


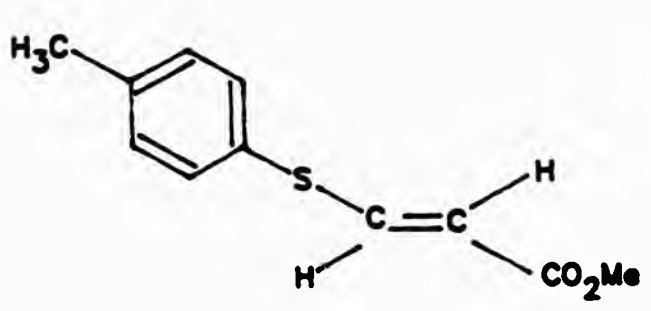
Although the formation of enols (21) and (22) are implied in the above mechanisms, only products of the more thermodynamically stable α-unsaturated carbonyl tautomers[10] were isolated.

Usually nucleophilic addition to a triple bond in the presence of protic solvents is stereoselective and gives product mixtures in which one of the pair of diastereoisomers predominates.[41] For example, the reaction of *p*-toluenethiolate with methyl propiolate gave a mixture which contained 92% methyl-(Z)-β-*p*-tolylmercaptoacrylate and only 8% of the corresponding E isomer (Reaction 5.1).

Reaction 5.1







	Z (cis)	E (trans)
Yield:	92 %	8 %

In contrast to the above example, the reaction of DMAD with 1,2-naphthoquinone-1-oxime was found to be largely non-stereoselective. This was bourne out by the occurrence of adducts (12) and (13) in almost equimolar amounts. This observation is not without precedent since several reports on the non-stereoselective addition to activated acetylenes have been published.[42-44] These reports allude to the fact that selectivity can be affected by the nature of the electron withdrawing group in the acetylene.

Previously, such reactions have been rationalized in term of (i) the postisomerization of the trans addition products (having the cis configuration) to the more stable E-trans isomer, or (ii) from the intermediacy of resonance stabilized or equilibrating carbanions in aprotic solvents.[45]

It is not certain which precise mechanism is operating in the system DMAD/1,2-quinone monooximes, but differences in the stability of

any intermediate carbanion can be ruled out since, in this study, the acetylenic substrate was symmetrical.

As regards the metal complexes or reaction in the presence of a metal ion, the results of this study show that main group and transition metal ions have fundamentally different effects on the reaction 1,2-naphthoquinone-1-oxime and possibly by extension, other 1,2-quinone monooximes with DMAD.

Although in both main group and transition metal complexes of 1,2-quinone monooximes, coordination of the metal ion involves the oximic nitrogen and carbonyl oxygen,[46-49] the degree of electron polarisation towards the metal ions is different.

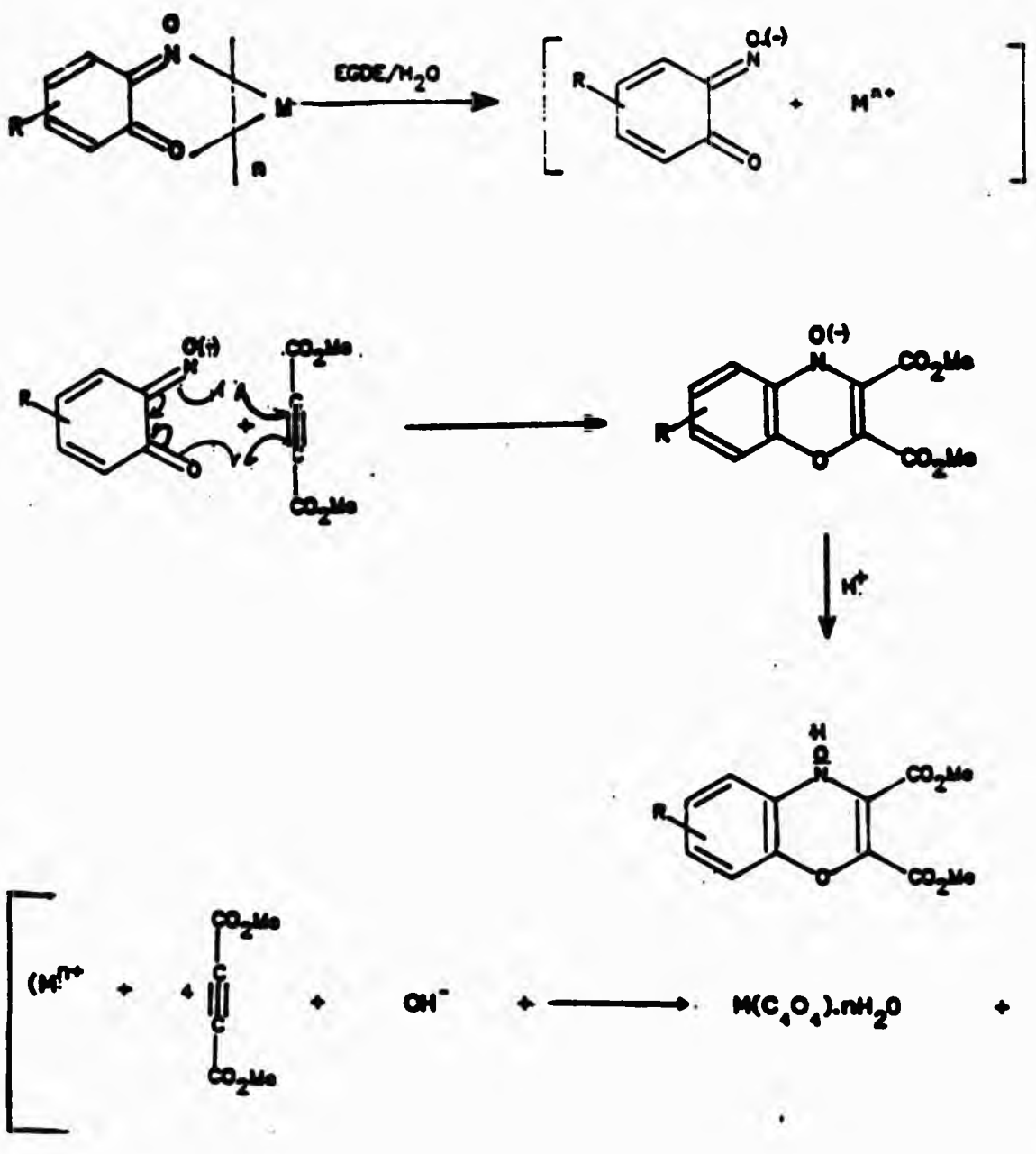
In the case of the main group metals, the degree of electron withdrawal from the oximic nitrogen and hence the oximic oxygen is less than for the transition metals. This can be attributed to the unavailability of suiltably energetic *d-orbitals* in the former to accomodate the extra ligand electrons.[50] The oximic oxygen in the main group metal complexes therefore retains a large amount of its electron density and hence can compete as a nucleophilic site. Thus the reaction of main group metal 1,2-quinone monooximates with DMAD, can be rationalized in terms of the nucleophilic attack of the electron-rich oximic oxygen at one of the acetylenic carbons giving a carbanion. The latter is then protonated to give the 1,2-addition product. The reaction being analogous to that observed with the free 1,2-quinone monooximes (Scheme 5.2).

By comparison, the transition metal ion fundamentally changes the reaction pathway by becoming strongly bound to the the 1,2-quinone monooximic moiety. The process of chelation is known to result in marked perturbation of the electron distribution in the ligand.[51] In these complexes therefore, electron density shifts from the oximic nitrogen

towards the metal ion and is compensated for by a concurrent movement of electrons from the oximic oxygen towards nitrogen. The partial double bond character of the N-O bond in the transition metal complexes (bond length 1.231 - 1.272 Å)[47] compared with that of and the main group metal complexes (bond length 1.308 - 1.351 Å)[48,49] is evidence of that shift. The latter results in lower electron density at oxygen and hence a reduced capacity of this site in the transition metal 1,2-quinone monooximates to participate in a nucleophilic reaction. Additionally in these complexes, the electron density at the oximic nitrogen is also reduced. The potential therefore, for reaction involving initial nucleophilic attack is diminished.

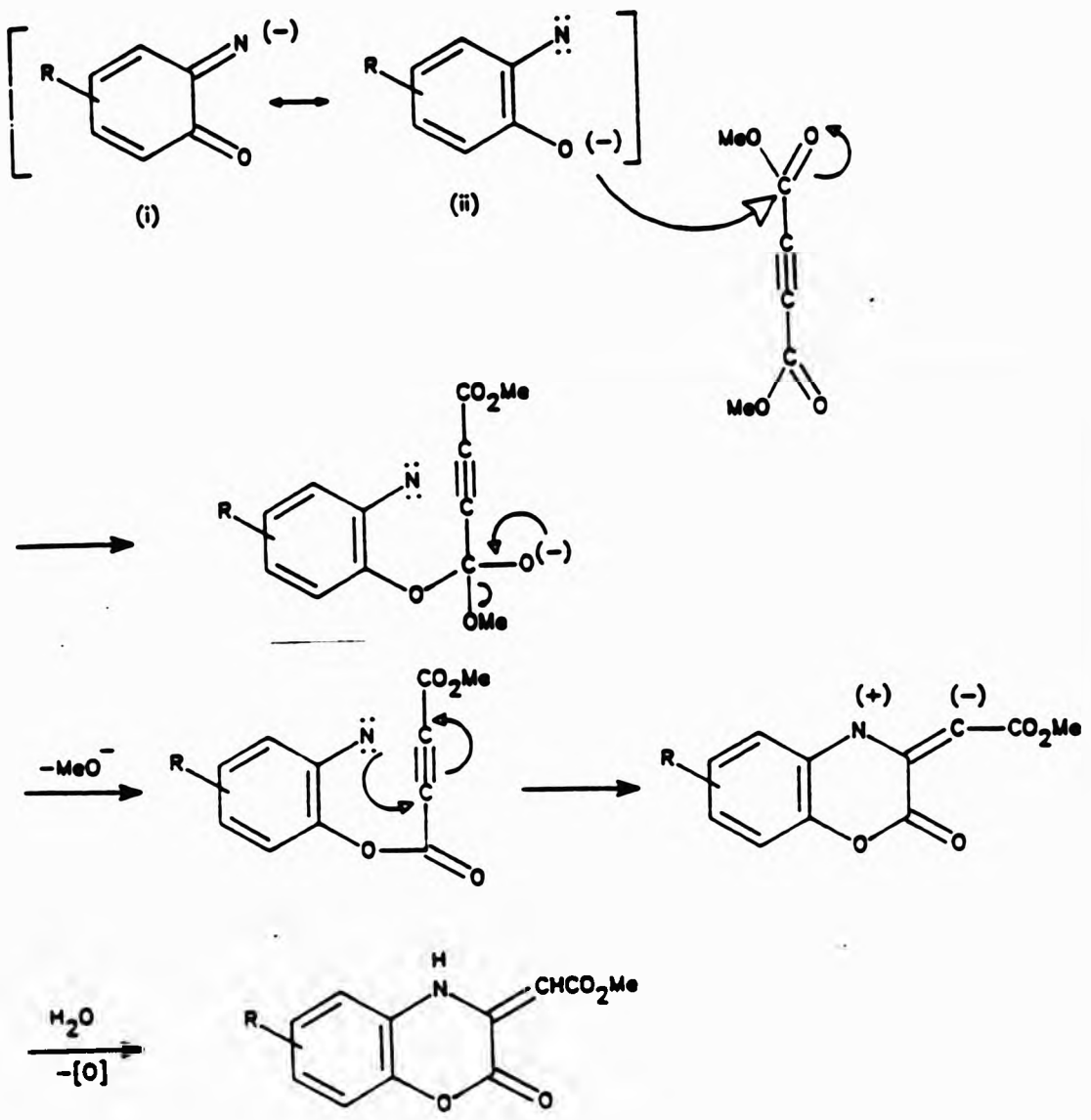
Transition metal ions are Lewis acids and they are known to catalyse Diels-Alder type cycloaddition reactions.[19] Their presence in the reaction system 1,2-quinone monooxime/DMAD would thus favour cycloadduct formation. The mechanism for the reaction of transition metal 1,2-quinone monooximates with DMAD can therefore be visualized as involving a concertive, single step addition of the 1,2-quinone monooximic anion to the dienophile giving the anion of the 1,4-benzoxazine. The latter is subsequently protonated by protons from water which acts as a reagent in these reactions (Scheme 5.4).

Scheme 5.4



Unlike the 1,4-oxazines which it is believed arise from a Diels-Alder type reaction, the origin of the 1,4-benzoxazinones (18 and 19) from the reaction of transition metal 1,2-quinone monooximates is unclear and cannot be rationalized in such terms. Instead, it is being proposed that these compounds arise from an initial nucleophilic substitution of the 1,2-quinone monooximic anion (or a species derived from it) for one of the two methoxy groups in DMAD followed by an intramolecular cyclisation (Scheme 5.5).

Scheme 5.5



The fact that the formation of the 1,4-benzoxazinones requires a reduction or deoxygenation of the 1,2-quinone monooximic moiety suggest that the nucleophile may not be the 1,2-quinone monooximic anion but rather some reduced or deoxygenated species derived from it. Such species could arise from abstraction of the oximic oxygen either by the transition metal ion or by DMAD.

Low valent, and early transition metal compounds have been widely used as oxygen abstractors in organic reactions.[52] In fact, titanium(II), titanium(III) and iron(II) compounds are reputed to effect the deoxygenation of nitroso compounds even under mild conditions. These reactions however lead to the formation of the corresponding metal oxide or a compound of that metal in an oxidation state one lower than the

starting compound. Since no such products were recovered from the reactions of $M(qo)_2$ with DMAD (M = Cu(II) and Ni(II)), it is safe to conclude that oxygen abstraction by the metal ion is not involved in the reaction mechanism.

In fact, a common metal containing product identified as the bis(butynedioate)metal(II) complexes (15) was recovered from all the reactions involving transition metal ions. The isolation of these complexes therefore precludes the occurrence of metal mediated oxidation or reduction reactions in the systems studied. In addition, the formation of butynedioate species, the hydrolysis product of DMAD, confirms the involvement of water and of hydrolytic processes in these reactions.

It was observed that the 1,4-benzoxazinones occured in higher yield when DMAD is used in considerable excess. This observation pointed to a mechanism for the formation of these compounds involving the abstraction of the relatively labile oximic oxygen by DMAD.

To check the hypothesis that excess of the multiple bonded system was responsible for the oxygen abstraction, and bearing in mind the reported use of $M(qo)_n$ as oxidation catalysts for alkenes and amines, the reaction of $Ni(4\text{-}Brqo)_2$ and $Ni(4\text{-}Clqo)_2$ with DMAD was repeated in the presence of octene. Separation of the products by column chromatography yielded the yellow 1,4-benzoxazinone in 90% recovery. The corresponding 1,4-benzoxazine was present only in trace amounts. These results supported the proposal of oxygen abstraction by the multiple bonded system but were not conclusive since they were not repeated when either $Ni(1\text{-}nqo)_2$ or $Ni(5\text{-}Buqo)_2.6H_2O$ were treated in the same way.

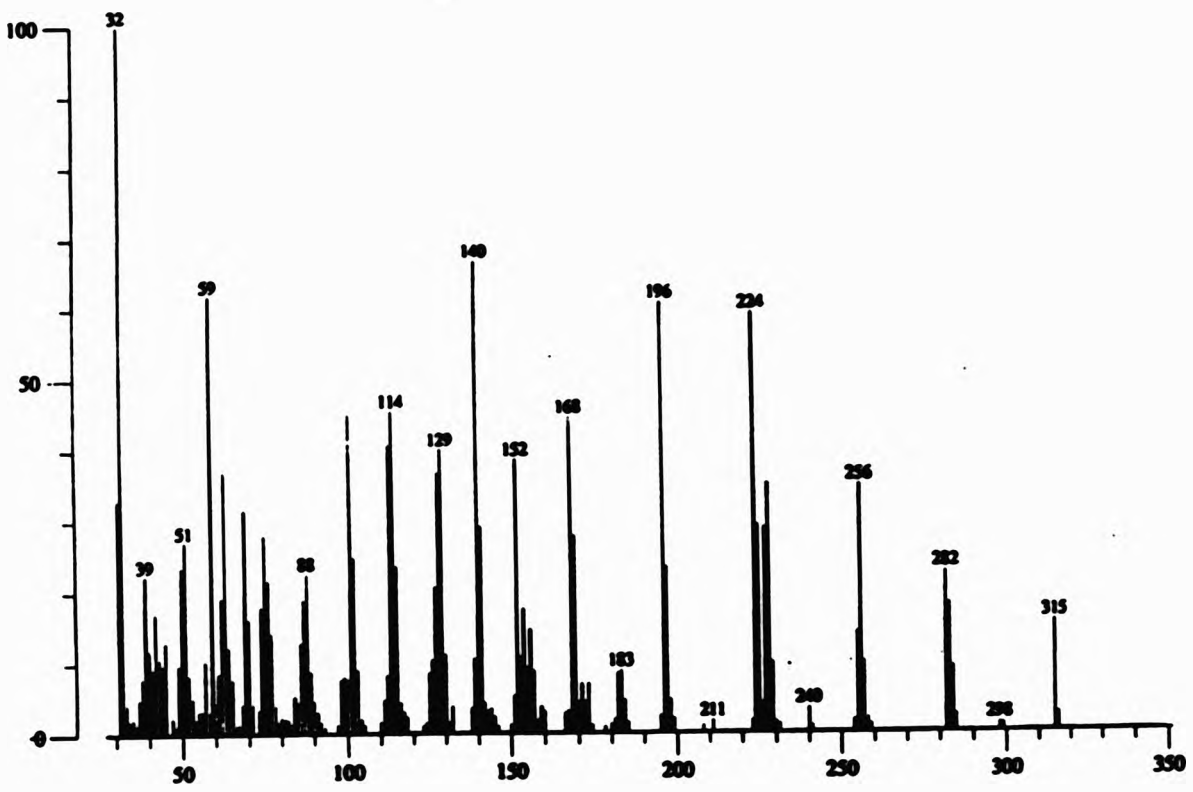
Thus, the involvement of other factors such as the nature of the ring substituent and its role in the stabilization of any intermediate important for the formation of the 1,4-oxazinones cannot be ruled out.

Although no attempt to establish the existence of such relationships was made during this study, the principle merits some attention.

5.7. Characterisation of the Products of the Reaction of DMAD with 1,2-Quinone Monooximes, Metal 1,2-Quinone Monooximates and their 1,2-Dioximic Analogues.

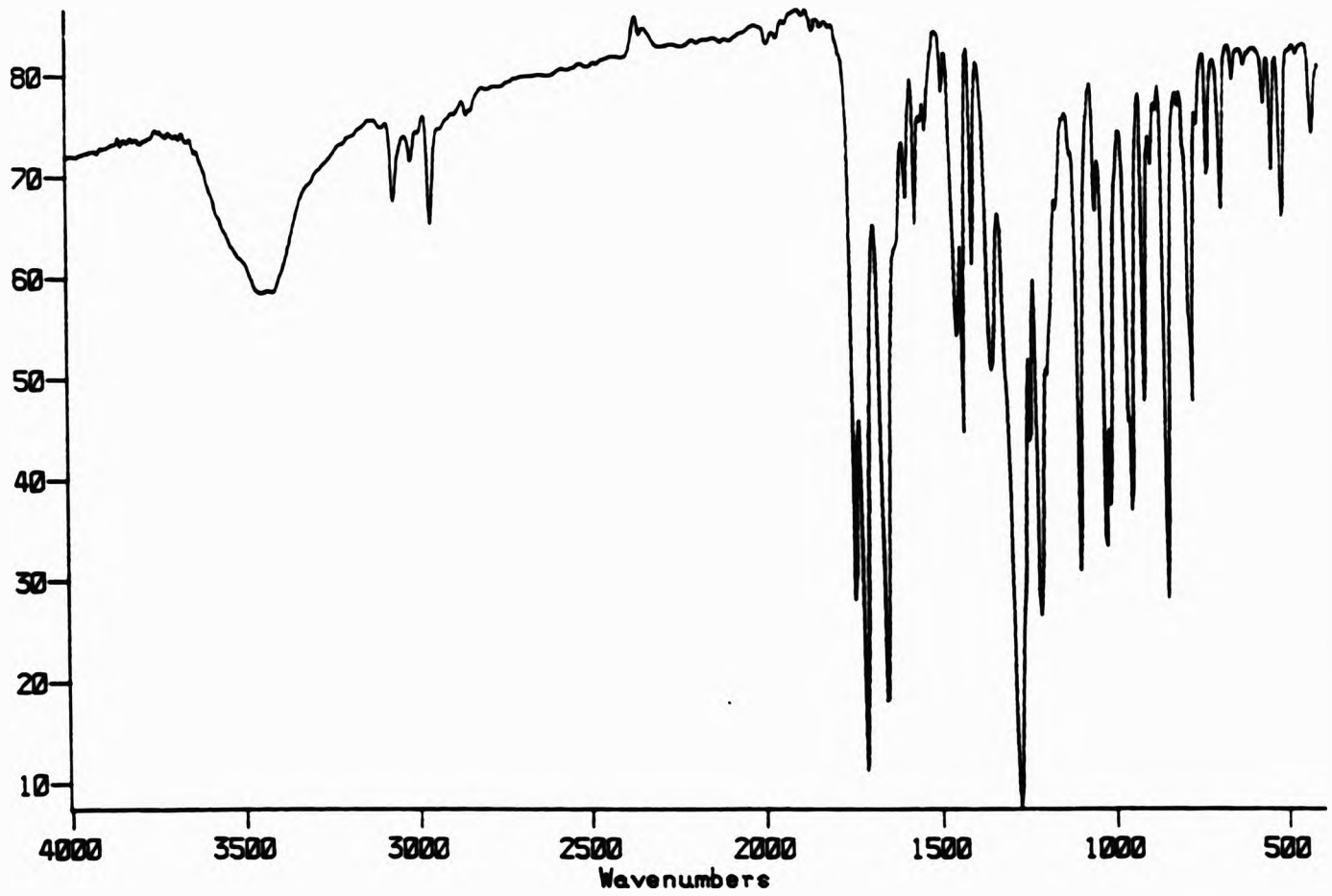
On the basis of elemental and mass spectral analysis, both compounds derived from the reaction of DMAD with 1,2-naphthoquinone-1-oxime were formulated as $C_{16}H_{13}NO_6$. The analogous yellow-orange solid recovered from the reaction of 5-hydroxy-1,2-benzoquinone-2-oxime were formulated as $C_{12}H_{11}NO_7$. The EI mass spectra of all three compounds (eg. Fig. 5.4) contained prominent molecular ion peaks at as well as peaks associated with the loss of such fragments as $CH_3O^{\cdot}$ and $CH_3CO_2^{\cdot}$.

Figure 5.4 *EI mass spectrum of trans-(O-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime.*



The IR spectra (eg Fig. 5.5) showed the common features of three absorption bands in the region between 1742 cm^{-1} and 1647 cm^{-1} assignable to the two ester and one quinoid carbonyl groups, moderately intense alkyl C-H stretching bands at 2956 cm^{-1} as well as well as a band at 3100 cm^{-1} assignable to a vinylic C-H stretch.

Figure 5.5 *Infrared spectrum of trans-(O-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime.*

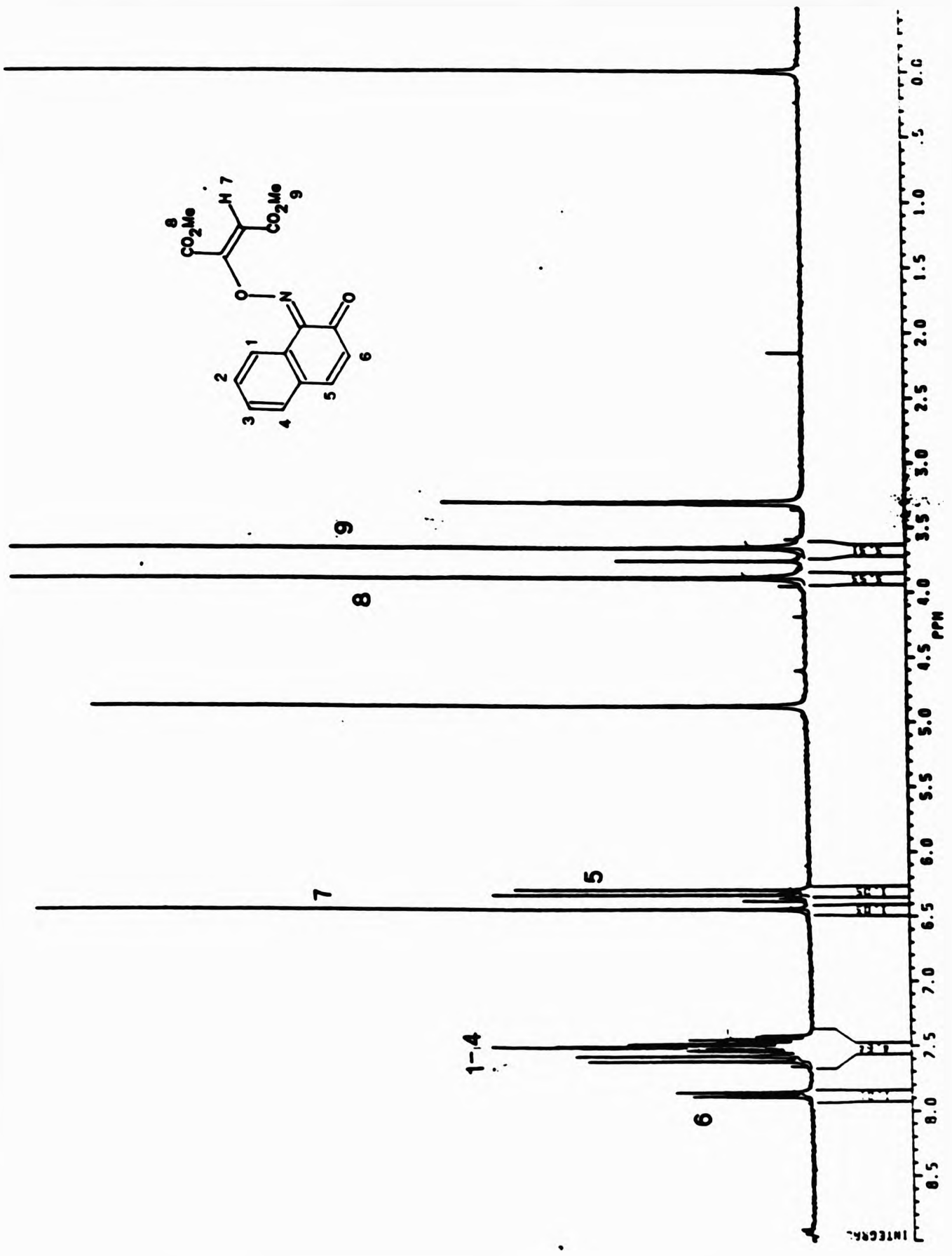


The ^{1}H NMR spectra of all three compounds (eg Fig. 5.6) contained two singlets integrating for three protons each between 3.60 ppm and 4.00 ppm. These signals were assigned to the two methoxy groups. Importantly, the spectra all contained a singlet integrating for one proton, between 5.90 ppm and 6.50 ppm. This signal, characteristic of vinylic protons was diagnostically important and is consistent with the the formulation of the compounds as the nucleophilic addition products of DMAD and the 1,2-quinone monoooxime, *cis*- and *trans*-(O-1,2-dicarbomethoxyethenyl)-1,2-quinone monooxime.

Although less informative, the ^{13}C NMR spectra confirm the presence of the two methoxy carbons as well as the vinylic C-H group by virtue of the appearance of signals attributable to these groups in the Dept 135 ^{13}C NMR spectra. The Dept 135 NMR experiment distinguishes

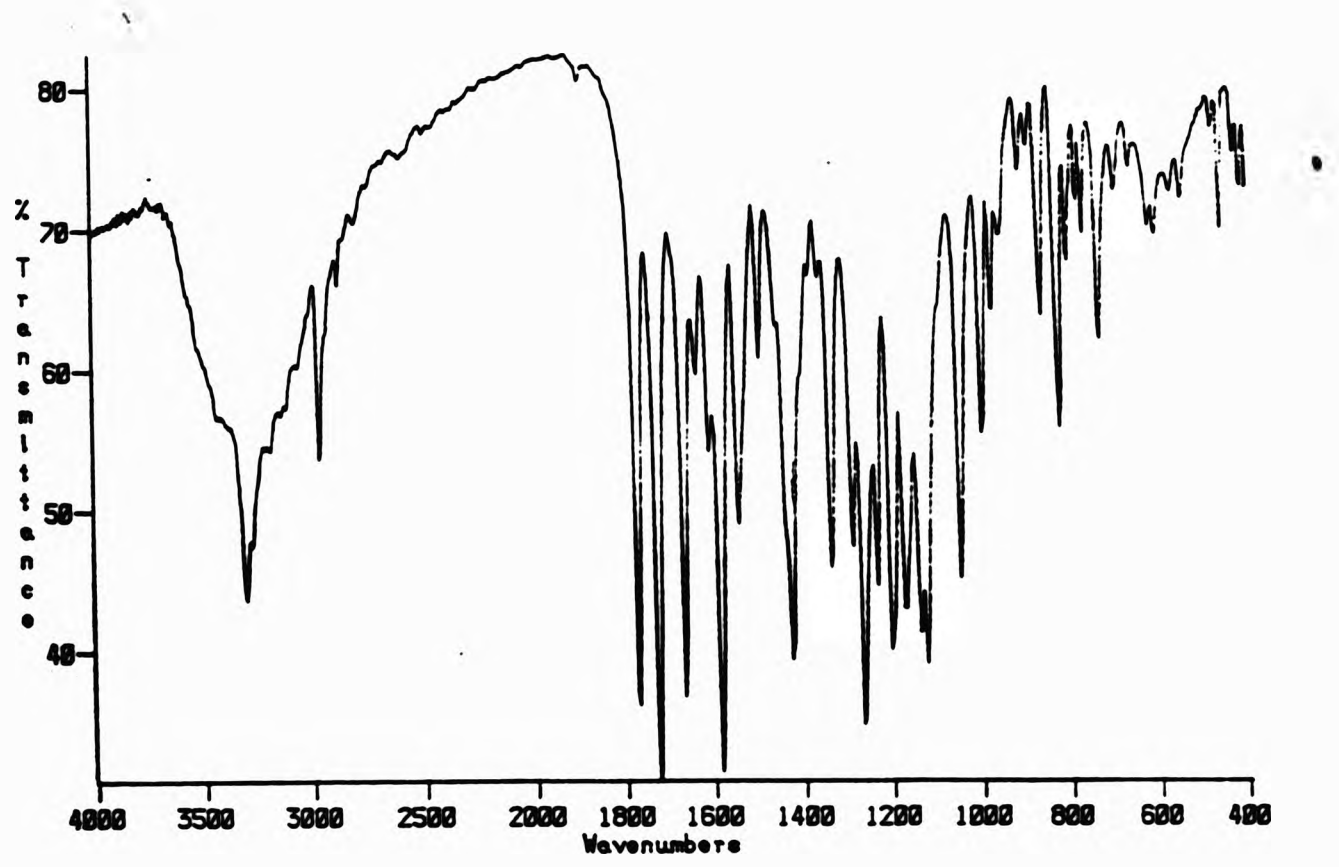
between carbon nuclei on the basis of the degree of substitution, showing CH_3 and CH as positive signals, CH_2 as negative signals while quarternary carbons are not observed.

Figure 5.6 *^1H NMR spectrum of trans-(O-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime.*



The IR spectra of the 1,4-oxazines prepared during this study were characterised by the presence of strong absorption bands due to νOH, and the ester νCO. This is exemplified by the IR spectrum of 7-butyrylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine (Fig. 5.7).

Figure 5.7. *IR spectrum of 7-butyrylamino-4-hydroxy-2,3-dimethoxy-carbonyl-1,4-benzoxazine.*



The ^{1}H NMR spectra are exemplified by Figure 5.8, (Table 5.1) which shows singlets between 1.00 ppm and 3.90 ppm due to the six methoxy protons, while the aromatic ring protons appear as multiplets between 7.20 ppm and 7.80 ppm.

Figure 5.8. ^{1}H *NMR spectrum of 7-butyrylamino-4-hydroxy-2,3-dimethoxycarbonyl-4-benzoxazine.*

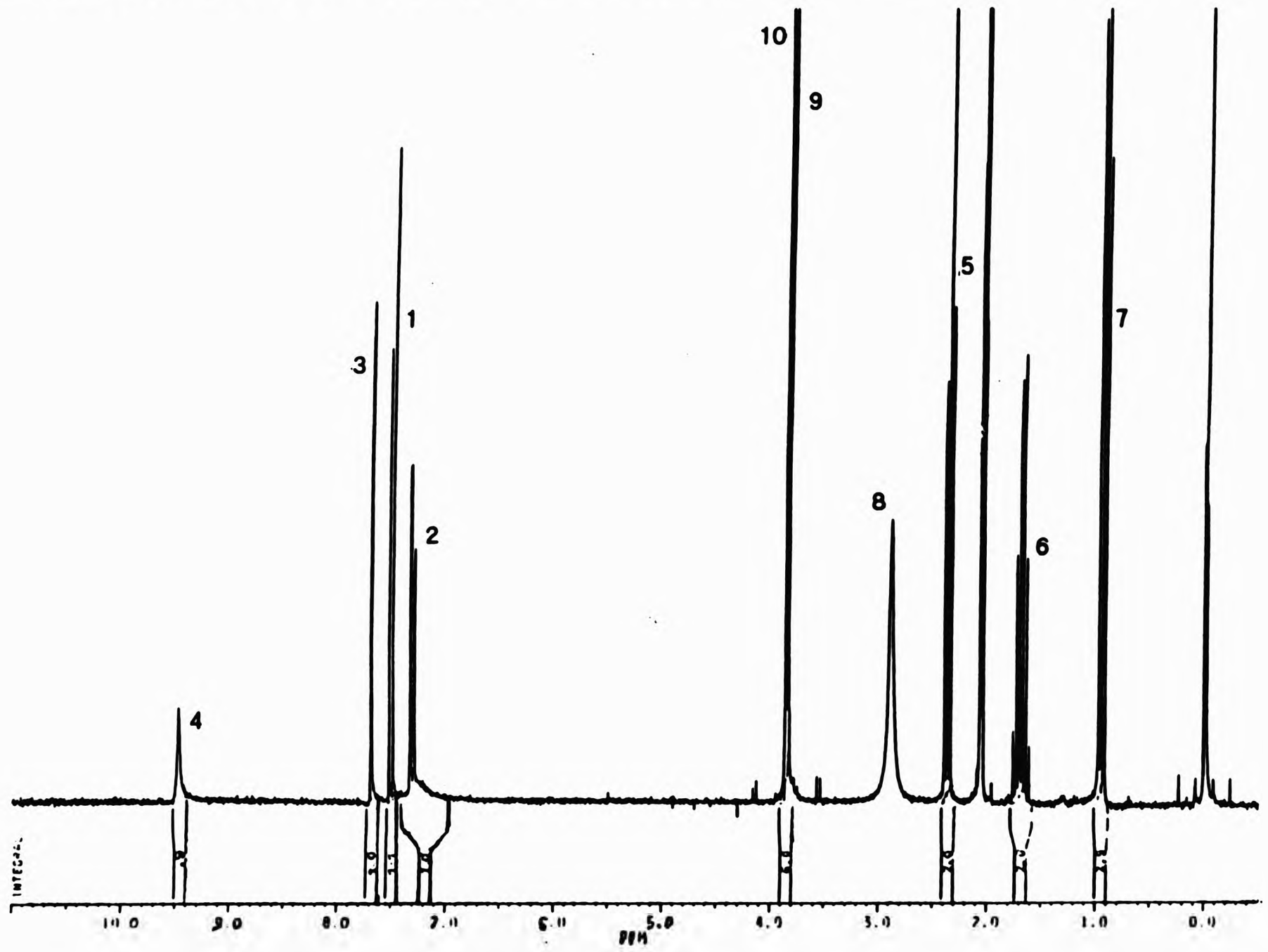


Table 5.1 ^{1}H NMR spectral assignment for 7-butyrylamino-4-hydroxy-2,3-dicarbomethoxy-1,4-benzooxazine.

Assignment	Multiplicity J/Hz	δppm
10	s	3.87
9	s	3.84
8	s	2.89
7	t $^{3}J_{7,6}$ (7.43)	0.95
6	sxt	1.65
5	t $^{3}J_{5,6}$ (7.25)	2.35
4	s	9.45
3	d $^{4}J_{2,3}$ (2.23)	7.69
2	d,d	7.29
1	d $^{3}J_{2,1}$ (8.60)	7.50

s singlet; d doublet; t triplet; sxt sextet; d,d doublet of doublets

The mass spectra all displayed prominent molecular ions, as well as ions due to the fragmentation of the carbomethoxy groups. For example the EI mass spectrum of 7-butyrylamino-4-hydroxy-2,3-dicarbomethoxy-1,4-benzooxazine (Fig. 5.9) contained a molecular ion peak at m/z = 350 and peaks assignable to the loss of $CH_3O^{\bullet}$, $CH_3CO_2^{\bullet}$, and CH_3CO_2H and $C_3H_7CONH^{\bullet}$ (Table 5.2).

Figure 5.9. *EI mass spectrum of 7-butyrylamino-2,3-dimethoxycarbonyl-4-benzoxazine.*

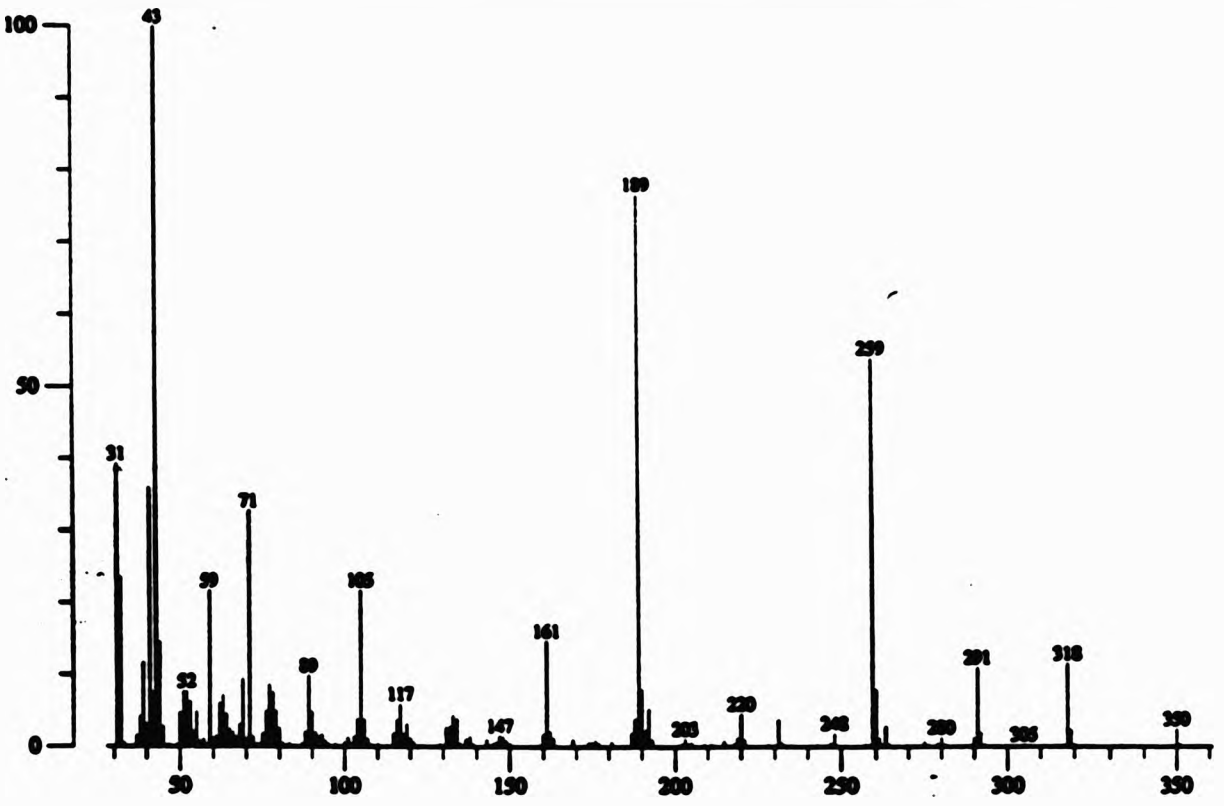


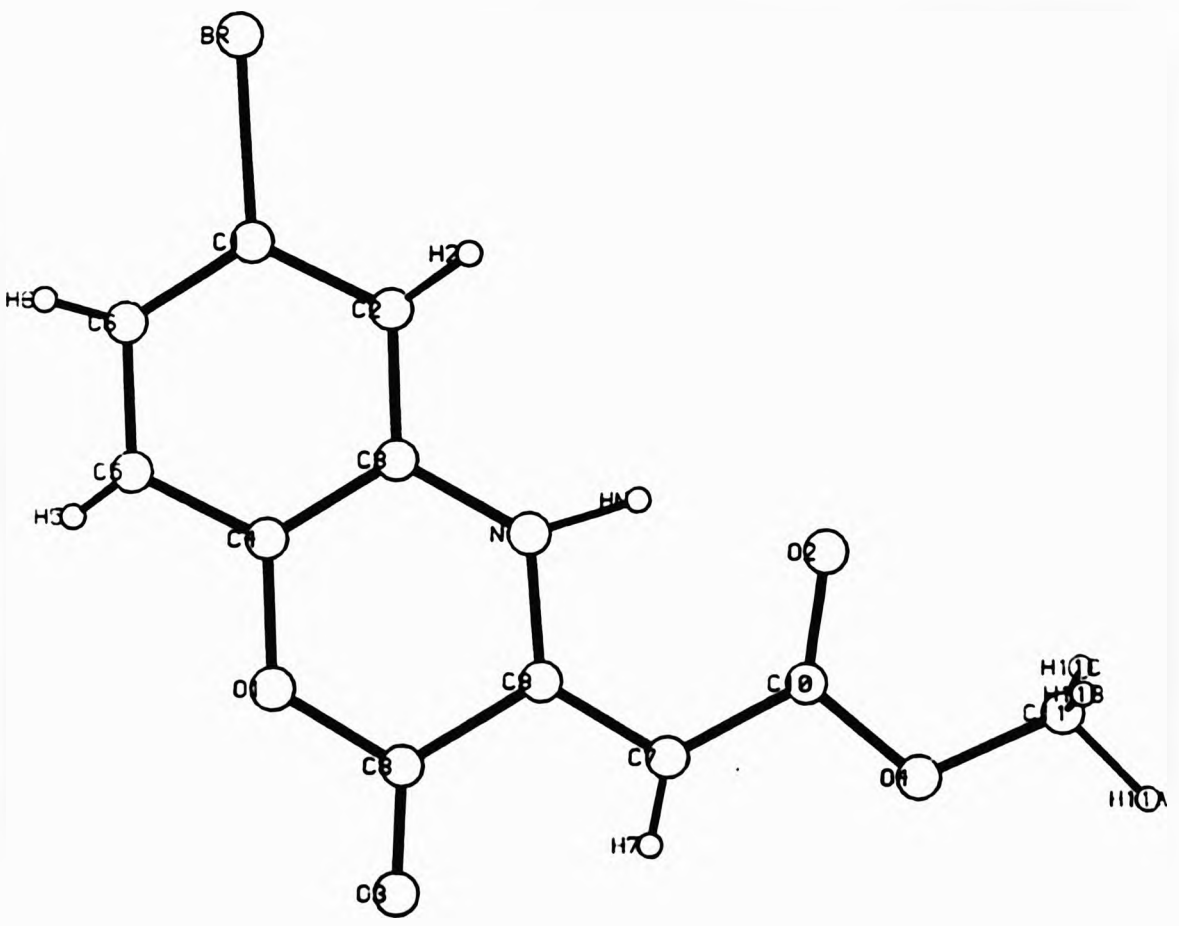
Table 5.2 *Ion abundances and assignment for the mass spectrum of 7-Butyrylamino-4-hydroxy-2,3-dicarbomethoxy-1,4-benzoxazine.*

Ion	Abundance %	m/z
$[M]^{+\cdot}$	3	350
$[M-OH^{\cdot}]^{+}$	1	333
$[M-CH_3OH]^{+\cdot}$	12	318
$[M-C_2H_4, OH^{\cdot}]^{+}$	1	305
$[M-CH_3CO_2^{\cdot}]^{+}$	11	291
$[M-CH_3CH_2CHCO^{\cdot}]^{+}$	1	280
$[M-CH_3CO_2^{\cdot} + CH_3OH]^{+}$	54	259
$[M-CH_3CH_2CHCO^{\cdot} + CH_3OH]^{+}$	2	248
$[M-CH_3CO_2^{\cdot} + CH_3CO_2H]^{+}$	4	231

The single crystal X-ray structure of 6-bromo-3,4-dihydro-3,2-oxo-2-methoxy-ethylidene-2H-1,4-benzoxazin-2-one (Fig. 5.10) has been reported.[29] Consequently, the EI mass spectra of this compound and of its 6-chloro analogue contained prominent molecular ion peaks at m/z = 297 and 257 respectively. The spectra also contained peaks associated with the loss of $CH_3O^{\cdot}$, CH_3OH, $HCO^{\cdot}$ and HCN. The base peak in both cases arose from the loss of the acetate radical $CH_3CO_2^{\cdot}$. The IR spectra showed a band at 3437 cm^{-1} assignable to νNH, at 2957 cm^{-1} due to νCH of the methoxy groups as well as intense absorption bands between 1758 cm^{-1} and 1650 cm^{-1} assignable to νCO of the acetate ester and the α-lactone carbonyl groups respectively.

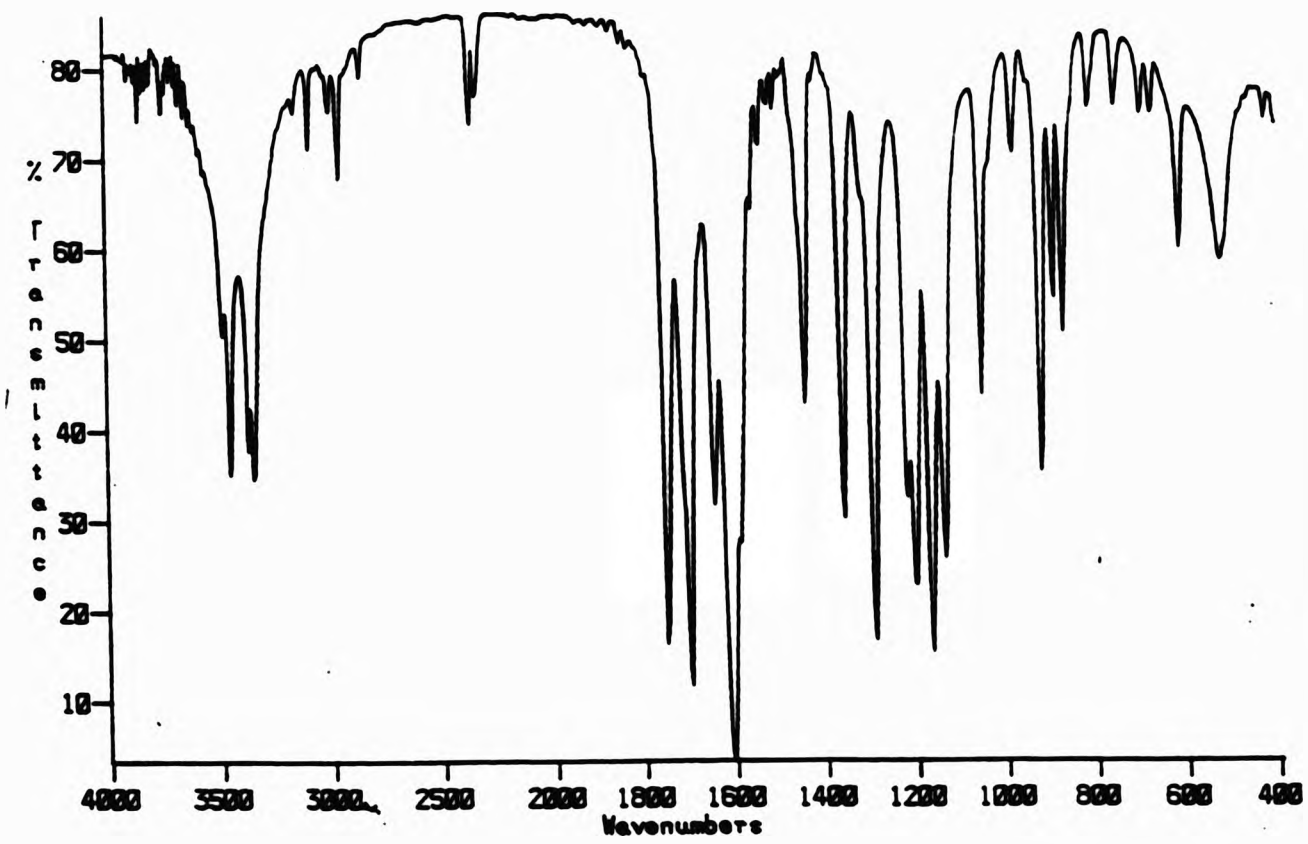
The ^1H NMR spectra show resonances at 3.80 ppm due to the methoxy protons, at 6.00 ppm due to the lone vinylic proton, and a multiplet between 6.90 ppm and 7.50ppm integrating for three protons assignable to the aromatic ring protons.

Figure 5.10



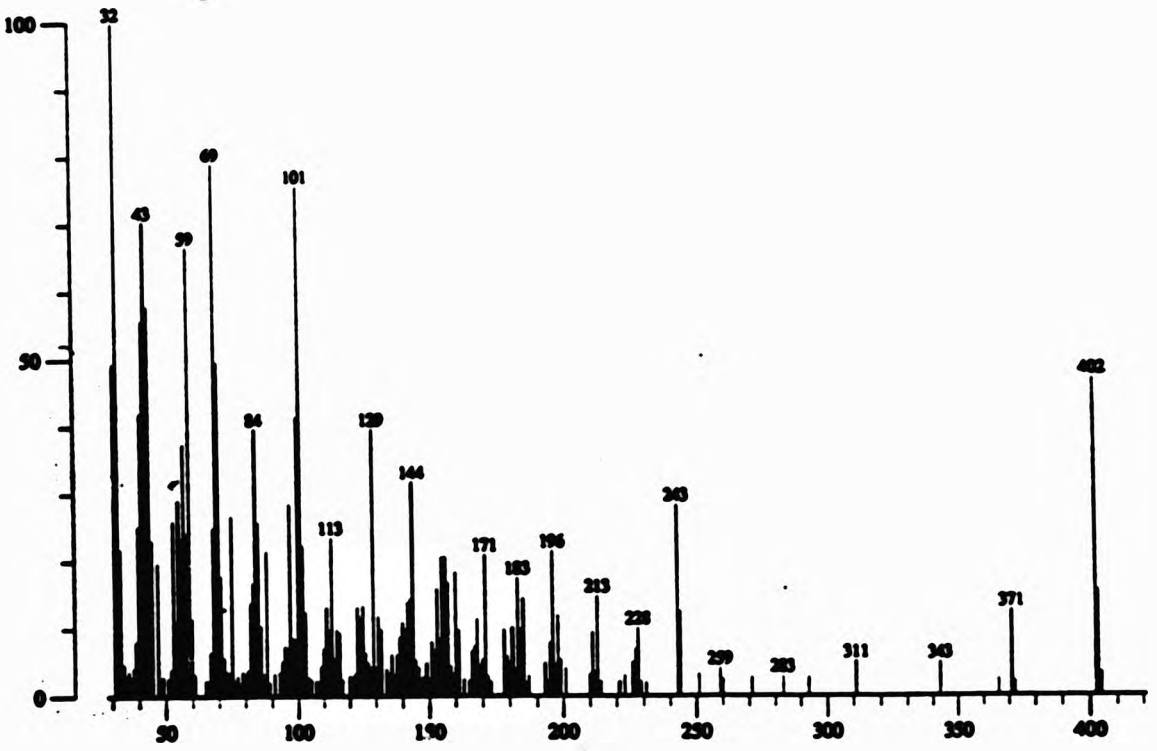
Single crystal X-ray analysis showed the solid labelled A, recovered from the reaction of 1,2-diaminoethanedione dioxime with DMAD to be the nucleophilic addition product, *trans*-bis(O-1,2-dicarbomethoxy-ethenyl)-1,2-diaminoethanedione dioxime (20). Consequently, the IR spectrum of this solid (Fig. 5.11) and of solid B contained bands at 3540 cm^{-1} and 3474 cm^{-1} due to the amino νNH as well as bands due to the ester carbonyls at 1750 and 1743 cm^{-1}.

Figure 5.11 *IR spectrum of trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime*



The EI mass spectra (eg. Fig 5.12) displayed prominent molecular ion peaks at m/z = 402 as well as fragment ions arising from the loss of such fragments as $CH_3O^{\cdot}$, and $CH_3CO_2^{\cdot}$, characteristic of all the DMAD adducts obtained during this study.

Figure 5.12 *EI mass spectrum of trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime*



The ^{1}H NMR spectra (eg. Fig. 5.13, Table 5.3) contain singlets at 3.60 ppm and 3.80 ppm due to the twelve methoxy protons. A third singlet integrating for two protons and which did not exchange with D_2O appears at 6.00 ppm. This signal is characteristic of vinylic protons. A signal at 104 ppm in the ^{13}C NMR spectra of both compounds is also indicative of alkene structure.

The similarities in the spectroscopic properties of solid B with that of solid A the structure of which was determined X-ray crystallographically, suggest that A and B were possibly a pair of isomers.

Figure 5.13 ^{1}H NMR spectrum of trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime

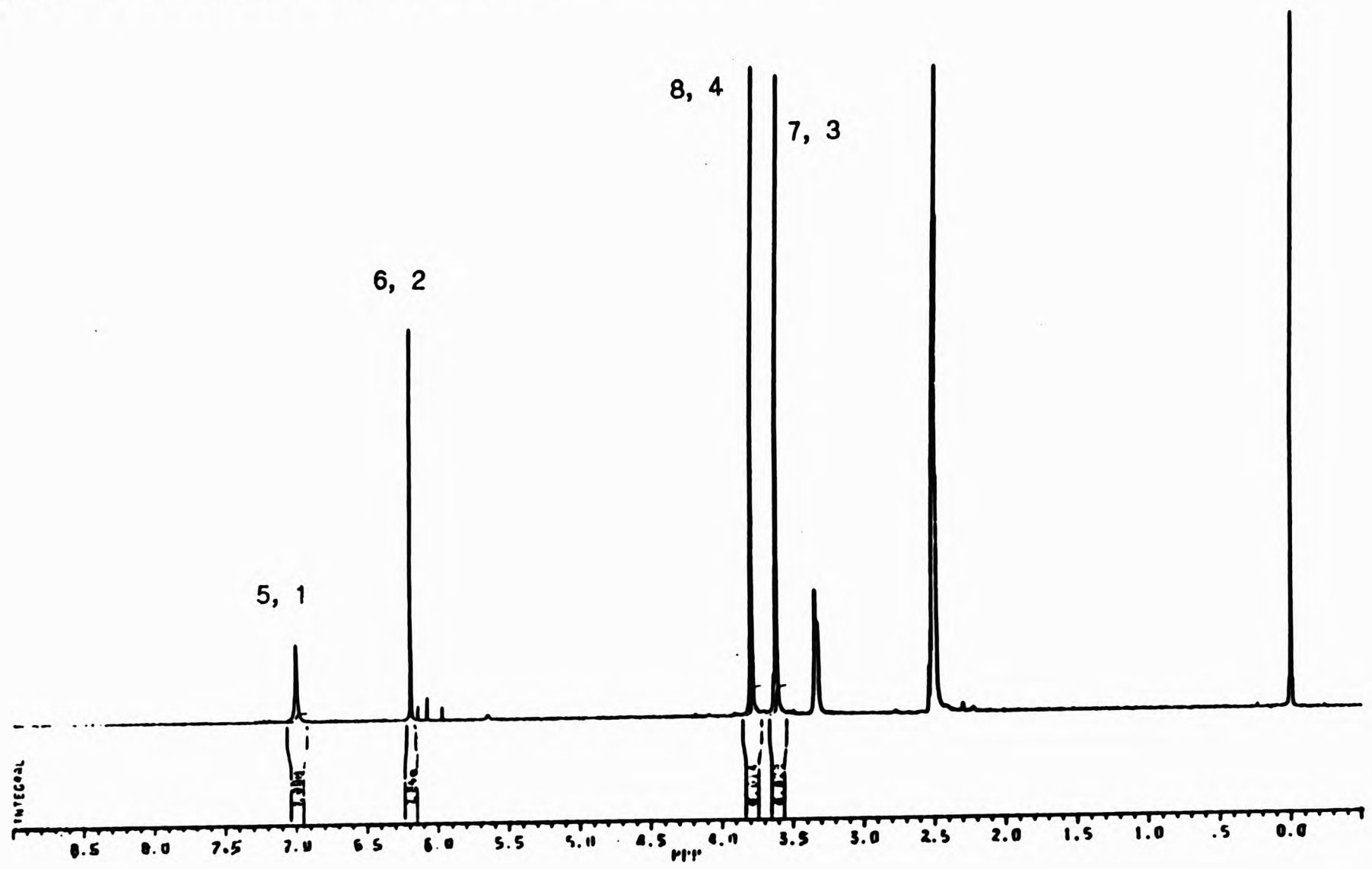
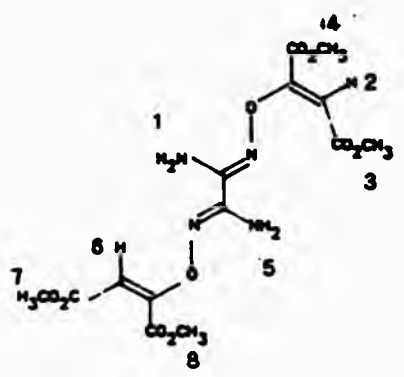


Table 5.3. ^{1}H *NMR spectral assignment for bis(O–1,2–dicarbomethoxy–ethenyl)–1,2–diaminoethanedione dioxime.*

	Assignment	*Multiplicity J/Hz*	*δppm*
	8, 4	s	3.80
	7, 3	s	3.68
	6, 2	s	6.20
	5, 1	s	7.00
	8, 4	s	3.80
	7, 3	s	3.68
	6, 2	s	6.20
	5, 1	s	7.00

s singlet;

5.8 Single Crystal X-ray Structure of *trans*–bis(O–1,2–dicarbomethoxy–ethenyl)–1,2–diaminoethanedione Dioxime.

Crystal preparation and data collection

Trans–bis(O–1,2–dicarbomethoxyethenyl)–1,2–diaminoethanedione (20) was obtained from the reaction of 1,2–diaminoethanedione dioxime with DMAD. The compound recrystallised from toluene:methanol 3:1 as colourless plate–like crystals. The crystal chosen for X–ray study had

dimensions 0.27 x 0.08 x 0.32mm. The unit cell parameters and intensity data were collected on a Phillips PW100 computer controlled, four circle diffractometer within the range 0 - 20^{0}. All relevant experimental parameters are given in Table 5.4. Lorentz polarization, empirical absorptions[53] and decay corrections were applied. The structure was solved by direct methods using MULTAN 77 computer package.[54] All atoms were refined by full matrix least-squares refinement on (F) with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. Atomic scattering factors were taken from published tables of X-ray data.[55] Atomic coordinates, relevant temperature factors, bond angles, bond lengths, inter and intramolecular contact distances are given in Appendix 5.

Table 5.4 *Crystal data, data collection and processing parameters for trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime.*

Formula	$C_{14}H_{18}N_4O_{10}$
MW	402.17
System	Monoclinic
Space group	$P2_1/C$
a	12.506(3) Å
b	9.697(2) Å
c	15.985(3) Å
V	1915.48 $Å^3$
Z	4
D_{calc}	1.397 g cm^{-3}
Radiation	Mo - K_α (l = 1.54184 Å)
	Graphite monochromated
μ	1.10 cm^{-1}

Table 5.4 cont'd...

F(000)	840
T	293(2) K
R	0.1306
R_w	0.1155
Crystal size	0.27x0.08x0.32 mm
Scan speed	0.05 min^{-1}
Scan width	0.90

Results and discussion.

A perspective view of the molecule together with the atomic numbering is presented in Figure 5.14. Selected bond lengths and bond angles are shown in Figures 5.15 and 5.16.

Figure 5.14 *Perspective view of trans-bis(O-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime.*

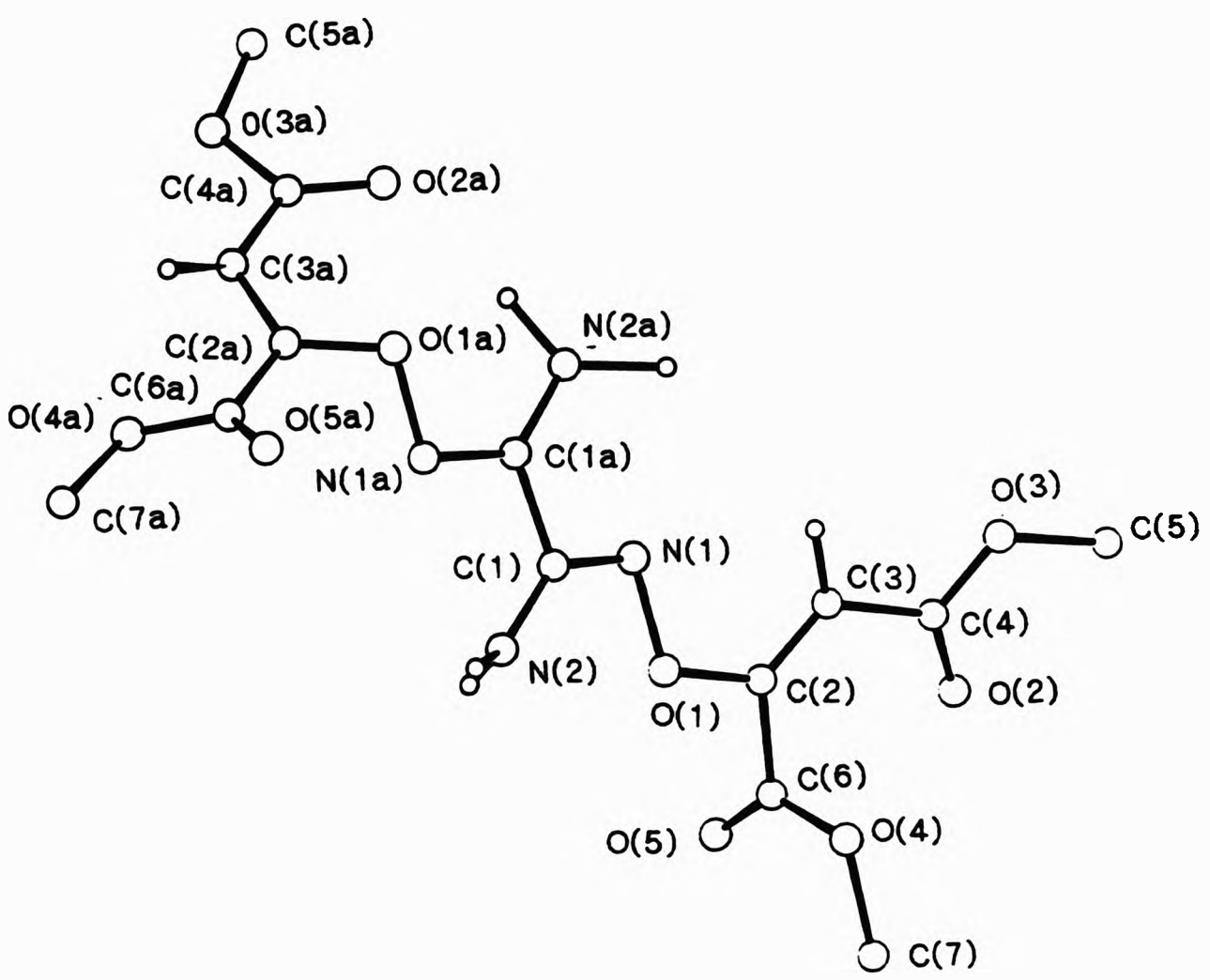


Figure 5.15 *Selected bond lengths in trans-bis(O-1,2-dicarbomethoxy-ethenyl)-1,2-diaminoethanedione dioxime.*

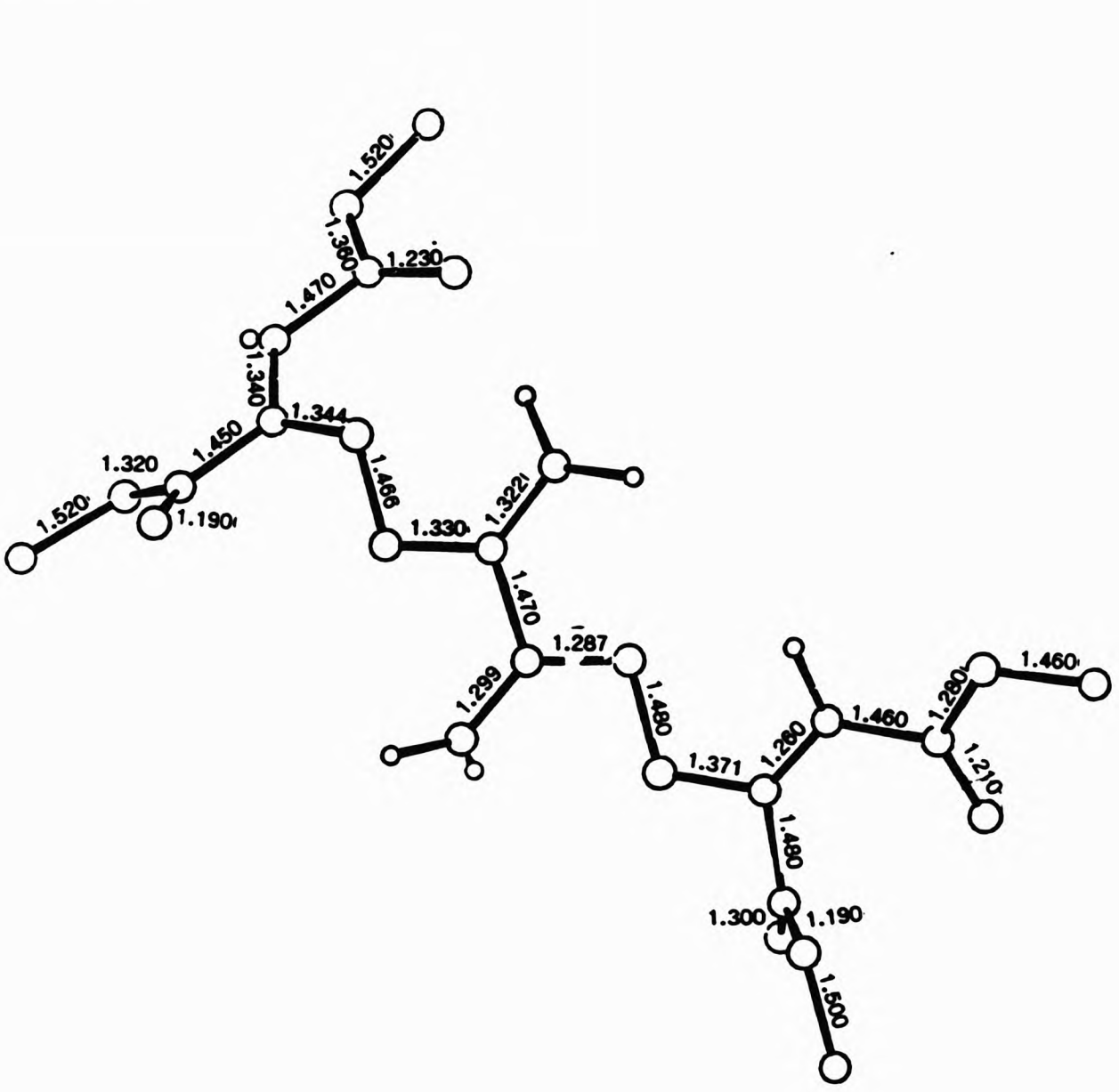
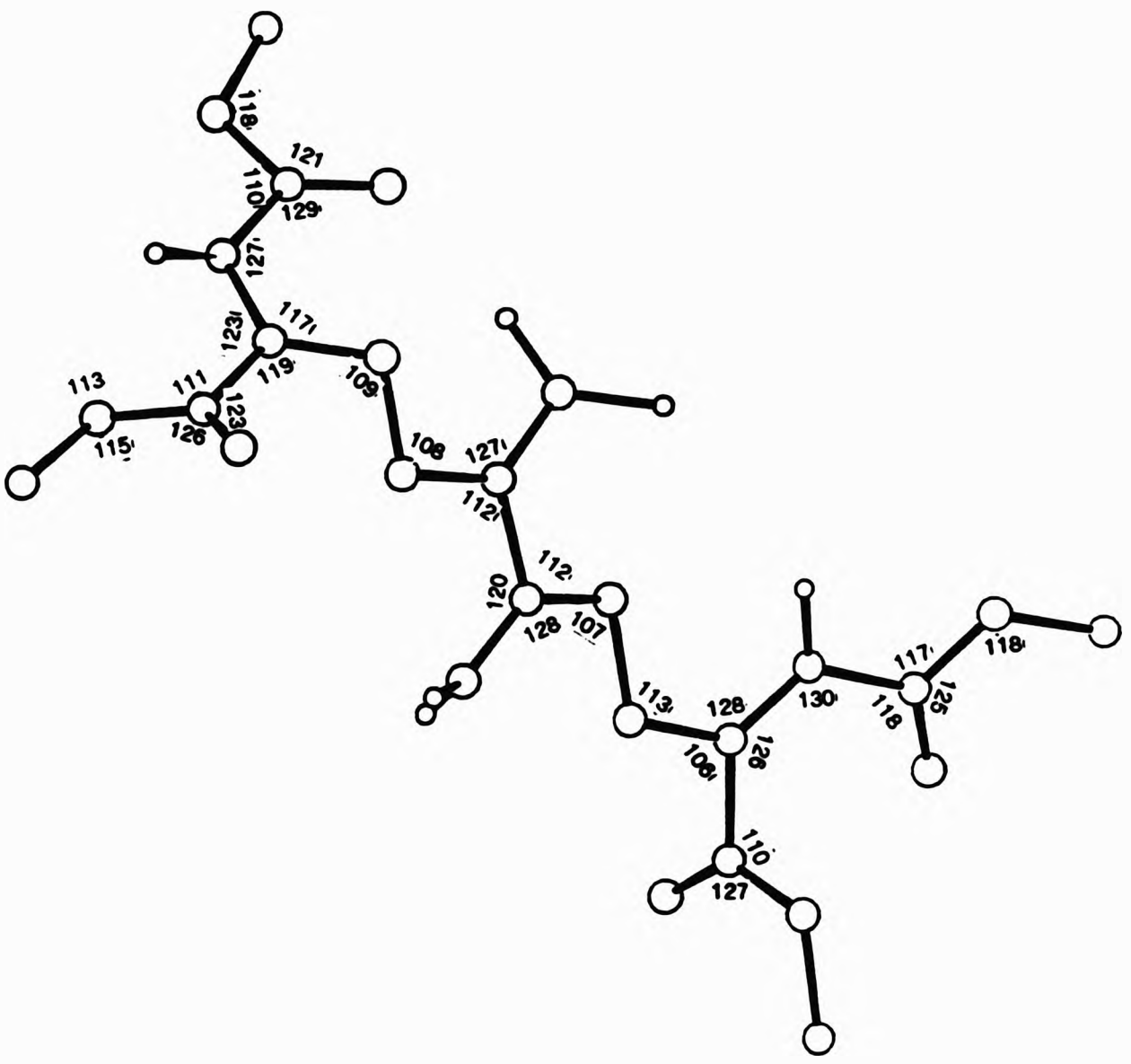


Figure 5.16 *Selected bond angles in trans-bis(O-1,2-dicarbomethoxy-ethenyl)-1,2-diaminoethanedione dioxime.*



The molecule is essentially planar with only a slight distortion of the C-C bond of the oximic moiety away from the ideal Csp^2 - Csp^2 geometry. Surprisingly, the molecule was found to be assymetrical with one of the two 1,2-carbomethoxyethenyl groups having the ester groups *cis* to each other while the other has the two groups in the *trans* conformation. This is interesting since it supports the proposal made earlier on the non-stereoselectivity of the addition of DMAD to oximic compounds.

The C-C bond length in the oximic moiety, C(1) - C(1a) was found to be 1.470 Å. This is within the range observed for related compounds. For example, the corresponding bond lengths in dithioxamide and dimethylglyoxime were 1.540 Å and 1.442 Å respectively.[56] The bond lengths C(1) - N(2) and C(1a) - N(2a) (1.322 (25) Å) agrees well with that reported for Csp^2 - NH_2 groups.[56,57] Similarly, the C - C bond lengths of the two ethenyl moieties C(2) - C(3) (1.26(3) Å) and C(2a) - C(3a) (1.34(3) Å) were in the range expected for such groups though the ethenyl group bearing the cis carbomethoxy substituents appeared longer than the analogous trans substituted group. Both bonds were however considerably shorter than the corresponding bond in maleic acid (1.440 Å). The shorter vinylic C=C bond lengths in the structure of trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime (Fig. 5.15) compared to maleic acid can be accounted for in terms of the effects of electron withdrawal by both the carbomethoxy groups and the oximic groups.

All the bond angles were well within the ranges observed for compounds containing related groups. The relatively short H(1Na)...O(1a), H(12N)...N(2a) and N(1)...H(3c) (Table 5, Appendix 5) points toward extensive intramolecular H-bonding in the molecule.

5.9. *References.*

1. J.Charalambous, M. J. Kensett, J. M. Jenkins, *J. Chem. Soc., Chem. Commun.,* 1977, 400.
2. J. Charalambous, M. J. Kensett, J. M. Jenkins, *J. Chem. Res.(S).,* 1982, 306-307.
3. H. Glaser, Houbenyl-Weyl, 'Methoden Der Organischen Chemie', Amine durch Austauschreaktion 160, Band XI/I, Georg Thieme Verlag, Stuttgart, 1957.
4. J. Morgan, PhD. Thesis, 1985, The Polytechnic of North London.
5. K. W. P. White, PhD. Thesis, 1987, The Polytechnic of North London.
6. G. Desmoni, G. Tacconi, *Chem. Rev.,* 1975, 75, 651.
7. J. Hamer, '1,4 Cycloaddition Reactions', Academic Press, New York, 1977.
8. A. S. Onischenko, 'Diene synthesis.', Academy of Sciences, USSR, 1964.
9. J. March, 'Advanced Organic Chemistry', J. Wiley and Sons Inc., USA, 1985.
10. A. Streatweiser, P. Hitchcock, 'Introduction to Organic Chemistry', Longmanns, London, 1987.
11. R. Huisgen, *Angew. Chem. Int. Ed. Engl.,* 1968, 7, 321.
12. G. Brieger, J. N. Bennet, *Chem. Rev.,* 1980, 80, 63.
13. K. Kobayashi, M. Itoh, H. Suginome, *J. Chem. Soc., Perkin Trans.1.,* 1991, 2135.
14. H. Kwart, K. King, *Chem. Rev.,* 1968, 68, 415.
15. H. H. Holmes, *Org. React.,* 1948, 4, 60.
16. D. L. Boger, *Tetrahedron* 1983, 39, 2869.
17. G. Martin, R. K. Hill, *Chem. Rev.,* 1961, 61, 537.
18. S. S. Sauer, G. C. Sustmann, *Angew. Chem. Int. Ed. Engl.,* 1980, 19, 779.

19. K. Furuta, S. Shimizu, Y. Miwa, Y. Yamamoto, *J. Org. Chem.*, 1989, 54, 1481.

20. X. Wang, *J. Chem. Soc., Chem. Commun.*, 1991, 1515.

21. S. S. Sauer, P. D. West, *Angew. Chem. Int. Ed. Engl.*, 1962, 1, 269.

22. H. Scharf, H. Plum, J. Fleischauer, W. Schleker, *Chem. Ber.*, 1979, 112, 862.

23. A. McKillop, T. S. B. Sayer, *J. Org. Chem.*, 1976, 41, 1079.

24. C. B. Castellani, R. Millini, *J. Chem. Soc., Dalton Trans.*, 1984, 1461.

25. P. Gaganatsou, PhD. Thesis, 1987, The Polytechnic of North London.

26. D. Baluch, J. Charalambous, L. I. B. Haines, *J. Chem. Soc. Chem. Commun.*, 1988, 1278.

27. E. G. Samser, K. Srinivasa, J. K. Kouli, *J. Am. Chem. Soc.*, 1985, 107, 7606.

28. B. Feringa, *J. Chem. Soc.*, 1986, 909.

29. H. Barjesteh, PhD. Thesis, 1991, University of North London.

30. G. C. Georgiou, PhD. Thesis, 1988, The Polytechnic of North London.

31. C. B. Castellani, O. Carugo, Personal Communication.

32. S. Yu Andreichikov, L. A. Voronova, A. P. Kozlov, *Zh. Org. Khim.*, 1979, 15, 520. Chem. Abs. 91:4773f

33. S. Yu Andreichikov, L. A. Voronova, L. A. Mulyutin, *Zh. Org. Khim.*, 1979, 15, 847. Chem. Abs. 91:74546h

34. J. F. Dellaria, B. D. Santarsiero, *Tetrahedron Letters*, 1988, 29(47), 6079.

35. R. M. Williams, M. Im, *Tetrahedron Letters*, 1988, 29(47), 6075.

36. E. Miller, R. Tanaka, *Sel. Org. Chem. Transform.*, 1970, 1, 143.

37. G. Bergman, E. Ginsburg, P. Pappo, *Org. React.*, 1959, 10, 179.

38. P. Armstrong, R. Grigg, S. Surendrakumar, W. Warnock, *J. Chem. Soc. Chem. Commun.*, 1987, 1327.

39. P. Armstrong, R. Grigg, W. Warnock, *J. Chem. Soc. Chem. Commun.*, 1987, 1325.

40. M. Makosza, *Tetrahedron Letters.*, 1966, 5489.

41. W. E. Truce, J. W. Tichenor, *J. Org. Chem.*, 1972, 37, 2391.

42. E. N. Prilezhaeva, *Zh. org. Khim*, 1971, 7, 1349.

43. M. C. Casiero, R. E. Pratt, R. J. Holland, *J. Am. Chem. Soc.*, 1966, 88, 1547.

44. F. Theron, R. Vassiere, *Bull. Chim. Soc.*, 1980, 5, 1527.

45. F. Prilezhaeva, D. Vasil'ev, G. Mikhaleshvili, D. Bogdanov, *Bull. Acad. Sci., USSR, Div. Chem. Sci.*, 1970, 1820.

46. M. McPartlin, *Inorg. Nucl. Chem. Lett.*, 1973, 9, 1207.

47. C. B. Castellani, G. Gatti, R. Millini, *Inorg. Chem*, 1984, 23, 4004.

48. J. Charalambous, P. G. T. Fogg, P. Gaganatsou, M. McPartlin, *Polyhedron*, 1993, 12, 879.

49. O. Carugo, J. Chakrabarty, J. Charalambous, T. A. Thomas, Unpublished results.

50. F. A. Cotton, G. Wilkinson, 'Advanced Inorganic Chemistry', 5th edn., J. Wiley and Sons, USA, 1988.

51. O. Carugo, C. B. Castellani, K. Djinovic, M. Rizzi, *J. Chem. Soc., Dalton Trans.*, 1991, 1255.

52. G. Fochi, C. Florani, *J. Chem. Soc. Dalton Trans.*, 1984, 2577, 2580.

53. A. C. T. North, D. C. Phillips, F. S. Matthews, *Acta. Cryst., A24*, 1968, 351.

54. G. M. Sheldrick, *Program for Crystal Structure Determination*, University of Cambridge, England, 1975.

55. M. K. Cooper, P. J. Guerney, H. J. Goodwin, M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 757.

56. H. J. M. Bower, et. al. 'Tables of Interatomic Distances and Configurations in Molecules and Ions', Chemical Society Special Pub. No. 11.

57. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, *J. Chem. Soc. Perkin Trans. 2,* 1987, S1.

CHAPTER SIX

Chapter 6

EXPERIMENTAL.

6.1. General.

All reagents used in this study were of G.P.R grade. Solvents were used as purchased, except where used for chromatographic purposes when they were redistilled and dried. For column chromatography, silica gel 60 (0.0063 - 0.200 mm, 70-230 mesh) obtained from BDH Merck was used as the stationary phase. Thin layer chromatography (TLC) was performed using commercially supplied silica coated plates.

6.2. Analytical.

Infra-red spectra

Infrared spectra in the range 4000 - 400 cm^{-1} were recorded on a *Bio-Rad FTS40* IR spectrometer. The samples were prepared as pressed KBr discs.

NMR spectra

Fourier transform ^{1}H and ^{13}C NMR spectra were recorded on a *Bruker AM250* NMR spectrometer. Trimethylsilane was used as the internal standard. ^{106}Pd and ^{195}Pt NMR spectra were recorded on a *Bruker AM400 (85.6 MHz)* NMR spectrometer using K_2PtCl_4 as reference.

UV spectra

Solution electronic spectra were recorded on a *Shimadzu UV-2100* UV-visible spectrophotometer. The pure solvent which in most cases was either methanol or dimethyl sulphoxide was used as reference.

Thermal gravimetric analysis

Thermal gravimetric analytical data at various heating rates were obtained by using a *Stanton HT-SM Thermobalance.*

Magnetic moments

Room temperature magnetic susceptibilities were recorded using a *Johnson Matthey* magnetic susceptibility balance calibrated with $Hg[Co(SCN)_4]$. Diamagnetic corrections for the metal and the ligands obtained from published tables[1] were applied in all cases.

Melting points

Melting points were recorded on an *Electrothermal* digital melting point apparatus. No corrections have been applied to the reported values.

Mass spectra

Mass spectra were recorded on a *Kratos Analytical* mass spectrometer. The LSIMS spectra of the metal complexes were recorded using a caesium ion source and either glycerol or 3-nitrobenzylalcohol as matrix.

Elemental analysis

Carbon, hydrogen and nitrogen analysis were carried out on a *Carlo Erba 1160* microanalytical apparatus. Metal analysis was carried out using a *Pye Unicam SP9 Atomic Absorption Spectrometer*, wet oxidation of the samples being achieved by the use of concentrated nitric acid and hydrogen peroxide in a *CEM Microwave Digester.*

6.3. Reactions.

6.3.1. Reaction of 3-aminophenol with carboxylic acids and carboxylic acid anhydrides.

To 3-aminophenol (10.9 g, 100 mmol) suspended in water (30 cm^3) the carboxylic acid or carboxylic acid anhydride (X g, Y mmol) was added. The mixture was gently refluxed (0.5 h) and the resulting solution allowed to cool slowly to room temperature affording a white crystalline solid. The latter was recovered by vacuum filtration and recrystallized from aqueous ethanol to afford the pure, white *3-acylaminophenols*. Relevant data for this series of reactions are given in Table 6.1.

Table 6.1 Yields, m.p's and analytical data of 3-acylaminophenols obtained from 3-aminophenol (10.0 mmol) with carboxylic acids or acid anhydrides.

Acid or Anhydride (g, mmol)	Yield (g, %)	3-Acylaminophenol m.p./^oC	Found % / Requires	C	H	N
Propionic anhydride	14.6, 89	183–185		65.8,	6.3,	8.5
(10.9, 100)				65.5,	6.3,	8.5
Butyric anhydride	18.0, 85	139–140		67.1,	7.2,	7.9
(12.9, 110)				67.0,	7.3,	7.8
Valeric anhydride	17.8, 86	123–125		68.3,	8.0,	7.3
(11.6, 107)				68.4,	7.8,	7.3
Heptanoic anhydride	18.0, 89	151–153		70.7,	8.9,	6.4
(10.0, 92)				70.6,	8.6,	6.3
Benzoic anhydride	16.8, 79	174–176		73.7,	5.2,	6.5
(10.8, 100)				73.2,	5.2,	6.6
Octanoic anhydride	7.9, 80	128–130		71.4,	9.0,	6.0
(4.6, 42)				71.5,	8.9,	6.0

6.3.2. Reaction of 3-aminophenol with n-Bromohexane.

To a solution of 3-aminophenol (10.9 g, 100 mmol) in absolute ethanol (20 cm^3), n-bromohexane (16.5 g, 100 mmol) was added. The mixture was gently refluxed (2 h) and the resulting solution poured into ice-cold water (200 cm^3) and stirred (0.5 h). The mixture was made alkaline by the addition of saturated sodium carbonate solution, and extracted with diethyl ether. The ethereal extract was acidified with 10% HCl. Addition of saturated sodium carbonate to the HCl extract gave *3-hexylaminophenol* 11.1 g, 58 %, m.p. 72-75 ^{0}C (Found: C, 74.4, H, 9.8, N, 6.9. Calc. for $C_{12}H_{19}NO$, C, 74.6, H, 9.8, 7.3%); ν_{max} (KBr) 3283 (NH); δ_H(250 MHz, CD_3OD) 0.90 (m, 3H, $C\underline{H}_3$), 1.30 (m, 6H, $C\underline{H}_2$ (x3)), 1.60 (m, 2H, $C\underline{H}_2$), 3.00 (t, 2H, $C\underline{H}_2$), 6.10 (m, 3H Ar), 6.90 (m, 1H Ar); m/z 193 (M^+ 80%).

Similarly reaction of 3-aminophenol (10.9 g, 100 mmol) with n-bromo-heptane (17.9 g, 100 mmol) gave *3-heptylaminophenol* 9.2 g, 44%, m.p. 55-57 ^{0}C (Found: C, 75.1, H, 10.0, N, 6.4% $C_{13}H_{21}NO$ requires C, 75.4, H 10.1, N 6.8%); ν_{max} (KBr) 3282 (NH); δ_H(250 MHz, CD_3OD) 0.90 (m, 3H, $C\underline{H}_3$), 1.30 (m, 8H, $C\underline{H}_2$ (x4)), 1.60 (m, 2H, $C\underline{H}_2$), 3.00 (t, 2H, $C\underline{H}_2$), 6.10 (m, 3H, Ar), 6.90 (m, 1H Ar); m/z 207 (M^+ 90%).

6.3.3. Reaction of 3-acylaminophenol with sodium nitrite/acetic acid in aqueous methanol.

To a solution of the 3-acylaminophenol (X g, Y mmol) in methanol:water (100 cm^3, 3:1) acetic acid (15 cm^3) was added. The solution was cooled to -10^0 C and sodium nitrite (1.5 g, 22 mmol) in water (50 cm^3) was

added dropwise (0.5 h) with stirring. After 24 h, concentration of the resultant solution to low volume gave a yellow-orange solid (three component by TLC). Qualitative test with aqueous ferrous ammonium sulphate gave a dark green precipitate. The solid was chromatographed with toluene:dichloromethane to give *3-acylamino-1,4-benzoquinone-4-oxime* and unreacted *3-acylaminophenol*. Relevant data for this series of reactions are given in Table 6.2.

Table 6.2. Yields, m.p's. and analytical data of 3-acylamino-1,4-benzoquinone-4-oximes obtained from the reaction of 3-acylaminophenol with sodium nitrite/acetic acid in water:methanol mixture.

3-Acylaminophenol (X g, Y mmol)	3-Acylamino-1,4-benzoquinone-4-oxime Yield (%)	m.p./^{0}C	Found % Requires C	H	N	Recovered Phenol (%)
3-Propionylamino-phenol (2.2, 13)	48	150-152	55.6, 55.6,	5.2, 5.2,	14.4 14.4	40
3-Butyrylamino-phenol (2.2, 12)	40	176-178	57.7, 57.7,	5.7, 5.8,	13.4 13.5	44
3-Pentanoylamino-phenol (2.0, 10)	30	132-135	59.5, 59.5,	6.3, 6.3,	12.6 12.6	63
3-Heptanoylamino-phenol (2.0, 9)	41	128-130	62.4, 62.2,	7.2, 7.1,	11.2 11.3	54

6.3.4. Reaction of 3-acylaminophenol with sodium nitrite/acetic acid.

A suspension of the 3-acylaminophenol (X g, Y mmol) in acetic acid (50 cm^3) was cooled to -10^{0}C before sodium nitrite (0.6 g, 9 mmol) in water (10 cm^3) was added. The mixture was stirred (24 h) during which time the

temperature was allowed to rise slowly to room temperature. The resultant orange solution was concentrated to low volume to give an orange paste which was dissolved in water (100 cm^3) and neutralized with saturated sodium carbonate solution to afford a yellow-orange solid (three component by TLC). Qualitative tests with aqueous ferrous ammonium sulphate gave a dark green precipitate. The solid was chromatographed with a toluene:ethylacetate (3:1) to give *3-acylamino-1,4-benzoquinone-4-oxime* and unreacted *3-acylaminophenol* both identified by elemental analysis and comparative m.p.'s (*cf* 6.3.3). The third fraction, an orange oil was eluted with methanol and was shown by comparative TLC to contain the *5-acylamino-1,2-benzoquinone-2-oxime* (see Table 6.3 for recovery).

In another experiment, 3-acylaminophenol was reacted (as above) with an excess of both acetic acid and sodium nitrite. Concentration of the reaction mixture after 24 h afforded a dark orange paste (multicomponent by TLC) which could not be adequately separated.

Table 6.3. Products and recovery obtained from the reaction of 3-acylaminophenols with sodium nitrite/neat acetic acid.

3-acylaminophenol (X g, Y mmol)	Recovery (%) 3-R-qOH*	Phenol	Other
3-Propionylaminophenol (2.2, 13)	53	27	17
3-Butyrylaminophenol (2.2, 12)	43	34	20
3-Pentanoylaminophenol (2.0, 10)	50	36	15
3-Heptanoylaminophenol (2.0, 9)	46	38	12

* 3-R-qOH = 3-Acylamino-1,4-benzoquinone-4-oxime.

6.3.5. Reaction of 3-acylaminophenol with amyl nitrite in the presence of potassium hydroxide.

3-Acylaminophenol (ca. 30 mmol) was added to a solution of potassium hydroxide (1.1 g, 20 mmol) in absolute ethanol (100 cm^3) with stirring. The mixture was cooled to -10 ^0C and amyl nitrite (3.5 g, 29 mmol) was added dropwise. The reaction was allowed to proceed (24 h) during which time the temperature was allowed to rise slowly to room temperature. The resultant orange-brown solution was concentrated to low volume giving a brown paste. The latter was dissolved in water and acidified with dilute acetic acid. Filtration afforded the *3-acylaminophenol* (89-95% recovery) identified by elemental analysis and comparative m.p.'s *cf* 6.3.1.

6.3.6. Reaction of 3-amino- and 3-alkylaminophenols with sodium nitrite/ acetic acid.

To a solution of the phenol (1.0 g, 9 mmol) in methanol:water (100 cm^3, 3:1), acetic acid (15 cm^3) was added. The solution was cooled to -10 ^0C and sodium nitrite (0.7 g, 22 mmol) in water (25 cm^3) was added dropwise (15 min) with stirring. The reaction was allowed to proceed (24 h). Filtration afforded brown solids (multicomponent by TLC; negative tests with aqueous ferrous ammonium sulphate).

6.3.7. Reaction of 3-alkylaminophenol with amyl nitrite in the presence of potassium ethoxide.

Potassium (0.7 g, 18 mmol) was dissolved in absolute ethanol and the solution cooled to -10 ^0C. To this, 3-alkylaminophenol (2.1 g, 11 mmol) was added followed by amyl nitrite (1.3 g, 11 mmol) dropwise (5 min). The mixture was stirred (24 h) during which time the temperature was allowed to rise slowly to room temperature. The resultant solution was concentrated to low volume under a stream of nitrogen, to afford an oily residue. The latter was stirred with diethyl ether. Filtration of the resultant mixture gave an orange-brown solid which was dissolved in water, acidified with dilute hydrochloric acid (5 cm^3, 4M) and filtered to give *3-hexylamino-1,4-benzoquinone-4-oxime* 1.2 g, 45%, m.p. 73 ^0C, (Found: C, 63.6, H, 7.9, N, 12.9%, $C_{12}H_{18}N_2O_2$ requires C, 64.1, H, 8.2, N, 12.6); ν_{max}(KBr) 3401 (NH), 1627 (C=O quinoid); δ_H(250 MHz, CD_3OD) 0.90 (m, 3H, C$\underline{H}_3$), 1.35 (m, 6H, C$\underline{H}_2$ (x3)), 1.70 (m, 2H, C$\underline{H}_2$), 3.21 (m, 2H, C$\underline{H}_2$), 6.40 (d, 1H, Ar), 6.22 (d,d, 1H, Ar), 7.5 (d, 1H, Ar); m/z 222

(M^+. 50%).

Similarly, 3-heptylaminophenol gave *3-heptylamino-1,4-benzoquinone-4-oxime* 2.5 g, 73 %, m.p. 67 ^{0}C (Found: C, 65.9, H, 8.7, N, 12.0% $C_{13}H_{20}N_2O_2$ requires C, 66.1, H, 8.4, N, 11.9%); ν_{max} (KBr) 3418 (NH), 1635 (C=O quinoid); δ_H(250 MHz, CD_3OD) 0.90 (m, 3H, C<u>H</u>$_3$), 1.35 (m, 8H, C<u>H</u>$_2$ (x4)), 1.70 (m, 2H, C<u>H</u>$_2$), 3.20 (m, 2H, C<u>H</u>$_2$), 6.40 (d, 1H, Ar), 6.82 (d,d, 1H, Ar), 7.70 (d, 1H, Ar); m/z 236 (M^+, 81%).

Using the same procedure 3-ethylamino-4-methylphenol (10.0 g, 66 mmol) and amyl nitrite (7.8 g, 67 mmol) gave product *5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime monohydrate* 9.5 g, 88%, m.p. 152-153 ^{0}C (Found: C, 54.6, H, 7.1, N, 14.1%, Calc. for $C_9H_{14}N_2O_3$ C, 54.5, H, 7.1, N, 14.1%); ν_{max} (KBr) 3400 (NH), 1635, 1610 (C=O quinoid); δ_H(250 MHz, CD_3OD) 1.30 (t, 3H, C<u>H</u>$_3$), 2.21 (s, 3H, C<u>H</u>$_3$), 3.53 (q, 2H, C<u>H</u>$_2$), 5.70 (s, 1H, Ar), 6.92 (s 1H, Ar), 19.1 (s, 1H, N<u>H</u>); m/z 180 (M^+, 65%).

6.3.8. Reaction of 3-amino and 3-alkylaminophenols with sodium nitrite in concentrated hydrochloric acid.

Concentrated hydrochloric acid (100 cm^3) was added to a solution of the phenol (X g, Y mmol) in methanol (minimum volume required to dissolve the compound). The solution was cooled to -10^{0}C before sodium nitrite (6.9 g, 100 mmol) in water (25 cm^3) was added dropwise (0.5 h) with stirring. The mixture was stirred for a further 1 h. Filtration afforded yellow *1,2-benzoquinone-2-oxime hydrochloride monohydrate* which were washed with dilute hydrochloric acid (3 x 50 cm^3) and diethyl ether (3 x

50 cm^3) and dried under vacuum at 20 ^{0}C. Relevant data for these reactions are given in Table 6.4).

Table 6.4 Yields, m.p.'s and analytical data of 1,2-benzoquinone-2-oxime hydrochloride monohydrate obtained from the reaction of 3-alkylamino-phenols with sodium nitrite in concentrated hydrochloric acid.

Phenol (X g, Y mmol)	1,2-benzoquinone-2-oxime hydrochloride monohydrate Yield %	m.p. /^{0}C	Found% Requires C	H	N
3-Aminophenol	63	150-160	37.4	5.0	14.3
(10.9, 100)		decomp.	37.4	4.7	14.5
3-Hexylaminophenol	78	120-130	52.1	7.6	10.2
(17.0, 88)		decomp.	52.1	7.6	10.1
3-Heptylaminophenol	69	90-100	53.9	8.0	9.4
(12.7, 61)		decomp.	53.7	7.9	9.6
3-Ethylamino-4-methyl-	93	240-250	46.5	6.2	11.9
phenol (10.1, 68)		decomp.	46.1	6.4	11.9

6.3.9. Interaction of 1,2-benzoquinone-2-oxime hydrochlorides with potassium carbonate.

To a solution of the 1,2-benzoquinone-2-oxime hydrochloride (X g, Y mmol) in methanol:water (1:4, 100 cm^3), saturated aqueous potassium sodium carbonate solution (5 cm^3) was added dropwise until a precipitate formed. The mixture was stirred for a further (0.5 h), filtered, washed with water (5 x 25 cm^3) and dried under vacuum to afford orange *1,2-benzoquinone-2-oximes* (see Table 6.5 for yields and elemental analysis).

Table 6.5 Yields, m.p.'s and analytical data of 1,2-benzoquinone-2-Oximes obtained from the interaction of 1,2-benzoquinone-2-oxime hydrochlorides with potassium carbonate.

5-R-qOH.HCl (g, mmol)	Substituted-1,2-benzoquinone-2-oxime Yield %	m.p./^{0}C	Found% Requires C	H	N
5-AqOH.HCl	90	183-185	52.2	4.5	20.1
(5.0, 29)			52.2	4.3	20.3
5-Et-4-MeqOH.HCl	91	152-153	60.0	6.7	15.6
(10.0, 43)			60.0	6.7	15.6
5-HxqOH.HCl	83	82-84	64.9	8.1	12.6
(10.0, 36)			64.9	8.1	12.6
5-HpqOH.HCl	86	70-73	66.1	8.4	11.9
(4.5, 15)			66.1	8.4	11.9

6.3.10. Nitrosation of 3-acylaminophenol in the presence of nickel(II) chloride hexahydrate.

Nickel(II) chloride hexahydrate (11.3 g, 50 mmol) in water (50 cm^3) was added to a solution of the phenol (X g, Y mmol), acetic acid (30 cm^3) and sodium acetate trihydrate (30.1 g, 195 mmol) in a mixture of water and methanol (200 cm^3 1:3). Sodium nitrite (16.5 g, 240 mmol) in water (50 cm^3) was added dropwise with stirring (1 h). The mixture was then stirred (48 h). Filtration gave a yellow orange solid which was washed with water (5 x 100 cm^3) and Soxhlet extracted with dichloromethane to afford orange *bis(5-acylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrate* (see Table 6.6 for yields and analytical data). Removal of the solvent from the extracts afforded yellow, *3-acylamino-1,4-benzoquinone-*

4-oxime (identified by comparative m.p. and IR). Further amounts of the 3-acylamino-1,4-benzoquinone-4-oxime were recovered by concentration of the original filtrate and subsequent column chromatography of the residue thus obtained.

Table 6.6. Yields, m.p.'s and analytical data for products of the nitrosation of 3-acylaminophenol in the presence of nickel(II) chloride hexahydrate.

Phenol (g, mmol)	Yield (%)	$M(qo)_2.nH_2O$ m.p. (dec.) /^{0}C	Found % Requires C	H	N	Ni	3-RqOH* (%)
3-Propionylamino-phenol (15.1, 90)	69	240-245	38.7 39.1	3.2 3.3	9.7 10.1	10.7 10.6	22
3-Butyrylamino-phenol (15.2, 91)	72	250-253	40.1 41.3	5.9 5.9	9.1 10.1	10.1 10.1	17
3-Pentanoylamino-phenol (17.8, 92)	68	232-240	45.8 46.1	5.6 5.9	9.5 9.8	10.1 10.3	19
3-Heptanoylamino-phenol (17.6, 90)	67	240-245	49.6 49.6	6.5 6.7	8.5 8.9	9.5 9.3	16

6.3.11. Nitrosation of 3-alkylaminophenol in the presence of nickel(II) chloride hexahydrate.

Nickel(II) chloride hexahydrate (6.2 g, 26 mmol) in water (50 cm^3) was added to a solution of the phenol (X g, Y mmol) and acetic acid (50 cm^3) in a mixture of methanol and water (100 cm^3, 3:1). Sodium nitrite (5.1 g, 74 mmol) in water (25 cm^3) was added dropwise (0.5 h) with stirring (48 h). Filtration afforded a brown solid. The latter was

washed with water (5 x 50 cm^3) and Soxhlet extracted with diethyl ether. The brown residue was dried under vacuum at 20 ^0C/0.1 mmHg to afford *bis(5-alkylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrates* (see Table 6.7 for yields and analytical data). Concentration of the ether extract afforded a second brown solid (multicomponent by TLC). Satisfactory separation of the latter was not achieved.

Table 6.7. Yields, m.p.'s and analytical data for the products of the nitrosation of 3-alkylaminophenols in the presence of nickel(II) chloride hexahydrate.

Phenol (g, mmol)	$Ni(qo)_2.nH_2O$ Yield (%)	m.p. (dec.) /^0C	Found % / Requires C	H	N	Ni
3-Ethylamino-4-methyl-	23	230–235	41.0	6.6	10.5	11.2
phenol (5.0, 33)			41.2	6.5	10.7	11.2
3-Hexylamino-	11	250–253	54.1	7.3	10.0	10.6
phenol (5.0, 26)			53.7	7.1	10.4	10.9
3-Heptylamino-	13	250–253	55.7	7.9	9.5	10.1
phenol (5.0, 25)			55.2	7.4	9.9	10.4

6.3.12. Interaction of 5-alkylamino-1,2-benzoquinone-2-oxime with nickel(II) chloride hexahydrate.

To nickel(II) chloride hexahydrate (1.0 g, 4.2 mmol) in water (50 cm^3), a methanolic solution of the 5-alkylamino-1,2-benzoquinone-2-oxime (X g, Y mmol) was added dropwise with stirring (24 h). Filtration afforded orange, solid *bis(5-alkylamino-1,2-benzoquinone-2-oximato)nickel(II)*

dihydrate which was washed with water and dried under vacuum at 20 ^{0}C/0.1 mmHg. Relevant data for this series of reactions are given in Table 6.8.

Table 6.8. Yields m.p.'s and analytical data for the complexes obtained by the interaction of 5-alkylamino-1,2-benzoquinone-2-Oximes with nickel(II) chloride hexahydrate

X-qOH (g, mmol)	Yield (%)	$Ni(qo)_2.nH_2O$ m.p. (dec.) /^{0}C	Found % / Requires			
			C	H	N	Ni
5-HxqoH	90	250-253	53.4	6.9	10.4	10.9
(2.0, 9)			53.7	7.1	10.4	10.9
5-HptqoH	87	250-253	55.2	7.6	10.0	10.4
(2.1, 9)			55.2	7.4	9.9	10.4
5-Et-4-MeqoH	93	230-235	47.7	5.7	12.4	13.0
(2.0, 11)			47.7	5.7	12.4	13.1

6.3.13. Nitrosation of 3-butyrylaminophenol in the presence of copper(II) chloride dihydrate.

Copper(II) chloride dihydrate (8.2 g, 48 mmol) in water (50 cm^3) was added to a solution of 3-butyrylaminophenol (16.4 g, 92 mmol), acetic acid (30 cm^3), sodium acetate trihydrate (15.1 g, 110 mmol) in a mixture of methanol and water (200 cm^3, 3:1). To this mixture, sodium nitrite (16.6 g, 240 mmol) in water (50 cm^3) was added with stirring. Filtration after 48 h afforded a brown solid which was washed with water (5 x 100 cm^3) and Soxhlet extracted with dichloromethane to give the brown

bis(5-butyrylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrate 16.5 g, 65%, m.p. 230-235 ^{0}C (decomp.); (Found: C, 47.6, H, 4.9, N, 10.8, Cu, 12.4%; $C_{20}H_{26}CuN_4O_8$ requires C, 46.7, H, 5.1, N, 10.9, Cu 12.2%); μ_B 1.79;. Concentration of the dichloromethane extract to low volume gave a yellow-brown solid. The latter was mixed with a similar solid obtained by concentration of the original filtrate and washings and chromatographed with a mixture of toluene and ethylacetate (3:1). This gave *3-butrylamino-1,4-benzoquinone-4-oxime* (2.1 g, 12%; confirmed by comparative m.p. and IR), and unreacted *3-butyrylaminophenol* (2 g, 11%) (confirmed by comparative m.p. and IR).

Similarly, 3-heptanoylaminophenol (16.4 g, 92 mmol) gave the brown *bis(5-heptanoylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrate* 14.2 g, 50%, m.p. 230-238 ^{0}C (decomp.) (Found: C, 52.0, H, 6.5, N, 9.3, Cu, 10.6% $C_{26}H_{38}CuN_4O_8$ requires C, 52.2, H, 6.4, N, 9.4, Cu, 10.4%); μ_B 1.86; and yellow *3-heptanoylamino-1,4-benzoquinone-2-oxime* (1.2 g, 6.1% confirmed by comparative m.p. and IR).

6.3.14. Nitrosation of 3-acylaminophenol in the presence of palladium(II) chloride.

To palladium(II) chloride (3.0 g, 17 mmol) in water:dilute hydrochloric acid (4M), (9:1, 100 cm^3), a solution of the phenol (5.0 g, 33 mmol) and sodium acetate trihydrate (7.0 g, 55 mmol) in a mixture of water and methanol (1:3, 100 cm^3) and acetic acid (15 cm^3) was added. Sodium nitrite (3.5 g, 51 mmol) in water (50 cm^3) was added dropwise (0.5 h), and the mixture stirred (24 h). Filtration gave a brown solid which was

washed with water (5 x 50 cm^3), Soxhlet extracted with dichloromethane and dried under vacuum at 20 ^0C/0.1 mmHg to afford *bis(5-acetylamino-1,2-benzoquinone-2-oximato)palladium(II)* 4.1 g, 53%, m.p. 250-255 ^0C (decomp.), (Found: C, 41.4, H, 3.0, N, 12.1, Pd, 23.0% $C_{16}H_{14}N_4O_6Pd$ requires C, 41.1, H, 3.0, N, 12.1, Pd 22.8%).

Similarly, 3-butyrylaminophenol (5.3 g, 30 mmol) gave *bis(5-butyryl-amino-1,2-benzoquinone-2-oximato)palladium(II)* 4.7 g, 60%, m.p. 270-275 ^0C (decomp.), (Found: C, 46.2, H, 4.2, N, 10.8, Pd, 20.4% $C_{20}H_{22}N_4O_6Pd$ requires C, 46.2, H, 4.2, N, 10.8, Pd 20.4%).

6.3.15. Nitrosation of 3-acylaminophenol in the presence of potassium tetrachloroplatinate(II).

To potassium tetrachloroplatinate(II) (1.2 g, 3 mmol) in water (50 cm^3), a solution of the phenol (1.0 g, 7 mmol), sodium acetate trihydrate (4.2 g, 31 mmol) in a mixture of water and methanol (1:3, 40 cm^3), and acetic acid (5 cm^3) was added. Sodium nitrite (1.5 g, 15 mmol) in water (25 cm^3) was added dropwise (15 min). The mixture was stirred for 7 days during which time no precipitate appeared. Concentration of the resultant mixture and filtration afforded a black solid (multicomponent by TLC). Satisfactory separation of which could not be achieved.

6.3.16. Interaction of 5-alkylamino-1,2-benzoquinone-2-oximes with copper(II) chloride dihydrate.

The procedure was the same as that for 6.3.12 except that copper(II)

chloride (0.5 g, 3 mmol) replaced nickel(II) chloride. The products obtained were the *bis(5-alkylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrates* (see Table 6.9 for yields and elemental analysis).

Table 6.9. Yields and analytical data for products of the interaction of 5-alkylamino-1,2-benzoquinone-2-oximes with copper(II) chloride dihydrate.

X-qOH (g, mmol)	Yield (%)	$Cu(qo)_2.2H_2O$ m.p. (dec.)	Found % / Requires C	H	N	Cu
5-HxqoH	90	215-220	53.2	7.0	10.3	11.7
(1.1, 5)			53.2	7.0	10.3	11.7
5-HptqoH	87	200-205	54.4	7.6	9.6	10.9
(1.0, 4)			54.8	7.4	9.8	11.1
5-Et-4-MeqoH	93	220-225	47.0	5.7	12.2	14.0
(1.0, 6)			47.2	5.7	12.2	13.9

6.3.17. Interaction of 5-acylamino and 5-alkylamino-1,2-benzoquinone-2-oxime with palladium(II) chloride.

To a solution of palladium(II) chloride (1.0 g, 5.6 mmol) in a mixture of water and hydrochloric acid (9:1, 100 cm^3), a methanolic solution of the 5-acyl or 5-alkylamino-1,2-benzoquinone-2-oximes (X g, Y mmol) was added dropwise with stirring (24 h). Filtration gave a brown solid which was washed with water (5 x 25 cm^3) and dried under vacuum to afford *bis(5-acylamino)-* and *bis(5-alkylamino-1,2-benzoquinone-2-oximato)-palladium(II)* (see Table 6.10 for yields and elemental analysis).

Table 6.10. Yields, and analytical data for products of the interaction of 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-Oxime with palladium(II) chloride.

X-qOH (g, mmol)	Yield (%)	$Pd(qo)_2$ m.p. (dec.) /^{0}C	Found % / Requires	C	H	N	Pd
5-AcqoH	71	250-255		41.3	3.0	12.1	22.8
(3.0, 16)				41.3	3.0	12.1	22.8
5-BuqoH	63	270-265		46.3	4.6	10.8	20.4
(3.2, 14)				46.2	4.2	10.8	20.4
5-Et-4-MeqoH	87	230-237		45.8	4.9	11.6	22.8
(4.0, 22)				46.0	4.7	11.9	22.6
5-HxqoH	68	240-245		52.3	6.2	10.2	19.3
(2.0, 11)				52.3	6.2	10.2	19.3

6.3.18. Interaction of 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-oxime with potassium tetrachloroplatinate(II).

The procedure was the same as for 6.3.18 except that potassium tetrachloroplatinate(II) (1.0 g, 3 mmol) replaced palladium(II) chloride and the reaction was done in the absence of hydrochloric acid. The product obtained was the *bis(1,2-benzoquinone-2-oximato)platinum(II)*. Relevant data for this series of reactions are given in Table 6.11.

Table 6.11. Yields, and analytical data for the product of the interaction of 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-Oxime with potassium tetrachloroplatinate(II) chloride.

X-qOH (g, mmol)	Yield (%)	$Pt(qo)_2$ m.p. (dec.) /^{0}C	Found % / Requires	C	H	N	Ni
5-AcqoH	63	230–233		34.7	2.5	10.1	35.4
(1.0, 6)				34.7	2.5	10.1	35.3
5-BuqoH	47	240–245		39.4	3.6	9.2	32.0
(0.4, 2)				39.4	3.6	9.2	32.0
5-Et-4-MeqoH	53	230–235		39.1	4.0	10.1	35.3
(1.1, 6)				39.1	4.0	10.1	35.3
5-HxqoH	52	240–245		45.4	5.2	9.0	30.8
(0.5, 2)				45.2	5.3	8.8	30.6

6.3.19. Reaction of bis(5-acylamino) and bis(5-alkylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrate with pyridine.

A suspension of bis(1,2-benzoquinone-2-oximato)nickel(II) hydrate (X g, Y mmol) and pyridine (0.5 g, 6 mmol) were stirred in acetone (24 h). Addition of light petroleum (100 cm^3, b.p. 30–40 ^{0}C) to the resultant solution gave *bis(1,2-benzoquinone-2-oximato)nickel(II)bispyridine* which was washed with light petroleum (6 x 25cm^3) and dried under vaccum at 20 ^{0}C, 0.1 mmHg. Relevant data for this series of reactions are given in Table 6.12.

Table 6.12. Yields and analytical data for the product of the reaction of pyridine with bis(5-acylamino) and bis(5-alkylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrates.

$Ni(X\text{-}qo)_2.nH_2O$ (g, mmol)	Yield (%)	$Ni(qo)_2(py)_2$ m.p. (dec.) /^{0}C	Found % / Requires	C	H	N	Ni
$Ni(5\text{-}Prqo).6H_2O$	96	240-245		55.3	4.8	13.5	9.8
(1.0, 2)				55.8	4.7	13.9	9.7
$Ni(5\text{-}Buqo)_2.6H_2O$	98	240-243		57.4	5.4	13.6	9.3
(1.0, 2)				57.1	5.1	13.3	9.3
$Ni(5\text{-}Peqo)_2.4H_2O$	95	235-240		58.3	5.5	12.6	8.7
(1.0, 2)				58.3	5.5	12.8	8.9
$Ni(5\text{-}Hpqo)_2.4H_2O$	93	230-236		60.6	5.9	11.9	8.2
(0.8, 0.5)				60.4	6.2	11.8	8.3
$Ni(5\text{-}Hxqo).2H_2O$	83	240-245		61.6	6.1	12.7	8.9
(0.5, 0.9)				61.9	6.7	12.8	8.9
$Ni(5\text{-}Hptqo)_2.2H_2O$	80	250-255		62.9	6.9	12.3	8.5
(0.5, 0.9)				62.9	7.0	12.2	8.6
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2.6H_2O$	90	250-255		58.3	5.5	14.7	10.2
(0.6, 1)				58.5	5.6	14.7	10.2

6.3.20. Reaction of bis(5-acylamino)- and bis(5-alkylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrates with 2,2-dipyridyl.

To a suspension of the bis(1,2-benzoquinone-2-oximato)nickel(II) hydrate (X g, Y mmol) in acetone (50 cm^3) 2,2-dipyridyl 0.3 g, 2.0 mmol) was added. The mixture was stirred at 20 ^{0}C (24 h). Subsequent filtration gave orange solids which were washed with acetone (2 x 25 cm^3) and

diethyl ether (2 x 25 cm^3), dried under vacuum at 20 ^0C, 0.1 mmHg to afford orange *bis(1,2-benzoquinone-2-oximato)nickel(II)2,2-dipyridyl.* Relevant data for this series of reactions are given in Table 6.13.

Table 6.13. Yields and analytical data for the product of the reaction of bis(5-acylamino-1,2-oximato)nickel(II) hydrates with 2,2-dipyridyl.

$Ni(qo)_2.nH_2O$ (g, mmol)	Yield (%)	$Ni(qo)_2(dipy)$ m.p. (dec.) /^0C	Found % / Requires			
			C	H	N	Ni
$Ni(5\text{-}Prqo).6H_2O$	93	250-260	55.9	4.4	13.9	9.8
(0.5, 0.9)			55.9	4.3	14.0	9.7
$Ni(5\text{-}Buqo)_2.6H_2O$	98	230-240	57.3	4.8	13.3	9.3
(0.5, 0.9)			57.3	4.8	13.3	9.3
$Ni(5\text{-}Peqo)_2.4H_2O$	93	240-245	58.6	5.3	12.8	8.7
(0.5, 0.9)			58.5	5.2	12.8	8.9
$Ni(5\text{-}Hpqo)_2.4H_2O$	94	230-237	60.7	5.9	11.7	8.3
(0.5, 0.8)			60.6	5.9	11.8	8.2
$Ni(5\text{-}Hxqo).2H_2O$	70	240-250	62.4	6.5	12.8	8.9
(0.5, 0.9)			62.3	6.4	12.8	8.9
$Ni(5\text{-}Hptqo)_2.2H_2O$	72	250-260	63.4	6.8	12.3	8.5
(0.5, 0.9)			63.3	6.7	12.3	8.6
$Ni(5\text{-}Et\text{-}4\text{-}Meqo)_2.6H_2O$	74	250-260	58.8	5.2	14.7	10.2
(0.5, 1)			58.7	5.2	14.7	10.2

6.3.21. Interaction of bis(5-acylamino-) and bis(5-alkylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrates with pyridine.

The procedure was the same as for 6.3.24 except that the copper(II) complexes replaced the nickel(II) complexes. The products obtained were

the *bis(1,2-benzoquinone-2-oximato)copper(II) pyridine* (see Table 6.14 for yields and elemental analysis).

Table 6.14 Yields and analytical data for the product of the reaction of bis(5-acylamino-) and bis(5-alkylamino-1,2-benzoquinone-2-oximato)-copper(II) dihydrates with pyridine.

$Cu(qo)_2.2H_2O$ (g, mmol)	Yield (%)	$Cu(qo)_2(py)$ m.p. (dec.) /°C	Found % / Requires			
			C	H	N	Cu
$Cu(5\text{-}Buqo)_2.2H_2O$ (0.5, 1)	82	240-243	52.2	4.5	12.9	11.4
			52.2	4.4	13.3	11.4
$Cu(5\text{-}Hpqo)_2.2H_2O$ (0.5, 0.9)	98	220-225	58.1	6.2	10.9	9.9
			58.1	6.1	10.9	9.9
$Cu(5\text{-}Hxqo)_2.2H_2O$ (0.5, 0.9)	70	240-245	59.5	6.7	12.0	10.9
			59.5	6.7	12.0	10.9
$Cu(5\text{-}Hptqo)_2.2H_2O$ (0.5, 0.9)	72	250-255	60.7	7.0	11.4	10.4
			60.7	7.0	11.4	10.4
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2.2H_2O$ (0.5, 1)	74	250-258	43.2	5.4	14.0	12.6
			43.2	5.4	14.0	12.7

6.3.22 Interaction of bis(5-acylamino-) and bis(5-alkylamino-1,2-benzo-quinone-2-oximato)copper(II) dihydrate with 2,2-dipyridyl.

The procedure was the same as for 6.3.20 except that the copper(II) complexe replaced the nickel(II) complexe. The product obtained was the *bis(1,2-benzoquinone-2-oximato)copper(II)2,2-dipyridyl* (see Table 6.16 for yields and analytical data).

Table 6.16 Yields and analytical data for products of the reaction of bis(5-acylamino-) and bis(5-alkylamino-1,2-benzoquinone-2-oximato)-copper(II) hydrates with 2,2-dipyridyl.

$Cu(qo)_2.nH_2O$ (g, mmol)	Yield (%)	$Cu(qo)_2(dipy)$ m.p. (dec.) /^{0}C	Found % / Requires	C	H	N	Cu
$Cu(5\text{-}Buqo)_2.2H_2O$	71	250–255		56.8	4.7	13.3	10.0
(0.5, 0.9)				56.8	4.7	13.3	10.2
$Cu(5\text{-}Hpqo)_2.2H_2O$	77	240–246		60.2	5.9	11.8	8.9
(0.5, 0.9)				60.2	5.9	11.7	8.9
$Cu(5\text{-}Hxqo)_2.2H_2O$	67	240–250		61.7	6.4	12.7	9.6
(0.5, 0.9)				61.7	6.4	12.7	9.6
$Cu(5\text{-}Hptqo)_2.2H_2O$	73	250–255		62.8	6.0	12.4	9.2
(0.5, 0.9)				62.7	6.2	12.2	9.2
$Cu(5\text{-}Et\text{-}4\text{-}Meqo)_2.2H_2O$	88	250–255		58.2	5.2	14.5	11.0
(0.5, 1)				58.2	5.2	14.5	11.0

6.3.23 Interaction of bis(5-acylamino)- and bis(5-alkylamino-1,2-benzoquinone-2-oximato)palladium(II) dihydrates with pyridine.

To the bis(1,2-benzoquinone-2-oximato)palladium(II) (0.6 g, 1.3 mmol) in a round bottom flask, pyridine (10 cm^3) was added. The mixture was gently refluxed (2 h) with stirring. The resulting mixture was stirred with light petroleum (b.p. 40–60 ^{0}C, 50 cm^3), filtered and dried to give unreacted complex (0.6 g, 100%).

6.3.24. Interaction of bis(5-acylamino) and bis(5-acetylamino-1,2-benzoquinone-2-oximato)platinum(II) with pyridine.

The procedure was similar to that described in 6.3.23 except that the bis(1,2-benzoquinone-2-oximato)platinum(II) complexes (0.5 g, 0.9 mmol) replaced the palladium complexes. The unreacted complex (0.5 g, 100%) was recovered.

6.3.25. Ion-exchange chromatography of bis(5-acylamino-1,2-benzoquinone-2-oximato)nickel(II) hydrates.

A solution of the bis(1,2-benzoquinone-2-oximato)nickel(II) hydrate (X g, Y mmol) in methanol (100 cm^3) was mounted on an ion-exchange column packed with Dowex 50W-X8(H) (40-60 mesh) ion-exchange resin to a length of 20 cm. Slow elution with a mixture of water and methanol (3:1) gave orange *5-acylamino-1,2-benzoquinone-2-oxime* on concentration of the the eluates. Relevant data for this reaction are given in Table 6.18.

Table 6.18 Yields m.p.'s and analytical data of 5-acylamino-1,2-benzoquinone-2-oximes obtained by ion-exchange chromatography of the corresponding nickel(II) complex.

$Ni(qo)_2.nH_2O$ (g, mmol)	5-Acylamino-1,2-benzoquinone-2-oxime Yield (%)	m.p./^{0}C	Found % / Requires C	H	N
$Ni(5\text{-}Prqo).6H_2O$	58	154-156	55.8	5.1	14.4
(0.2, 0.4)			55.7	5.2	14.4
$Ni(5\text{-}Buqo)_2.6H_2O$	58	110-112	57.6	5.8	13.4
(0.3, 0.6)			57.7	5.8	13.4
$Ni(5\text{-}Peqo)_2.4H_2O$	50	104-106	59.4	6.3	12.7
(0.3, 0.4)			59.5	6.3	12.6
$Ni(5\text{-}Hpqo)_2.4H_2O$	65	98-100	60.8	7.2	11.8
(0.3, 0.4)			60.8	7.2	11.8

6.3.26. Acidolysis of bis(5-butyrylamino-1,2-benzoquinone-2-oximato)-copper(II) hydrates.

To a suspension of bis(5-butyrylamino-1,2-benzoquinone-2-oximato)-copper(II) dihydrate (1.0 g, 2 mmol) in water (100 cm^3), dilute HCl (4M, 25 cm^3) was added. The mixture was stirred (0.5 h) and then extracted with ethylacetate. Concentration of the ethylacetate extract afforded orange *5-butyrylamino-1,2-benzoquinone-2-oxime* (0.6 g, 77%; confirmed by elemental analysis and comparative IR, and m.p.).

6.3.27. Reaction of 1,2-naphthoquinone-1-oxime with dimethylacetylene-dicarboxylate in aqueous ethyleneglycol dimethlyether (EGDE).

To a solution of 1,2-naphthoquinone-1-oxime (1.1 g, 6.6 mmol) in EGDE:water (80 cm^3, 7:1), DMAD (2.5 g, 17.6 mmol) was added. The mixture was stirred at 40 ^0C (5 h) giving an orange brown solution. Removal of the solvent afforded an orange paste which was chromatographed with toluene to give orange *cis-(O-1,2-dicarbomethoxyethenyl)-1,2-naphtho-quinone-1-Oxime* 0.4 g, 43%, m.p. 106-108 ^0C (Found: C, 60.9, H, 4.1, N, 4.4% $C_{16}H_{13}NO_6$ requires C, 61.0, H, 4.1, N, 4.4%); ν_{max} (KBr) 1724, 1715 (C=O ester), 1657 (C=O, quinoid); δ_H(250 MHz, DMSO) 3.66 (s, 3H, C$\underline{H}_3$), 3.89 (s, 3H, C$\underline{H}_3$), 6.30 (d, 1H, C$\underline{H}$ Ar), 6.44 (s, 1H, C$\underline{H}$ vinylic); 7.46-7.64 (m, 4H, C$\underline{H}$ Ar), 7.86 (d, 1H, C$\underline{H}$ Ar); m/z 315 (M^+, 53%). Further elution with a mixture of toluene and dichloromethane afforded yellow *trans-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime* 0.4 g, 49%, mp 125-127 ^0C (Found: C, 60.9, H, 4.2, N, 4.5% $C_{16}H_{13}NO_6$; requires C, 61.0, H, 4.1, N 4.4%); ν_{max} (KBr) 1739, 1717 (C=O ester), 1658 (C=O, quinoid); δ_H(250 MHz, DMSO) 3.66 (s, 3H, C$\underline{H}_3$), 3.89 (s, 3H, C$\underline{H}_3$), 6.30 (d, 1H, C$\underline{H}$ Ar), 6.44 (s, 1H, C$\underline{H}$ vinylic); 7.41-7.62 (m, 4H, C$\underline{H}$ Ar), 7.86 (d, 1H, C$\underline{H}$ Ar); m/z 315 (M^+, 47%).

6.3.28. Reaction of 1,2-naphthoquinone-1-oxime with DMAD in aqueous EGDE in the presence of sodium chloride.

To a solution of 1,2-naphthoquinone-1-oxime (1.03 g, 6 mmol) and sodium chloride (0.1 g, 2 mmol) in EGDE:water (80 cm^3, 7:1), DMAD (2.5 g, 17.6 mmol) was added. The mixture was stirred at 40 ^0C for 5 h. Concentration

of the resultant solution to low volume afforded a yellow-orange solid (multicomponent by TLC). The latter was chromatographed with toluene to give *cis-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime* (0.6 g 32%; confirmed by elemental analysis and comparative IR and m.p.). Further Further elution with a mixture of toluene and dichloromethane afforded *trans-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime* (1.2 g, 60%; confirmed by by elemental analysis and comparative IR and m.p.). Elution with methanol afforded an orange residue (0.1 g; multi-component by TLC).

Similarly, reaction of 1,2-naphthoquinone-1-oxime and DMAD in the presence of lithium, potassium, magnesium and aluminium chloride all afforded a yellow-orange solid (X g, Y%). TLC showed that the composition of this solid to be similar to that obtained from the involving sodium chloride. Recovery of the yellow-orange from these reactions are given in Table 6.19.

Table 6.19. Reagents and recovery from the reaction of 1-nqOH (6.0 mmol) with DMAD (14.0 mmol) in the presence of selected main group metal chlorides.

MCl_n (g, mmol)	Recovery (%)
LiCl (0.1, 2.6)	94
KCl (0.2, 2.7)	68
$MgCl_2$ (0.3, 2.7)	54
$AlCl_3$ (0.3, 2.5)	50

6.3.29. Reaction of 1,2-naphthoquinone-1-oxime with DMAD in aqueous EGDE in the presence of nickel(II) chloride hexahydrate.

To a solution of 1,2-naphthoquinone-1-oxime (1.1 g, 6.3 mmol) in EGDE:water (80 cm^3, 7:1), nickel(II) chloride (0.3g, 1.4 mmol) and DMAD (2.0 g, 14 mmol) were added. The mixture was stirred at 40 ^0C (5 h). Filtration afforded a green-brown solid which was washed with EGDE (2 x 10 cm^3) and water (3 x 50 cm^3) and dried under vacuum at room temperature to give *bis(1,2-naphthoquinone-1-oximato)nickel(II)* 0.6g, 100%, mp 230-235 dec. ^0C, (Found: C 59.6, H 3.1, N 7.0% Calc. for $C_{20}H_{12}N_2O_4Ni$: C 59.6, H 3.0, N 7.0%). Concentration of the filtrate gave a yellow-orange residue which was chromatographed to give *cis-(O-1,2-dicarbo-methoxyethenyl)-1,2-naphthoquinone-1-oxime* 0.1 g, 7%, and *trans-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime* 0.4

g, 20% both identified by elemental analysis, comparative IR and m.p.

In another experiment, 1,2-naphthoquinone-1-oxime (1.1 g, 6 mmol) nickel(II) chloride hexahydrate (0.4 g, 1.7 mmol) and DMAD (2.0 g, 14 mmol) in EGDE:water (80 cm^3, 7:1) were refluxed (24 h). Filtration of the cold reaction mixture gave a pink solid which was washed with EGDE (2 x 10 cm^3), methanol (2 x 25 cm^3) and water (2 x 25 cm^3) and dried under vacuum at room temperature to afford *nickel(II) butynedioate octahydrate* 0.3 g, 38%, m.p. 200–210 ^{0}C decomp. (Found: C, 14.2, H, 4.2, Ni, 18.6% Calc. for $C_8H_{16}O_{12}Ni$: C, 15.3, H, 5.1, Ni, 18.8%). Concentration of the combined filtrate and washings gave a brown paste which was chromatographed using toluene and dichloromethane to give *4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine* 1.0 g, 55%, m.p. 162–164 ^{0}C (Found: C 60.8, H 4.2, N 4.5% Calc. for $C_{16}H_{13}NO_6$: C 60.9, H 4.1, N 4.4%); m/z 315 (M^+, 67). Further elution with methanol gave a red solid (0.1 g; multicomponent by TLC).

6.3.30. Reaction of 1-naphthoquinone-2-oxime with DMAD in aqueous EGDE in the presence of copper(II) chloride dihydrate.

To a solution of 1,2-naphthoquinone-1-oxime (1.0 g, 6 mmol) in EGDE:water (80 cm^3, 7:1), copper(II) chloride (0.2 g, 1.4 mmol) and DMAD (2.0 g, 14 mmol) were added. The mixture was stirred at 40 ^{0}C (5 h). Filtration of the reaction mixture after that time gave a brown solid which was washed with EGDE (2 x 10 cm^3), water (2 x 25 cm^3) and methanol (2 x 25 cm^3) and dried under vacuum at room temperature to afford *bis(1,2-naphthoquinone-1-oximato)copper(II)* 0.6 g, 100% m.p. 215-220 ^{0}C

decomp. (Found: C, 58.9, H 3.0, N 6.9% Calc. for $C_{20}H_{12}N_2O_4Cu$: C 58.9, H 3.0, N 6.9%). Concentration of the combined washings and filtrate gave a brown paste which was flash chromatographed with toluene and dichloromethane to give *trans-(O-1,2-dicarbomethoxyethenyl)-1,2-naphtho-quinone-1-oxime* 0.2 g, 12% and *cis-(O-1,2-dicarbomethoxyethenyl)-1,2-naphthoquinone-1-oxime* 0.2 g, 12% both identified by elemental analysis, comparative IR and m.p.

In another experiment, 1,2-naphthoquinone-1-oxime (1.0 g, 6.2 mmol), copper(II) chloride dihydrate (0.2 g, 1.4 mmol) and DMAD (2.0 g, 14 mmol) in EGDE:water (80 cm^3, 7:1) were refluxed (24 h). Filtration afforded a green solid which was washed with EGDE (2 x 10 cm^3), water (2 x 25 cm^3) and methanol (2 x 25 cm^3) and dried under vacuum at room temperature to give crude *copper(II) butynedioate tetrahydrate* 0.1 g, 15% (confirmed by elemental analysis, and comparative IR). Concentration of the combined washings and filtrate gave a brown paste which was chromatographed with toluene and dichloromethane to give *4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine* 0.8 g, 42%, m.p. 163-165 ^0C, (Found: C, 60.9, H, 4.1, N, 4.5%, Calc. for $C_{16}H_{13}NO_6$: C, 60.9, H, 4.1, N, 4.4%) m/z 315 (M^+ 53). Further elution with methanol gave a red solid (0.1 g; multicomponent by TLC).

6.3.31. Reaction of Bis(5-butyrylamino-1,2-benzoquinone-2-oximato) nickel(II) hexahydrate with DMAD in aqueous EGDE.

Bis(5-butyrylamino-1,2-benzoquinone-2-oximato)nickel(II) hexahydrate (1.0 g, 1.8 mmol) and DMAD (0.8 g, 5.6 mmol) were refluxed with

EGDE:water (80 cm^3, 7:1) (24 h). Filtration afforded a pink solid which was washed with EGDE (2 x 10 cm^3), methanol (2 x 10 cm^3) and water (3 x 25 cm^3) and dried under vacuum at room temperature to give *nickel(II) butynedioate octahydrate* 0.2 g, 23% (confirmed by elemental analysis and comparative IR). Concentration of the combined washings and filtrate gave an orange paste which was chromatographed with a mixture of toluene and ethylacetate (3:1) to give pale yellow *7-butyrylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine* 0.6 g, 48%, m.p. 200-202 ^{0}C, (Found: C, 54.9, H, 5.1, N, 8.0% $C_{16}H_{18}N_2O_7$ requires C, 54.8, H, 5.2, N, 8.0%); ν_{max} (KBr) 3424 (NH), 1773, 1728 (C=O ester); δ_H(250 MHz, CD_3OD) 0.95 (t, 3H, C$\underline{H}_3$ acyl), 1.70 (sxt, 2H, C$\underline{H}_2$), 2.36 (t, 2H, C$\underline{H}_2$), 3.84 (s, 3H, C$\underline{H}_3$ methoxy), 3.87 (s, 3H, C$\underline{H}_3$ methoxy), 7.31 (d,d, 2H, C$\underline{H}$ Ar), 7.50 (d, 1H, C$\underline{H}$ Ar), 7.68 (d,d, 1H, C$\underline{H}$ aromatic), 9.47 (s, 1H, N$\underline{H}$); m/z 350 (M^+, 25%). Further elution with methanol gave a red oil (0.1 g; multicomponent by TLC).

6.3.32. Reaction of Bis(5-butyrylamino-1,2-benzoquinone-2-oximato) copper(II) dihydrate with DMAD in aqueous EGDE.

Bis(5-butyrylamino-1,2-benzoquinone-2-oximato)copper(II) dihydrate (1.0 g, 2 mmol) and DMAD (0.8 g, 5.6 mmol) were refluxed with EGDE:water (80 cm^3, 7:1) (24 h). Filtration afforded a green solid which was washed with EGDE (2 x 10 cm^3), methanol (2 x 10 cm^3) and water (3 x 25 cm^3) and dried under vacuum at room temperature to give *copper(II) butynedioate tetrahydrate* 0.2 g, 21% identified by elemental analysis and comparative IR. Concentration of the combined washings and filtrate gave an orange paste which was chromatographed with a mixture of toluene and

ethylacetate (3:1) to give pale yellow *7-butyrylamino-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine* 0.8 g, 60%, m.p. 200-202 ^{0}C, (Found: C, 54.9, H, 5.1, N, 8.0%, $C_{16}H_{18}N_2O_7$ requires C, 54.8, H, 5.2, N, 8.0%); ν_{max} (KBr) 3424 (NH), 1773, 1728 (C=O ester); δ_H(250 MHZ, CD_3OD) 0.95 (t, 3H, C$\underline{H}_3$ acyl), 1.70 (sxt, 2H, C$\underline{H}_2$), 2.36 (t, 2H, C$\underline{H}_2$), 3.84 (s, 3H, C$\underline{H}_3$ methoxy), 3.87 (s, 3H, C$\underline{H}_3$ methoxy), 7.31 (d,d, 2H, C$\underline{H}$ Ar), 7.50 (d, 1H, C$\underline{H}$ Ar), 7.68 (d,d, 1H, C$\underline{H}$ Ar), 9.47 (s, 1H, N$\underline{H}$); m/z 350 (M^+, 33%). Further elution with methanol afforded a red oil (0.1 g; multicomponent by TLC).

6.3.33. Reaction of Bis(4-bromo-1,2-benzoquinone-2-oximato)nickel(II) with DMAD in aqueous EGDE.

To a solution of Ni(4-Brqo)$_2$ (1.1 g, 2.3 mmol) in EGDE:water (80 cm^3, 7:1), DMAD (1.0 g, 9.2 mmol) was added. The mixture was refluxed (24 h). Filtration afforded a pink solid which was washed with EGDE (2 x 10 cm^3), methanol (2 x 25 cm^3) and water (3 x 25 cm^3) and dried to give *nickel(II) butynedioate octahydrate* (0.3 g, 41% identified by elemental analysis, and comparative IR). Concentration of the combined filtrate and washings gave a brown solid which was chromatographed with toluene and dichloromethane to give *6-bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one* 0.5 g, 36%, m.p. 178-180 ^{0}C, (Found: C, 44.5, H, 2.7, N, 4.8% Calc. for $C_{11}H_8BrNO_4$: C, 44.4, H, 2.7, N, 4.7%) ν_{max} (KBr) 3458 (NH), 1780 (C=O ester), 1606-1668 (C=O ester); δ_H(250 MHz, DMSO) 3.97 (s, 3H, C$\underline{H}_3$ methoxy), 5.97 (s, 1H, C$\underline{H}$ vinylic), 7.00 (m, 1H C$\underline{H}$ Ar), 7.10 (m, 2H, C$\underline{H}$ Ar), 10.65 (s, 1H, N$\underline{H}$); m/z 297 (M^+, 56%). Further elution with dichloromethane gave a second yellow solid

identified as *6-bromo-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine* 0.3 g, 28%, m.p. 198-200 ^{0}C, (Found: C, 41.9, H, 2.9, N, 4.1% Calc. for $C_{12}H_{10}BrNO_6$: C, 42.0, H, 2.9, N, 4.1%); ν_{max} (KBr) 3243 (OH), 1769, 1727 (C=O ester); δ_H(250 MHz, DMSO) 3.93 (s, 3H, C$\underline{H}_3$ methoxy), 3.96 (s, 3H, C$\underline{H}_3$ methoxy), 6.93 (d, 1H, C$\underline{H}$ Ar), 7.50 (d,d, 1H, C$\underline{H}$ Ar), 7.83 (d, 1H C$\underline{H}$ Ar); m/z 343 (M^+, 53%). Further elution with ethylacetate and methanol afforded red-brown solids (0.3 g; multicomponent by TLC).

6.3.34. Reaction of Bis(4-bromo-1,2-benzoquinone-2-oximato)copper(II) with DMAD in aqueous EGDE.

To a solution of Cu(4-Brqo)$_2$ (1.1 g, 2 mmol) in EGDE:water (80 cm^3, 7:1) DMAD (1.0 g, 9.0 mmol) was added. The mixture was refluxed (24 h). Filtration gave a green solid which was washed with EGDE (2 x 10 cm^3), water (3 x 25 cm^3) and methanol (2 x 25 cm^3) and dried to afford crude *copper(II) butynedioate* 0.2 g, 28% (identified by elemental analysis and comparative IR). Concentration of the combined washings and filtrate gave a brown paste which was chromatographed with a mixture toluene and dichloromethane to afford yellow-orange *6-bromo-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benoxazin-2-one* (0.4 g, 48%), identified by elemental analysis and comparative m.p. Further elution with dichloro-methane gave a second yellow solid *6-bromo-4-hydroxy-2,3-dimethoxy-carbonyl-1,4-benzoxazine* (0.4 g, 27%) identified by elemental analysis and comparative m.p. Elution with ethylacetate and methanol afforded red-brown residues (0.3 g; mulcomponent by TLC).

6.3.35. Reaction of Bis(4-chloro-1,2-benzoquinone-2-oximato)nickel(II) with DMAD in aqueous EGDE.

To a solution of $Ni(4\text{-}Clqo)_2$ (1.0 g, 2.3 mmol) in EGDE:water (80 cm^3, 7:1), DMAD (1.1 g, 10 mmol) was added. The mixture was refluxed (24 h) and then filtered to give a pink solid which was washed with EGDE (2 x 10 cm^3), water (3 x 25 cm^3) and methanol (2 x 25 cm^3). This gave pure *nickel(II) butynedioate* (0.3 g, 41%; identified by elemental analysis and comparative IR). Concentration of the combined washings and filtrate gave a brown paste which was chromatographed with a mixture of toluene and dichloromethane to give yellow-orange *6-chloro-3,4-dihydro-3-(2-oxo-2-methoxyethylidene)-2H-1,4-benzoxazin-2-one* 0.4 g, 30%, m.p. 188-190 ^0C, (Found: C, 52.2, H, 3.2, N, 5.6% Calc. for $C_{11}H_8ClNO_4$: C, 52.2, H, 3.2, N, 5.5%); ν_{max} (KBr) 3430 (NH), 1779 (C=O ester), 1609-1653 (C=O lactone); δ_H(250 MHz, DMSO) 3.85 (s, 3H, C<u>H</u>$_3$ methoxy), 5.95 (s, 1H, C<u>H</u> vinylic), 7.05 (m, 1H, C<u>H</u> Ar), 7.15 (m, 2H, C<u>H</u> Ar), 10.65 (s, 1H, N<u>H</u>); m/z 253 (M^+, 67%). Further elution with dichloromethane gave a second yellow solid identified as *6-chloro-4-hydroxy-1,4-benzoxazine* 0.4 g, 28%, m.p. 190-192 ^0C (Found: C, 48.2, H, 3.4, N, 4.7% Calc. for $C_{12}H_{10}ClNO_6$: C, 48.2, H, 3.3, N, 4.7%); ν_{max} (KBr) 3239 (OH), 1769, 1728 (C=O ester); δ_H(250 MHz, DMSO) 3.93 (s, 3H, C<u>H</u>$_3$ methoxy), 3.96 (s, 3H, C<u>H</u>$_3$ methoxy), 5.10 (s, 1H, O<u>H</u>), 6.92 (d, 1H, C<u>H</u> Ar), 7.18 (d,d, 1H, C<u>H</u> Ar), 7.15 (d, 1H, C<u>H</u> Ar); m/z 299 (M^+, 53%). Elution with ethylacetate and methanol gave red-brown (0.3 g; multicomponent by TLC).

6.3.36. Reaction of Bis(4-chloro-1,2,benzoquinone-2-oximato)copper(II) with DMAD in aqueous EGDE.

To a solution of $Cu(4\text{-}Clqo)_2$ (1.1 g, 2.3 mmol) in EGDE:water (80 cm^3, 7:1), DMAD was added. The mixture was refluxed (24 h) and then filtered to give a green solid which was washed with EGDE (2 x 10cm^3), water (3 x 25 cm^3) and methanol (2 x 25 cm^3) and dried. This afforded crude *copper(II) butynedioate* (0.3 g, 28%) identified by comparative IR with an authentic sample *cf* 6.3.34. Concentration of the combined washings and filtrate gave a brown paste which was chromatographed with a mixture of toluene and dichloromethane to give a yellow-orange solid, *6-chloro-3,4-dihydro-3-(2-oxo-2-methoxy-ethylidene)-2H-1,4-benzoxazin-2-one* (0.4 g, 39%). Further elution with dichloromethane afforded a second yellow solid, *6-chloro-4-hydroxy-2,3-dimethoxycarbonyl-1,4-benzoxazine* (0.33 g, 27%). Both compounds were identified by elemental analysis, comparative m.p. and IR with authentic samples *cf* 6.3.35. Elution with ethylacetate and methanol afforded red-brown multicomponent (TLC) residues (0.2 g).

6.3.37. Reaction of Bis(4-bromo-1,2-benzoquinone-2-oximato)nickel(II) with DMAD and octene in aqueous EGDE.

To a solution of $Ni(4\text{-}Brqo)_2$ (1.1 g) in EGDE:water (80 cm^3, 7:1), octene (10 cm^3) and DMAD (0.9 g, 6 mmol) were added. The mixture was refluxed (24 h). Filtration gave a pink solid which was washed with EGDE (2 x 10 cm^3), methanol (2 x 25 cm^3) and water (3 x 25 cm^3) and dried to afford *nickel(II) butynedioate octahydrate* (0.3 g, 40%; identified by elemental analysis and comparative IR). Concentration of the combined washings and

and filtrate gave a yellow-brown solid which was chromatographed with a mixture of toluene and dichloromethane to give a yellow *6-bromo-3,4-dihydro-3-(2-oxo-2-methoxyethylidene)-2H-1,4-benzoxazin-2-one* (1.5 g, 95%; identified by elemental analysis and comparative m.p. and IR). Further elution with ethylacetate and methanol afforded a brown solid (0.3 g; multicomponent by TLC).

6.3.38. Reaction of Bis(1,2-Naphthoquinone-1-oximato)nickel(II) with DMAD and octene in aqueous EGDE.

To bis(1,2-naphthoquinone-1-oximato)nickel(II) (1.1 g, 2.7 mmol) in EGDE:water (80 cm^3, 7:1), octene (10 cm^3) and DMAD (0.9 g, 6 mmol) were added. The mixture was refluxed (24 h). Filtration of the reaction mixture gave a pink solid which was washed with EGDE (2 x 10 cm^3), methanol (2 x 25 cm^3) and water (3 x 25 cm^3) to afford *nickel(II) butynedioate octahydrate* (0.3 g, 41%; identified by comparative IR). Concentration of the combined washings and filtrate gave a brown paste which was chromatographed with a mixture toluene and dichloromethane to afford the yellow *4-hydroxy-2,3-dimethoxycarbonyl-1,4-naphthoxazine* (1.0 g, 60%; identified by elemental analysis and comparative m.p. and IR). Further elution with ethylacetate and methanol gave a red-brown residue (0.2 g; multicomponent by TLC).

6.3.39. Reaction of 1,2-diaminoethanedione dioxime with DMAD in aqueous EGDE.

To a solution of 1,2-diaminoethanedione dioxime (1.04 g) in EGDE:water

(80 cm^3, 7:1) DMAD (2.0 g, 14 mmol) was added. The mixture was refluxed (24 h). Concentration of the reaction mixture gave a yellow paste which was stirred with a mixture of toluene and methanol (50 cm^3, 6:4) and then filtered to afford a white powdery solid. The latter was recrystallised from a mixture of toluene and methanol to afford *cis-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime* 1.0 g, 29%, m.p. 136-138 ^0C, (Found: 402; C, 42.0, H, 4.7, N, 13.8% $C_{14}H_{18}N_4O_6$ requires C, 41.8, H, 4.5, N, 13.9%); ν_{max} (KBr) 3500-3400 (NH), 1700-1800 (C=O ester), 1610 (C=N); δ_H(250 MHz, CD_3OD) 3.64 (m, 6H, 2 x C<u>H</u>$_3$ methoxy), 3.80 (m, 6H, 2 x C<u>H</u>$_3$ methoxy), 6.00 (s, 2H, 2 x C<u>H</u> vinylic); m/z 402 (M^+, 23%) and white plate like crystals of *trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime* 1.2 g, 34%, m.p. 192-194 ^0C, (Found: C, 41.8, H, 4.6, N, 13.8% requires C, 41.8, H, 4.5, N, 13.9%); ν_{max} (KBr) 3500-3400 (NH), 1700-1800 (C=O ester), 1610 (C=N); δ_H(250 MHz, CD_3OD) 3.63 (s, 6H, 2 x C<u>H</u>$_3$ methoxy), 3.79 (s, 6H, 2 x C<u>H</u>$_3$ methoxy), 6.18 (s, 2H, 2 x C<u>H</u> vinylic), 7.00 (s, 4H, N<u>H</u>); m/z 402 (M^+, 58%).

6.3.40. Reaction of dimethylglyoxime with DMAD in aqueous EGDE.

To a solution of dimethylglyoxime (1.0 g, 2 mmol) in EGDE:water (80 cm^3, 7:1), DMAD (1.8 g, 13 mmol) was added. The mixture was refluxed (24 h). Concentration of the resultant solution gave an orange paste. The latter was redissolved in a mixture of toluene and methanol (50 cm^3, 6:4) and allowed to stand. A white solid was precipitated after several hours. This solid was filtered off and washed with cold acetone (3 x 50 cm^3) to afford pure unreacted *dimethylglyoxime* (1.0 g, 94%; identified by

comparative IR and m.p. with an authentic sample).

In another experiment dimethylglyoxime (1.0 g, 2 mmol) and DMAD (2.0 g, 14 mmol) were refluxed for 72 h. Concentration of the resultant solution gave a yellow paste which was precipitated with a mixture of toluene and methanol to afford a white solid (multicomponent by TLC). The components of this solid could not be adequately separated.

Similarly, reaction of DMAD (14 mmol) with benzil *anti* monooxime (2 mmol) and cyclohexanedione dioxime (2 mmol) gave white multicomponent solids.

6.3.41. Reaction of Bis(1,2-diaminoethanedionedioximato)nickel(II) with DMAD in aqueous EGDE.

To a solution of bis(1,2-diaminoethanedione dioximato)nickel(II) (1.6 g, 5 mmol) in EGDE:water (80 cm^3, 7:1) DMAD (2.0 g, 14 mmol) was added. The mixture was refluxed (24 h) and then filtered to give a pink solid and an orange filtrate. The solid was washed with EGDE (2 x 10 cm^3), water (3 x 25 cm^3) and methanol (2 x 25 cm^3) and dried to afford *nickel(II) butynedioate octahydrate* 0.3 g 33% (identified by comparative IR with an authentic sample. Concentration of the combined washings and filtrate gave an orange paste which was dissolved in a mixture of toluene and methanol (50 cm^3, 6:4) and allowed to stand for several days. This afforded white powdery *cis-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diamino-ethanedione dioxime* (0.6 g, 29%) and white plate-like crystals of *trans-bis(O-1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione dioxime* (0.9 g,

43%). Both were identified by elemental analysis and comparative m.p. and IR.

6.3.42. Reaction of bis(dimethyglyoximato)nickel(II) with DMAD in aqueous EGDE.

To a suspension of bis(dimethylglyoximato)nickel(II) (1.5 g, 5 mmol) in EGDE:water (80 cm^3, 7:1), DMAD (2.0 g, 14 mmol) was added. The mixture was refluxed (24 h). Filtration of the reaction mixture gave a brown solid which was washed with EGDE (2 x 10 cm^3), water (5 x 25 cm^3) and methanol (5 x 25 cm^3) and dried to give unreacted *bis(dimethylglyoximato)nickel(II)* (1.4 g, 95%; identified by comparative IR with an authentic sample).

6.3.43. Reaction of 5-hydroxy-1,2-benzoquinone-2-oxime with DMAD.

5-Hydroxy-1,2-benzoquinone-2-oxime (1.1 g, 7 mmol) and DMAD (2.3 g, 16 mmol) in EGDE:water (80 cm^3, 7:1) was gently refluxed with stirring (3 h). Filtration of the hot mixture afforded a brown multicomponent solid (0.4 g), which could not be separated. Concentration of the filtrate afforded a brown paste which was with dichloromethane to afford *trans-(O-1,2-dicarbomethoxyethenyl)-5-hydroxy-1,2-benzoquinone-2-oxime* 0.6 g, 28%g, m.p. 135-136; (Found: C, 50.4, H, 4.1, N, 5.0% $C_{12}H_{11}NO_7$ requires C, 50.5, H, 3.9, N, 4.9%); ν_{max} (KBr) 3231 (OH), 1743, 1679 (C=O ester), 1626 (C=O quinoid); δ_H(250 MHz, CD_3OD) 3.67 (s, 3H, C<u>H</u>$_3$ methoxy), 3.92 (s, 3H, C<u>H</u>$_3$ methoxy), 5.91, (s, 1H, C<u>H</u> vinylic), 6.44 (d, 1H, C<u>H</u> Ar), 6.53 (d,d, 1H, C<u>H</u> Ar), 7.26 (d, 1H, C<u>H</u> Ar). Further elution with ethylacetate afforded oily residues which could not be

characterised.

6.4 References.

1. F. N. Figgis, 'Magnetochemistry', J. Wiley and Sons, New York, 1968, pp. 172.
2. P. Gaganatsou, PhD Thesis, 1987, The Polytechnic of North London.

APPENDICES

APPENDIX 1.

General spectroscopic characteristics of 3-acyl and 3-alkylaminophenols.

3-Acyl and 3-alkylaminophenols have been reported previously.[1-4] However, little spectroscopic data for these compounds have been published. Presented in this appendix are the general IR, NMR and mass spectral characteristics of these compounds determined during this study.

The IR spectra are exemplified by Figures A1 and A2. These spectra contain bands assignable to νNH between 3306 and 3311 cm^{-1} for the acylamino substituted compounds and between 3283 and 3290 cm^{-1} for their alkylamino analogues.

Figure A1. *IR spectrum of 3-propionylaminophenol*

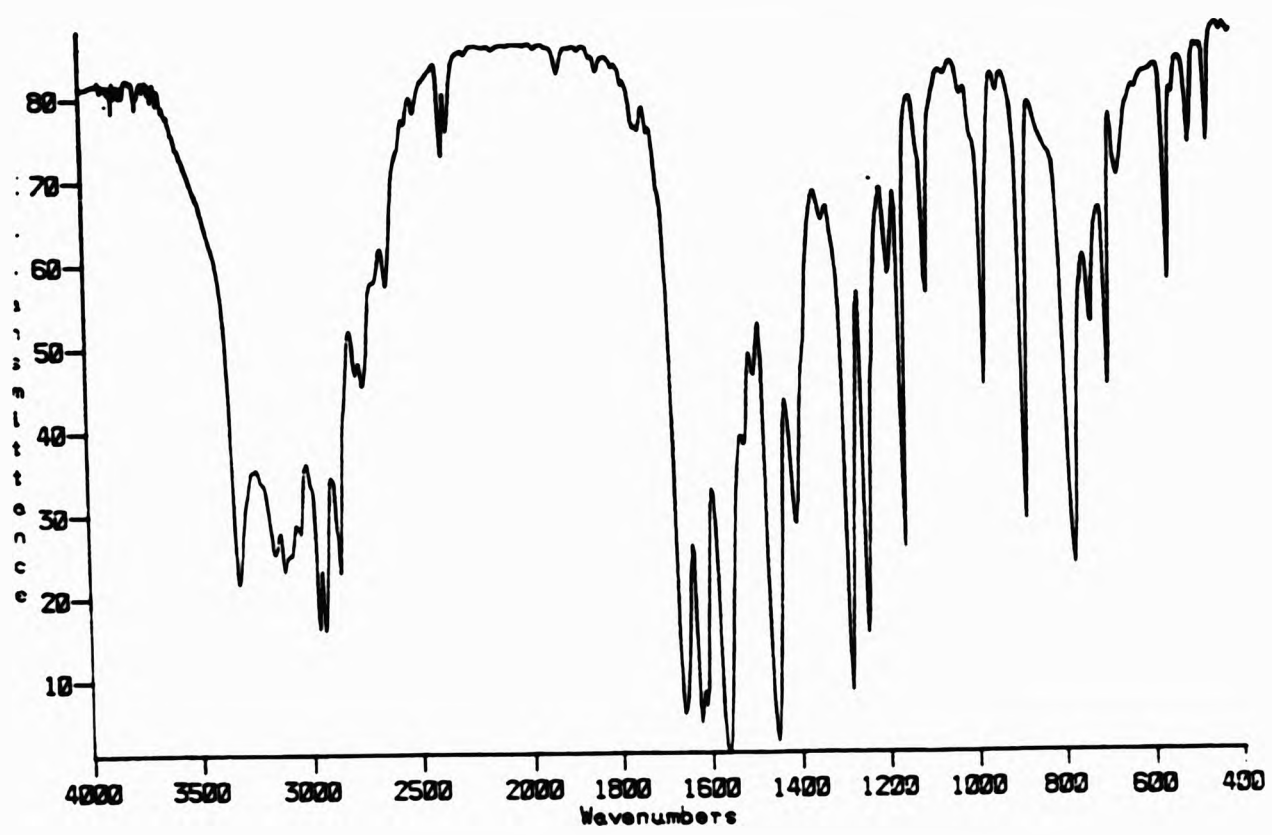
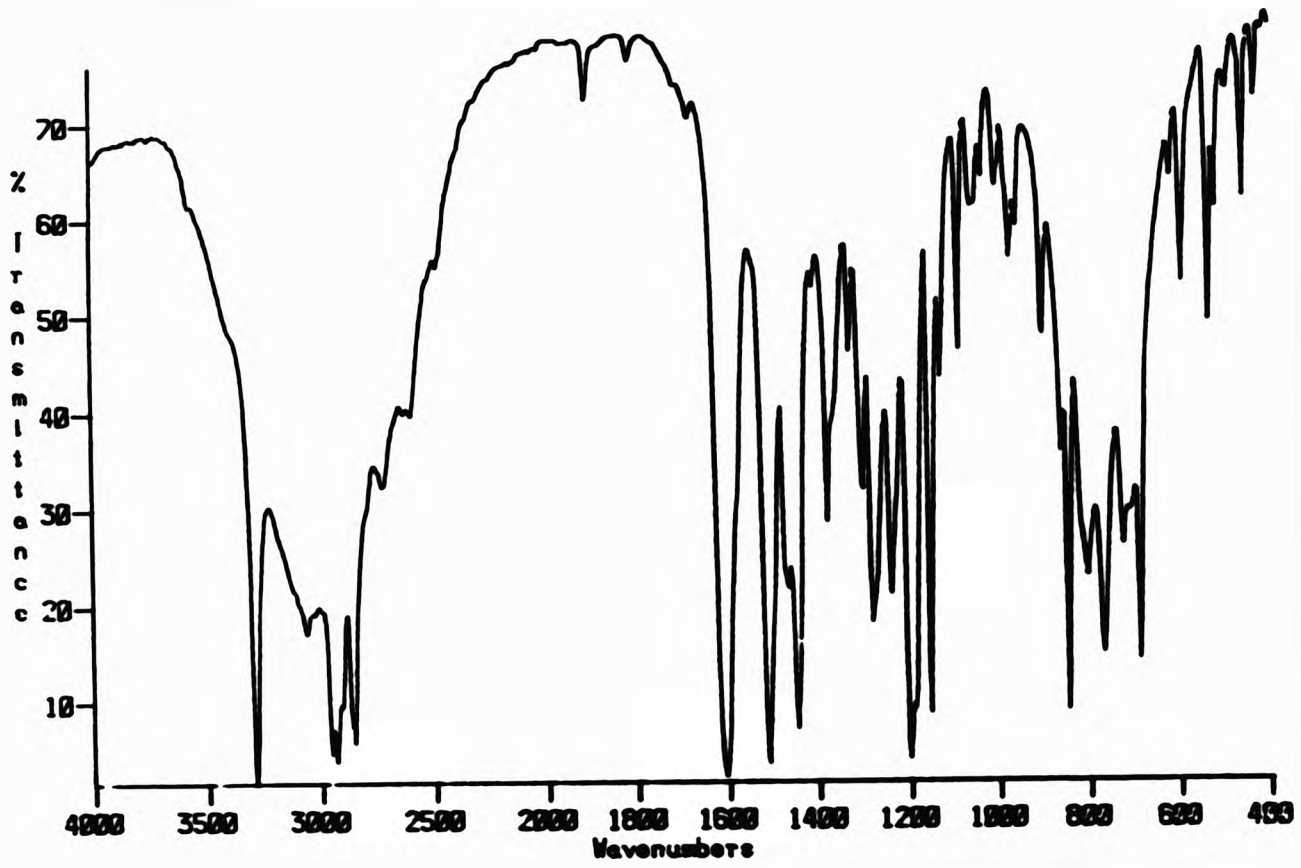
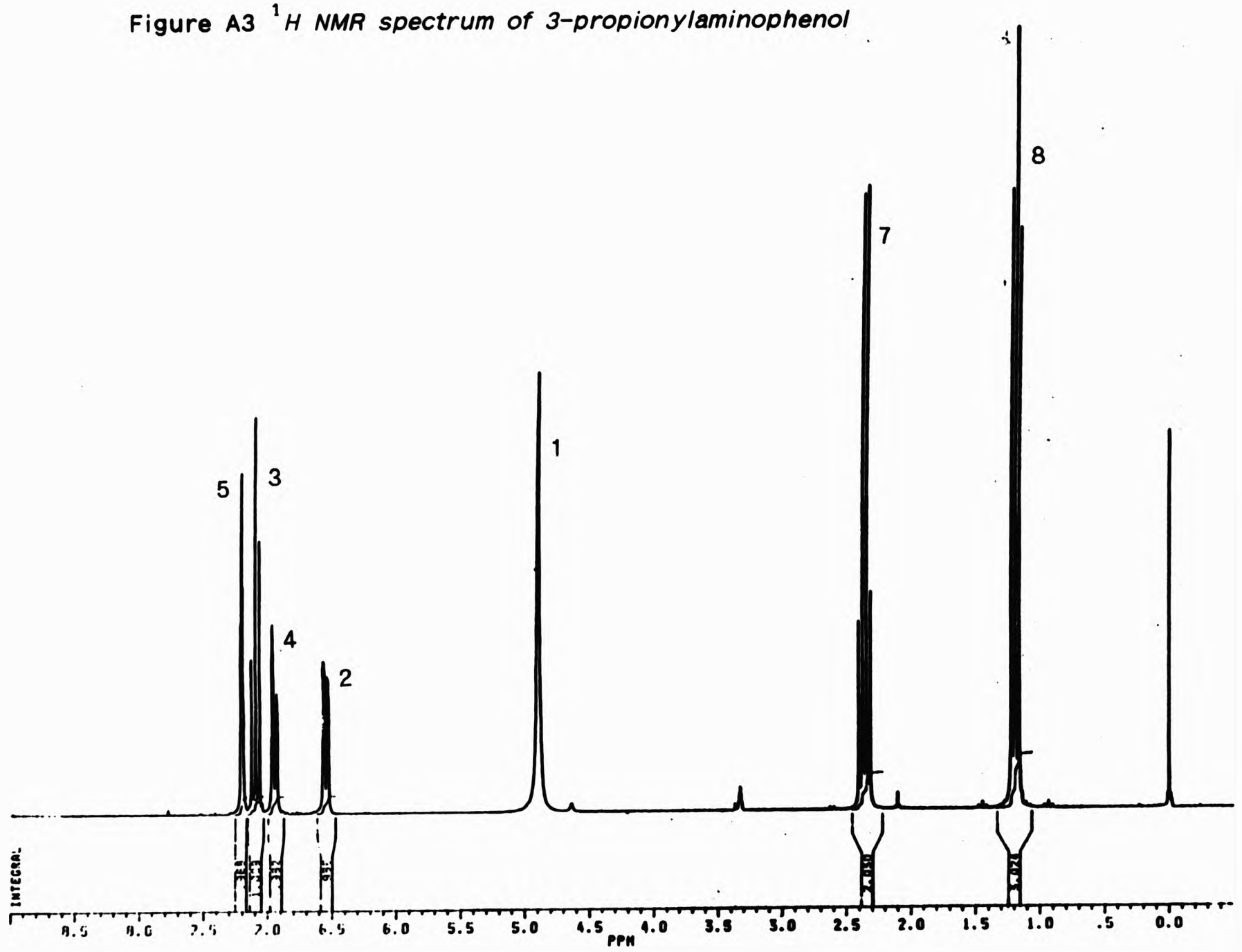


Figure A2 *IR spectrum of 3-hexylaminophenol.*



The ^{1}H NMR spectra of both sets of compounds in deuterated methanol displayed signals due to the OH and NH protons at approximately 5.00 ppm and 11.91 ppm respectively. The ^{1}H NMR spectra of the acylaminophenols (eg. Fig. A3) showed all four aromatic protons as individual multiplets between 6.80 and 7.30 ppm (Table A1.1). By contrast, the spectra of the alkylamino analogues (eg. Fig. A4) contained two multiplets in the aromatic region (Table A1.1).

Figure A3 ^{1}H *NMR spectrum of 3-propionylaminophenol*



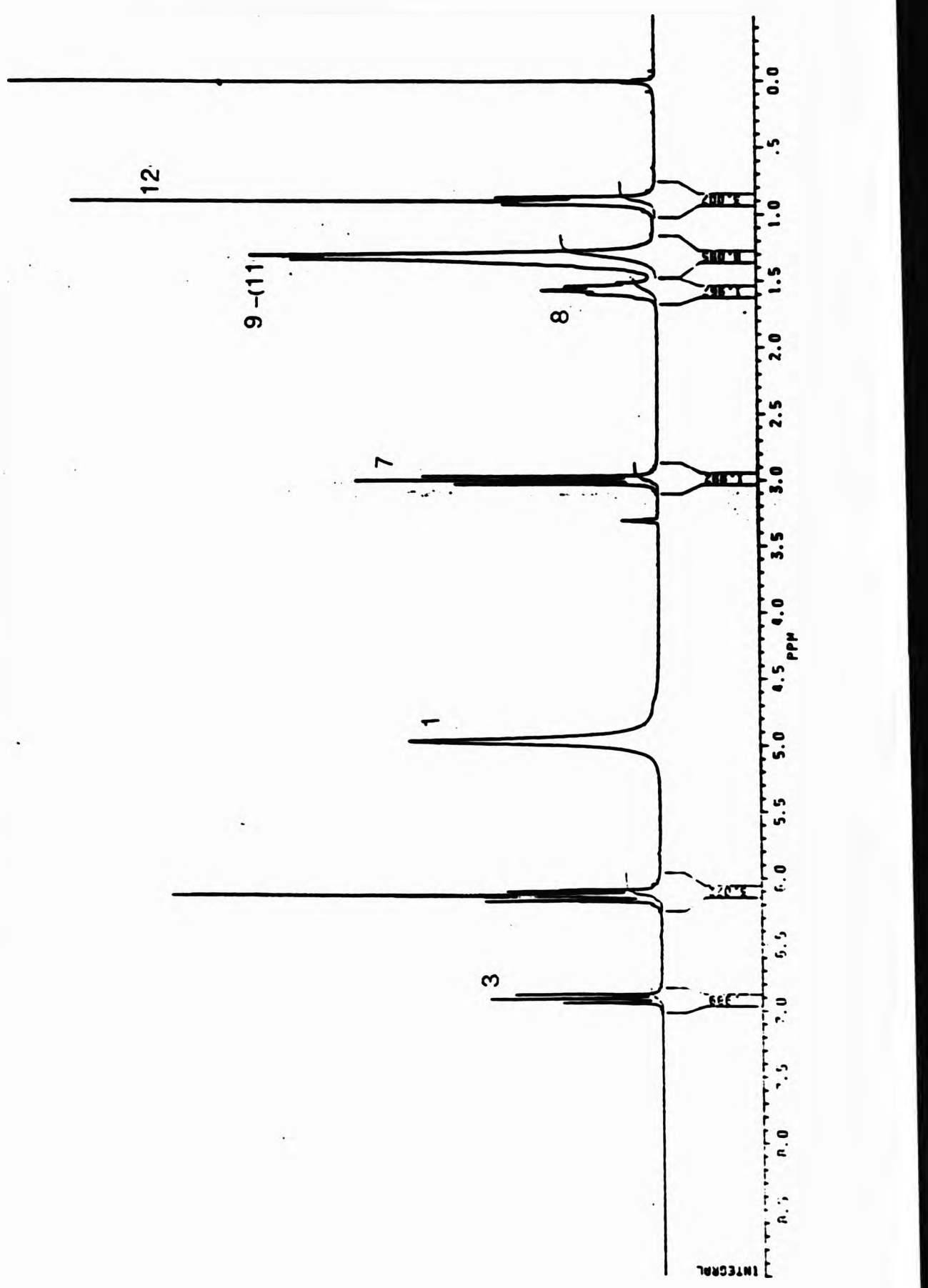
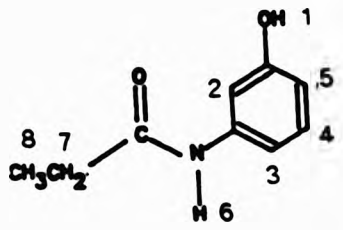
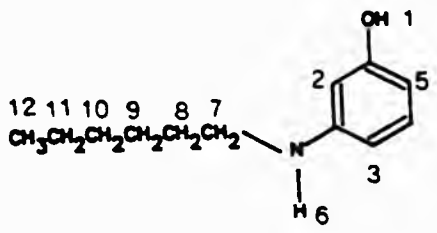


Figure A4 ^{1}H *NMR spectrum of 3-hexylaminophenol*

Table A1.1 ^{1}H *NMR spectral assignments for 3-propionylaminophenol and 3-hexylaminophenol.*

Compound	Assignment	Multiplicity	δppm
	8	t $^{3}J_{7,8}$ (7.04)	1.20
	7	q	2.35
	6	s	9.81
	5	m	7.20
	4	m $^{3}J_{4,3}$ (7.04)	6.95
	3	t	7.00
	2	m	6.55
	1	s	5.00
	12	m	0.90
	9–11	m	1.35
	8	m	1.60
	7	t $^{3}J_{7,8}$ (8.00)	3.05
	6	s	9.81
	5, 4, 2	m	6.10
	3	m $^{3}J_{2,3}$ (7.40)	6.90
	1	s	5.00

s, singlet; t, triplet; q, quartet; m. multiplet.

The EI mass spectra of both the acylamino and alkylaminophenols (eg. Fig. A5) contained relatively prominent molecular ions (Table A 1.2). The spectra are dominated by fragmentation of the substituents with the base peak (m/z = 109) arising from the loss of these groups.

Figure A5 *EI mass spectrum of 3-heptanoylaminophenol*

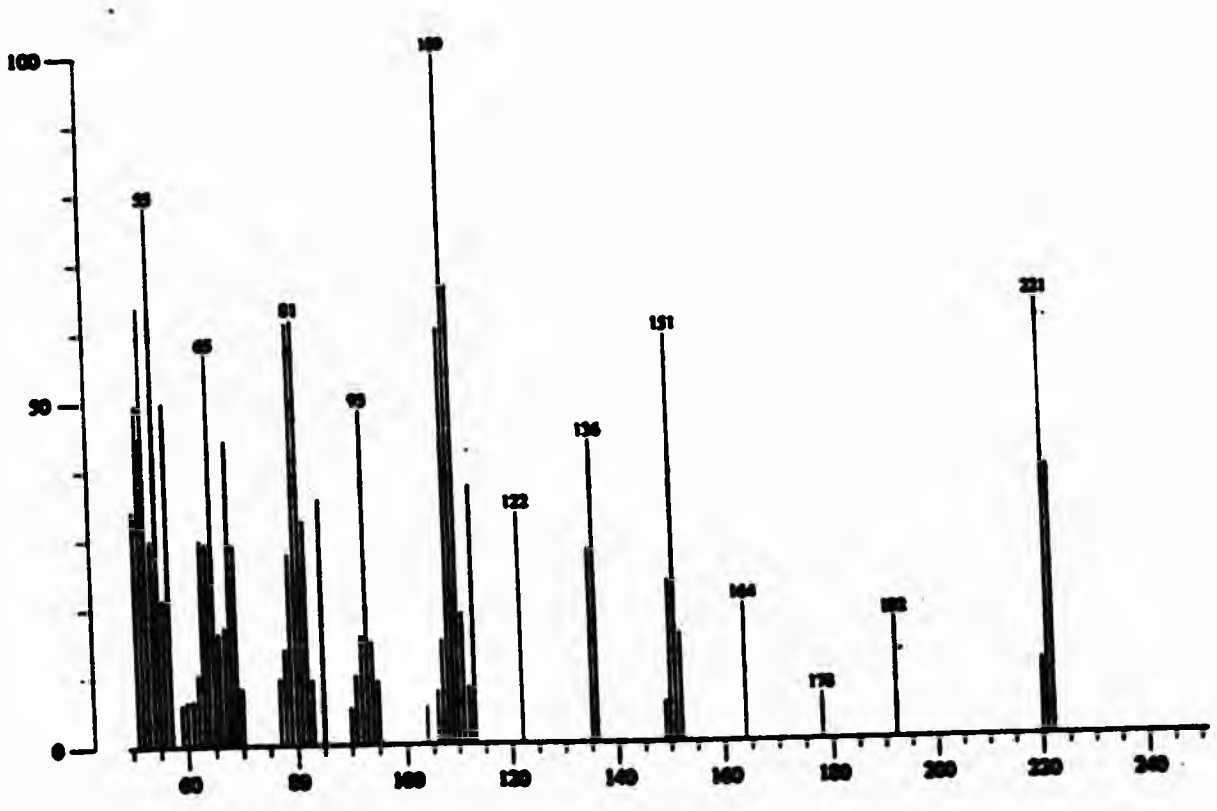


Table A1.2 *Relative abundances and assignments of ions in the mass spectrum of 3-heptanoylaminophenol*

Ion assignment	Relative abundance %	m/z
$[M]^{+\cdot}$	37	221
$[M-CH_3]^+$	5	206
$[M-C_2H_5]^+$	21	192
$[M-C_3H_7]^+$	10	178
$[M-C_4H_9]^+$	10	164
$[M-C_5H_{11}]^+$	37	151
$[M-C_6H_{13}]^+$	27	136
$[M-C_6H_{12}CO]^{+\cdot}$	100	109
$[M-C_6H_{13}CONH]^{+\cdot}$	30	93

References.

1. Jaromir Socha, Czech. Pat. CS.260,431, 15 Apr. 1989.
2. E. Felder, D. Pitre, *Ed. Sci.*, 1960, 15, 609-31.
3. H. Harada, H. Maki, S. Sasaki, Jap. Pat. JP 62,48,653 (87,48,653) 03 Mar. 1987.
4. H. Harada, H. Maki, S. Sasaki, Jap. Pat. JP 62,48,654 (87,48,654) 03 Mar. 1987.

APPENDIX 2 X-ray Crystal data for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Table A2.1

Positional Parameters and their Estimated Standard Deviations for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Atom	x	y	z	B(A2)
O1	0.0250(3)	0.4315(2)	0.3845(2)	5.31(5)
O2	0.4983(3)	0.3162(2)	0.4012(1)	4.13(4)
O3	-0.1687(4)	0.2634(2)	0.4387(2)	5.37(5)
N1	0.1814(4)	0.3877(2)	0.3909(2)	4.24(5)
N7	0.6521(4)	0.6188(2)	0.1952(2)	4.63(6)
C1	0.2938(4)	0.4537(3)	0.3528(2)	3.80(6)
C2	0.4664(4)	0.4084(3)	0.3551(2)	3.61(5)
C3	0.5874(5)	0.4655(3)	0.3023(2)	3.94(6)
C4	0.5469(5)	0.5650(3)	0.2520(2)	3.96(6)
C5	0.3804(5)	0.6145(3)	0.2593(2)	4.55(7)
C6	0.2608(5)	0.5625(3)	0.3076(2)	4.39(6)
C8	0.8157(5)	0.5774(3)	0.1725(2)	5.20(7)
C9	0.8157(7)	0.4900(4)	0.0942(3)	6.80(1)
C10	0.9844(8)	0.4393(4)	0.0644(3)	7.60(1)
C11	1.0361(9)	0.3411(5)	0.1239(3)	8.70(1)
C12	1.1940(1)	0.2751(5)	0.0889(3)	9.20(1)
C13	1.3500(1)	0.3476(6)	0.0912(4)	11.10(2)

Table A2.2. Table of Bond Distances in Angstroms for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N1	1.355(4)	C3	C4	1.397(4)
O2	C2	1.281(4)	C4	C5	1.456(5)
N1	C1	1.302(4)	C5	C6	1.328(5)
N7	C4	1.330(4)	C8	C9	1.514(6)
N7	C8	1.463(5)	C9	C10	1.535(8)
C1	C2	1.479(5)	C10	C11	1.481(7)
C1	C6	1.440(5)	C11	C12	1.560(1)
C2	C3	1.398(5)	C12	C13	1.500(1)

Table A2.3. Table of Bond Angles in Degrees for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	N1	C1	113.1(3)	N7	C4	C5	116.3(3)
C4	N7	C8	124.6(3)	C3	C4	C5	119.9(3)
N1	C1	C2	115.5(3)	C4	C5	C6	121.4(3)
N1	C1	C6	125.1(3)	C1	C6	C5	120.0(3)
C2	C1	C6	119.4(3)	N7	C8	C9	111.4(3)
O2	C2	C1	119.4(3)	C8	C9	C10	116.4(4)
O2	C2	C3	122.4(3)	C9	C10	C11	112.2(4)
C1	C2	C3	118.0(3)	C10	C11	C12	114.5(5)
C2	C3	C4	120.6(3)	C11	C12	C13	113.5(5)
N7	C4	C3	123.8(3)				

Table A2.4. Table of General Displacement Parameters Expressions - B's for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beq
O1	2.96(9)	5.90(1)	7.00(1)	0.60(1)	0.50(1)	1.10(1)	5.3
O2	3.31(8)	3.96(8)	5.13(8)	-0.02(9)	-0.07(9)	0.69(8)	4.1
O3	3.70(1)	6.80(1)	5.64(9)	-0.10(1)	-0.20(1)	1.90(1)	5.3
N1	3.10(1)	4.90(1)	4.82(9)	0.10(1)	0.10(1)	0.00(1)	4.2
N7	4.40(1)	4.10(1)	5.40(1)	0.10(1)	0.60(1)	0.70(1)	4.6
C1	3.60(1)	3.60(1)	4.10(1)	-0.10(1)	-0.10(1)	-0.10(1)	3.8
C2	3.30(1)	3.40(1)	4.10(1)	-0.00(1)	-0.30(1)	-0.20(1)	3.6
C3	3.40(1)	3.90(1)	4.40(1)	0.20(1)	-0.20(1)	0.40(1)	3.9
C4	3.90(1)	3.70(1)	4.30(1)	-0.40(1)	0.10(1)	0.10(1)	3.9
C5	4.40(1)	3.70(1)	5.50(1)	0.50(1)	-0.00(2)	0.30(1)	4.5
C6	3.50(1)	4.20(1)	5.50(1)	0.40(1)	0.00(1)	0.30(1)	4.3
C8	4.00(1)	5.30(2)	6.30(1)	-0.40(2)	1.00(1)	1.20(1)	5.2
C9	5.70(2)	6.80(2)	8.00(2)	1.30(2)	1.00(2)	0.00(2)	6.8
C10	6.90(2)	7.20(2)	8.60(2)	0.80(2)	1.80(2)	1.60(2)	7.6
C11	6.70(3)	8.90(3)	10.40(3)	1.00(3)	0.10(3)	1.70(3)	8.7
C12	8.30(3)	9.30(3)	10.00(3)	2.50(3)	-1.20(3)	-0.90(3)	9.2
C13	7.00(3)	13.20(4)	13.20(3)	2.50(3)	-2.20(4)	-4.80(3)	11.1

Table A2.5. Table of Refined Displacement Parameter Expressions - Beta's for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
O1	0.0115(3)	0.0111(2)	0.0085(1)	0.0033(5)	0.0020(5)	0.0032(3)
O2	0.0129(3)	0.0074(2)	0.00617(9)	-0.0001(5)	-0.0003(4)	0.0021(2)
O3	0.0144(4)	0.0127(2)	0.0068(1)	-0.0008(6)	-0.0007(4)	0.0058(3)
N1	0.0119(4)	0.0091(2)	0.0058(1)	0.0004(6)	0.0006(5)	0.0001(3)
N7	0.0171(5)	0.0077(2)	0.0065(1)	0.0003(6)	0.0027(6)	0.0021(3)
C1	0.0141(5)	0.0068(2)	0.0050(1)	-0.0008(6)	-0.0006(5)	-0.0004(3)
C2	0.0129(5)	0.0063(2)	0.0050(1)	-0.0002(6)	-0.0014(5)	-0.0007(3)
C3	0.0134(5)	0.0074(2)	0.0053(1)	0.0010(7)	-0.0008(6)	0.0013(4)
C4	0.0152(5)	0.0069(2)	0.0052(1)	-0.0021(7)	0.0006(6)	0.0003(3)
C5	0.0173(6)	0.0070(2)	0.0066(2)	0.0027(7)	-0.0002(7)	0.0009(4)
C6	0.0135(5)	0.0079(3)	0.0066(2)	0.0022(7)	0.0002(6)	0.0009(4)
C8	0.0155(5)	0.0100(3)	0.0076(2)	-0.0023(9)	0.0045(7)	0.0036(4)
C9	0.0221(8)	0.0128(4)	0.0096(2)	0.0070(1)	0.0040(1)	0.0001(6)
C10	0.0270(1)	0.0135(4)	0.0104(2)	0.0040(1)	0.0080(1)	0.0047(6)
C11	0.0260(1)	0.0167(5)	0.0125(3)	0.0060(1)	0.0000(1)	0.0050(8)
C12	0.0320(1)	0.0175(6)	0.0120(3)	0.0130(2)	-0.0050(1)	-0.0028(8)
C13	0.0270(1)	0.0247(8)	0.0159(4)	0.0140(2)	-0.0100(2)	-0.0145(9)

Table A2.6. Table of General Displacement Parameters Expressions - U's for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.037(1)	0.075(1)	0.089(1)	0.008(1)	0.006(1)	0.013(1)
O2	0.042(1)	0.050(1)	0.065(1)	-0.000(1)	-0.001(1)	0.009(1)
O3	0.047(1)	0.086(2)	0.071(1)	-0.002(1)	-0.002(1)	0.024(1)
N1	0.039(4)	0.062(1)	0.061(1)	0.001(1)	0.002(1)	0.000(1)
N7	0.056(2)	0.052(1)	0.068(1)	0.001(1)	0.008(2)	0.009(1)
C1	0.046(2)	0.046(1)	0.053(1)	-0.002(1)	-0.002(2)	-0.002(1)
C2	0.042(2)	0.043(1)	0.052(1)	-0.000(1)	-0.004(2)	-0.003(1)
C3	0.044(2)	0.050(2)	0.056(1)	0.002(2)	-0.002(2)	0.005(1)
C4	0.049(2)	0.046(1)	0.055(1)	-0.005(2)	0.002(2)	0.001(1)
C5	0.056(2)	0.047(2)	0.069(2)	0.006(2)	-0.001(2)	0.004(2)
C6	0.044(2)	0.053(2)	0.069(2)	0.005(2)	0.002(6)	0.004(2)
C8	0.051(2)	0.068(2)	0.080(2)	-0.005(2)	0.013(2)	0.015(2)
C9	0.072(2)	0.086(3)	0.101(2)	0.017(3)	0.013(3)	0.000(2)
C10	0.088(3)	0.091(3)	0.109(3)	0.010(3)	0.022(3)	0.020(3)
C11	0.085(3)	0.113(4)	0.131(3)	0.013(3)	0.001(4)	0.021(3)
C12	0.105(4)	0.118(4)	0.127(3)	0.031(4)	-0.015(4)	-0.012(3)
C13	0.089(4)	0.167(5)	0.167(4)	0.032(4)	-0.028(5)	-0.061(4)

Table A2.7. Table of Root-mean-square Amplitudes of Anisotropic Displacement in Angstroms for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Atom	Min	Int'med	Max
O1	0.189	0.259	0.314
O2	0.205	0.215	0.263
O3	0.216	0.230	0.323
N1	0.196	0.248	0.248
N7	0.217	0.232	0.274
C1	0.208	0.218	0.231
C2	0.200	0.207	0.233
C3	0.204	0.221	0.244
C4	0.206	0.230	0.235
C5	0.209	0.244	0.264
C6	0.204	0.234	0.265
C8	0.202	0.256	0.303
C9	0.241	0.305	0.329
C10	0.270	0.284	0.366
C11	0.281	0.323	0.382
C12	0.281	0.339	0.395
C13	0.277	0.326	0.490

Table A2.8. Table of Positional Parameters and their Estimated Standard Deviations for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Atom	x	y	z	B(A2)
HO1	-0.047(7)	0.361(3)	0.408(2)	3.8(9)
HO3B	-0.160(1)	0.227(5)	0.503(5)	7.0(1)
H3	0.700(7)	0.433(3)	0.299(2)	3.4(9)
HO3A	-0.290(7)	0.283(3)	0.432(2)	3.7(9)
H5	0.358(9)	0.675(3)	0.220(2)	3.6(9)
H6	0.156(9)	0.593(4)	0.311(2)	5.0(1)
HN7	0.616(7)	0.683(3)	0.161(2)	3.6(9)
H8A	0.890(1)	0.542(4)	0.231(3)	6.0(1)
H8B	0.869(8)	0.650(3)	0.146(2)	5.0(1)
H9A	0.770(1)	0.535(4)	0.038(2)	6.0(1)
H9B	0.727(8)	0.433(3)	0.125(2)	4.0(1)
H10B	0.970(2)	0.408(5)	-0.008(3)	9.0(2)
H10A	1.074(9)	0.498(4)	0.074(2)	6.0(1)
H11A	0.940(1)	0.272(4)	0.123(3)	8.0(1)
H11B	1.065(9)	0.367(4)	0.192(2)	6.0(1)
H12A	1.190(2)	0.247(7)	0.023(3)	10.0(2)
H12B	1.250(1)	0.209(4)	0.125(3)	8.0(1)
H13C	1.380(2)	0.389(5)	0.148(3)	12.0(2)
H13A	1.470(3)	0.302(5)	0.069(3)	14.0(3)
H13B	1.320(1)	0.406(4)	0.050(3)	11.0(2)

Table A2.9. Table of Torsion Angles in Degrees for 5-Hexylamino-1,2-benzoquinone-2-oxime Monohydrate.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
HO1	O1	N1	C1	171.12 (1.73)
O1	N1	C1	C2	-178.14 (0.23)
O1	N1	C1	C6	-0.17 (0.42)
C8	N7	C4	C3	4.35 (0.49)
C8	N7	C4	C5	-174.74 (0.29)
HN7	N7	C4	C3	176.95 (2.51)
HN7	N7	C4	C5	-2.14 (2.53)
C4	N7	C8	C9	84.51 (0.39)
C4	N7	C8	H8A	-40.06 (3.03)
C4	N7	C8	H8B	-163.38 (2.20)
HN7	N7	C8	C9	88.45 (2.56)
HN7	N7	C8	H8A	146.98 (3.93)
HN7	N7	C8	H8B	23.66 (3.37)
N1	C1	C2	O2	-7.18 (0.39)
N1	C1	C2	C3	169.58 (0.26)
C6	C1	C2	O2	174.73 (0.26)
C6	C1	C2	C3	-8.51 (0.40)
N1	C1	C6	C5	-170.08 (0.31)
N1	C1	C6	H6	7.88 (2.87)
C2	C1	C6	C5	7.82 (0.45)
C2	C1	C6	H6	-174.22 (2.84)
O2	C2	C3	C4	179.17 (0.27)
O2	C2	C3	H3	1.65 (2.40)
C1	C2	C3	C4	2.52 (0.42)

Table A2.9 cont'd...

C1	C2	C3	H3	-175.01 (2.37)
C2	C3	C4	N7	-174.92 (0.29)
C2	C3	C4	C5	4.14 (0.45)
H3	C3	C4	N7	2.57 (2.47)
H3	C3	C4	C5	-178.38 (2.44)
N7	C4	C5	C6	174.07 (0.31)
N7	C4	C5	H5	5.37 (2.52)
C3	C4	C5	C6	-5.06 (0.48)
C3	C4	C5	H5	173.75 (2.50)
C4	C5	C6	C1	-1.09 (0.49)
C4	C5	C6	H6	-179.01 (2.95)
H5	C5	C6	C1	166.89 (2.44)
H5	C5	C6	H6	-11.03 (3.84)
N7	C8	C9	C10	-179.56 (0.33)
N7	C8	C9	H9A	64.03 (4.36)
N7	C8	C9	H9B	-53.55 (2.88)
H8A	C8	C9	C10	-52.76 (4.37)
H8A	C8	C9	H9A	-169.18 (6.15)
H8A	C8	C9	H9B	73.25 (5.21)
H8B	C8	C9	C10	72.30 (3.77)
H8B	C8	C9	H9A	-44.12 (5.75)
H8B	C8	C9	H9B	-161.69 (4.72)
C8	C9	C10	C11	83.61 (0.52)
C8	C9	C10	H10B	-157.13 (3.36)
C8	C9	C10	H10A	-31.05 (2.31)
H9A	C9	C10	C11	-160.22 (2.98)

Table A2.9 cont'd...

H9A	C9	C10	H10B	-40.96 (4.49)
H9A	C9	C10	H10A	85.12 (3.74)
H9B	C9	C10	C11	-30.82 (2.39)
H9B	C9	C10	H10B	88.44 (4.09)
H9B	C9	C10	H10A	-145.48 (3.25)
C9	C10	C11	C12	172.05 (0.45)
C9	C10	C11	H11A	58.02 (3.27)
C9	C10	C11	H11B	-67.83 (4.09)
H10B	C10	C11	C12	53.36 (6.68)
H10B	C10	C11	H11A	-60.67 (7.41)
H10B	C10	C11	H11B	173.48 (7.79)
H10A	C10	C11	C12	-70.00 (2.99)
H10A	C10	C11	H11A	175.97 (4.38)
H10A	C10	C11	H11B	50.12 (5.03)
C10	C11	C12	C13	65.57 (0.62)
C10	C11	C12	H12A	-54.18 (5.29)
C10	C11	C12	H12B	175.80 (4.47)
H11A	C11	C12	C13	-174.88 (2.41)
H11A	C11	C12	H12A	65.37 (5.78)
H11A	C11	C12	H12B	-64.65 (5.08)
H11B	C11	C12	C13	-58.53 (2.67)
H11B	C11	C12	H12A	-178.28 (5.88)
H11B	C11	C12	H12B	51.70 (5.21)
C11	C12	C13	H13C	50.30 (5.60)
C11	C12	C13	H13A	177.65 (3.47)
C11	C12	C13	H13B	-62.19 (3.96)

Table A2.9 cont'd...

H12A	C12	C13	H13C	174.86 (7.77)
H12A	C12	C13	H13A	-57.79 (6.45)
H12A	C12	C13	H13B	62.37 (6.72)
H12B	C12	C13	H13C	-77.71 (6.19)
H12B	C12	C13	H13A	49.64 (4.40)
H12B	C12	C13	H13B	169.80 (4.77)

Table A2.10. Values of 10*Fobs and 10*F calc

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	0	-16	48	38	0	2	-11	96	90	0	3	6	116	104
0	0	-14	45	47	0	2	-9	17	15	0	3	7	317	320
0	0	-12	17	21	0	2	-8	60	51	0	3	8	93	94
0	0	-10	112	111	0	2	-7	359	358	0	3	8	94	94
0	0	-6	486	485	0	2	-6	243	248	0	3	9	108	115
0	0	-4	965	971	0	2	-5	282	281	0	3	9	109	115
0	0	-2	325	328	0	2	-4	28	22	0	3	11	22	20
0	0	2	325	328	0	2	-3	1472	1461	0	3	11	21	20
0	0	4	961	971	0	2	-2	730	706	0	3	13	45	44
0	0	6	489	485	0	2	-1	224	214	0	3	13	42	44
0	0	10	115	111	0	2	0	591	584	0	3	14	63	56
0	0	10	109	111	0	2	1	226	214	0	3	14	58	56
0	0	12	17	21	0	2	2	730	706	0	3	16	45	45
0	0	12	16	21	0	2	3	1453	1461	0	3	16	40	45
0	0	14	45	47	0	2	4	29	22	0	3	17	41	35
0	0	14	43	47	0	2	5	286	281	0	3	17	37	35
0	0	16	46	38	0	2	6	247	248	0	4	-15	51	55
0	0	16	44	38	0	2	7	358	358	0	4	-14	44	44
0	1	-13	28	29	0	2	8	58	51	0	4	-13	115	110
0	1	-11	22	23	0	2	8	59	51	0	4	-12	17	14
0	1	-10	155	158	0	2	9	15	15	0	4	-11	20	26
0	1	-9	28	27	0	2	11	94	90	0	4	-10	26	25
0	1	-8	38	35	0	2	11	99	90	0	4	-9	94	94
0	1	-7	37	36	0	2	13	62	53	0	4	-8	161	161
0	1	-6	228	241	0	2	13	57	53	0	4	-7	34	48
0	1	-5	52	47	0	2	15	35	43	0	4	-6	86	91
0	1	-4	375	366	0	2	15	38	43	0	4	-5	281	267
0	1	-3	289	277	0	2	16	17	14	0	4	-4	56	63
0	1	-2	265	266	0	2	16	16	14	0	4	-3	147	153
0	1	-1	319	329	0	2	17	37	39	0	4	-2	398	420
0	1	1	324	329	0	2	17	34	39	0	4	-1	162	163
0	1	2	277	266	0	3	-17	39	35	0	2	0	300	284
0	1	3	293	277	0	3	-16	41	45	0	4	1	164	163
0	1	4	380	366	0	3	-14	60	56	0	4	2	408	420
0	1	5	53	47	0	3	-13	43	44	0	4	3	152	153
0	1	6	229	241	0	3	-11	21	20	0	4	4	54	63
0	1	7	33	36	0	3	-9	111	115	0	4	5	286	267
0	1	8	33	35	0	3	-8	94	94	0	4	6	85	91
0	1	9	27	27	0	3	-7	315	320	0	4	7	40	48
0	1	9	29	27	0	3	-6	116	104	0	4	7	37	48
0	1	10	149	158	0	3	-5	67	70	0	4	8	158	161
0	1	10	154	158	0	3	-4	526	524	0	4	8	160	161
0	1	11	22	23	0	3	-3	722	716	0	4	9	90	94
0	1	11	24	23	0	3	-2	104	104	0	4	9	92	94
0	1	13	28	29	0	3	-1	176	188	0	4	10	24	25
0	1	13	27	29	0	3	1	178	188	0	4	10	24	25
0	2	-17	35	39	0	3	2	105	104	0	4	11	20	26
0	2	-16	17	14	0	3	3	726	716	0	4	11	21	26
0	2	-15	37	43	0	3	4	534	524	0	4	12	16	14
0	2	-13	58	53	0	3	5	66	70	0	4	12	17	14
0	4	13	121	110	0	9	1	57	53	1	1	15	21	12

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	4	13	112	110	0	9	2	59	63	1	1	16	23	25
0	4	14	42	44	0	9	3	44	47	1	1	17	19	23
0	4	14	46	44	0	9	4	89	90	1	2	8	107	114
0	4	15	57	55	0	9	5	115	113	1	2	9	112	116
0	5	5	26	23	0	9	6	22	22	1	2	10	61	68
0	5	6	245	253	0	9	7	71	73	1	2	11	87	88
0	5	6	244	253	0	9	8	46	42	1	2	12	37	35
0	5	7	116	121	0	9	9	32	33	1	2	13	43	48
0	5	7	118	121	0	9	10	29	29	1	2	14	45	51
0	5	8	49	48	0	9	12	50	47	1	2	16	56	48
0	5	8	52	48	0	10	0	26	25	1	2	17	31	32
0	5	9	54	56	0	10	3	30	32	1	3	8	173	165
0	5	9	56	56	0	10	4	24	27	1	3	9	106	107
0	5	10	109	105	0	10	7	54	54	1	3	10	95	106
0	5	10	106	105	0	10	8	33	37	1	3	11	48	53
0	5	11	87	86	0	10	9	18	15	1	3	12	91	86
0	5	11	92	86	0	10	10	19	18	1	3	13	23	22
0	5	12	36	37	0	10	11	22	19	1	3	14	51	46
0	5	12	35	37	0	11	1	24	21	1	3	15	35	35
0	5	13	35	35	0	11	2	15	11	1	4	7	90	90
0	5	13	32	35	0	11	3	47	44	1	4	8	141	138
0	5	14	31	30	0	11	4	38	38	1	4	9	34	23
0	5	14	28	30	0	11	5	39	42	1	4	10	71	64
0	6	4	32	39	0	11	6	46	50	1	4	11	101	103
0	6	5	51	62	0	11	7	17	21	1	4	12	51	51
0	6	6	69	64	0	11	8	18	21	1	4	13	38	42
0	6	9	73	71	0	12	1	38	43	1	4	14	76	78
0	6	10	112	118	0	12	2	42	44	1	4	15	19	16
0	6	11	19	15	0	12	4	39	36	1	5	6	152	159
0	6	13	25	27	0	12	5	23	22	1	5	7	107	100
0	7	1	74	72	0	13	1	26	26	1	5	8	69	73
0	7	2	255	252	0	13	2	45	41	1	5	9	207	207
0	7	5	33	32	0	13	3	19	20	1	5	10	20	22
0	7	6	44	51	0	13	6	26	23	1	5	11	116	122
0	7	8	22	24	0	14	0	23	30	1	5	12	35	33
0	7	9	46	40	0	14	1	34	35	1	5	13	71	72
0	7	10	42	46	1	0	9	36	33	1	5	16	20	20
0	7	13	22	23	1	0	10	41	48	1	6	3	259	263
0	7	14	28	29	1	0	11	42	40	1	6	4	226	226
0	8	0	142	139	1	0	12	64	72	1	6	5	48	52
0	8	1	102	99	1	0	13	58	48	1	6	6	60	59
0	8	2	48	46	1	0	15	28	22	1	6	7	52	59
0	8	3	112	111	1	0	17	18	25	1	6	8	34	31
0	8	4	98	88	1	1	8	160	163	1	6	9	128	122
0	8	6	30	32	1	1	9	74	77	1	6	10	81	84
0	8	7	29	20	1	1	10	43	42	1	6	11	61	62
0	8	8	49	47	1	1	11	77	73	1	6	12	50	46
0	8	9	52	61	1	1	12	37	42	1	6	13	47	44
0	8	13	28	33	1	1	13	67	72	1	6	14	18	13
1	7	0	38	33	1	10	12	21	20	2	3	13	22	23

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
1	7	1	55	61	1	11	0	24	21	2	3	14	35	37
1	7	2	167	160	1	11	1	44	49	2	3	16	21	21
1	7	3	34	22	1	11	2	36	40	2	4	6	100	97
1	7	4	108	107	1	11	3	28	31	2	4	7	217	217
1	7	5	83	80	1	11	4	49	50	2	4	8	98	102
1	7	6	30	31	1	11	5	49	49	2	4	9	80	88
1	7	7	32	33	1	11	6	17	20	2	4	10	93	87
1	7	8	96	100	1	11	7	25	24	2	4	11	20	19
1	7	9	107	108	1	11	8	16	12	2	4	12	42	43
1	7	10	66	61	1	11	9	42	40	2	4	13	56	55
1	7	11	89	98	1	12	0	83	80	2	4	14	57	54
1	7	12	24	29	1	12	1	46	44	2	4	15	15	14
1	7	13	26	24	1	12	2	21	22	2	5	5	52	51
1	7	14	18	17	1	12	3	30	28	2	5	6	101	96
1	8	0	75	73	1	12	4	30	27	2	5	7	36	40
1	8	1	60	56	1	12	5	23	19	2	5	8	182	181
1	8	2	48	48	1	12	6	32	32	2	5	9	118	115
1	8	3	52	48	1	12	7	20	17	2	5	10	137	132
1	8	4	57	56	1	12	8	15	15	2	5	11	62	64
1	8	5	28	29	1	13	0	27	31	2	5	12	80	81
1	8	6	59	53	1	13	2	36	36	2	5	13	70	72
1	8	7	69	70	1	13	6	28	27	2	5	14	21	15
1	8	8	80	80	2	0	8	260	262	2	6	0	87	87
1	8	9	55	57	2	0	9	123	117	2	6	1	96	94
1	8	10	62	56	2	0	10	29	24	2	6	2	113	119
1	8	12	29	31	2	0	11	101	87	2	6	3	92	100
1	8	13	34	32	2	0	13	60	63	2	6	4	49	50
1	9	0	51	47	2	0	14	16	20	2	6	5	26	29
1	9	1	64	61	2	0	15	34	31	2	6	6	21	23
1	9	2	26	24	2	1	8	169	173	2	6	7	81	81
1	9	3	30	26	2	1	9	146	147	2	6	8	113	105
1	9	4	80	85	2	1	10	48	59	2	6	9	93	96
1	9	5	19	22	2	1	11	138	138	2	6	10	86	86
1	9	6	74	76	2	1	12	39	35	2	6	11	76	80
1	9	7	40	44	2	1	14	52	44	2	6	12	19	20
1	9	8	70	73	2	1	15	44	40	2	6	13	30	31
1	9	9	25	22	2	1	17	28	25	2	6	14	26	21
1	9	11	27	26	2	2	7	200	191	2	6	15	34	28
1	9	12	33	32	2	2	8	191	184	2	7	0	26	25
1	10	0	40	38	2	2	9	88	91	2	7	1	100	101
1	10	1	39	37	2	2	10	84	85	2	7	2	69	74
1	10	2	39	31	2	2	11	68	72	2	7	3	19	18
1	10	3	78	75	2	2	12	72	68	2	7	4	27	27
1	10	4	54	52	2	2	13	34	32	2	7	5	77	83
1	10	5	31	33	2	2	14	25	27	2	7	6	169	168
1	10	7	51	46	2	2	16	39	34	2	7	7	184	180
1	10	8	44	47	2	3	8	37	40	2	7	8	127	132
1	10	10	19	14	2	3	10	239	47	2	7	9	67	66
1	10	11	22	23	2	3	11	29	40	2	7	10	58	59
2	7	11	85	82	2	12	4	37	40	3	4	11	19	17
2	7	13	58	59	2	12	5	21	24	3	4	12	29	31

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
2	8	0	196	199	2	12	7	23	20	3	4	13	18	19
2	8	1	39	42	2	12	8	31	30	3	5	0	69	67
2	8	2	84	85	2	13	1	27	29	3	5	1	40	38
2	8	3	38	36	2	13	2	20	23	3	5	2	157	162
2	8	4	75	71	2	13	3	23	22	3	5	3	84	87
2	8	5	137	133	2	13	4	16	20	3	5	4	58	52
2	8	6	192	188	2	13	5	24	25	3	5	5	87	90
2	8	7	80	75	3	0	7	94	103	3	5	6	226	235
2	8	8	54	55	3	0	8	18	19	3	5	7	92	86
2	8	9	55	58	3	0	9	38	44	3	5	8	88	80
2	8	10	47	44	3	0	10	35	36	3	5	9	17	19
2	8	11	27	27	3	0	11	51	53	3	5	10	83	89
2	9	0	16	15	3	0	12	50	49	3	5	12	43	37
2	9	1	90	91	3	0	13	73	69	3	5	13	39	35
2	9	2	42	38	3	0	14	21	23	3	5	14	36	32
2	9	3	83	84	3	0	16	18	18	3	5	15	36	34
2	9	4	81	79	3	1	7	78	86	3	6	0	191	187
2	9	5	113	114	3	1	8	113	121	3	6	1	68	69
2	9	6	33	33	3	1	10	42	48	3	6	2	176	176
2	9	7	55	57	3	1	12	20	22	3	6	3	43	37
2	9	8	51	52	3	1	13	22	20	3	6	4	49	48
2	9	9	46	48	3	1	15	19	16	3	6	6	53	54
2	9	11	37	34	3	1	16	35	32	3	6	7	83	81
2	9	12	33	26	3	2	6	115	117	3	6	8	61	54
2	10	0	17	22	3	2	7	28	23	3	6	9	45	46
2	10	1	83	83	3	2	8	21	20	3	6	10	26	24
2	10	2	46	51	3	2	9	60	71	3	6	11	52	59
2	10	3	137	136	3	2	10	90	95	3	7	0	79	88
2	10	4	91	91	3	2	12	25	27	3	7	1	25	23
2	10	5	61	65	3	2	13	36	38	3	7	2	62	66
2	10	6	59	60	3	2	14	15	17	3	7	3	113	121
2	10	7	25	22	3	2	16	28	23	3	7	4	71	69
2	10	8	23	28	3	3	5	205	216	3	7	5	79	77
2	10	9	21	17	3	3	6	56	50	3	7	6	55	51
2	10	10	21	23	3	3	7	45	47	3	7	7	90	89
2	11	0	35	33	3	3	8	39	38	3	7	8	55	57
2	11	1	33	35	3	3	9	92	92	3	7	9	29	31
2	11	2	98	99	3	3	10	29	24	3	7	10	17	20
2	11	3	28	31	3	3	11	49	47	3	7	11	31	32
2	11	4	35	34	3	3	13	34	36	3	7	12	59	59
2	11	6	71	72	3	3	14	32	36	3	7	13	44	42
2	11	8	37	37	3	3	15	18	19	3	8	0	138	128
2	11	9	32	28	3	3	16	18	17	3	8	1	81	82
2	11	10	16	19	3	4	4	153	150	3	8	2	18	10
2	12	0	45	49	3	4	5	197	202	3	8	3	187	186
2	12	1	20	17	3	4	6	125	125	3	8	4	118	109
2	12	2	37	35	3	4	7	27	32	3	8	5	28	22
2	12	3	17	17	3	4	9	78	78	3	8	6	49	52
3	8	7	26	25	4	0	8	114	114	4	4	13	39	35
3	8	8	20	19	4	0	9	66	64	4	5	0	27	21

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
3	8	10	25	33	4	0	11	30	34	4	5	1	121	118
3	8	13	39	36	4	0	15	51	49	4	5	2	108	107
3	9	0	86	88	4	1	4	114	116	4	5	3	112	114
3	9	1	83	82	4	1	5	174	180	4	5	4	140	138
3	9	2	113	113	4	1	6	94	98	4	5	5	33	31
3	9	3	81	82	4	1	7	56	54	4	5	6	43	44
3	9	4	79	78	4	1	8	76	72	4	5	7	128	139
3	9	5	47	46	4	1	9	84	82	4	5	8	60	64
3	9	6	17	14	4	1	11	29	31	4	5	9	24	24
3	9	7	43	45	4	1	12	47	48	4	5	11	53	55
3	9	9	23	23	4	1	13	36	37	4	5	13	25	25
3	9	10	38	37	4	1	14	26	27	4	5	14	44	44
3	9	11	18	19	4	1	15	39	37	4	6	0	41	41
3	9	12	24	19	4	2	4	23	18	4	6	1	123	131
3	10	0	117	112	4	2	5	113	119	4	6	2	233	230
3	10	1	72	69	4	2	6	67	73	4	6	3	210	218
3	10	2	63	65	4	2	7	119	125	4	6	4	29	31
3	10	3	124	119	4	2	8	75	77	4	6	5	101	99
3	10	4	57	59	4	2	9	62	60	4	6	6	63	64
3	10	5	77	77	4	2	10	77	82	4	6	7	106	107
3	10	6	31	24	4	2	11	22	19	4	6	9	17	21
3	10	7	37	33	4	2	12	27	26	4	6	10	23	26
3	10	8	17	12	4	2	13	26	24	4	6	14	25	25
3	10	11	23	22	4	2	14	25	24	4	7	0	118	117
3	11	0	68	69	4	2	15	15	13	4	7	1	98	97
3	11	1	87	81	4	3	2	99	113	4	7	2	74	76
3	11	2	34	37	4	3	3	40	40	4	7	3	71	69
3	11	3	55	54	4	3	4	59	62	4	7	4	147	151
3	11	4	27	28	4	3	5	141	144	4	7	5	71	72
3	11	5	44	43	4	3	6	48	48	4	7	6	53	64
3	11	6	53	55	4	3	7	113	115	4	7	7	15	14
3	11	7	43	43	4	3	8	67	70	4	7	8	53	52
3	11	8	16	15	4	3	9	38	38	4	7	9	31	26
3	11	9	23	17	4	3	10	90	90	4	7	11	35	35
3	12	0	110	104	4	3	11	79	86	4	7	12	23	20
3	12	1	62	61	4	3	12	50	51	4	8	0	261	266
3	12	2	30	34	4	3	13	56	57	4	8	1	60	63
3	12	3	23	21	4	3	14	22	22	4	8	2	46	42
3	12	4	45	46	4	4	0	43	45	4	8	3	46	46
3	12	6	27	29	4	4	1	213	213	4	8	4	87	88
3	12	7	31	31	4	4	2	153	157	4	8	5	63	62
3	13	0	16	19	4	4	3	108	108	4	8	6	73	77
3	13	1	30	30	4	4	4	103	105	4	8	7	25	27
3	13	2	41	39	4	4	5	98	99	4	8	8	15	13
3	13	3	38	39	4	4	6	44	48	4	8	9	38	46
4	0	5	151	154	4	4	8	23	22	4	8	10	32	33
4	0	6	29	32	4	4	9	83	84	4	8	11	15	15
4	0	7	124	129	4	4	11	47	48	4	9	0	142	142
4	9	1	138	140	5	1	8	65	69	5	5	2	82	79
4	9	2	64	69	5	1	9	130	127	5	5	3	67	71

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
4	9	3	41	45	5	1	10	43	48	5	5	4	53	55
4	9	5	62	62	5	1	11	56	61	5	5	5	175	172
4	9	7	48	44	5	1	12	38	35	5	5	6	133	129
4	9	8	41	36	5	1	13	59	59	5	5	7	80	75
4	9	9	29	31	5	1	14	36	38	5	5	8	61	62
4	9	10	19	17	5	2	1	122	129	5	5	9	102	108
4	10	0	27	24	5	2	2	77	77	5	5	10	25	27
4	10	1	65	68	5	2	3	104	95	5	5	11	33	33
4	10	2	33	37	5	2	4	67	78	5	5	12	41	36
4	10	3	107	107	5	2	5	24	22	5	6	0	33	24
4	10	4	24	28	5	2	6	76	82	5	6	1	63	64
4	10	5	40	35	5	2	7	66	67	5	6	2	119	117
4	10	6	18	22	5	2	8	28	32	5	6	3	120	114
4	10	7	18	17	5	2	9	77	75	5	6	4	106	104
4	11	0	24	28	5	2	10	69	71	5	6	5	120	116
4	11	1	27	32	5	2	11	59	64	5	6	6	42	41
4	11	2	70	70	5	2	12	52	54	5	6	7	60	65
4	11	4	57	56	5	2	13	38	39	5	6	8	48	51
4	11	5	23	23	5	3	1	23	29	5	6	9	20	21
4	11	6	22	23	5	3	2	101	104	5	6	12	28	20
4	11	8	26	25	5	3	3	50	55	5	6	13	18	20
4	12	0	44	44	5	3	4	64	65	5	7	0	49	52
4	12	1	48	48	5	3	5	44	41	5	7	1	24	23
4	12	2	58	55	5	3	6	68	75	5	7	2	111	107
4	12	3	45	49	5	3	7	159	163	5	7	3	62	52
4	12	4	25	20	5	3	8	83	81	5	7	4	112	109
4	12	5	22	28	5	3	9	156	158	5	7	5	42	38
5	0	1	174	170	5	3	10	26	24	5	7	6	88	87
5	0	2	86	90	5	3	11	55	56	5	7	7	28	23
5	0	3	103	105	5	3	12	102	98	5	7	8	30	33
5	0	4	163	165	5	3	13	34	30	5	7	9	25	26
5	0	5	102	106	5	4	0	113	117	5	7	10	18	14
5	0	6	39	29	5	4	1	63	61	5	7	11	34	32
5	0	7	30	29	5	4	2	89	90	5	8	1	80	79
5	0	8	46	49	5	4	3	68	71	5	8	2	89	88
5	0	9	53	55	5	4	4	50	45	5	8	3	60	63
5	0	10	16	10	5	4	5	74	71	5	8	4	54	56
5	0	11	17	17	5	4	6	144	139	5	8	5	30	34
5	0	12	45	57	5	4	7	81	83	5	8	6	26	26
5	0	15	39	43	5	4	8	33	32	5	8	7	56	52
5	1	0	150	139	5	4	9	71	63	5	8	8	33	34
5	1	1	83	88	5	4	10	111	114	5	8	9	20	16
5	1	2	46	54	5	4	11	34	30	5	8	10	19	22
5	1	3	70	62	5	4	12	23	22	5	8	11	23	16
5	1	4	170	178	5	4	13	26	29	5	9	1	59	56
5	1	5	70	70	5	4	14	36	33	5	9	3	36	26
5	1	6	140	148	5	5	0	22	19	5	9	4	40	42
5	1	7	66	64	5	5	1	112	111	5	9	5	21	18
5	9	7	29	25	6	2	8	81	77	6	7	2	20	28
5	9	8	29	30	6	2	9	34	36	6	7	3	42	41

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
5	9	9	18	18	6	2	10	31	27	6	7	4	40	49
5	9	10	25	22	6	2	11	32	26	6	7	5	52	58
5	10	0	50	49	6	2	12	48	48	6	7	6	24	29
5	10	2	33	34	6	2	13	18	21	6	7	7	51	53
5	10	3	18	17	6	3	0	30	30	6	7	8	29	25
5	10	4	42	40	6	3	1	58	58	6	7	9	17	15
5	10	5	35	36	6	3	2	135	123	6	7	10	27	28
5	10	6	23	19	6	3	3	160	160	6	8	0	17	21
5	10	7	33	30	6	3	4	84	85	6	8	1	25	22
5	10	8	44	38	6	3	5	29	33	6	8	2	25	23
5	11	1	30	31	6	3	6	37	32	6	8	3	29	32
5	11	3	16	14	6	3	7	61	66	6	8	4	30	31
5	11	4	19	17	6	3	8	64	69	6	8	5	18	22
5	12	0	28	26	6	3	9	43	39	6	8	8	35	35
5	12	1	16	14	6	3	10	100	98	6	9	1	30	36
6	0	0	368	361	6	3	11	25	22	6	9	2	18	16
6	0	2	156	156	6	3	12	42	44	6	9	3	46	52
6	0	3	34	34	6	3	13	28	26	6	9	6	17	18
6	0	4	227	229	6	4	0	67	62	6	10	0	39	48
6	0	6	125	128	6	4	1	20	22	6	10	1	35	38
6	0	7	70	64	6	4	2	99	93	6	10	2	28	32
6	0	8	22	16	6	4	3	43	38	6	10	3	18	17
6	0	9	45	49	6	4	4	91	87	7	0	1	18	13
6	0	10	30	28	6	4	5	36	35	7	0	2	126	133
6	0	11	38	32	6	4	6	54	55	7	0	3	36	32
6	0	13	26	30	6	4	7	19	24	7	0	4	42	43
6	1	0	41	43	6	4	8	76	73	7	0	5	21	23
6	1	1	169	163	6	4	9	41	38	7	0	6	89	95
6	1	2	52	51	6	4	10	56	53	7	0	7	47	47
6	1	3	74	75	6	4	12	50	53	7	0	9	37	35
6	1	4	157	153	6	5	0	62	62	7	0	12	21	26
6	1	5	122	116	6	5	2	21	22	7	1	0	17	15
6	1	6	148	150	6	5	5	62	63	7	1	1	133	132
6	1	7	151	155	6	5	6	66	72	7	1	2	60	59
6	1	8	34	33	6	5	7	79	83	7	1	3	96	94
6	1	9	27	24	6	5	8	17	16	7	1	4	140	141
6	1	10	89	87	6	5	9	44	45	7	1	5	80	86
6	1	11	29	26	6	5	10	51	52	7	1	6	22	21
6	1	12	22	25	6	6	0	51	51	7	1	7	63	61
6	1	13	41	40	6	6	1	47	41	7	1	8	65	63
6	2	0	119	119	6	6	3	37	31	7	1	9	19	19
6	2	1	96	101	6	6	5	32	31	7	1	10	24	21
6	2	2	58	59	6	6	6	46	41	7	1	11	30	27
6	2	3	185	184	6	6	8	35	35	7	1	12	50	48
6	2	4	84	84	6	6	9	27	30	7	2	1	123	120
6	2	5	73	72	6	6	10	30	31	7	2	2	151	159
6	2	6	41	43	6	7	0	21	25	7	2	3	61	61
6	2	7	141	135	6	7	1	41	40	7	2	4	62	56
7	2	5	62	60	7	7	7	28	31	8	4	8	15	15
7	2	6	54	56	7	7	8	42	43	8	5	1	48	52

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
7	2	7	32	29	7	8	1	48	48	8	5	2	37	38
7	2	9	41	44	7	8	2	19	18	8	5	3	35	35
7	2	10	25	22	7	8	3	40	41	8	5	4	70	63
7	2	11	27	26	7	8	4	22	17	8	5	5	34	33
7	3	0	33	33	7	8	5	35	35	8	5	6	43	43
7	3	1	206	217	7	8	6	26	26	8	6	0	32	36
7	3	2	25	28	7	8	7	36	39	8	6	1	22	21
7	3	3	48	45	7	9	1	22	30	8	6	3	16	16
7	3	4	58	57	7	9	2	42	41	8	6	4	27	31
7	3	5	42	41	7	9	3	27	27	8	6	5	17	16
7	3	6	60	57	8	0	0	31	36	8	6	6	52	54
7	3	7	24	22	8	0	2	16	13	8	7	0	37	34
7	3	8	19	23	8	0	4	22	27	8	7	1	27	34
7	3	9	33	28	8	0	5	50	54	8	7	2	22	19
7	3	10	34	34	8	0	7	24	29	8	7	4	37	34
7	4	0	105	109	8	1	0	69	62	8	8	0	26	29
7	4	1	133	128	8	1	1	39	41	8	8	0	26	29
7	4	2	70	69	8	1	2	15	15	8	8	1	30	31
7	4	3	56	65	8	1	4	30	35	9	0	1	56	56
7	4	4	97	90	8	1	5	32	29	9	0	2	33	34
7	4	5	40	36	8	1	6	22	19	9	0	3	63	61
7	4	6	21	19	8	1	7	47	44	9	0	4	40	38
7	4	7	18	16	8	1	8	45	40	9	0	6	41	35
7	4	8	17	15	8	1	9	32	30	9	1	0	68	64
7	4	9	28	33	8	2	0	31	32	9	1	1	34	29
7	4	10	20	21	8	2	1	63	62	9	1	2	59	53
7	4	11	18	20	8	2	2	29	27	9	1	3	23	18
7	5	1	64	67	8	2	3	21	18	9	1	4	61	58
7	5	2	99	100	8	2	4	39	40	9	1	6	17	16
7	5	3	50	56	8	2	5	44	44	9	2	0	29	28
7	5	4	90	93	8	2	8	38	36	9	2	2	23	23
7	5	5	56	53	8	2	9	16	9	9	2	3	32	29
7	5	8	38	35	8	3	1	45	44	9	2	4	35	32
7	5	9	18	19	8	3	2	71	73	9	2	5	48	40
7	6	1	41	41	8	3	3	76	74	9	2	6	32	29
7	6	2	54	56	8	3	4	57	57	9	3	0	24	25
7	6	3	62	64	8	3	6	28	28	9	3	1	40	36
7	6	4	42	39	8	3	7	24	16	9	3	2	17	19
7	6	5	47	41	8	3	8	19	16	9	3	5	32	31
7	6	6	69	70	8	3	9	29	26	9	4	0	30	31
7	6	7	39	34	8	4	0	41	38	9	4	1	21	21
7	6	8	32	31	8	4	1	24	28	9	4	2	22	16
7	6	9	15	15	8	4	2	21	21	9	4	3	27	25
7	7	0	17	14	8	4	3	38	37	9	4	4	31	28
7	7	2	26	24	8	4	4	57	53	9	5	1	19	19
7	7	4	77	79	8	4	5	22	22	9	5	2	17	13
7	7	5	16	17	8	4	6	45	46					
7	7	6	18	17	8	4	7	45	37					

APPENDIX 3 X-ray Crystal Data for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Table A3.1. Positional Parameters and their Estimated Standard Deviations for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom	x	y	z	B(A2)
O1	0.5692(5)	0.0114(1)	0.7776(1)	6.03(5)
O2	0.2943(5)	0.1361(1)	0.8192(1)	4.67(4)
N1	0.4724(6)	0.0208(1)	0.6733(2)	4.58(5)
N7	-0.2307(5)	0.2769(1)	0.5347(1)	3.44(4)
C1	0.3001(6)	0.0832(1)	0.6480(2)	3.38(4)
C2	0.1987(6)	0.1432(1)	0.7217(2)	3.45(5)
C3	0.0101(6)	0.2049(1)	0.6809(2)	3.36(4)
C4	-0.0662(5)	0.2142(1)	0.5732(2)	2.98(4)
C5	0.0339(6)	0.1551(1)	0.4993(2)	3.10(4)
C6	0.2051(6)	0.0933(1)	0.5374(2)	3.36(4)
C8	-0.3453(6)	0.3392(1)	0.6017(2)	3.79(5)
C9	-0.5188(7)	0.4024(2)	0.5378(2)	4.99(6)
C10	-0.0624(7)	0.1640(4)	0.3838(2)	4.14(5)

Table A3.2. Table of Bond Distances in Angstroms for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N1	1.367(3)	C5	C6	1.335(3)
O1	HO1	0.990(3)	C5	C10	1.503(3)
O2	C2	1.281(3)	C6	HC6	0.970(2)
N1	C1	1.304(3)	C8	C9	1.496(3)
N7	C4	1.337(3)	C8	HC8A	1.050(2)
N7	C8	1.469(3)	C8	HC8B	1.010(3)
N7	HN7	1.040(3)	C9	HC9A	0.990(3)
C1	C2	1.476(3)	C9	HC9B	0.970(3)
C1	C6	1.444(3)	C9	HC9C	1.050(3)
C2	C3	1.381(3)	C10	HC10A	0.950(3)
C3	C4	1.394(3)	C10	HC10B	1.020(2)
C3	HC3	0.910(2)	C10	HC10C	1.000(3)
C4	C5	1.467(3)			

Table A3.3. Table of Bond Angles in Degrees for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	O1	HO1	105.0(2)	C1	C6	HC6	122.0(1)
O1	N1	C1	116.3(2)	C5	C6	HC6	116.0(1)
C4	N7	C8	122.8(1)	N7	C8	C9	111.4(2)
C4	N7	HN7	122.0(2)	N7	C8	HC8A	108.0(1)
C8	N7	HN7	115.0(2)	N7	C8	HC8B	109.0(1)
N1	C1	C2	125.9(2)	C9	C8	HC8A	109.0(1)
N1	C1	C6	115.7(2)	C9	C8	HC8B	107.0(1)
C2	C1	C6	118.4(2)	HC8A	C8	HC8B	112.0(2)
O2	C2	C1	118.5(2)	C8	C9	HC9A	109.0(2)
O2	C2	C3	123.6(2)	C8	C9	HC9B	112.1(2)
C1	C2	C3	117.9(1)	C8	C9	HC9C	106.0(2)
C2	C3	C4	122.0(2)	HC9A	C9	HC9B	111.0(2)
C2	C3	HC3	118.0(1)	HC9A	C9	HC9C	109.0(2)
C4	C3	HC3	120.0(1)	HC9B	C9	HC9C	109.0(2)
N7	C4	C3	121.2(1)	C5	C10	HC10A	109.0(2)
N7	C4	C5	118.3(2)	C5	C10	HC10B	111.0(1)
C3	C4	C5	120.4(2)	C5	C10	HC10C	106.0(2)
C4	C5	C6	118.5(2)	HC10A	C10	HC10B	106.0(2)
C4	C5	C10	120.0(2)	HC10A	C10	HC10C	117.0(2)
C6	C5	C10	121.6(2)	HC10B	C10	HC10C	109.0(2)
C1	C6	C5	122.7(2)				

Table A3.4. Table of General Displacement Parameters Expressions - B's for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beq
O1	8.40(1)	5.02(8)	4.46(8)	1.64(9)	-0.72(8)	1.22(7)	6.0
O2	6.55(9)	4.60(8)	2.77(6)	0.20(8)	-0.12(6)	0.38(6)	4.6
N1	5.80(1)	3.62(8)	4.22(9)	0.71(8)	-0.06(1)	0.60(1)	4.5
N7	4.66(9)	2.67(7)	3.00(7)	0.28(7)	0.42(7)	-0.19(6)	3.4
C1	4.00(1)	2.85(8)	3.30(8)	-0.19(8)	0.24(8)	0.20(8)	3.3
C2	4.20(1)	3.42(9)	2.74(8)	-0.51(9)	0.42(8)	0.14(8)	3.4
C3	4.40(1)	3.06(8)	2.66(8)	-0.12(8)	0.55(7)	-0.30(7)	3.3
C4	3.51(9)	2.61(8)	2.82(8)	-0.31(7)	0.36(7)	-0.11(7)	2.9
C5	3.81(9)	2.90(8)	2.63(7)	-0.31(8)	0.51(7)	-0.20(1)	3.1
C6	4.10(1)	2.97(8)	3.07(8)	-0.10(8)	0.56(8)	-0.29(7)	3.3
C8	4.90(1)	2.90(9)	3.59(9)	0.20(9)	0.77(8)	-0.44(8)	3.7
C9	6.40(1)	3.60(1)	5.10(1)	1.20(1)	1.20(1)	0.30(1)	4.9
C10	5.80(1)	4.00(1)	2.62(8)	0.40(1)	0.26(9)	-0.19(8)	4.1

Table A3.5. Table of Refined Displacement Parameter Expressions - Beta's for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
O1	0.1270(2)	0.00430(7)	0.0069(1)	0.0118(6)	-0.0069(8)	0.0028(2)
O2	0.0090(1)	0.00393(6)	0.00426(9)	0.0015(6)	-0.0012(6)	0.0009(1)
N1	0.0880(2)	0.00310(7)	0.0065(1)	0.0051(6)	-0.0006(8)	0.0014(2)
N7	0.0700(1)	0.00228(6)	0.0046(1)	0.0020(5)	0.0040(6)	-0.0004(1)
C1	0.0600(1)	0.00244(7)	0.0051(1)	-0.0014(6)	0.0023(8)	0.0005(2)
C2	0.0640(2)	0.00293(8)	0.0042(1)	-0.0036(6)	0.0041(7)	0.0003(3)
C3	0.0660(2)	0.00262(7)	0.0041(1)	-0.0008(6)	0.0053(7)	-0.0007(2)
C4	0.0530(1)	0.00223(7)	0.0043(1)	-0.0022(5)	0.0034(7)	-0.0003(2)
C5	0.0580(1)	0.00248(7)	0.0041(1)	-0.0022(6)	0.0049(7)	-0.0005(2)
C6	0.0620(1)	0.00254(7)	0.0047(1)	-0.0007(6)	0.0054(7)	-0.0007(2)
C8	0.0750(2)	0.00248(7)	0.0055(1)	0.0014(6)	0.0074(8)	-0.0010(4)
C9	0.0960(2)	0.00311(9)	0.0078(2)	0.0088(7)	0.0110(1)	0.0007(2)
C10	0.0880(2)	0.00340(9)	0.0040(1)	0.0027(7)	0.0025(8)	-0.0004(26)

Table A3.6. Table of General Displacement Parameters Expressions - U's for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.106(1)	0.064(1)	0.056(1)	0.021(1)	-0.009(1)	0.0154(9)
O2	0.083(1)	0.058(1)	0.0351(8)	0.003(1)	-0.0016(8)	0.0048(8)
N1	0.073(1)	0.046(1)	0.053(1)	0.009(1)	-0.001(1)	0.008(1)
N7	0.059(1)	0.0338(9)	0.0380(9)	0.0035(9)	0.0053(8)	-0.0025(8)
C1	0.050(1)	0.036(1)	0.042(1)	-0.002(1)	0.003(1)	0.003(1)
C2	0.053(1)	0.043(1)	0.035(1)	-0.006(1)	0.005(1)	0.002(1)
C3	0.056(1)	0.039(1)	0.034(1)	-0.001(1)	0.0069(9)	-0.0038(9)
C4	0.045(1)	0.033(1)	0.036(1)	-0.0039(9)	0.0045(9)	-0.0015(9)
C5	0.048(1)	0.037(2)	0.0333(9)	-0.004(1)	0.0064(9)	-0.0026(9)
C6	0.052(1)	0.038(2)	0.039(1)	-0.001(1)	0.007(1)	-0.004(1)
C8	0.063(1)	0.037(2)	0.045(1)	0.003(1)	0.010(1)	-0.006(1)
C9	0.081(2)	0.046(3)	0.064(1)	0.016(1)	0.015(1)	0.004(1)
C10	0.074(2)	0.050(3)	0.033(1)	0.005(1)	0.003(1)	-0.002(1)

Table A3.7. Table of Root-mean-square Amplitudes of Anisotropic Displacement in Angstroms for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom	Min	Int'med	Max
O1	0.191	0.274	0.343
O2	0.183	0.243	0.291
N1	0.196	0.241	0.278
N7	0.179	0.198	0.244
C1	0.187	0.206	0.226
C2	0.183	0.203	0.238
C3	0.177	0.201	0.237
C4	0.178	0.189	0.214
C5	0.178	0.190	0.224
C6	0.185	0.202	0.229
C8	0.182	0.217	0.252
C9	0.200	0.245	0.299
C10	0.181	0.223	0.273

Table A3.8. Table of Positional Parameters and their Estimated Standard Deviations for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom	x	y	z	B(A2)
HO1	0.481(7)	0.057(2)	0.813(2)	5.4(8)
HN7	-0.270(7)	0.287(2)	0.455(2)	3.8(7)
HC3	-0.049(6)	0.242(1)	0.727(2)	2.1(5)
HC6	0.255(6)	0.054(1)	0.486(2)	2.5(6)
HC8A	-0.139(6)	0.363(1)	0.645(2)	2.9(5)
HC8B	-0.508(8)	0.317(1)	0.648(2)	2.8(6)
HC9A	-0.360(7)	0.430(2)	0.497(2)	4.6(7)
HC9B	-0.700(7)	0.382(2)	0.492(2)	3.8(7)
HC9C	-0.610(7)	0.442(2)	0.592(2)	4.9(8)
HC10A	0.009(6)	0.214(2)	0.362(2)	3.4(6)
HC10B	-0.311(6)	0.164(2)	0.369(2)	3.2(6)
HC10C	0.026(7)	0.117(2)	0.349(2)	4.9(8)

Table A3.9. Table of Torsion Angles in Degrees for

5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
HO1	O1	N1	C1	-0.05 (1.87)
O1	N1	C1	C2	-0.78 (0.35)
O1	N1	C1	C6	178.77 (0.20)
C8	N7	C4	C3	-0.78 (0.33)
C8	N7	C4	C5	179.34 (0.20)
HN7	N7	C4	C3	174.25 (1.77)
HN7	N7	C4	C5	-5.62 (1.78)
C4	N7	C8	C9	179.42 (0.21)
HN7	N7	C8	C9	4.09 (1.68)
N1	C1	C2	O2	2.43 (0.36)
N1	C1	C2	C3	-178.69 (0.23)
C6	C1	C2	O2	-177.11 (0.21)
C6	C1	C2	C3	1.76 (0.32)
N1	C1	C6	C5	-178.66 (0.23)
N1	C1	C6	HC6	3.93 (1.69)
C2	C1	C6	C5	0.93 (0.34)
C2	C1	C6	HC6	-176.47 (1.67)
O2	C2	C3	C4	174.47 (0.22)
C1	C2	C3	C4	-4.34 (0.34)
C2	C3	C4	N7	-175.57 (0.21)
C2	C3	C4	C5	4.30 (0.34)
N7	C4	C5	C6	178.42 (0.21)
N7	C4	C5	C10	-2.78 (0.31)
C3	C4	C5	C6	-1.46 (0.32)

Table A3.9 cont'd...

C3	C4	C5	C10	177.34 (0.21)
C4	C5	C6	C1	-1.08 (0.34)
C4	C5	C6	HC6	176.47 (1.58)
C10	C5	C6	C1	-179.86 (0.20)
C10	C5	C6	HC6	-2.31 (1.60)
C4	C5	C10	HC10A	54.46 (1.68)
C4	C5	C10	HC10C	-178.67 (1.76)
C6	C5	C10	HC10A	-126.78 (1.67)
C6	C5	C10	HC10C	0.09 (1.79)

Table A3.10. Values of 10*Fobs and 10*F calc For 5-Ethylamino-4-methyl-benzoquinone-2-oxime.

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	0	2	48	73	0	4	1	199	212	0	7	12	37	41
0	0	4	133	149	0	4	2	244	240	0	7	13	15	12
0	0	6	334	333	0	4	3	268	252	0	8	0	208	215
0	0	8	115	110	0	4	4	114	103	0	8	1	31	38
0	0	10	35	35	0	4	5	154	143	0	8	2	221	230
0	0	14	74	70	0	4	6	159	148	0	8	3	337	347
0	1	1	195	211	0	4	7	74	71	0	8	4	208	211
0	1	3	111	114	0	4	8	112	107	0	8	5	119	117
0	1	4	332	335	0	4	9	167	166	0	8	6	21	25
0	1	5	28	27	0	4	10	79	70	0	8	7	183	186
0	1	6	336	326	0	4	11	83	87	0	8	8	53	51
0	1	7	248	228	0	4	14	18	14	0	8	9	30	26
0	1	8	62	61	0	5	1	90	92	0	8	11	27	27
0	1	9	64	60	0	5	2	357	368	0	9	1	111	110
0	1	10	40	38	0	5	3	199	199	0	9	2	221	223
0	1	11	15	2	0	5	4	45	43	0	9	3	182	176
0	1	12	34	35	0	5	5	13	5	0	9	4	23	23
0	1	13	40	34	0	5	6	27	25	0	9	5	184	180
0	1	14	49	50	0	5	7	14	11	0	9	6	93	97
0	1	15	16	18	0	5	8	248	241	0	9	7	59	56
0	2	0	200	221	0	5	9	131	130	0	9	8	119	116
0	2	1	469	489	0	5	10	101	100	0	9	9	122	122
0	2	2	470	467	0	5	11	191	199	0	9	10	34	35
0	2	3	527	515	0	5	12	66	68	0	9	11	84	86
0	2	4	134	130	0	5	13	19	16	0	9	12	28	27
0	2	5	72	72	0	5	14	40	38	0	9	13	23	22
0	2	6	69	76	0	5	15	44	44	0	9	14	24	24
0	2	7	335	317	0	6	0	344	347	0	9	14	24	24
0	2	8	25	24	0	6	1	112	122	0	10	0	91	87
0	2	9	111	105	0	6	3	80	85	0	10	1	305	296
0	2	10	57	61	0	6	4	89	83	0	10	2	38	36
0	2	11	93	96	0	6	5	77	70	0	10	3	64	61
0	2	14	28	29	0	6	6	45	44	0	10	4	42	52
0	2	15	20	20	0	6	7	52	51	0	10	5	54	63
0	3	1	75	86	0	6	8	107	106	0	10	7	42	42
0	3	2	24	28	0	6	9	105	107	0	10	8	121	121
0	3	3	82	77	0	6	10	216	216	0	10	9	160	164
0	3	4	115	104	0	6	11	67	70	0	10	10	128	137
0	3	5	96	90	0	6	12	67	67	0	10	12	32	28
0	3	6	112	104	0	7	1	25	27	0	10	13	27	27
0	3	7	131	128	0	7	2	38	41	0	11	1	113	107
0	3	8	103	95	0	7	3	397	410	0	11	2	105	102
0	3	9	283	271	0	7	4	229	232	0	11	3	51	55
0	3	10	120	112	0	7	5	61	50	0	11	4	22	17
0	3	11	101	93	0	7	6	113	111	0	11	5	24	24
0	3	12	61	62	0	7	7	122	122	0	11	6	45	41
0	3	13	90	91	0	7	8	66	70	0	11	7	121	122
0	3	14	22	15	0	7	9	120	122	0	11	8	110	111

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	3	15	61	58	0	7	10	167	171	0	11	9	112	121
0	4	0	337	343	0	7	11	67	66	0	11	10	73	78
0	11	12	60	56	0	17	3	31	31	1	1	3	77	84
0	11	13	82	79	0	17	4	86	89	1	1	4	32	30
0	12	0	103	102	0	17	5	66	68	1	1	5	201	204
0	12	1	44	43	0	17	6	94	95	1	1	6	83	84
0	12	2	68	63	0	17	7	14	7	1	1	7	103	106
0	12	3	53	51	0	18	2	104	109	1	1	8	80	87
0	12	4	26	28	0	18	3	14	11	1	1	10	95	93
0	12	6	44	36	0	18	5	19	21	1	1	11	123	137
0	12	7	46	42	0	18	6	68	71	1	1	12	31	32
0	12	8	175	176	0	18	7	23	26	1	1	13	63	63
0	12	9	27	32	0	19	1	19	22	1	1	14	32	32
0	12	10	13	13	0	19	2	16	19	1	2	-14	46	46
0	12	11	38	36	0	19	3	24	24	1	2	-13	21	24
0	12	12	41	39	0	19	4	24	28	1	2	-12	26	27
0	13	1	30	26	0	19	5	22	26	1	2	-11	99	97
0	13	2	38	36	0	19	6	24	27	1	2	-10	28	27
0	13	3	16	14	0	20	0	19	21	1	2	-9	204	204
0	13	4	30	25	0	20	1	25	29	1	2	-8	64	59
0	13	7	73	76	0	20	3	25	24	1	2	-7	40	41
0	13	8	137	130	0	20	4	45	45	1	2	-6	69	79
0	13	9	40	40	1	0	-15	37	31	1	2	-5	36	35
0	13	10	32	33	1	0	-13	24	19	1	2	-3	444	443
0	13	11	16	16	1	0	-11	16	8	1	2	-2	227	226
0	13	12	41	41	1	0	-9	142	151	1	2	-1	379	378
0	14	0	236	222	1	0	-7	41	41	1	2	0	758	752
0	14	2	55	54	1	0	-5	53	59	1	2	1	421	427
0	14	3	99	96	1	0	-3	272	274	1	2	2	33	42
0	14	4	42	39	1	0	-1	649	633	1	2	3	177	190
0	14	5	20	19	1	0	1	98	108	1	2	4	104	108
0	14	6	12	10	1	0	3	50	55	1	2	5	102	97
0	14	7	24	26	1	0	5	418	419	1	2	6	371	376
0	14	8	37	37	1	0	7	265	270	1	2	7	188	191
0	14	9	31	35	1	0	9	138	142	1	2	8	82	75
0	14	11	59	59	1	0	11	30	40	1	2	9	72	68
0	15	2	153	149	1	0	13	31	39	1	2	10	41	46
0	15	3	26	30	1	1	-14	16	16	1	2	11	86	97
0	15	4	49	46	1	1	-13	76	78	1	2	14	17	18
0	15	5	31	27	1	1	-12	75	75	1	3	-15	42	42
0	15	6	51	53	1	1	-10	166	172	1	3	-14	14	15
0	15	7	39	44	1	1	-9	140	144	1	3	-13	21	24
0	15	8	63	63	1	1	-8	75	80	1	3	-12	34	39
0	15	10	15	17	1	1	-7	68	74	1	3	-13	167	162
0	16	0	254	252	1	1	-6	28	29	1	3	-10	231	235
0	16	1	221	218	1	1	-5	41	33	1	3	-9	83	76
0	16	2	161	161	1	1	-4	64	64	1	3	-8	21	17
0	16	4	16	14	1	1	-3	183	177	1	3	-7	153	154
0	16	5	25	25	1	1	-2	814	803	1	3	-5	102	101
0	16	7	59	60	1	1	-1	281	273	1	3	-4	254	255

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	17	1	94	96	1	1	0	42	44	1	3	-3	325	328
0	17	2	42	42	1	1	1	275	296	1	3	-2	22	16
1	3	-1	777	787	1	5	-2	36	42	1	7	-5	64	55
1	3	0	942	941	1	5	-1	94	102	1	7	-4	26	18
1	3	1	97	91	1	5	0	60	61	1	2	-2	130	132
1	3	2	163	174	1	5	1	90	84	1	7	-1	63	61
1	3	3	96	92	1	5	2	32	35	1	7	0	252	252
1	3	4	177	183	1	5	3	105	111	1	7	1	258	256
1	3	5	49	42	1	5	4	168	166	1	7	2	246	251
1	3	6	103	102	1	5	5	75	72	1	7	3	17	17
1	3	7	112	116	1	5	6	56	59	1	7	4	38	41
1	3	8	82	82	1	5	7	27	14	1	7	5	152	165
1	3	9	23	27	1	5	8	19	19	1	7	6	68	67
1	3	10	37	40	1	5	9	53	53	1	7	8	398	406
1	3	11	93	95	1	5	10	46	45	1	7	12	28	25
1	3	12	26	29	1	5	11	100	102	1	7	13	13	7
1	4	-14	51	52	1	5	13	17	15	1	8	-13	56	53
1	4	-13	18	16	1	5	14	17	15	1	8	-12	113	118
1	4	-11	104	101	1	6	-13	13	15	1	8	-11	37	37
1	4	-10	231	225	1	6	-11	26	26	1	8	-10	48	49
1	4	-9	65	59	1	6	-9	86	80	1	8	-8	61	58
1	4	-8	21	10	1	6	-8	148	142	1	8	-7	14	7
1	4	-7	373	379	1	6	-7	68	66	1	8	-6	15	14
1	4	-6	59	60	1	6	-6	35	24	1	8	-4	17	16
1	4	-5	206	207	1	6	-5	155	144	1	8	-3	61	57
1	4	-4	289	293	1	6	-4	30	32	1	8	-1	41	39
1	4	-3	111	119	1	6	-3	38	35	1	8	0	73	73
1	4	-2	218	216	1	6	-2	203	210	1	8	1	98	93
1	4	-1	414	414	1	6	-1	154	151	1	8	2	325	321
1	4	0	51	49	1	6	0	198	199	1	8	3	54	55
1	4	1	437	447	1	6	1	208	193	1	8	4	115	115
1	4	2	96	97	1	6	2	319	317	1	8	5	54	54
1	4	4	40	41	1	6	3	179	177	1	8	6	106	109
1	4	5	81	78	1	6	4	47	44	1	8	7	86	89
1	4	6	30	31	1	6	5	117	116	1	8	8	106	103
1	4	8	21	20	1	6	6	26	19	1	8	9	126	134
1	4	9	52	55	1	6	7	16	20	1	8	10	159	162
1	4	10	75	73	1	6	8	16	11	1	8	11	55	59
1	4	11	45	40	1	6	9	166	173	1	8	12	40	40
1	5	-15	18	24	1	6	10	86	88	1	9	-13	94	89
1	5	-15	18	24	1	6	11	50	51	1	9	-11	30	31
1	5	-13	58	63	1	6	12	47	46	1	9	-10	29	27
1	5	-12	116	124	1	6	14	26	25	1	9	-8	22	23
1	5	-11	61	54	1	7	-14	47	48	1	9	-6	127	124
1	5	-10	62	60	1	7	-13	20	22	1	9	-5	30	45
1	5	-9	29	27	1	7	-12	70	72	1	9	-4	14	19
1	5	-8	66	64	1	7	-11	52	55	1	9	-3	81	55
1	5	-7	150	148	1	7	-10	90	90	1	9	-1	45	45
1	5	-6	44	42	1	7	-9	31	31	1	9	0	118	118
1	5	-5	104	101	1	7	-8	45	46	1	9	1	304	300

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
1	5	-4	330	337	1	7	-7	123	120	1	9	2	115	120
1	5	-3	524	541	1	7	-6	58	66	1	9	3	117	117
1	9	4	55	46	1	12	-11	48	48	1	14	1	37	37
1	9	5	63	65	1	12	-10	81	83	1	14	2	48	48
1	9	6	116	123	1	12	-9	179	181	1	14	3	66	67
1	9	7	161	158	1	12	-8	21	15	1	14	4	72	73
1	9	8	238	238	1	12	-7	81	88	1	14	5	135	131
1	9	11	20	17	1	12	-4	117	117	1	14	8	21	22
1	10	-11	22	19	1	12	-3	159	150	1	14	9	16	13
1	10	-7	84	92	1	12	-2	74	74	1	15	-9	34	31
1	10	-6	53	45	1	12	-1	59	58	1	15	-8	104	102
1	10	-5	48	51	1	12	0	174	166	1	15	-4	54	53
1	10	-4	47	51	1	12	1	50	48	1	15	-3	92	92
1	10	-3	31	33	1	12	2	16	12	1	15	-2	149	142
1	10	-2	45	46	1	12	3	28	23	1	15	-1	17	16
1	10	-1	126	130	1	12	4	25	20	1	15	0	68	69
1	10	0	38	38	1	12	6	19	20	1	15	1	54	60
1	10	2	27	23	1	12	9	22	22	1	15	2	19	18
1	10	3	226	219	1	12	10	41	42	1	15	3	23	27
1	10	4	79	67	1	12	11	16	19	1	15	5	79	86
1	10	5	37	36	1	13	-10	120	112	1	15	6	43	44
1	10	6	69	67	1	13	-9	113	116	1	15	8	33	30
1	10	7	129	133	1	13	-8	62	64	1	16	-9	59	54
1	10	8	115	109	1	13	-7	45	47	1	16	-8	38	33
1	10	9	81	78	1	13	-5	85	85	1	16	-9	20	20
1	10	10	28	31	1	13	-4	29	32	1	16	-5	17	18
1	10	12	45	41	1	13	-3	65	66	1	16	-3	21	17
1	11	-13	52	53	1	13	-2	201	202	1	16	-2	79	83
1	11	-12	35	34	1	13	-1	291	281	1	16	-1	35	35
1	11	-11	19	16	1	13	0	44	41	1	16	0	62	64
1	11	-10	70	68	1	13	1	61	57	1	16	1	44	47
1	11	-9	67	68	1	13	2	18	19	1	16	2	30	32
1	11	-8	29	32	1	13	3	51	47	1	16	3	72	71
1	11	-7	41	42	1	13	4	26	25	1	16	4	36	39
1	11	-5	18	24	1	13	5	70	65	1	16	6	77	75
1	11	-4	74	83	1	13	6	25	23	1	16	8	47	46
1	11	-3	182	178	1	13	7	26	30	1	17	-5	34	33
1	11	-2	203	197	1	13	8	26	26	1	17	-4	37	34
1	11	0	19	24	1	13	9	58	55	1	17	-3	42	41
1	11	1	15	20	1	14	-11	16	15	1	17	-2	58	60
1	11	2	39	32	1	14	-10	83	82	1	17	-1	77	80
1	11	3	109	100	1	14	-9	42	43	1	17	0	69	71
1	11	4	47	39	1	14	-8	49	47	1	17	1	23	26
1	11	5	57	57	1	14	-7	63	58	1	17	3	23	19
1	11	6	75	72	1	14	-6	22	27	1	17	4	59	62
1	11	7	61	58	1	14	-4	84	87	1	17	5	30	34
1	11	8	64	63	1	14	-3	91	90	1	17	6	23	25
1	11	10	57	53	1	14	-2	158	153	1	17	7	54	46
1	11	11	26	25	1	14	-1	167	163	1	17	8	17	17

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
1	11	12	47	46	1	14	0	99	98	1	18	-7	20	27
1	18	-6	33	37	2	1	-1	26	30	2	3	-2	162	157
1	18	-5	27	28	2	1	0	60	60	2	3	-1	175	173
1	18	-4	16	10	2	1	1	15	5	2	3	0	53	53
1	18	-3	33	31	2	1	2	18	8	2	3	1	290	293
1	18	-2	47	50	2	1	3	22	24	2	3	2	12	24
1	18	-1	44	46	2	1	4	50	46	2	3	3	23	15
1	18	0	37	36	2	1	5	125	131	2	3	4	132	138
1	18	1	102	108	2	1	6	13	18	2	3	5	86	87
1	18	2	60	67	2	1	7	92	94	2	3	6	42	37
1	18	3	24	24	2	1	8	45	43	2	3	7	15	13
1	18	4	46	43	2	1	9	73	74	2	3	8	37	34
1	18	6	20	19	2	1	10	104	116	2	3	9	16	13
1	19	-5	33	36	2	1	11	82	89	2	3	11	38	42
1	19	-3	61	56	2	1	12	16	15	2	3	12	31	33
1	19	-2	33	34	2	2	-14	37	40	2	4	-13	24	21
1	19	-1	26	25	2	2	-13	23	24	2	4	-12	19	17
1	19	0	116	122	2	2	-12	53	56	2	4	-10	16	16
1	19	1	101	112	2	2	-11	25	19	2	4	-9	54	55
1	19	2	25	27	2	2	-10	62	62	2	4	-8	47	42
1	19	5	16	10	2	2	-9	58	52	2	4	-7	61	65
1	20	-3	20	18	2	2	-8	25	22	2	4	-6	86	81
1	20	-3	20	18	2	2	-7	60	59	2	4	-5	83	74
1	20	-3	20	18	2	2	-6	32	31	2	4	-4	56	48
1	20	-1	23	22	2	2	-5	237	229	2	4	-3	214	213
1	20	0	57	55	2	2	-4	277	265	2	4	-2	538	532
1	20	2	31	37	2	2	-3	101	97	2	4	-1	103	99
2	0	-12	167	168	2	2	-2	141	139	2	4	0	265	261
2	0	-10	129	118	2	2	-1	188	189	2	4	1	23	26
2	0	-8	62	52	2	2	0	68	72	2	4	2	162	160
2	0	-6	26	27	2	2	1	167	169	2	4	3	86	86
2	0	-4	39	39	2	2	2	24	28	2	4	4	92	91
2	0	-2	33	39	2	2	3	45	48	2	4	5	231	233
2	0	0	79	85	2	2	4	38	42	2	4	6	122	121
2	0	2	58	69	2	2	5	176	185	2	4	7	139	133
2	0	4	26	27	2	2	7	63	64	2	4	8	178	176
2	0	6	44	48	2	2	8	64	59	2	4	9	21	25
2	0	8	36	40	2	2	9	83	88	2	4	10	20	15
2	0	10	50	51	2	2	11	22	26	2	4	11	28	28
2	1	-13	38	39	2	2	12	30	29	2	4	12	39	37
2	1	-12	26	25	2	2	13	13	11	2	4	13	37	34
2	1	-11	201	197	2	3	-14	18	18	2	5	-14	37	42
2	1	-10	238	223	2	3	-13	40	41	5	5	-13	45	48
2	1	-9	20	17	2	3	-12	62	68	2	5	-12	15	14
2	1	-8	66	61	2	3	-11	111	105	2	5	-11	13	11
2	1	-7	37	38	2	3	-9	111	106	2	5	-10	33	35
2	1	-6	47	53	2	3	-8	69	69	2	5	-9	85	80
2	1	-5	170	161	2	3	-7	61	59	2	5	-8	93	87
2	1	-4	229	221	2	3	-6	154	147	2	5	-6	95	92
2	1	-3	197	192	2	3	-5	18	19	2	5	-4	18	16
2	1	-2	27	25	2	3	-4	48	44	2	5	-3	84	83

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
2	5	-2	83	79	2	7	8	83	78	2	10	0	112	106
2	5	-1	395	394	2	7	9	28	34	2	10	1	121	114
2	5	0	86	83	2	7	11	69	71	2	10	2	34	29
2	5	1	278	273	2	8	-13	68	85	2	10	3	56	54
2	5	2	34	36	2	8	-11	15	21	2	10	4	24	28
2	5	3	137	138	2	8	-10	52	54	2	10	6	31	28
2	5	5	97	92	2	8	-9	85	89	2	10	7	119	114
2	5	7	49	51	2	8	-8	68	67	2	10	8	130	131
2	5	8	113	113	2	8	-7	23	19	2	10	9	59	55
2	5	9	119	114	2	8	-6	20	16	2	11	-12	39	48
2	5	11	20	21	2	8	-5	75	75	2	11	-10	15	19
2	5	12	43	35	2	8	-3	31	33	2	11	-9	54	55
2	5	13	26	20	2	8	-2	20	17	2	11	-5	28	25
2	6	-13	61	65	2	8	-1	20	17	2	11	-4	28	35
2	6	-9	36	38	2	8	0	59	53	2	11	-3	30	27
2	6	-8	21	22	2	8	1	54	55	2	11	-2	209	206
2	6	-7	142	143	2	8	2	20	16	2	11	-1	168	165
2	6	-6	30	28	2	8	4	22	21	2	11	0	54	50
2	6	-5	136	133	2	8	6	23	22	2	11	1	188	183
2	6	-4	54	53	2	8	7	26	29	2	11	2	74	65
2	6	-3	26	27	2	8	8	33	33	2	11	3	55	52
2	6	-2	202	195	2	9	-13	16	19	2	11	4	50	52
2	6	-1	392	383	2	9	-11	34	36	2	11	5	110	101
2	6	0	230	223	2	9	-10	35	36	2	11	7	34	25
2	6	1	179	180	2	9	-9	59	65	2	11	8	19	20
2	6	2	65	66	2	9	-8	44	51	2	11	9	88	81
2	6	3	54	56	2	9	-7	19	27	2	11	10	63	59
2	6	5	32	32	2	9	-5	46	52	2	11	11	20	18
2	6	6	180	179	2	9	-4	69	75	2	11	11	20	18
2	6	7	228	222	2	9	-3	55	55	2	11	11	20	18
2	6	8	81	77	2	9	-2	64	63	2	12	-11	21	22
2	6	9	35	325	2	9	-1	13	12	2	12	-10	38	41
2	6	12	17	18	2	9	0	56	49	2	12	-9	46	47
2	7	-13	51	57	2	9	2	24	26	2	12	-7	32	30
2	7	-12	20	23	2	9	3	24	30	2	12	-6	16	9
2	7	-11	22	23	2	9	4	34	35	2	12	-4	184	187
2	7	-10	52	52	2	9	5	19	20	2	12	-3	167	167
2	7	-8	71	71	2	9	6	90	84	2	12	-2	59	58
2	7	-7	82	85	2	9	7	37	36	2	12	-1	67	65
2	7	-6	43	42	2	9	8	135	128	2	12	1	90	85
2	7	-5	32	33	2	9	9	112	115	2	12	2	30	29
2	7	-4	62	64	2	9	10	28	25	2	12	3	64	63
2	7	-3	73	72	2	10	-12	12	13	2	12	5	170	167
2	7	-2	75	70	2	10	-9	26	31	2	12	6	19	13
2	7	-1	114	115	2	10	-8	32	39	2	12	8	80	76
2	7	0	84	78	2	10	-6	19	31	2	12	9	78	79
2	7	2	14	12	2	10	-5	45	47	2	12	10	23	24
2	7	4	24	20	2	10	-3	135	140	2	13	-10	32	37
2	7	5	48	45	2	10	-2	242	241	2	13	-9	41	40
2	7	7	217	216	2	10	-1	48	52	2	13	-8	39	38
2	13	-7	29	31	2	17	-5	36	36	3	2	-10	64	65

Table A2.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
2	13	-6	49	50	2	17	-4	27	24	3	2	-9	46	46
2	13	-5	20	17	2	17	-3	46	48	3	2	-8	37	37
2	13	-3	58	59	2	17	-2	32	25	3	2	-7	16	19
2	13	-2	92	92	2	17	2	29	29	3	2	-6	40	32
2	13	-1	50	47	2	17	4	19	18	3	2	-5	36	35
2	13	0	62	59	2	18	-5	84	83	3	2	-3	49	48
2	13	1	61	63	2	18	-4	18	22	3	2	-2	55	53
2	13	2	39	31	2	18	0	34	32	3	2	-1	92	90
2	13	3	141	141	2	18	2	37	36	3	2	0	159	153
2	13	4	23	24	2	19	-1	38	44	3	2	1	46	45
2	13	5	44	45	2	19	-1	38	44	3	2	2	26	24
2	13	7	44	42	2	19	0	19	26	3	2	4	28	30
2	13	8	23	19	2	19	0	19	26	3	2	5	16	9
2	14	-10	24	25	3	0	-13	58	62	3	2	7	15	11
2	14	-8	15	15	3	0	-11	127	126	3	2	8	72	74
2	14	-7	18	15	3	0	-9	105	103	3	2	9	71	73
2	14	-5	38	35	3	0	-7	85	80	3	2	10	14	7
2	14	-4	49	50	3	0	-5	127	119	3	3	-13	38	37
2	14	-3	126	128	3	0	-1	76	71	3	3	-13	38	37
2	14	-1	37	32	3	0	1	128	122	3	3	-12	75	79
2	14	0	34	37	3	0	3	61	65	3	3	-11	69	70
2	14	1	26	27	3	0	5	36	40	3	3	-8	38	35
2	14	2	42	39	3	0	7	41	41	3	3	-6	38	39
2	14	3	50	54	3	1	-13	55	60	3	3	-5	45	43
2	14	4	40	45	3	1	-12	42	41	3	3	-3	27	27
2	14	5	26	26	3	1	-11	54	54	3	3	-1	15	15
2	14	6	42	37	3	1	-10	31	34	3	3	0	128	125
2	14	9	48	44	3	1	-9	57	56	3	3	1	60	59
2	15	-9	88	83	3	1	-8	27	26	3	3	3	43	36
2	15	-8	37	36	3	1	-7	60	56	3	3	4	16	18
2	15	-7	44	43	3	1	-6	45	41	3	3	5	82	82
2	15	-5	23	17	3	1	-5	206	195	3	3	6	198	191
2	15	-4	74	73	3	1	-4	100	97	3	3	7	75	73
2	15	-3	21	24	3	1	-3	47	47	3	3	8	47	43
2	15	2	17	19	3	1	-2	53	48	3	3	9	16	15
2	15	4	37	39	3	1	-1	52	45	3	3	10	26	24
2	15	5	19	18	3	1	0	16	10	3	3	11	33	31
2	15	6	27	28	3	1	1	42	41	3	4	-11	17	23
2	15	7	26	26	3	1	2	24	17	3	4	-10	41	45
2	15	8	18	17	3	1	3	51	50	3	4	-8	13	8
2	16	-8	26	24	3	1	4	48	40	3	4	-5	36	34
2	16	-7	18	15	3	1	5	23	19	3	4	-4	40	36
2	16	-3	15	16	3	1	6	55	53	3	4	-3	24	22
2	16	-2	15	17	3	1	7	48	45	3	4	-2	19	16
2	16	-1	15	11	3	1	8	49	48	3	4	-1	26	30
2	16	0	18	11	3	1	9	74	76	3	4	0	26	23
2	16	5	25	17	3	2	-13	15	17	3	4	1	43	42
2	16	6	43	37	3	2	-12	67	68	3	4	2	37	30
2	17	-6	35	33	3	2	-12	101	99	3	4	3	15	16
3	4	5	75	74	3	8	-10	46	48	3	10	6	25	23
3	4	6	101	97	3	8	-9	32	31	3	10	7	50	53
3	4	7	154	146	3	8	-8	28	29	3	11	-9	30	30

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
3	4	8	48	48	3	8	-7	17	14	3	11	-8	16	18
3	4	9	39	34	3	8	-6	43	41	3	11	-3	20	17
3	4	10	35	35	3	8	-5	29	30	3	11	-1	14	14
3	4	11	31	30	3	8	-4	15	12	3	11	2	29	32
3	5	-11	33	33	3	8	-3	125	125	3	11	3	88	89
3	5	-10	55	56	3	8	-2	265	267	3	11	4	38	41
3	5	-5	34	34	3	8	-1	95	95	3	11	5	20	26
3	5	-4	24	23	3	8	0	93	98	3	11	6	35	33
3	5	-3	19	20	3	8	1	16	11	3	11	8	51	50
3	5	-2	70	71	3	8	4	73	73	3	12	-6	19	18
3	5	3	61	60	3	8	5	21	22	3	12	-5	22	21
3	5	4	102	99	3	8	7	19	18	3	12	-2	23	24
3	5	7	66	61	3	8	8	25	18	3	12	-1	28	25
3	5	8	17	18	3	8	10	16	15	3	12	0	27	31
3	5	9	56	56	3	8	10	16	15	3	12	1	16	17
3	5	10	25	24	3	9	-11	15	14	3	12	3	36	39
3	6	-12	26	26	3	9	-10	19	19	3	12	4	30	31
3	6	-10	18	21	3	9	-9	50	49	3	12	7	48	45
3	6	-9	50	55	3	9	-8	58	59	3	13	-7	25	24
3	6	-5	73	72	3	9	-7	20	16	3	13	-6	19	21
3	6	-3	184	183	3	9	-6	53	54	3	13	-3	15	15
3	6	-2	154	154	3	9	-5	33	33	3	13	-2	20	25
3	6	-1	88	89	3	9	-4	134	130	3	13	-1	17	17
3	6	0	30	30	3	9	-3	49	50	3	13	1	45	44
3	6	1	80	78	3	9	-2	69	68	3	13	2	38	45
3	6	2	27	27	3	9	-1	125	123	3	13	3	20	25
3	6	3	56	53	3	9	0	29	30	3	13	6	67	64
3	6	4	51	44	3	9	2	53	48	3	14	-7	27	30
3	6	5	35	35	3	9	3	25	25	3	14	-2	19	20
3	6	6	87	85	3	9	4	66	66	3	14	0	41	38
3	6	9	29	29	3	9	5	81	78	3	14	1	63	65
3	7	-11	27	26	3	9	7	15	12	3	14	2	40	40
3	7	-10	13	8	3	9	8	14	12	3	14	5	15	12
3	7	-9	20	19	3	10	-10	21	22	3	15	-6	38	48
3	7	-8	64	66	3	10	-9	36	35	3	15	-5	73	79
3	7	-7	16	14	3	10	-8	51	53	3	15	-4	28	30
3	7	-6	59	59	3	10	-7	18	22	3	15	-2	17	13
3	7	-5	34	28	3	10	-6	21	29	3	15	0	21	22
3	7	-4	82	79	3	10	-4	134	131	3	15	3	25	29
3	7	-3	58	55	3	10	-3	155	153	3	15	4	35	35
3	7	-2	185	182	3	10	-2	21	14	3	16	-3	31	35
3	7	0	100	103	3	10	-1	57	58	3	16	0	15	10
3	7	2	53	56	3	10	0	64	58	3	16	2	45	48
3	7	3	35	30	3	10	1	44	47	4	0	-4	28	31
3	7	5	107	102	3	10	2	35	35	4	0	0	113	111
3	7	10	25	23	3	10	3	61	64	4	0	2	51	50
3	8	-11	27	28	3	10	5	45	48	4	0	4	45	46
4	0	6	131	133	4	5	-6	37	44	4	10	-3	41	49
4	0	8	52	51	4	5	-5	26	30	4	10	-1	35	41
4	1	-10	13	10	4	5	-4	29	29	4	10	0	26	31

Table A3.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
4	1	-8	32	29	4	5	-3	56	63	4	10	1	28	28
4	1	-6	32	33	4	5	-2	60	67	4	10	4	21	20
4	1	-5	26	31	4	5	0	17	15	4	11	-2	51	62
4	1	-4	26	26	4	5	1	15	15	4	11	-1	45	46
4	1	-3	16	14	4	5	2	12	5	4	11	0	12	12
4	1	-2	30	24	4	5	6	23	20	4	11	1	13	9
4	1	-1	44	46	4	6	-9	29	31	4	12	-3	17	22
4	1	0	31	33	4	6	-8	16	16	4	12	-2	34	46
4	1	3	27	22	4	6	-6	29	28	4	12	-1	10	6
4	1	5	49	49	4	6	-5	54	56					
4	1	6	106	103	4	6	-4	53	63					
4	1	7	28	26	4	6	-3	19	23					
4	1	8	34	32	4	6	-2	41	46					
4	2	-10	27	27	4	6	-1	28	36					
4	2	-9	25	25	4	6	1	23	26					
4	2	-8	22	21	4	6	3	39	42					
4	2	-7	54	57	4	6	4	40	40					
4	2	-6	34	38	4	6	6	21	17					
4	2	-4	17	9	4	7	-5	37	42					
4	2	-3	21	16	4	7	-4	83	93					
4	2	-1	47	51	4	7	-3	83	99					
4	2	0	15	18	4	7	-2	29	34					
4	2	1	25	27	4	7	-1	34	32					
4	2	4	44	40	4	7	1	24	25					
4	2	5	34	31	4	7	2	18	19					
4	2	7	49	50	4	7	5	35	38					
4	3	-9	20	23	4	8	-7	12	11					
4	3	-5	54	60	4	8	-6	18	21					
4	3	-4	52	58	4	8	-5	33	36					
4	3	-3	27	25	4	8	-4	42	45					
4	3	-2	21	20	4	8	-3	47	59					
4	3	-1	20	20	4	8	-2	20	30					
4	3	3	22	21	4	8	-1	26	32					
4	3	4	32	30	4	8	1	43	44					
4	3	5	56	57	4	8	2	30	32					
4	4	-9	35	36	4	8	3	104	102					
4	4	-7	21	20	4	8	4	34	31					
4	4	-6	42	43	4	9	-4	31	32					
4	4	-5	38	36	4	9	-3	77	98					
4	4	-4	22	22	4	9	-2	53	68					
4	4	-3	39	43	4	9	-1	51	56					
4	4	-1	30	29	4	9	1	24	21					
4	4	3	25	23	4	9	2	23	26					
4	4	4	26	23	4	9	3	17	20					
4	4	5	19	19	4	9	4	17	19					
4	4	6	30	34	4	10	-6	13	9					
4	5	-7	19	16	4	10	-4	50	62					

APPENDIX 4 X-ray Crystal Data for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Table A4.1. Positional Parameters and their Estimated Standard Deviations for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

Atom	x	y	z	B(A2)
Cl	0.2415(1)	0.8739(1)	0.50318(9)	4.67(2)
O1	0.2433(3)	0.6293(3)	1.2398(2)	4.62(6)
O2	0.4024(3)	0.8239(3)	0.9503(2)	4.36(5)
O3	0.5574(3)	0.9232(3)	0.7760(2)	4.77(6)
N1	0.2965(3)	0.7030(3)	1.1434(3)	3.62(6)
N7	0.2482(4)	0.2742(3)	0.6365(3)	4.14(6)
C1	0.2785(4)	0.5941(4)	1.0231(3)	3.22(6)
C2	0.3373(4)	0.6599(3)	0.9141(3)	3.27(6)
C3	0.3239(4)	0.5547(4)	0.7860(3)	3.60(7)
C4	0.2560(4)	0.3789(4)	0.7578(3)	3.36(6)
C5	0.1955(4)	0.3102(4)	0.8651(3)	3.32(6)
C6	0.2092(4)	0.4149(4)	0.9914(3)	3.51(7)
C8	0.3104(5)	0.3129(5)	0.5175(4)	5.33(9)
C9	0.1556(7)	0.3408(6)	0.4051(5)	7.70(1)
C10	0.1218(5)	0.1244(4)	0.8337(4)	4.44(8)

Table A4.2. Table of Bond Distances in Angstroms for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N1	1.363(4)	C2	C3	1.356(4)
O2	C2	1.326(3)	C3	C4	1.425(4)
N1	C1	1.302(4)	C4	C5	1.461(5)
N7	C4	1.310(4)	C5	C6	1.339(4)
N7	C8	1.468(5)	C5	C10	1.508(4)
C1	C2	1.458(5)	C8	C9	1.480(6)
C1	C6	1.450(3)			

Table A4.3. Table of Bond Angles in Degrees for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	N1	C1	112.1(2)	N7	C4	C3	121.2(3)
C4	N7	C8	127.5(3)	N7	C4	C5	118.2(3)
N1	C1	C2	116.3(3)	C3	C4	C5	120.6(3)
N1	C1	C6	125.3(3)	C4	C5	C6	118.7(3)
C2	C1	C6	118.4(3)	C4	C5	C10	120.2(3)
O2	C2	C1	115.6(2)	C6	C5	C10	121.1(3)
O2	C2	C3	124.3(3)	C1	C6	C5	121.9(3)
C1	C2	C3	120.0(2)	N7	C8	C9	111.8(3)
C2	C3	C4	120.4(3)				

Table A4.4. Table of General Displacement Parameters Expressions - B's for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beq
Cl	4.60(3)	4.46(3)	4.51(3)	0.46(3)	1.29(3)	0.24(3)	4.6
O1	6.20(1)	4.05(8)	4.02(9)	0.60(9)	1.93(8)	1.28(7)	4.6
O2	5.70(1)	2.92(8)	4.65(9)	0.46(8)	1.70(8)	1.17(7)	4.3
O3	5.50(1)	3.85(9)	5.20(1)	0.39(8)	1.85(8)	1.34(8)	4.7
N1	3.80(1)	3.61(9)	3.80(1)	0.93(8)	1.09(8)	1.47(8)	3.6
N7	4.10(1)	4.10(1)	4.10(1)	0.01(9)	1.35(9)	0.63(9)	4.1
C1	2.90(1)	3.20(1)	3.60(1)	1.06(9)	0.54(9)	1.16(9)	3.2
C2	3.00(1)	3.00(1)	3.90(1)	0.79(9)	0.67(9)	1.36(9)	3.2
C3	3.40(1)	3.60(1)	4.00(1)	0.70(1)	0.90(1)	1.30(1)	3.6
C4	2.60(1)	3.80(1)	3.60(1)	0.78(9)	0.65(9)	0.80(1)	3.3
C5	2.90(1)	3.10(1)	4.00(1)	0.68(9)	0.58(9)	1.18(9)	3.3
C6	3.50(1)	3.30(1)	3.90(1)	0.91(9)	0.80(1)	1.44(9)	3.5
C8	5.70(2)	5.50(2)	4.80(1)	-0.70(1)	2.60(1)	0.50(1)	5.3
C9	7.80(2)	9.90(2)	7.80(2)	2.30(2)	3.00(2)	6.00(1)	7.7
C10	5.10(2)	3.10(1)	5.10(8)	0.40(1)	1.20(1)	1.30(1)	4.4

Table A4.5. Table of Refined Displacement Parameter Expressions - Beta's for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Cl	0.0220(2)	0.0179(1)	0.0128(1)	0.0041(3)	0.0095(2)	0.0017(2)
O1	0.0296(5)	0.0163(4)	0.0114(3)	0.0053(8)	0.0142(6)	0.0086(5)
O2	0.0274(5)	0.0117(3)	0.0132(3)	0.0040(7)	0.0125(6)	0.0079(5)
O3	0.0265(5)	0.0154(4)	0.0147(3)	0.0034(7)	0.0136(6)	0.0090(5)
N1	0.0182(5)	0.0145(4)	0.0107(3)	0.0081(7)	0.0080(6)	0.0099(5)
N7	0.0194(5)	0.0163(5)	0.0117(3)	0.0001(8)	0.0099(6)	0.0043(6)
C1	0.0140(5)	0.0130(4)	0.0101(3)	0.0093(8)	0.0040(7)	0.0078(6)
C2	0.0144(5)	0.0121(4)	0.0111(3)	0.0069(8)	0.0049(7)	0.0092(6)
C3	0.0161(5)	0.0144(5)	0.0114(4)	0.0060(9)	0.0067(7)	0.0086(6)
C4	0.0126(5)	0.0153(5)	0.0101(3)	0.0069(8)	0.0048(7)	0.0056(7)
C5	0.0137(5)	0.0125(4)	0.0112(3)	0.0060(8)	0.0043(7)	0.0080(6)
C6	0.0167(6)	0.0133(4)	0.0111(3)	0.0080(8)	0.0058(7)	0.0097(6)
C8	0.0271(8)	0.0222(7)	0.0135(4)	-0.0060(1)	0.0192(9)	0.0032(9)
C9	0.0380(1)	0.0396(9)	0.0219(2)	0.0200(2)	0.0220(1)	0.0405(9)
C10	0.0244(7)	0.0125(5)	0.0144(4)	0.0040(1)	0.0089(9)	0.0087(7)

Table A4.6. Table of General Displacement Parameters Expressions - U's for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Mono-hydrate.

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Cl	0.0582(4)	0.0565(4)	0.0572(4)	0.0059(4)	0.0163(4)	0.0031(4)
O1	0.078(1)	0.051(1)	0.051(1)	0.008(1)	0.024(1)	0.0162(9)
O2	0.073(1)	0.037(1)	0.059(8)	0.006(1)	0.022(1)	0.0148(9)
O3	0.070(1)	0.049(1)	0.066(1)	0.005(1)	0.023(1)	0.017(1)
N1	0.048(1)	0.046(1)	0.048(1)	0.012(1)	0.014(1)	0.019(1)
N7	0.051(1)	0.052(1)	0.052(1)	0.000(1)	0.017(1)	0.008(1)
C1	0.037(1)	0.041(1)	0.045(1)	0.013(1)	0.007(1)	0.015(1)
C2	0.038(1)	0.038(1)	0.050(1)	0.010(1)	0.008(1)	0.017(1)
C3	0.043(1)	0.045(1)	0.051(2)	0.009(1)	0.012(1)	0.016(1)
C4	0.033(1)	0.048(1)	0.045(1)	0.010(1)	0.008(1)	0.011(1)
C5	0.036(1)	0.039(1)	0.050(2)	0.009(1)	0.007(1)	0.015(1)
C6	0.044(1)	0.042(1)	0.050(2)	0.012(1)	0.010(1)	0.018(1)
C8	0.072(2)	0.070(2)	0.060(2)	-0.009(2)	0.033(1)	0.006(1)
C9	0.099(3)	0.125(3)	0.098(2)	0.029(2)	0.039(1)	0.076(1)
C10	0.065(2)	0.040(1)	0.064(2)	0.006(1)	0.015(1)	0.016(1)

Table A4.7. Table of Root-mean-square Amplitudes of Anisotropic Displacement in Angstroms for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Atom	Min	Int'med	Max
Cl	0.219	0.241	0.267
O1	0.208	0.230	0.282
O2	0.188	0.238	0.271
O3	0.214	0.250	0.271
N1	0.192	0.218	0.231
N7	0.211	0.222	0.252
C1	0.167	0.214	0.221
C2	0.172	0.204	0.230
C3	0.199	0.211	0.230
C4	0.177	0.213	0.225
C5	0.179	0.201	0.231
C6	0.181	0.218	0.231
C8	0.206	0.241	0.319
C9	0.210	0.307	0.391
C10	0.194	0.250	0.261

Table A4.8. Table of Positional Parameters and their Estimated Standard Deviations for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Monohydrate.

Atom	x	y	z	B(A2)
HO1	0.245(6)	0.725(5)	1.315(4)	6.0(1)
HN7	0.205(5)	0.162(5)	0.617(4)	4.0(1)
HO2	0.447(5)	0.849(5)	0.872(4)	5.0(1)
HO3A	0.601(6)	1.040(5)	0.805(4)	5.0(1)
HO3B	0.484(6)	0.918(6)	0.677(5)	8.0(1)
H3	0.3604	0.5991	0.7139	5.0
H6	0.1721	0.3701	1.0631	5.0
H8A	0.3675	0.2219	0.4767	7.0
H8B	0.3998	0.4134	0.5518	7.0
H9C	0.0982	0.4317	0.4431	10.0
H9B	0.0660	0.2402	0.3680	10.0
H9A	0.1988	0.3661	0.3289	10.0
H10B	0.0150	0.0950	0.7531	6.0
H10A	0.0879	0.0991	0.9131	6.0
H10C	0.2134	0.0574	0.8126	6.0

Table A4.9. Table of Torsion Angles in Degrees for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
HO1	O1	N1	C1	-171.11 (2.76)
HO2	O2	C2	C1	174.75 (2.57)
HO2	O2	C2	C3	-5.08 (2.60)
O1	N1	C1	C2	-178.20 (0.25)
O1	N1	C1	C6	0.40 (0.42)
C8	N7	C4	C3	2.70 (0.51)
C8	N7	C4	C5	-176.44 (0.31)
HN7	N7	C4	C3	-179.70 (2.86)
HN7	N7	C8	C5	1.17 (2.91)
C4	N7	C8	C9	-98.01 (0.42)
C4	N7	C8	H8A	140.88 (0.35)
C4	N7	C8	H8B	22.04 (0.53)
HN7	N7	C8	C9	84.16 (2.63)
HN7	N7	C8	H8A	-36.95 (2.64)
HN7	N7	C8	H8B	155.79 (2.62)
N1	C1	C2	O2	-0.11 (0.41)
N1	C1	C2	C3	179.73 (0.30)
C6	C1	C2	O2	-178.80 (0.27)
C6	C1	C2	C3	1.03 (0.44)
N1	C1	C6	C5	-179.61 (0.31)
N1	C1	C6	H6	0.37 (0.51)
C2	C1	C6	C5	-1.04 (0.46)
C2	C1	C6	H6	178.94 (0.29)
O2	C2	C3	C4	178.49 (0.29)

Table 4.9. cont'd...

O2	C2	C3	H3	−1.46 (0.52)
C1	C2	C3	C4	−1.32 (0.46)
C1	C2	C3	H3	178.72 (0.29)
C2	C3	C4	N7	−177.53 (0.30)
C2	C3	C4	C5	1.58 (0.46)
H3	C3	C4	N7	2.42 (0.50)
H3	C3	C4	C5	−178.46 (0.29)
N7	C4	C5	C6	177.59 (0.30)
N7	C4	C5	C10	−1.60 (0.44)
C3	C4	C5	C6	−1.55 (0.45)
C3	C4	C5	C10	179.26 (0.29)
C4	C5	C6	C1	1.29 (0.46)
C4	C5	C6	H6	−178.69 (0.29)
C10	C5	C6	C1	−179.53 (0.29)
C10	C5	C6	H6	0.49 (0.50)
C4	C5	C10	H10B	−59.81 (0.43)
C4	C5	C10	H10A	−179.80 (0.30)
C4	C5	C10	H10C	59.68 (0.41)
C6	C5	C10	H10B	121.02 (0.36)
C6	C5	C10	H10A	1.02 (0.49)
C6	C5	C10	H10C	−119.50 (0.35)
N7	C8	C9	H9C	59.00 (0.53)
N7	C8	C9	H9B	−60.79 (0.49)
N7	C8	C9	H9A	179.78 (0.36)
H8A	C8	C9	H9C	−179.12 (0.41)
H8A	C8	C9	H9B	61.10 (0.52)

Table 4.9. cont'd...

H8A	C8	C9	H9A	-58.33 (0.54)
H8B	C8	C9	H9C	-61.49 (0.53)
H8B	C8	C9	H9B	178.72 (0.38)
H8B	C8	C9	H9A	59.29 (0.52)

Table A4.10. Values of 10*Fobs and 10*F calc for 5-Ethylamino-4-methyl-1,2-benzoquinone-2-oxime Chloridrate Monohydrate.

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	0	1	90	93	0	2	6	61	59	0	5	-4	12	10
0	0	2	190	180	0	2	8	13	18	0	5	-3	29	33
0	0	3	332	335	0	2	9	52	56	0	5	-2	50	50
0	0	4	316	316	0	3	-11	20	19	0	5	-1	245	245
0	0	5	11	10	0	3	-10	36	43	0	5	0	117	118
0	0	6	97	98	0	3	-9	38	44	0	5	1	73	68
0	0	7	154	146	0	3	-8	16	17	0	5	2	42	43
0	0	8	164	160	0	3	-7	53	54	0	5	3	313	314
0	0	9	30	30	0	3	-6	139	148	0	5	4	137	134
0	0	10	9	9	0	3	-5	67	58	0	5	5	76	72
0	0	11	53	54	0	3	-4	227	232	0	5	6	73	68
0	1	-11	6	9	0	3	-3	51	52	0	5	7	48	50
0	1	-9	166	173	0	3	-2	262	271	0	5	8	18	21
0	1	-8	55	51	0	3	-1	180	179	0	6	-10	27	32
0	1	-7	67	70	0	3	0	159	145	0	6	-9	47	49
0	1	-6	153	166	0	3	1	36	29	0	6	-8	16	17
0	1	-5	24	23	0	3	2	163	153	0	6	-7	29	27
0	1	-4	134	147	0	3	3	12	9	0	6	-6	91	95
0	1	-3	126	128	0	3	4	58	56	0	6	-5	204	219
0	1	-2	12	11	0	3	5	112	105	0	6	-4	74	82
0	1	-1	447	417	0	3	6	73	69	0	6	-3	76	79
0	1	0	215	188	0	3	7	68	62	0	6	-2	109	110
0	1	1	15	16	0	3	8	63	65	0	6	-1	19	23
0	1	2	148	138	0	3	9	50	50	0	6	1	8	7
0	1	3	308	311	0	3	10	17	16	0	6	2	15	12
0	1	4	101	88	0	4	-11	39	40	0	6	3	122	116
0	1	5	259	259	0	4	-9	16	20	0	6	4	48	46
0	1	6	41	40	0	4	-8	79	85	0	6	5	10	7
0	1	7	103	99	0	4	-7	28	28	0	6	7	19	19
0	1	8	16	14	0	4	-6	46	42	0	7	-10	13	12
0	1	9	15	13	0	4	-5	112	113	0	7	-9	24	30
0	1	10	31	35	0	4	-4	261	272	0	7	-8	35	42
0	1	11	22	25	0	4	-3	78	86	0	7	-7	25	29
0	2	-11	15	14	0	4	-2	208	207	0	7	-6	210	227
0	2	-10	78	84	0	4	-1	91	80	0	7	-5	54	55
0	2	-9	176	181	0	4	0	415	404	0	7	-4	37	36
0	2	-8	36	34	0	4	1	100	97	0	7	-3	32	31
0	2	-7	12	1	0	4	2	37	35	0	7	-2	122	122
0	2	-6	26	15	0	4	3	189	186	0	7	-1	30	33
0	2	-5	273	304	0	4	4	227	224	0	7	0	78	80
0	2	-4	264	283	0	4	6	55	53	0	7	1	66	70
0	2	-3	120	122	0	4	7	71	71	0	7	2	61	67
0	2	-2	67	64	0	4	8	46	49	0	7	3	28	32
0	2	-1	302	300	0	4	9	46	46	0	7	4	23	21
0	2	0	240	240	0	5	-11	13	14	0	7	5	47	49
0	2	1	175	161	0	5	-10	15	19	0	7	6	24	26
0	2	2	221	212	0	5	-9	54	66	0	8	-9	31	32
0	2	3	107	106	0	5	-8	71	77	0	8	-8	22	23
0	2	4	181	161	0	5	-6	85	92	0	8	-7	16	16

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	2	5	47	45	0	5	-5	130	138	0	8	-5	23	26
0	8	-4	52	53	1	-7	8	20	26	1	-4	11	18	12
0	8	-3	48	52	1	-6	-7	41	42	1	-3	-10	14	18
0	8	-2	10	11	1	-6	-6	39	40	1	-3	-9	29	30
0	8	-1	126	128	1	-6	-5	42	41	1	-3	-8	54	50
0	8	0	13	9	1	-6	-4	74	73	1	-3	-7	112	110
0	8	1	35	35	1	-6	-3	141	141	1	-3	-6	22	19
0	8	2	20	21	1	-6	-2	60	63	1	-3	-5	134	136
0	8	3	14	18	1	-6	-1	134	134	1	-3	-4	167	172
0	8	4	34	37	1	-6	0	43	37	1	-3	-3	14	22
0	9	-7	7	1	1	-6	1	130	113	1	-3	-2	23	15
0	9	-6	23	21	1	-6	2	63	60	1	-3	-1	458	471
0	9	-5	46	57	1	-6	3	100	104	1	-3	0	163	158
0	9	-2	25	30	1	-6	4	106	108	1	-3	1	9	10
0	9	-1	41	42	1	-6	6	27	25	1	-3	2	167	164
0	9	1	11	11	1	-6	8	44	24	1	-3	3	271	273
1	-9	-2	49	45	1	-6	10	35	32	1	-3	4	35	36
1	-9	-1	16	16	1	-5	-8	18	18	1	-3	5	60	64
1	-9	0	16	15	1	-5	-7	55	55	1	-3	6	170	161
1	-9	1	74	62	1	-5	-6	19	18	1	-3	7	96	94
1	-9	2	20	20	1	-5	-5	56	59	1	-3	8	84	76
1	-9	3	24	19	1	-5	-4	35	37	1	-3	9	12	13
1	-9	4	45	46	1	-5	-3	45	50	1	-3	10	56	52
1	-9	5	48	48	1	-5	-2	6	9	1	-2	-10	54	54
1	-9	7	24	28	1	-5	-1	47	57	1	-2	-9	68	74
1	-8	-4	19	18	1	-5	0	109	108	1	-2	-8	87	89
1	-8	-3	10	9	1	-5	1	108	106	1	-2	-7	107	107
1	-8	-2	12	9	1	-5	2	145	143	1	-2	-6	51	53
1	-8	0	65	57	1	-5	3	21	20	1	-2	-5	151	155
1	-8	1	23	24	1	-5	4	159	161	1	-2	-4	106	112
1	-8	2	20	19	1	-5	5	83	78	1	-2	-3	241	243
1	-8	3	26	21	1	-5	7	78	72	1	-2	-2	282	283
1	-8	4	13	13	1	-5	8	97	85	1	-2	-1	542	545
1	-8	5	23	20	1	-5	10	13	13	1	-2	0	221	210
1	-8	6	27	27	1	-4	-9	7	8	1	-2	1	286	281
1	-8	7	48	49	1	-4	-8	11	11	1	-2	2	266	266
1	-8	8	13	13	1	-4	-7	55	58	1	-2	3	27	27
1	-7	-6	31	27	1	-4	-6	74	68	1	-2	4	182	191
1	-7	-5	24	23	1	-4	-2	98	100	1	-2	5	31	34
1	-7	-4	89	87	1	-4	-1	10	10	1	-2	6	191	184
1	-7	-3	17	17	1	-4	0	151	130	1	-2	7	38	34
1	-7	-2	79	78	1	-4	1	45	33	1	-2	8	103	91
1	-7	-1	98	96	1	-4	2	117	105	1	-2	9	12	6
1	-7	0	40	36	1	-4	3	80	75	1	-2	10	33	30
1	-7	1	29	24	1	-4	4	89	89	1	-2	11	32	31
1	-7	2	10	11	1	-4	5	53	52	1	-1	-11	40	38
1	-7	3	116	116	1	-4	6	46	47	1	-1	-10	10	10
1	-7	4	27	25	1	-4	7	74	71	1	-1	-8	60	61
1	-7	5	51	56	1	-4	8	30	26	1	-1	-7	50	47
1	-7	6	43	50	1	-4	9	19	17	1	-6	-6	73	70
1	-7	7	10	17	1	-4	10	15	14	1	-1	-5	139	143
1	-1	-4	199	201	1	1	2	285	291	1	4	-10	29	34

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
1	-1	-3	11	11	1	1	3	103	104	1	4	-9	18	20
1	-1	-2	95	100	1	1	4	183	182	1	4	-8	41	38
1	-1	-1	30	23	1	1	5	109	110	1	4	-7	113	112
1	-1	0	142	130	1	1	6	72	74	1	4	-6	87	89
1	-1	1	310	323	1	1	7	9	6	1	4	-5	71	69
1	-1	2	309	317	1	1	8	40	38	1	4	-4	21	16
1	-1	3	183	178	1	1	9	28	27	1	4	-3	179	175
1	-1	4	259	260	1	1	10	21	23	1	4	-2	104	100
1	-1	5	45	44	1	2	-10	16	9	1	4	-1	25	25
1	-1	6	38	39	1	2	-9	90	89	1	4	0	142	135
1	-1	7	93	85	1	2	-8	31	28	1	4	1	93	100
1	-1	8	52	44	1	2	-7	77	75	1	4	2	70	74
1	-1	9	43	42	1	2	-6	128	140	1	4	3	30	27
1	-1	10	21	22	1	2	-5	262	276	1	4	4	26	25
1	-1	11	37	37	1	2	-4	279	279	1	4	5	29	28
1	0	-10	46	50	1	2	-3	50	38	1	4	7	11	10
1	0	-9	26	26	1	2	-2	470	480	1	4	8	16	17
1	0	-8	76	81	1	2	-1	442	458	1	5	-10	22	30
1	0	-7	37	39	1	2	0	174	180	1	5	-9	64	70
1	0	-6	38	41	1	2	1	165	173	1	5	-8	33	29
1	0	-5	25	21	1	2	2	502	525	1	5	-7	104	110
1	0	-4	188	184	1	2	3	137	138	1	5	-6	59	58
1	0	-3	126	132	1	2	4	29	31	1	5	-5	66	70
1	0	-2	66	64	1	2	5	136	138	1	5	-4	10	6
1	0	-1	294	300	1	2	6	122	127	1	5	-3	88	83
1	0	0	222	226	1	2	7	34	34	1	5	-2	125	126
1	0	2	102	97	1	2	8	83	86	1	5	-1	14	20
1	0	3	141	138	1	2	9	64	64	1	5	0	128	125
1	0	4	79	71	1	2	10	38	35	1	5	1	15	17
1	0	5	6	10	1	3	-10	24	28	1	5	2	133	132
1	0	6	63	61	1	3	-9	27	28	1	5	3	77	73
1	0	7	91	87	1	3	-8	120	124	1	5	4	61	61
1	0	8	39	38	1	3	-7	91	98	1	5	5	65	68
1	0	10	30	28	1	3	-6	45	46	1	5	6	21	18
1	0	11	17	17	1	3	-5	14	11	1	5	7	21	21
1	0	11	17	17	1	3	-4	127	120	1	6	-9	25	27
1	0	11	17	17	1	3	-3	116	103	1	6	-7	16	11
1	1	-10	28	29	1	3	-2	137	139	1	6	-6	42	43
1	1	-9	65	67	1	3	-1	251	241	1	6	-5	36	33
1	1	-8	43	45	1	3	0	193	188	1	6	-4	137	137
1	1	-7	92	95	1	3	1	96	103	1	6	-3	15	13
1	1	-6	9	9	1	3	2	152	152	1	6	-2	195	190
1	1	-5	256	270	1	3	3	34	32	1	6	-1	58	52
1	1	-4	79	82	1	3	4	65	64	1	6	0	47	42
1	1	-3	310	314	1	3	5	65	64	1	6	1	41	39
1	1	-2	33	34	1	3	6	22	23	1	6	2	69	63
1	1	-1	11	13	1	3	7	101	102	1	6	3	103	95
1	1	0	12	10	1	3	8	13	3	1	6	4	25	26
1	1	1	202	214	1	3	9	25	26	1	6	5	90	87
1	6	6	35	33	1	-8	5	51	50	2	-5	10	18	15

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
1	7	-9	11	13	2	-8	6	79	80	2	-4	-9	38	37
1	7	-8	10	16	2	-8	7	104	99	2	-4	-8	100	106
1	7	-7	20	18	2	-7	-6	35	32	2	-4	-7	17	18
1	7	-6	86	90	2	-7	-5	44	42	2	-4	-6	64	60
1	7	-4	35	38	2	-7	-4	27	31	2	-4	-5	88	87
1	7	-3	28	30	2	-7	-3	33	31	2	-4	-4	133	136
1	7	-2	64	64	2	-7	-2	92	93	2	-4	-3	137	143
1	7	-1	52	43	2	-7	-1	73	73	2	-4	-2	77	80
1	7	0	17	19	2	-7	0	54	51	2	-4	-1	217	226
1	7	1	120	109	2	-7	1	40	33	2	-4	0	154	153
1	7	2	71	65	2	-7	2	17	14	2	-4	1	26	18
1	7	3	37	34	2	-7	3	117	115	2	-4	2	128	121
1	7	4	30	27	2	-7	4	42	37	2	-4	3	139	140
1	7	5	50	46	2	-7	5	80	81	2	-4	4	25	25
1	8	-9	30	27	2	-7	6	192	187	2	-4	5	165	155
1	8	-8	50	51	2	-6	-7	12	10	2	-4	6	38	32
1	8	-7	11	11	2	-6	-6	9	12	2	-4	7	54	48
1	8	-6	21	21	2	-6	-5	20	20	2	-4	8	54	47
1	8	-5	45	48	2	-6	-4	83	84	2	-4	9	18	15
1	8	-4	25	29	2	-6	-3	212	215	2	-4	10	29	22
1	8	-3	41	42	2	-6	-2	129	133	2	-3	-10	6	5
1	8	-2	30	28	2	-6	-1	10	8	2	-3	-9	47	49
1	8	-1	47	43	2	-6	0	33	31	2	-3	-8	37	42
1	8	0	40	35	2	-6	1	12	5	2	-3	-7	31	33
1	8	2	12	13	2	-6	2	109	104	2	-3	-6	33	31
1	8	3	22	18	2	-6	3	13	7	2	-3	-5	151	155
1	9	-7	23	24	2	-6	4	14	15	2	-3	-4	68	68
1	9	-6	39	40	2	-6	5	68	63	2	-3	-3	107	102
1	9	-4	63	59	2	-6	6	29	24	2	-3	-2	50	52
1	9	-3	33	29	2	-6	7	24	18	2	-3	-1	190	197
1	9	-1	26	24	2	-6	8	30	29	2	-3	0	153	148
1	9	0	47	44	2	-6	9	14	12	2	-3	1	124	116
1	9	1	8	9	2	-5	-8	50	47	2	-3	2	309	305
2	-9	-2	20	22	2	-5	-7	45	45	2	-3	3	194	188
2	-9	-1	12	16	2	-5	-6	99	94	2	-3	4	163	159
2	-9	0	18	19	2	-5	-5	82	78	2	-3	5	130	121
2	-9	1	25	21	2	-5	-4	51	54	2	-3	6	184	175
2	-9	2	83	77	2	-5	-3	169	178	2	-3	7	31	27
2	-9	3	13	9	2	-5	-2	178	192	2	-3	9	27	22
2	-9	5	27	30	2	-5	-1	73	73	2	-3	10	123	113
2	-9	6	9	15	2	-5	0	29	25	2	-2	-10	20	19
2	-8	-4	69	64	2	-5	1	306	289	2	-1	-9	40	40
2	-8	-2	24	23	2	-5	2	48	45	2	-2	-8	16	18
2	-8	-1	47	45	2	-5	3	65	63	2	-2	-7	43	38
2	-8	0	41	35	2	-5	4	17	10	2	-2	-6	30	29
2	-8	1	116	104	2	-5	5	138	133	2	-2	-5	98	94
2	-8	2	21	19	2	-5	6	111	110	2	-2	-4	203	199
2	-8	3	77	79	2	-5	8	19	21	2	-2	-3	171	175
2	-8	4	30	29	2	-5	9	54	55	2	-2	-2	8	2
2	-2	-1	31	25	2	0	8	102	95	2	3	-1	189	181

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
2	-2	0	43	52	2	0	9	49	47	2	3	0	195	187
2	-2	1	235	229	2	1	-10	16	14	2	3	1	195	188
2	-2	2	113	111	2	1	-9	222	228	2	3	2	90	92
2	-2	3	23	24	2	1	-8	103	99	2	3	3	20	19
2	-2	4	43	39	2	1	-7	10	7	2	3	4	70	69
2	-2	5	26	20	2	1	-6	77	83	2	3	5	136	139
1	-2	6	111	103	2	1	-5	130	131	2	3	6	24	22
2	-2	7	11	5	2	1	-4	362	364	2	3	7	25	23
2	-2	8	29	22	2	1	-3	152	156	2	3	8	14	12
2	-2	9	133	123	2	1	-2	257	270	2	4	-10	25	39
2	-2	10	73	68	2	1	-1	170	176	2	4	-9	21	36
2	-1	-10	66	73	2	1	0	18	21	2	4	-8	31	36
2	-1	-9	8	5	2	1	1	64	71	2	4	-7	119	117
2	-1	-8	20	23	2	1	2	267	275	2	4	-6	15	12
2	-1	-7	122	124	2	1	3	34	38	2	4	-5	111	111
2	-1	-6	189	191	2	1	4	68	56	2	4	-4	263	267
2	-1	-5	200	207	2	1	5	141	139	2	4	-3	173	180
2	-1	-4	63	52	2	1	6	80	80	2	4	-2	176	179
2	-1	-3	287	288	2	1	7	15	12	2	4	-1	87	78
2	-1	-2	273	278	2	1	8	26	27	2	4	0	244	256
2	-1	-1	104	95	2	1	9	13	13	2	4	1	147	156
2	-1	0	578	586	2	1	10	34	38	2	4	2	84	86
2	-1	1	749	734	2	2	-10	15	10	2	4	4	273	311
2	-1	2	97	102	2	2	-9	67	63	2	4	5	29	29
2	-1	3	68	67	2	2	-8	81	81	2	4	6	29	39
2	-1	4	184	178	2	2	-7	13	19	2	4	7	48	58
2	-1	5	194	187	2	2	-6	54	48	2	4	8	34	46
2	-1	6	44	40	2	2	-5	177	163	2	5	-9	82	93
2	-1	7	26	27	2	2	-4	200	185	2	5	-8	11	12
2	-1	8	25	24	2	2	-3	88	83	2	5	-6	60	62
2	-1	9	92	91	2	2	-2	103	100	2	5	-5	203	204
2	-1	10	18	18	2	2	-1	208	219	2	5	-4	156	155
2	0	-10	41	42	2	2	0	270	281	2	5	-3	40	47
2	0	-8	222	231	2	2	1	38	31	2	5	-2	180	176
2	0	-7	72	74	2	2	2	75	65	2	5	-1	7	9
2	0	-6	105	100	2	2	3	57	57	2	5	0	105	107
2	0	-5	264	261	2	2	4	49	48	2	5	1	98	95
2	0	-4	88	85	2	2	5	57	57	2	5	2	67	64
2	0	-3	339	349	2	2	8	47	47	2	5	3	118	120
2	0	-2	342	367	2	2	9	65	62	2	5	4	62	65
2	0	-1	138	136	2	3	-10	52	56	2	5	5	42	49
2	0	0	611	636	2	3	-9	51	56	2	5	6	26	31
2	0	1	172	170	2	3	-8	10	16	2	5	7	25	31
2	0	2	91	86	2	3	-7	132	136	2	6	-9	14	9
2	0	3	52	52	2	3	-6	100	94	2	6	-8	16	17
2	0	4	260	254	2	3	-5	81	63	2	6	-7	29	31
2	0	5	54	45	2	3	-4	38	35	2	6	-6	155	154
2	0	6	156	149	2	3	-3	235	225	2	6	-5	258	250
2	0	7	67	62	2	3	-2	48	44	2	6	-4	15	12
2	6	-3	14	10	3	-8	0	51	49	3	-5	8	39	38

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
2	6	-2	14	4	3	-8	1	13	10	3	-5	9	26	26
2	6	-1	125	115	3	-8	3	27	26	3	-4	-9	9	7
2	6	0	27	32	3	-8	4	51	52	3	-4	-7	21	23
2	6	1	11	8	3	-8	5	21	26	3	-4	-6	63	66
2	6	2	46	38	3	-8	6	9	9	3	-4	-5	44	44
2	6	3	57	51	3	-8	7	28	29	3	-4	-4	17	21
2	6	4	25	23	3	-7	-6	44	40	3	-4	-3	59	62
2	6	5	42	34	3	-7	-5	33	30	3	-4	-2	47	45
2	6	6	10	12	3	-7	-4	40	37	3	-4	-1	158	161
2	7	-8	50	50	3	-7	-3	30	31	3	-4	0	125	129
2	7	-7	61	61	3	-7	-2	140	143	3	-4	1	66	59
2	7	-6	76	71	3	-7	-1	41	38	3	-4	2	9	9
2	7	-4	28	26	3	-7	0	72	75	3	-4	3	26	27
2	7	-3	32	28	3	-7	1	17	17	3	-4	4	81	78
2	7	-2	74	69	3	-7	2	28	31	3	-4	5	44	45
2	7	-1	40	37	3	-7	3	21	22	3	-4	6	60	58
2	7	0	130	120	3	-7	4	22	23	3	-4	7	16	10
2	7	1	32	28	3	-7	5	65	72	3	-4	9	15	13
2	7	2	43	41	3	-7	6	15	21	3	-4	10	10	11
2	7	3	27	27	3	-6	-7	18	19	3	-3	-10	21	24
2	8	-9	38	38	3	-6	-6	69	66	3	-3	-9	41	39
2	8	-8	18	17	3	-6	-5	26	24	3	-3	-8	70	68
2	8	-7	29	28	3	-6	-4	64	66	3	-3	-7	101	100
2	8	-6	17	20	3	-6	-3	85	85	3	-3	-6	119	120
2	8	-5	26	24	3	-6	-2	38	43	3	-3	-5	60	66
2	8	-4	79	78	3	-6	-1	47	49	3	-3	-4	155	168
2	8	-3	32	30	3	-6	0	50	50	3	-3	-3	70	80
2	8	-2	19	15	3	-6	1	104	91	3	-3	-2	103	99
2	8	-1	48	44	3	-6	2	41	37	3	-3	-1	95	94
2	8	0	67	57	3	-6	3	115	111	3	-3	0	271	277
2	8	1	26	22	3	-6	4	25	5	3	-3	1	104	100
2	8	2	16	16	3	-6	5	51	50	3	-3	2	115	113
2	9	-6	16	10	3	-6	6	41	38	3	-3	3	187	187
2	9	-5	30	32	3	-6	8	29	30	3	-3	4	21	22
2	9	-4	17	21	3	-6	9	40	37	3	-3	5	103	102
2	9	-3	15	16	3	-5	-8	24	24	3	-3	6	40	31
2	9	-2	36	34	3	-5	-7	9	6	3	-3	7	91	85
2	9	-1	29	22	3	-5	-6	98	100	3	-3	8	10	11
3	-9	-2	28	28	3	-5	-4	24	27	3	-3	9	40	41
3	-9	-1	30	29	3	-5	-3	51	53	3	-3	10	11	11
3	-9	0	26	29	3	-5	-2	13	12	3	-2	-10	74	77
3	-9	1	9	6	3	-5	-1	88	89	3	-2	-9	58	57
3	-9	2	17	15	3	-5	0	33	29	3	-2	-8	47	45
3	-9	3	40	36	3	-5	1	134	127	3	-2	-7	112	110
3	-9	5	33	34	3	-5	2	150	141	3	-6	-6	128	123
3	-8	-4	13	11	3	-5	3	34	33	3	-2	-5	17	16
3	-8	-3	44	39	3	-5	4	31	31	3	-2	-4	116	119
3	-8	-2	16	20	3	-5	5	99	94	3	-2	-3	305	312
3	-8	-1	9	7	3	-5	7	22	23	3	-2	-2	203	207
3	-2	-1	182	177	3	1	-9	8	6	3	3	7	31	30

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
3	-2	0	145	141	3	1	-8	92	89	3	3	8	21	22
3	-2	1	301	297	3	1	-7	57	54	3	4	-8	40	48
3	-2	2	168	158	3	1	-6	45	41	3	4	-6	78	81
3	-2	3	80	79	3	1	-5	113	116	3	4	-5	47	49
3	-2	4	77	72	3	1	-4	189	183	3	4	-4	48	54
3	-2	5	117	111	3	1	-3	287	286	3	4	-3	8	3
3	-2	6	72	65	3	1	-2	184	171	3	4	-2	35	26
3	-2	7	36	36	3	1	-1	159	166	3	4	-1	107	112
3	-2	8	99	91	3	1	0	203	213	3	4	0	8	1
3	-2	9	10	10	3	1	1	34	42	3	4	1	73	79
3	-2	10	16	17	3	1	2	29	33	3	4	2	8	7
3	-1	-9	11	11	3	1	3	259	268	3	4	3	79	81
3	-1	-8	29	30	3	1	4	132	134	3	4	4	51	56
3	-1	-7	34	36	3	1	5	28	27	3	4	5	22	25
3	-1	-6	44	45	3	1	6	62	56	3	4	6	18	26
3	-1	-5	7	5	3	1	7	57	54	3	5	-9	52	58
3	-1	-4	9	7	3	1	9	23	24	3	5	-8	65	72
3	-1	-3	234	227	3	2	-9	567	50	3	5	-7	37	40
3	-1	-2	38	36	3	2	-8	27	21	3	5	-6	19	16
3	-1	-1	123	113	3	2	-7	154	150	3	5	-5	62	64
3	-1	0	50	50	3	2	-6	164	163	3	5	-4	40	45
3	-1	1	144	143	3	2	-5	217	208	3	5	-3	97	97
3	-1	2	172	161	3	2	-4	197	197	3	5	-2	16	19
3	-1	3	31	32	3	2	-3	262	265	3	5	-1	118	127
3	-1	4	132	133	3	2	-2	80	81	3	5	0	62	64
3	-1	5	71	71	3	2	-1	186	191	3	5	1	31	35
3	-1	6	56	50	3	2	0	201	205	3	5	2	37	40
3	-1	7	21	19	3	2	1	180	181	3	5	4	41	49
3	-1	8	28	26	3	2	2	154	153	3	5	5	7	7
3	-1	9	34	36	3	2	3	150	154	3	5	6	38	44
3	0	-10	19	19	3	2	4	73	70	3	6	-8	23	20
3	0	-9	13	12	3	2	5	71	68	3	6	-7	41	39
3	0	-8	114	112	3	2	6	73	70	3	6	-6	17	16
3	0	-7	96	95	3	2	7	20	21	3	6	-5	115	108
3	0	-6	14	15	3	2	8	77	76	3	6	-4	87	80
3	0	-5	118	116	3	3	-8	21	25	3	6	-3	64	58
3	0	-4	75	72	3	3	-7	151	144	3	6	-2	72	68
3	0	-3	105	98	3	3	-6	51	45	3	6	-1	87	80
3	0	-2	161	160	3	3	-5	101	98	3	6	0	90	82
3	0	-1	120	112	3	3	-4	84	83	3	6	1	32	29
3	0	0	14	14	3	3	-3	98	96	3	6	2	87	77
3	0	1	17	21	3	3	-2	73	74	3	6	3	81	73
3	0	2	166	163	3	3	-1	149	148	3	6	4	44	41
3	0	3	42	37	3	3	0	172	174	3	6	5	39	35
3	0	4	81	76	3	3	1	44	32	3	7	-9	19	19
3	0	5	16	13	3	3	2	45	40	3	7	-8	40	32
3	0	6	35	27	3	3	4	52	48	3	7	-7	48	51
3	0	8	27	27	3	3	5	9	4	3	7	-6	24	27
3	1	-10	31	32	3	3	6	40	44	3	7	-5	15	10
3	7	-4	93	92	4	-6	-2	43	39	4	-3	-1	99	99

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
3	7	-3	31	29	4	-6	-1	69	65	4	-3	0	36	39
3	7	-2	15	17	4	-6	0	42	40	4	-3	1	48	55
3	7	0	71	60	4	-6	1	73	72	4	-3	2	194	187
3	7	1	23	17	4	-6	2	145	135	4	-3	3	89	86
3	7	2	40	30	4	-6	3	14	13	4	-3	4	71	70
3	7	3	53	44	4	-6	5	44	44	4	-3	5	18	13
3	8	-8	37	33	4	-6	7	27	26	4	-3	6	16	17
3	8	-7	11	8	4	-6	8	9	10	4	-3	7	56	51
3	8	-6	13	12	4	-5	-8	35	29	4	-3	8	21	22
3	8	-5	34	31	4	-5	-7	104	105	4	-3	9	39	36
3	8	-4	20	15	4	-5	-6	29	27	4	-2	-9	56	60
3	8	-3	53	51	4	-5	-5	51	47	4	-2	-7	80	81
3	8	-2	51	44	4	-5	-4	57	56	4	-2	-6	11	9
3	8	-1	13	15	4	-5	-3	87	84	4	-2	-5	23	21
3	8	1	28	22	4	-5	-2	105	103	4	-2	-4	130	118
3	9	-5	42	38	4	-5	-1	44	45	4	-2	-3	130	122
3	9	-4	9	76	4	-5	0	82	83	4	-2	-2	63	63
3	9	-3	27	25	4	-5	1	115	113	4	-2	-1	99	99
4	-9	0	17	20	4	-5	2	16	8	4	-2	0	165	161
4	-9	1	19	15	4	-5	3	57	57	4	-2	1	417	429
4	-9	2	65	62	4	-5	4	58	62	4	-2	2	280	271
4	-9	3	19	18	4	-5	6	92	97	4	-2	3	22	22
4	-8	-4	50	45	4	-4	-9	16	14	4	-2	4	52	50
4	-8	-3	42	43	4	-4	-8	87	89	4	-2	6	25	26
4	-8	-2	14	15	4	-4	-6	37	35	4	-2	9	35	36
4	-8	-1	43	42	4	-4	-5	29	27	4	-1	-9	55	56
4	-8	0	51	54	4	-4	-4	143	145	4	-1	-8	34	32
4	-8	1	56	53	4	-4	-3	141	137	4	-1	-7	171	168
4	-8	2	28	25	4	-4	-2	19	23	4	-1	-6	138	139
4	-8	4	45	47	4	-4	-1	86	84	4	-1	-5	96	96
4	-8	5	54	54	4	-4	0	182	176	4	-1	-4	188	186
4	-8	6	79	85	4	-4	1	36	33	4	-1	-3	36	36
4	-7	-6	32	32	4	-4	2	20	11	4	-1	-2	154	150
4	-7	-5	26	24	4	-4	3	106	96	4	-1	-1	167	164
4	-7	-4	39	38	4	-4	4	48	49	4	-1	0	159	141
4	-7	-3	77	79	4	-4	5	137	127	4	-1	1	395	400
4	-7	-2	158	161	4	-4	6	55	51	4	-1	2	162	160
4	-7	-1	10	10	4	-4	7	75	73	4	-1	3	107	107
4	-7	0	21	26	4	-4	8	38	34	4	-1	4	30	29
4	-7	1	53	53	4	-4	9	25	25	4	-1	5	159	148
4	-7	2	49	52	4	-3	-10	16	17	4	-1	6	18	17
4	-7	3	12	8	4	-3	-9	9	11	4	-1	7	44	42
4	-7	4	35	36	4	-3	-8	16	17	4	-1	8	12	12
4	-7	5	14	15	4	-3	-7	26	27	4	-1	9	37	36
4	-7	6	62	63	4	-3	-6	46	50	4	0	-9	48	46
4	-6	-7	18	15	4	-3	-5	19	20	4	0	-8	273	271
4	-6	-5	39	40	4	-3	-4	162	154	4	0	-7	42	33
4	-6	-4	69	70	4	-3	-3	107	96	4	0	-6	54	48
4	-6	-3	114	114	4	-3	-2	77	70	4	0	-5	167	163
4	0	-4	290	286	4	3	-6	117	113	4	6	4	20	21

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
4	0	-3	62	60	4	3	-5	17	18	4	6	4	20	21
4	0	-2	113	102	4	3	-4	27	27	4	7	-8	36	29
4	0	-1	229	227	4	3	-3	135	136	4	7	-7	43	39
4	0	0	245	236	4	3	-2	105	110	4	7	-6	40	36
4	0	1	100	97	4	3	-1	165	164	4	7	-5	30	31
4	0	2	16	14	4	3	0	112	97	4	7	-4	40	36
4	0	3	141	134	4	3	1	127	121	4	7	-3	58	51
4	0	4	103	94	4	3	2	102	98	4	7	-2	39	34
4	0	5	27	21	4	3	3	57	56	4	7	0	42	36
4	0	6	85	84	4	3	4	63	59	4	7	1	55	43
4	0	7	59	59	4	3	5	173	171	4	7	2	34	25
4	0	8	28	28	4	3	7	6	5	4	8	-7	31	29
4	1	-9	72	67	4	4	-8	80	89	4	8	-6	21	21
4	1	-7	50	46	4	4	-7	78	75	4	8	-5	10	10
4	1	-6	47	44	4	4	-6	47	43	4	8	-4	35	28
4	1	-5	107	93	4	4	-5	89	88	4	8	-3	36	30
4	1	-4	163	148	4	4	-4	277	275	4	8	-2	26	21
4	1	-3	151	138	4	4	-3	25	24	4	8	-1	39	33
4	1	-2	24	22	4	4	-2	51	53	5	-8	-3	16	12
4	1	-1	207	203	4	4	-1	142	143	5	-8	-2	19	26
4	1	0	82	72	4	4	0	45	39	5	-8	-1	74	78
4	1	1	88	80	4	4	1	100	91	5	-8	0	21	25
4	1	2	51	54	4	4	2	98	93	5	-8	1	22	24
4	1	3	77	73	4	4	3	38	39	5	-7	-5	50	47
4	1	4	14	10	4	4	4	155	150	5	-7	-4	14	13
4	1	5	36	35	4	4	5	9	9	5	-7	-3	20	26
4	1	6	53	52	4	4	6	34	35	5	-7	-2	70	78
4	1	7	22	23	4	5	-9	30	36	5	-7	0	20	27
4	1	8	26	29	4	5	-6	43	44	5	-7	1	9	14
4	2	-9	46	40	4	5	-5	219	242	5	-7	2	38	43
4	2	-8	51	53	4	5	-4	125	135	5	-7	3	10	6
4	2	-7	57	54	4	5	-2	60	72	5	-7	4	44	51
4	2	-6	68	65	4	5	-1	63	73	5	-7	5	17	17
4	2	-5	87	78	4	5	0	15	23	5	-7	6	12	17
4	2	-4	95	87	4	5	1	44	53	5	-6	-7	24	25
4	2	-3	31	26	4	5	2	42	53	5	-6	-6	7	4
4	2	-2	113	112	4	5	3	23	27	5	-6	-5	78	77
4	2	-1	18	14	4	5	4	11	13	5	-6	-4	39	43
4	2	0	157	147	4	6	-8	17	14	5	-6	-3	35	37
4	2	1	99	96	4	6	-7	19	17	5	-6	-2	51	55
4	2	2	17	10	4	6	-6	19	20	5	-6	-1	24	26
4	2	3	19	14	4	6	-5	96	93	5	-6	0	62	63
4	2	4	51	48	4	6	-4	21	24	5	-6	1	25	16
4	2	5	38	34	4	6	-3	35	37	5	-6	2	32	29
4	2	6	35	36	4	6	-1	64	64	5	-6	3	84	84
4	2	7	5	2	4	6	0	53	55	5	-6	4	16	16
4	3	-9	83	84	4	6	1	54	54	5	-6	5	12	10
4	3	-8	9	6	4	6	2	14	13	5	-6	6	46	48
4	3	-7	21	19	4	6	3	20	18	5	-6	7	9	6
5	-5	-8	27	25	5	-2	0	106	102	5	1	6	29	28

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
5	-5	-7	9	7	5	-2	1	49	45	5	1	7	30	28
5	-5	-6	71	72	5	-2	2	14	8	5	2	-9	58	51
5	-5	-5	12	12	5	-2	3	87	83	5	2	-8	38	36
5	-5	-4	48	51	5	-2	4	29	27	5	2	-7	57	56
5	-5	-3	36	34	5	-2	5	64	63	5	2	-6	216	198
5	-5	-1	47	43	5	-2	6	39	41	5	2	-5	131	120
5	-5	0	108	111	5	-2	7	47	50	5	2	-4	38	34
5	-5	1	33	35	5	-2	8	14	17	5	2	-3	128	118
5	-5	2	49	46	5	-1	-9	12	8	5	2	-2	127	121
5	-5	3	50	51	5	-1	-8	43	41	5	2	-1	14	9
5	-5	4	27	27	5	-1	-7	124	112	5	2	0	92	82
5	-5	6	10	11	5	-1	-6	76	69	5	2	1	152	144
5	-5	7	34	35	5	-1	-5	10	4	5	2	2	66	61
5	-4	-6	34	33	5	-1	-4	78	71	5	2	3	76	70
5	-4	-5	38	37	5	-1	-3	16	13	5	2	4	44	42
5	-4	-4	11	7	5	-1	-2	136	138	5	2	5	53	51
5	-4	-3	59	61	5	-1	-1	61	59	5	2	6	8	6
5	-4	-1	8	2	5	-1	0	34	15	5	3	-8	17	17
5	-4	1	82	79	5	-1	1	62	61	5	3	-7	12	14
5	-4	2	18	10	5	-1	2	36	35	5	3	-6	31	31
5	-4	4	49	46	5	-1	3	94	89	5	3	-5	22	22
5	-4	5	27	26	5	-1	4	11	5	5	3	-3	11	5
5	-4	8	22	20	5	-1	5	44	45	5	3	-2	52	49
5	-3	-9	66	64	5	-1	6	46	47	5	3	-1	79	70
5	-3	-8	67	63	5	0	-7	9	9	5	3	1	46	43
5	-3	-7	56	53	5	0	-5	51	50	5	3	2	8	5
5	-3	-6	108	105	5	0	-4	15	16	5	3	3	34	32
5	-3	-5	135	125	5	0	-2	193	183	5	3	4	35	32
5	-3	-4	30	28	5	0	-1	64	63	5	3	5	16	17
5	-3	-3	21	20	5	0	0	14	13	5	3	6	37	42
5	-3	-2	147	142	5	0	1	50	48	5	4	-8	32	30
5	-3	-1	79	79	5	0	2	51	45	5	4	-7	47	43
5	-3	0	92	94	5	0	3	56	55	5	4	-6	46	41
5	-3	1	58	63	5	0	4	24	23	5	4	-5	19	16
5	-3	2	208	198	5	0	5	28	28	5	4	-4	100	92
5	-3	3	18	15	5	1	-8	75	65	5	4	-3	50	49
5	-3	4	43	43	5	1	-7	20	15	5	4	-2	59	49
5	-3	5	42	40	5	1	-6	96	87	5	4	-1	18	19
5	-3	6	30	32	5	1	-5	68	65	5	4	0	43	37
5	-3	7	24	25	5	1	-4	112	108	5	4	1	25	23
5	-2	-9	67	64	5	1	-3	128	126	5	4	3	30	28
5	-2	-8	34	30	5	1	-2	119	123	5	4	4	25	24
5	-2	-7	77	73	5	1	-1	49	51	5	5	-8	33	44
5	-2	-6	37	31	5	1	0	95	93	5	5	-7	19	26
5	-2	-5	85	75	5	1	1	94	94	5	5	-6	25	33
5	-2	-4	76	71	5	1	2	88	85	5	5	-5	28	38
5	-2	-3	52	46	5	1	3	83	76	5	5	-4	17	24
5	-2	-2	186	187	5	1	4	97	87	5	5	-3	44	64
5	-2	-1	62	60	5	1	5	40	39	5	5	-2	20	24
5	5	-1	30	44	6	-5	-6	61	67	6	-1	1	141	135

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
5	5	0	33	48	6	-4	-8	35	34	6	-1	2	91	85
5	5	1	52	77	6	-4	-6	32	32	6	-1	3	42	27
5	5	2	14	20	6	-4	-5	38	40	6	-1	4	42	42
5	5	3	10	16	6	-4	-4	25	26	6	-1	5	60	63
5	6	-8	42	48	6	-4	-3	138	137	6	-1	6	17	20
5	6	-6	36	42	6	-4	-1	35	34	6	0	-9	8	6
5	6	-5	50	60	6	-4	0	68	67	6	0	-8	108	103
5	6	-3	74	87	6	-4	1	29	29	6	0	-7	77	72
5	6	-2	45	47	6	-4	3	65	62	6	0	-6	61	54
5	6	-1	42	44	6	-4	4	40	40	6	0	-5	24	21
5	6	0	27	27	6	-4	5	57	63	6	0	-4	158	149
5	6	1	38	39	6	-3	-8	24	24	6	0	-3	41	36
5	6	2	28	28	6	-3	-6	61	61	6	0	-2	85	81
5	7	-8	45	34	6	-3	-5	40	39	6	0	-1	39	33
5	7	-8	45	34	6	-3	-4	64	62	6	0	0	106	106
5	7	-8	45	34	6	-3	-3	48	41	6	0	1	95	93
5	7	-7	45	40	6	-3	-2	90	91	6	0	3	43	43
5	7	-6	25	22	6	-3	-1	50	50	6	0	4	58	58
5	7	-5	17	18	6	-3	0	43	42	6	0	6	23	25
5	7	-3	52	48	6	-3	1	83	86	6	1	-8	12	9
5	7	-1	25	21	6	-3	2	212	217	6	1	-7	42	42
5	7	0	32	23	6	-3	3	29	27	6	1	-6	39	35
6	-8	-1	63	74	6	-3	5	25	27	6	1	-4	55	52
6	-8	0	19	18	6	-3	6	16	19	6	1	-3	87	84
6	-8	1	14	16	6	-2	-9	20	20	6	1	-2	68	65
6	-7	-4	15	16	6	-2	-8	38	36	6	1	-1	18	19
6	-7	-3	51	56	6	-2	-7	74	70	6	1	0	68	67
6	-7	-2	82	90	6	-2	-6	21	19	6	1	1	60	53
6	-7	-1	14	18	6	-2	-5	47	47	6	1	2	42	41
6	-7	1	7	5	6	-2	-4	27	28	6	1	3	19	22
6	-7	2	65	75	6	-2	-3	61	62	6	1	5	20	21
6	-7	3	28	30	6	-2	-1	37	38	6	1	6	36	40
6	-6	-6	45	45	6	-2	0	101	101	6	2	-8	61	60
6	-6	-5	15	15	6	-2	1	171	173	6	2	-7	13	10
6	-6	-4	18	17	6	-2	2	97	92	6	2	-6	12	14
6	-6	-2	15	15	6	-2	3	30	28	6	2	-5	79	72
6	-6	-1	36	35	6	-2	4	17	16	6	2	-3	51	51
6	-6	0	19	20	6	-2	5	25	26	6	2	-2	35	31
6	-6	2	52	57	6	-2	6	46	49	6	2	-1	15	14
6	-6	3	15	18	6	-1	-9	65	60	6	2	0	100	93
6	-5	-7	84	84	6	-1	-8	67	65	6	2	1	80	74
6	-5	-6	22	21	6	-1	-7	186	182	6	2	3	21	18
6	-5	-5	29	30	6	-1	-6	81	78	6	2	4	23	22
6	-5	-3	53	55	6	-1	-5	28	30	6	2	5	77	73
6	-5	-2	76	79	6	-1	-4	74	75	6	3	-7	36	33
6	-5	-1	14	20	6	-1	-3	166	165	6	3	-6	49	48
6	-5	0	23	29	6	-1	-2	20	22	6	3	-5	13	12
6	-5	1	84	94	6	-1	-1	42	39	6	3	-4	13	9
6	-5	4	35	37	6	-1	0	64	70	6	3	-3	155	152
6	3	-2	60	57	7	-4	-2	9	13	7	0	1	16	4

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
6	3	-1	45	44	7	-4	-1	43	45	7	0	3	8	9
6	3	0	68	68	7	-4	0	10	9	7	1	-7	20	20
6	3	1	31	29	7	-4	1	18	14	7	1	-6	18	17
6	3	2	42	40	7	-4	2	13	18	7	1	-5	84	86
6	3	3	49	50	7	-4	3	65	70	7	1	-4	87	87
6	3	4	26	18	7	-4	4	15	15	7	1	-3	43	41
6	4	-7	63	60	7	-3	-8	55	53	7	1	-2	73	75
6	4	-6	58	53	7	-3	-7	32	31	7	1	-1	75	79
6	4	-5	34	31	7	-3	-6	66	70	7	1	0	20	20
6	4	-4	233	226	7	-3	-5	33	34	7	1	1	30	30
6	4	-2	12	9	7	-3	-4	38	39	7	1	2	72	72
6	4	-1	64	62	7	-3	-3	36	38	7	1	3	32	28
6	4	0	71	69	7	-3	-2	36	26	7	1	4	30	30
6	4	1	11	14	7	-3	-1	73	77	7	2	-7	55	54
6	4	2	42	40	7	-3	0	27	33	7	2	-6	46	42
6	4	3	52	46	7	-3	1	51	59	7	2	-5	73	70
6	5	-7	15	20	7	-3	2	68	75	7	2	-4	39	38
6	5	-5	35	54	7	-3	3	15	17	7	2	-3	36	34
6	5	-4	28	37	7	-3	4	27	33	7	2	-2	10	10
6	5	-1	21	31	7	-2	-8	25	24	7	2	-1	29	32
6	5	0	23	31	7	-2	-7	82	83	7	2	0	55	57
6	5	1	38	50	7	-2	-6	47	49	7	2	1	33	33
6	6	-6	28	34	7	-2	-5	61	60	7	2	2	39	41
6	6	-5	33	40	7	-2	-4	38	36	7	2	3	21	20
6	6	-4	31	42	7	-2	-3	46	46	7	3	-7	13	7
6	6	-3	11	18	7	-2	-2	20	18	7	3	-4	20	21
6	6	-2	14	19	7	-2	-1	62	66	7	3	-3	55	54
6	6	-1	18	24	7	-2	0	58	66	7	3	-2	52	53
6	6	0	12	20	7	-2	2	13	18	7	3	0	15	18
7	-7	-1	13	19	7	-2	3	23	28	7	4	-7	27	24
7	-6	-4	15	16	7	-2	4	45	47	7	4	-6	31	26
7	-6	-3	29	34	7	-2	5	13	12	7	4	-5	41	40
7	-6	-2	35	37	7	-1	-7	11	11	7	4	-4	10	5
7	-6	0	24	25	7	-1	-6	16	17	7	4	-3	26	23
7	-6	1	33	34	7	-1	-5	9	6	7	4	-2	27	26
7	-6	2	13	14	7	-1	-4	48	52	7	4	0	7	4
7	-6	3	28	29	7	-1	-3	22	25	7	5	-7	28	35
7	-5	-6	35	36	7	-1	-2	88	89	7	5	-4	24	31
7	-5	-5	7	6	7	-1	-1	29	33	7	5	-2	31	46
7	-5	-3	30	34	7	-1	0	31	31	7	5	-1	19	27
7	-5	-1	24	25	7	-1	1	26	30	8	-5	-4	13	18
7	-5	-0	24	28	7	-1	3	30	32	8	-5	-2	56	65
7	-5	1	35	39	7	-1	4	24	25	8	-5	-1	9	15
7	-5	3	14	20	7	-1	5	15	19	8	-5	0	9	11
7	-4	-7	17	16	7	0	-7	20	19	8	-5	1	26	34
7	-4	-6	7	5	7	0	-6	13	12	8	-4	-5	30	32
7	-4	-5	33	36	7	0	-5	26	26	8	-4	-4	21	24
7	-5	-4	47	53	7	0	-2	57	57	8	-4	-1	54	61
7	-4	-3	17	20	7	0	-1	28	29	8	-4	-1	26	32
8	-4	0	25	28	8	2	-1	14	15					

Table A4.10. cont'd...

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
8	-4	1	37	47	8	2	0	11	11
8	-4	2	41	57	8	2	1	10	8
8	-3	-6	44	46	8	3	-7	25	26
8	-3	-5	27	31	8	3	-6	33	33
8	-3	-4	12	14	8	3	-5	41	42
8	-3	-3	15	13	8	3	-4	46	46
8	-3	-1	24	28	8	3	-3	120	124
8	-3	0	22	26	8	3	-2	32	34
8	-3	1	52	65	8	4	-5	9	5
8	-3	2	85	100	8	4	-4	67	71
8	-2	-7	71	70	9	-2	-4	9	10
8	-2	-6	53	56	9	-2	-3	19	25
8	-2	-5	37	42	9	-2	-1	42	54
8	-2	-3	11	12	9	-1	-5	18	22
8	-2	-2	49	58	9	-1	-2	31	38
8	-2	1	21	25	9	0	-4	15	14
8	-2	2	29	31	9	0	-3	19	22
8	-2	3	19	19	9	0	-2	8	8
8	-1	-7	66	66	9	1	-4	39	44
8	-1	-6	49	52	9	1	-3	29	33
8	-1	-5	41	45					
8	-3	-4	9	9					
8	-1	-3	92	101					
8	-1	-1	34	38					
8	-1	0	22	24					
8	-1	1	39	41					
8	-1	2	49	55					
8	0	-7	33	33					
8	0	-6	12	9					
8	0	-5	29	33					
8	0	-4	35	38					
8	0	-3	22	28					
8	0	-2	36	41					
8	0	-1	29	34					
8	0	0	16	19					
8	0	1	56	63					
8	1	-7	32	33					
8	1	-5	26	29					
8	1	-4	16	17					
8	1	-2	40	44					
8	1	-1	12	13					
8	1	0	24	30					
8	1	1	40	41					
8	1	2	26	30					
8	2	-6	7	4					
8	2	-5	23	24					
8	2	-4	11	11					
8	2	-3	42	45					
8	2	-2	37	38					

APPENDIX 5. X-ray Crystal data for *trans*-Bis(1,2-dicarbomethoxyethenyl)-1,2-diaminoethanedione Dioxime

Table A5.1 Table of Fractional Atomic Coordinates and Thermal Parameters for *trans*-Bis(1,2-dicarbomethoxyethenyl)-1,2-ethanedione Dioxime.

Atom	x	y	z	U_{iso} or U_{eq}
N(1)	0.2552(11)	−0.0429(16)	1.2407(9)	0.029(4)
N(2)	0.2512(12)	0.1460(18)	1.1512(10)	0.041(4)
C(1)	0.2991(14)	0.0488(21)	1.1987(12)	0.025(4)
O(1)	0.1382(10)	−0.0110(13)	1.2301(8)	0.040(3)
C(2)	0.0843(14)	−0.0809(20)	1.2855(12)	0.024(4)
C(3)	0.1245(15)	−0.1507(21)	1.3490(13)	0.034(5)
C(4)	0.0723(20)	−0.2273(24)	1.4100(16)	0.060(5)
O(2)	−0.0238(13)	−0.2508(16)	1.3922(10)	0.075(4)
O(3)	0.1309(12)	−0.2597(17)	1.4797(11)	0.076(4)
C(5)	0.0794(19)	−0.3312(27)	1.5437(16)	0.091(6)
C(6)	−0.0321(16)	−0.0529(23)	1.2575(15)	0.050(5)
O(4)	−0.0706(12)	0.0204(16)	1.3138(10)	0.068(4)
O(5)	−0.0801(12)	−0.0953(18)	1.1926(10)	0.082(5)
C(7)	−0.1898(18)	0.0509(24)	1.2943(14)	0.071(5)
N(1a)	0.4580(11)	0.1077(16)	1.1492(10)	0.031(4)
N(2a)	0.4664(11)	−0.0733(17)	1.2499(10)	0.034(4)
C(1a)	0.4154(14)	0.0236(21)	1.2010(12)	0.031(4)
O(1a)	0.5737(9)	0.0759(12)	1.1570(8)	0.032(3)
C(2a)	0.6067(14)	0.0967(20)	1.0819(12)	0.026(4)
C(3a)	0.6648(15)	−0.0037(21)	1.0528(12)	0.035(5)
C(4a)	0.6873(16)	−0.1418(22)	1.0900(15)	0.044(5)

Table A5.1 cont'd....

O(2a)	0.6615(10)	-0.1902(14)	1.1554(9)	0.049(4)
O(3a)	0.7437(11)	-0.2184(16)	1.0402(9)	0.057(4)
C(5a)	0.7841(18)	-0.3598(27)	1.0717(15)	0.077(5)
C(6a)	0.5859(14)	0.2288(23)	1.0398(14)	0.035(5)
O(4a)	0.5819(10)	0.2173(15)	0.9570(9)	0.043(4)
O(5a)	0.5785(10)	0.3334(16)	1.0777(9)	0.048(4)
C(7a)	0.5706(16)	0.3550(24)	0.9110(14)	0.060(5)

Table A5.2. Table of Fractional atomic Coordinate for the Hydrogen Atoms in *trans*-Bis(1,2-dicarbomethoxyethenyl)-1,2-ethanedione Dioxime

Atom	x	y	z
H(25)	0.0143	−0.2691	1.5606
H(35)	0.1385	−0.3498	1.5993
H(27)	−0.2232	0.0083	1.2334
H(37)	−0.2041	0.1607	1.2941
H(25a)	0.8286	−0.3541	1.1351
H(35a)	0.8343	0.4067	1.0302
H(27a)	0.5705	0.3371	0.8443
H(37a)	0.6375	0.4214	0.9352
H(1na)	0.5364	−0.1187	1.2233
H(2na)	0.4375	−0.0966	1.3225
H(12n)	0.2712	0.2553	1.1424
H(22n)	0.2014	0.1027	1.1010
H(13)	0.1998	−0.1420	1.3630
H(13a)	0.6765	−0.0002	1.0021
H(15a)	0.7057	−0.4132	1.0705
H(17a)	0.5020	0.3987	0.9185
H(15)	0.0435	−0.4415	1.5139
H(17)	−0.2255	0.0025	1.3416

Table A5.3. Table of Bond Distances in Angstroms for *trans*-Bis(1,2-dicarbomethoxyethenyl)-1,2-ethanedione Dioxime.

N(1) - C(1)	1.287(25)	N(1) - O(1)	1.480(19)
N(2) - C(1)	1.299(25)	C(1) - C(1a)	1.470(3)
O(1) - C2)	1.371(24)	C(2) - C(3)	1.260(3)
C(2) - C(6)	1.480(3)	C(3) - C(4)	1.460(3)
C(4) - O(2)	1.210(3)	C(4) - O(3)	1.280(3)
O(3) - C(5)	1.460(3)	C(6) - O(4)	1.300(3)
C(6) - O(5)	1.190(3)	O(4) - C(7)	1.500(3)
N(1a) - C(1a)	1.330(3)	N(1a) - O(1a)	1.466(18)
N(2a) - C(1a)	1.322(24)	O(1a) - C(2a)	1.344(24)
C(2a) - C(3a)	1.340(3)	C(2a) - C(6a)	1.450(3)
C(3a) - C(4a)	1.470(3)	C(4a) - O(2a)	1.230(3)
C(4a) - O(3a)	1.360(3)	O(3a) - C(5a)	1.520(3)
C(6a) - O(4a)	1.320(3)	C(6a) - O(5a)	1.190(3)
O(4a) - C(7a)	1.520(3)		

Table A5.4. Table of Bond Angles in Degrees for

trans-Bis(1,2-dicarbomethoxyethenyl)-1,2-ethanedione Dioxime.

O(1) - N(1) - C(1)	107(1)	N(2) - C(1) - N(1)	128(2)
C(1a) - C(1) - N(1)	112(2)	C(1a) - C(1) - N(2)	120(2)
C(2) - O(1) - N(1)	113(1)	C(3) - C(2) - O(1)	128(2)
C(6) - C(2) - O(1)	106(2)	C(6) - C(2) - C(3)	126(2)
C(4) - C(3) - C(2)	130(2)	O(2) - C(4) - C(3)	118(2)
O(3) - C(4) - C(3)	117(2)	O(3) - C(4) - O(2)	125(2)
C(5) - O(3) - C(4)	118(2)	O(4) - C(6) - C(2)	110(2)
O(5) - C(6) - C(2)	123(2)	O(5) - C(6) - O(4)	127(2)
C(7) - O(4) - C(6)	115(2)	O(1a) - N(1a) - C(1a)	108(1)
N(1a) - C(1a) - C(1)	112(2)	N(2a) - C(1a) - C(1)	121(2)
N(2a) - C(1a) - N(1a)	127(2)	C(2a) - O(1a) - N(1a)	109(1)
C(3a) - C(2a) - O(1a)	117(2)	C(6a) - C(2a) - O(1a)	119(2)
C(6a) - C(2a) - C(3a)	123(2)	C(4a) - C(3a) - C(2a)	127(2)
O(2a) - C(4a) - C(3a)	129(2)	O(3a) - C(4a) - C(3a)	110(2)
O(3a) - C(4a) - O(2a)	121(2)	C(5a) - O(3a) - C(4a)	118(2)
O(4a) - C(6a) - C(2a)	111(2)	O(5a) - C(6a) - C(2a)	123(2)
O(5a) - C(6a) - O(4a)	126(2)	C(7a) - O(4a) - C(6a)	113(2)

Table A5.5. Table of Intermolecular Contact Distances for *trans*-Bis(1,2-dicarbomethoxyethenyl)-1,2-ethanedione Dioxime.

Atom 1	Atom 2	Dist.	s	a	b	c
H(37) ...	N(1)	2.98	2	0.0	0.0	2.0
H(25a)...	N(1)	3.01	2	1.0	-1.0	2.0
H(35) ...	N(1)	2.70	-2	0.0	0.0	1.0
O(3a) ...	N(2)	3.15	-1	1.0	0.0	2.0
O(2) ...	N(2)	2.99	2	0.0	-1.0	2.0
H(35) ...	C(1)	3.05	-2	0.0	0.0	1.0
H(25a)...	O(1)	2.62	2	1.0	-1.0	2.0
C(5) ...	O(1)	3.33	-2	0.0	0.0	1.0
H(35) ...	O(1)	2.49	-2	0.0	0.0	1.0
C(5a) ...	C(2)	3.37	2	1.0	-1.0	2.0
H(25a)...	C(2)	2.68	2	1.0	-1.0	2.0
C(5a) ...	C(3)	3.23	2	1.0	-1.0	2.0
H(25a)...	C(3)	2.94	2	1.0	-1.0	2.0
H(35a)...	C(3)	3.05	2	1.0	-1.0	2.0
H(22n)...	O(2)	2.65	2	0.0	0.0	2.0
H(15) ...	C(5)	2.76	-1	0.0	-1.0	3.0
O(5) ...	C(5)	3.41	-2	0.0	0.0	0.0
O(5) ...	H(25)	2.89	-2	0.0	0.0	0.0
C(4a) ...	O(5)	3.14	1	1.0	0.0	0.0
O(2a) ...	O(5)	3.33	1	1.0	0.0	0.0
O(3a) ...	O(5)	3.25	1	1.0	0.0	0.0
H(25a)...	O(5)	2.85	1	1.0	0.0	0.0
O(1a) ...	C(7)	3.41	1	1.0	0.0	0.0
O(1a) ...	H(27)	2.72	1	1.0	0.0	0.0

Table A5.5 cont'd...

C(3a) ... H(27)	3.01	1	1.0	0.0	0.0
C(4a) ... H(27)	2.80	1	1.0	0.0	0.0
O(2a) ... H(27)	2.61	1	1.0	0.0	0.0
H(13a)... N(1a)	2.92	−1	1.0	0.0	2.0
H(27a)... N(2a)	2.97	−1	1.0	0.0	2.0
O(5a) ... N(2a)	3.03	2	1.0	0.0	2.0
C(7a) ... N(2a)	3.43	−2	0.0	1.0	0.0
H(27a)... N(2a)	2.93	−2	0.0	1.0	0.0
H(27a)... C(1a)	3.08	−2	0.0	1.0	0.0
O(4a) ... C(4a)	3.41	−1	1.0	0.0	2.0
O(4a) ... O(2a)	3.30	−1	1.0	0.0	2.0
C(7a) ... O(2a)	3.34	−1	1.0	0.0	2.0
H(17a)... O(2a)	2.99	−1	1.0	0.0	2.0
H(12n)... O(3a)	2.92	−1	1.0	0.0	2.0
H(22n)... O(3a)	2.70	−1	1.0	0.0	2.0
H(13) ... C(5a)	2.92	2	1.0	0.0	2.0
H(2na)... C(6a)	2.83	2	1.0	−1.0	2.0
H(15a)... O(5a)	2.94	1	0.0	−1.0	0.0
H(17a)... O(5a)	2.79	−1	1.0	1.0	2.0
H(2na)... O(5a)	1.77	2	1.0	−1.0	2.0
H(13) ... O(5a)	2.80	2	1.0	−1.0	2.0

Table A5.6. Table of Intramolecular Contact Distances for *trans*-Bis(1,2-dicarbomethoxyethenyl)-1,2-ethanedione Dioxime.

N(2)	... N(1)	2.32	C(4)	... C(2)	2.47
C(3)	... N(1)	2.76	O(4)	... C(2)	2.28
C(1a)	... N(1)	2.29	H(13)	... C(2)	1.85
H(22n)	... N(1)	2.64	O(3)	... C(3)	2.33
O(1)	... N(2)	2.54	O(4)	... C(3)	2.93
C(1a)	... N(2)	2.40	C(5)	... C(4)	2.35
C(2)	... C(1)	3.44	C(6)	... C(4)	3.09
N(2a)	... C(1)	2.43	H(13)	... C(4)	2.04
H(12n)	... C(1)	2.20	O(3)	... O(2)	2.21
C(3)	... O(1)	2.36	H(25)	... O(2)	2.67
O(4)	... O(1)	3.13	O(4)	... O(2)	2.93
H(22n)	... O(1)	2.57	H(25)	... O(3)	2.09
C(2)	... N(1)	2.38	H(13)	... O(3)	2.45
N(2a)	... N(1)	2.64	O(2)	... C(2)	2.86
H(2na)	... N(1)	2.50	O(5)	... C(2)	2.35
H(13)	... N(1)	2.38	O(2)	... C(3)	2.29
N(1a)	... N(2)	2.62	O(6)	... C(3)	2.45
O(1)	... C(1)	2.22	O(5)	... C(3)	3.33
N(1a)	... C(1)	2.32	H(25)	... C(4)	2.65
H(2na)	... C(1)	2.80	O(4)	... C(4)	3.24
H(22n)	... C(1)	1.90	H(15)	... C(4)	2.72
C(6)	... O(1)	2.28	C(5)	... O(2)	2.68
O(5)	... O(1)	2.82	C(6)	... O(2)	2.88
H(13)	... O(1)	2.49	H(15)	... O(2)	2.72

Table A5.6 cont'd...

H(35) ... O(3)	2.09	H(27) ... C(6)	2.43
H(15) ... O(3)	2.19	O(5) ... O(4)	2.23
C(7) ... C(6)	2.37	H(37) ... O(4)	2.14
H(17) ... C(6)	2.99	C(7) ... O(5)	2.69
H(27) ... O(4)	2.13	N(2a) ... N(1a)	2.37
H(17) ... O(4)	2.06	C(3a) ... N(1a)	3.38
H(27) ... O(5)	2.23	O(5a) ... N(1a)	2.98
C(2a) ... N(1a)	2.29	H(12n)... N(1a)	2.73
C(6a) ... N(1a)	2.80	O(2a) ... N(2a)	3.27
H(1na)... N(1a)	2.61	C(2a) ... C(1a)	3.35
O(1a) ... N(2a)	2.59	H(2na)... C(1a)	2.24
O(1a) ... C(1a)	2.26	H(22n)... C(1a)	3.00
H(1na)... N(1a)	2.04	C(4a) ... O(1a)	2.84
H(12n)... C(1a)	2.94	C(6a) ... O(1a)	2.41
C(3a) ... O(1a)	2.29	H(1na)... O(1a)	2.25
O(2a) ... O(1a)	2.81	O(2a) ... C(2a)	3.06
O(5a) ... O(1a)	2.81	O(5a) ... C(2a)	2.32
C(4a) ... C(2a)	2.52	O(2a) ... C(3a)	2.45
O(4a) ... C(2a)	2.29	C(6a) ... C(3a)	2.46
H(13a)... C(2a)	1.90	C(5a) ... C(4a)	2.48
O(3a) ... C(3a)	2.33	H(1na)... C(4a)	3.06
O(4a) ... C(3a)	2.74	H(15a)... C(4a)	2.66
H(25a)... C(4a)	2.74	C(5a) ... O(2a)	2.73
H(13a)... C(4a)	1.95	H(1na)... O(2a)	2.15
O(3a) ... O(2a)	2.26	H(25a)... O(3a)	2.16
H(25a)... O(2a)	2.68	H(13a)... O(3a)	2.32

Table A5.6. cont'd...

H(15a)... O(2a)	2.66	C(7a) ... C(6a)	2.38
H(35a)... O(3a)	2.17	H(13a)... C(6a)	2.61
H(15a)... O(3a)	2.02	O(5a) ... O(4a)	2.24
H(37a)... C(6a)	2.65	H(37a)... O(4a)	2.14
H(17a)... C(6a)	2.64	H(17a)... O(4a)	2.07
H(27a)... O(4a)	2.13	H(37a)... O(5a)	2.64
H(13a)... O(4a)	2.47	H(17a)... O(5a)	2.65
C(7a) ... O(5a)	2.66		

Erratum

Page 43 Scheme 2.3

The phenol in the scheme should be 3-ethylamino-4-methylphenol and NOT 3-ethylamino-2-methylphenol as shown.

DX

179051