II

STUDIES OF OXIME COMPLEXES

A thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

by

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The Polytechnic of
North London

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For my Family

We do not ask for what useful purpose the birds do sing, for song is their pleasure since they were created for singing. Similarly, we ought not to ask why the human mind troubles to fathom the secrets of the heavens..... The diversity of the phenomena of Nature is so great, and the treasures hidden in the heavens so rich, precisely in order that the human mind shall never be lacking in fresh nourishment.

Johannes Kepler, *Mysterium Cosmographicum.*

Declaration

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

W.M.SHUTIE

Winston Michael Shutie
Studies of oxime complexes.

Abstract

The reaction of 5-hydroxy-2-nitrosophenol (mnrH), 5-hydroxy-6-methyl-2-nitrosophenol (6-MemnrH), 2,4-dinitrosooresorcinol ($dnrH_2$) and substituted dinitrosoresorcinols ($X\text{-}dnrH_2$) with various metal salts gave monomeric, dimeric and polymeric metal complexes such as $M(mnr)_2$ (M=Cu, Ni and Fe); Cu(OH)(mnr); M(dnr) (M=Ni or Cu). The complexes of type $M(mnr)_2$, $M(6\text{-}Memnr)_2$ and M(dnr) (M=Cu or Ni) form 1:2 adducts with pyridine. These complexes were investigated using spectroscopic, thermogravimetric and magnetochemical techniques, and where appropriate by Mössbauer spectroscopy.

The complexing behaviour of 3-methyl-4-oxime-1H-pyrazol-4,5-dione (poH) and 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione (PpoH) with nickel(II) and copper(II) has been reinvestigated. Three new iron(II) complexes derived from these ligands have been prepared either by the reaction of PpoH with iron(II) under aqueous conditions or by the reaction of poH with iron pentacarbonyl in anhydrous THF. The latter reaction also afforded a number of organic products, the formation of which has been rationalised in terms of nitrene intermediates. The complexes $Fe(Ppo)_2.H_2O$, $Fe(Ppo)_2.2py$ and $Fe(po)_2.H_2O$ were found to be high spin. This property contrasts the behaviour of iron(II) complexes derived from 2-nitrosophenols, which are low spin, and is rationalised in terms of conjugation effects and the bonding character of the pyrazol-4,5-dione monooxime ligand.

The interaction of $Cu(mnr)_2.2py$ with triphenylphosphine gave several products including a phenoxazinone and a novel phenoxazinone phosphorus ylid whose structure was elucidated by X-ray crystallography. The complex $Cu(6\text{-}Memnr)_2.2py$ behaved similarly towards triphenylphosphine. The synthetic significance of these reactions is discussed.

Kinetic studies on the reaction between triphenylphosphine and $Cu(mnr)_2.2py$ indicate that adduct formation takes place initially. It is suggested that subsequent deoxygenative decomposition of this adduct leads to the products. Attempts to clarify the proposed mechanism through the use of insoluble polymer supports were not fruitful.

Acknowledgments

May I express my sincere thanks for the guidance and encouragement given to me (and patience shown!) by my supervisors Dr John Charalambous and Dr Ian Haines.

Also my thanks are due to Dr Kim Henrick of The Polytechnic of North London, and Dr Ernst Egert of The University Chemical Laboratory, Cambridge, for their invaluable assistance in the solution of the crystal structure.

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CONTENTS

INTRODUCTION

2-Nitrosophenols, their derivatives and their metal complexes pose some interesting structural problems and have shown considerable promise as substrates for syntheses and catalysis. Their chemistry has been the subject of extensive current investigations both within these laboratories and elsewhere.

This thesis extends the work on 2-nitrosophenols to include nitrosoresorcinols with particular attention to the synthesis and reactions of monomeric and polymeric metal complexes derived from them. Furthermore the work contrasts these results with those obtained for the related pyrazol-4,5-dione monooxime ligands.

2-Nitrosophenols, mononitrosoresorcinols and pyrazol-4,5-dione monooximes exhibit tautomeric behaviour and thus the nomenclature of these compounds varies and may appear confusing. It should be noted that throughout this thesis both the terms 'nitrosophenol' and 'quinoneoxime' are freely used. This does not necessarily imply that the particular compound possesses one structure or the other, or exists in that form. When only one structure is being discussed attention will be drawn to it in the text. For the convenience of the reader the list below summarises the common abbreviations used for the compounds in this thesis.

poH	3-methyl-4-oxime-1H-pyrazol-4,5-dione
PpoH	3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione
mnrH	5-hydroxy-2-nitrosophenol
6-MemnrH	5-hydroxy-6-methyl-2-nitrosophenol

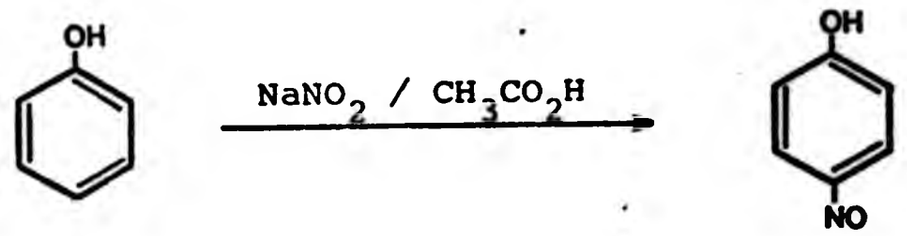
$dnrH_2$	2,4-dinitrosoresorcinol
$M(L)_n$	Metal complex derived from one of the above ligands.

CHAPTER 1

METAL COMPLEXES OF NITROSORESORCINOLS AND THEIR DERIVATIVES

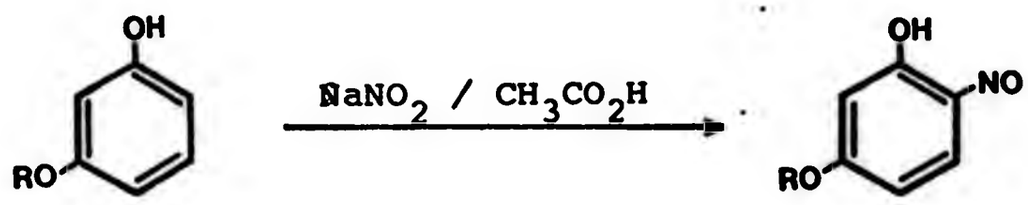
1.1 Introduction

The reaction of a phenol with a mixture of sodium or potassium nitrite and glacial acetic acid, usually gives the corresponding 4-nitrosophenol (Reaction 1)[1,2].



Reaction 1

2-Nitrosophenols are formed in certain cases only, e.g. when a 5-alkoxyphenol is nitrosated (Reaction 2)[3-6]



R = alkyl

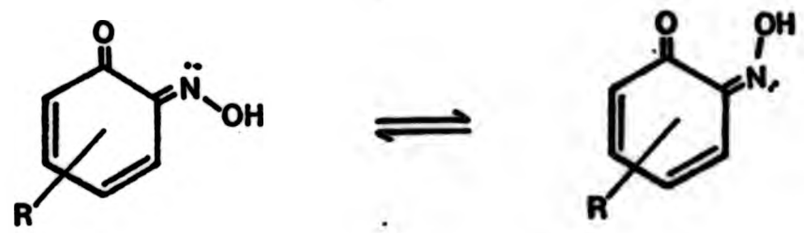
Reaction 2

4-Nitrosophenol has been obtained in a colourless form and a yellow form. It has been suggested that in solution 4-nitrosophenol exists in a tautomeric equilibrium involving

the nitrosophenolic and quinoneoximic structures (1a) and (1b).Similar behaviour is shown by other 4-nitrosophenols.[7]

(1a) (1b)

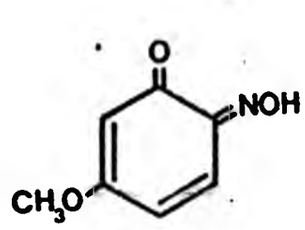
In the case of 2-nitrosophenols, in addition to the quinoneoximic - nitrosophenolic tautomerism, there is also the possibility of geometrical isomerism in the oxime form (2a) and (2b). Henrich and Eisenach[8] prepared



(2a) (2b)

5-methoxy-2-nitrosophenol and found that it could be recrystallised from benzene as green plates or from alcohol as brown needles. The two forms have different melting points. The former melts at 128°C while the latter has a melting point of 145°C. The green product slowly converts

to the brown at room temperature and more rapidly at elevated temperatures. In solution both forms give identical ultra violet and visible spectra. Henrich ascribed the brown form to the quinoneoxime structure (3a) and the

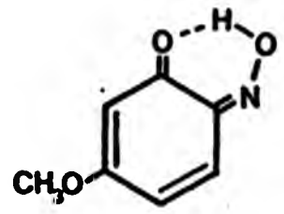


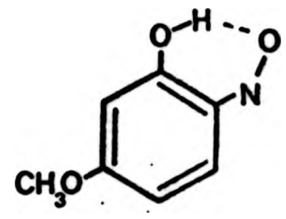
(3a)

(3b)

yellow modification to the nitrosophenolic structure(3b). By analogy to 4-nitrosophenol, a tautomeric equilibrium for 5-methoxy-2-nitrosophenol between the nitrosophenolic and quinoneoximic structures was suggested.

Burawoy et. al.[7] found that the X-ray powder photographs of the green and brown forms of 5-methoxy-2-nitrosophenol were different but that their solution electronic spectra were identical. The spectra showed absorbtions that were characteristic of both the nitroso and the oximic forms. They concluded that in solution 5-methoxy-2-nitrosophenol shows a solvent dependent tautomeric equilibrium between the intramolecularly hydrogen-bonded species (4a) and (4b). Several X-ray





(4a) (4b)

crystallographic studies of the two forms of 5-alkoxy-1,2-benzoquinone-2-oximes have been undertaken.[9-11] Bartindale et. al.[9] established that the structure of 5-methoxy-2-nitroso-phenol was essentially quinoneoximic and that the oximic oxygen was in an anti configuration with respect to the quinonic oxygen (Figure 1)

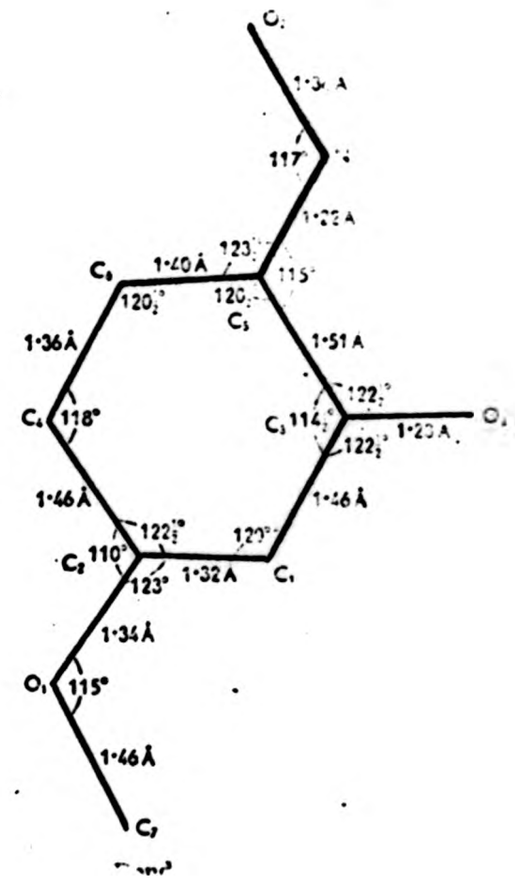
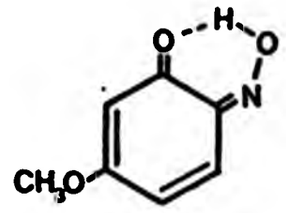
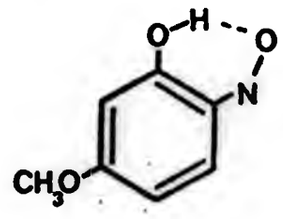


Figure 1





(4a) (4b)

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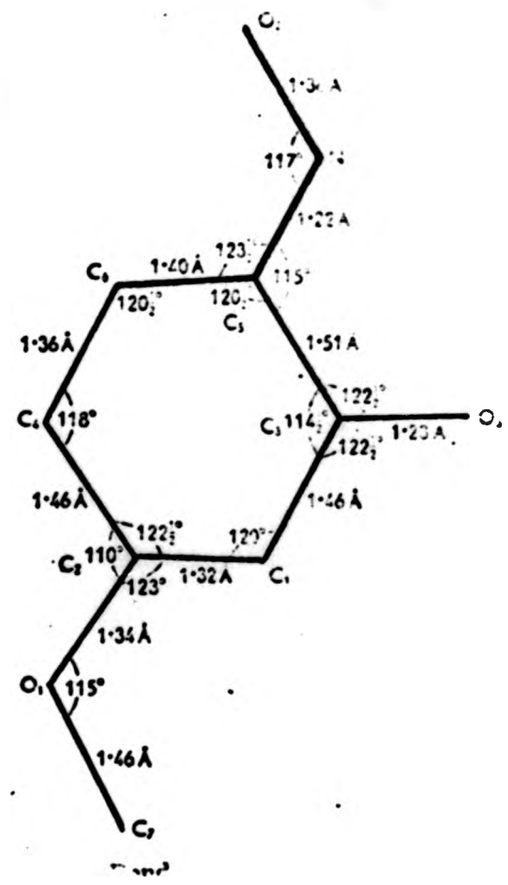
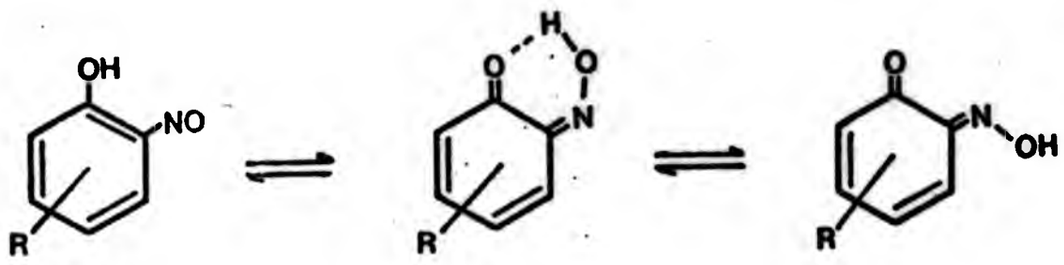


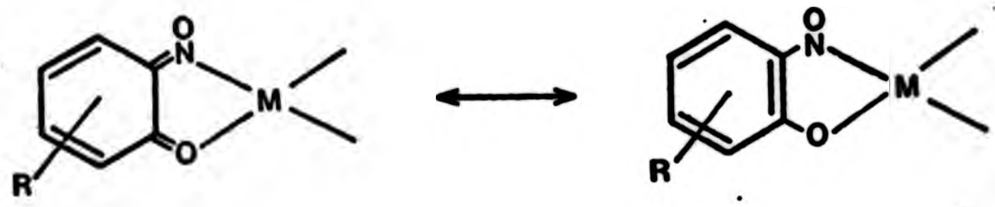
Figure 1

On the basis of the above, the 2-nitrosophenol/ 1,2-benzoquinone monooxime system is best described as shown in Scheme 1.



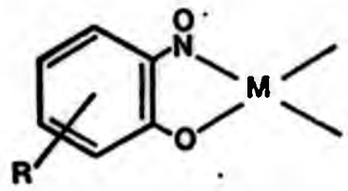
Scheme 1

The chelate compounds formed by replacing the acidic proton in this tautomeric system by a metal may be represented in valence bond terms as involving resonance between structures (5a) and (5b). Recent X-ray studies

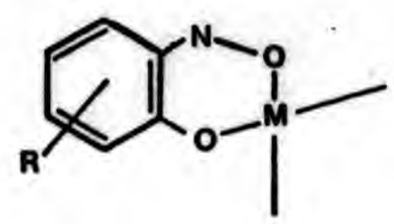


(5a) (5b)

of a number of 2-nitrosophenol complexes[12-16], indicate that the contribution of the quinoneoximic structure (5a) is significant. In addition to the tautomeric structures (5a) and (5b), the possibility arises that within each structure the ligand may be coordinated to the metal via the nitrogen atom (N-bonded) or the oxygen atom (O-bonded). These structures are exemplified by (6a) and (6b)



(6a)



(6b)

respectively. However for all the compounds investigated, X-ray crystallography has established that the mode of bonding of the NO group to the metal is through the nitrogen atom. For example studies on bis(4-methyl-2-nitrosophenol) copper(II)-monopyridine[15] and ferroverdin[16] (Figures 2 and 3)

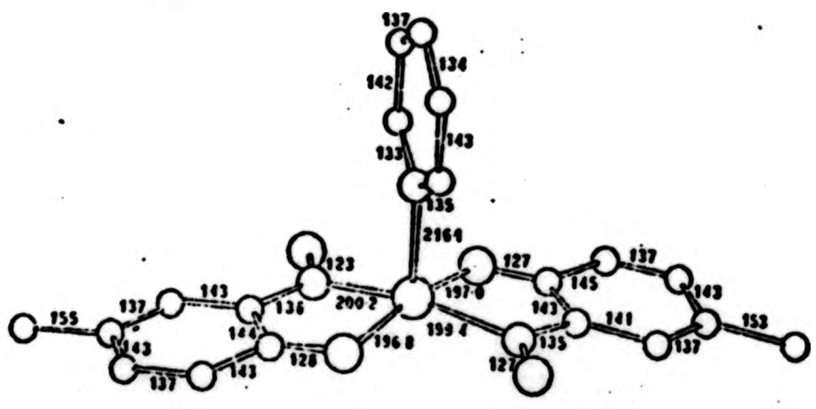


Figure 2

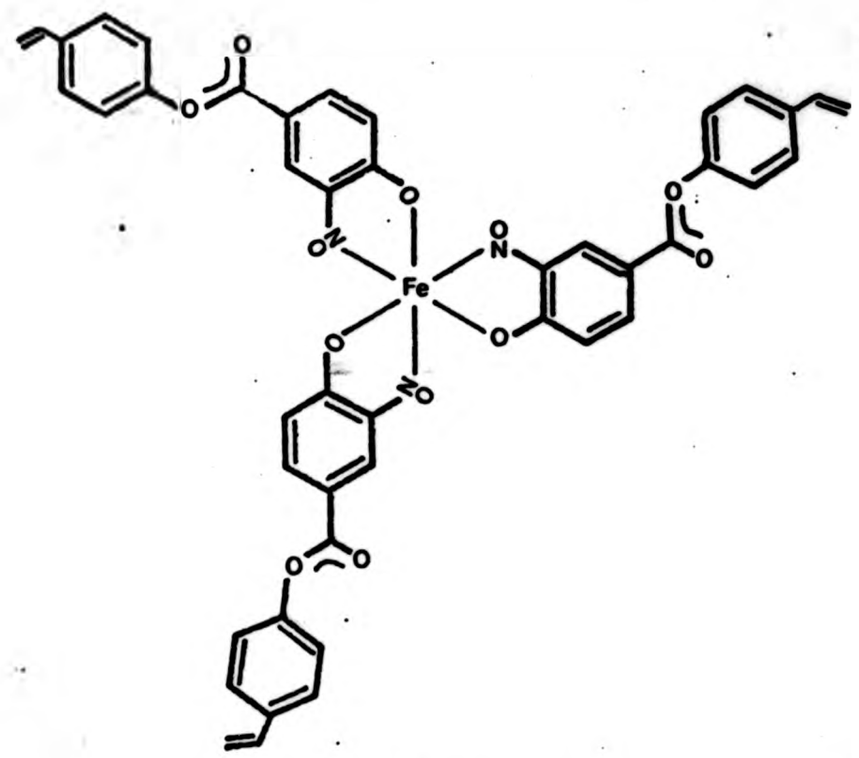


Figure 3

indicate this mode of bonding.

2-Nitrosophenols and their derivatives readily afford metal complexes. The reactions resulting in complex formation may be classified into four groups: a) the direct method, b) the nitrosation method, c) the Baudisch reaction, d) the interaction with metal carbonyls.

The direct method involves the interaction of a 2-nitrosophenol with a metal salt (Reaction 3). This method

$$M^{n+} + n\ qoH \longrightarrow M(qo)_n$$

(qoH = a 2-nitrosophenol)

Reaction 3

has limited applicability since only relatively few 2-nitrosophenols are readily available (Table 1)[17-20]

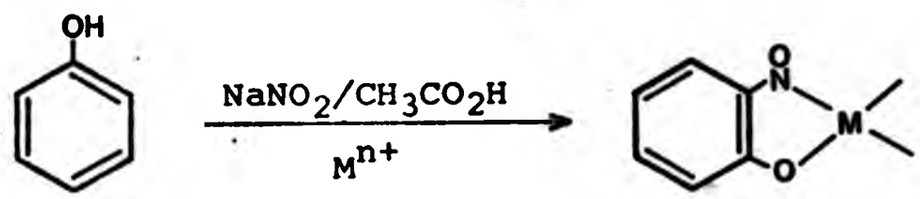
Table 1 Metal complexes of 2-nitrosophenols prepared by the direct method

2-Nitrosophenol	Metal	Proposed formulation	Data reported	Applications	Ref.
5-Methoxy-2-nitrosophenol	Fe(II)	$Fe(qo)_3$	Elemental analyses	Dyes	18
	Cu(II)	$Cu(qo)_2$	Elemental analyses		34
	Ni(II)	$Ni(qo)_2$	Elemental analyses		34
	Zn(II)	$Zn(qo)_2$	Elemental analyses		42
4-Methyl-2-nitrosophenol	Fe(II)	$Na[Fe(qo)_3]$	Elemental analyses. Mössbauer data	Dyes	43
	Cu(II)	$Cu(qo)_2$	Elemental analyses X-ray.		42
1-Nitroso-2-naphthol	Fe(II)	$Fe(qo)_3$	Elemental analyses	Analytical	17
	Cu(II)	$Cu(qo)_2$	Elemental analyses X-ray		35

Table 1 continued

2-Nitrosophenol	Metal	Proposed formulation	Data reported	Applications	Ref.
1-Nitroso-2-naphthol	Zn(II)	$Zn(qo)_2$	Elemental analyses		35
	Co(III)	$Co(qo)_3$	Elemental analyses		
	Fe(III)	$Fe(qo)_3$	Elemental analyses Mössbauer data UV/Vis. spectra	Analytical	22
2-Nitroso-1-naphthol	Fe(III)	$Fe(qo)_3$	Elemental analyses	Analytical	17
	Cu(II)	$Cu(qo)_2$	Elemental analyses		35
	Zn(II)	$Zn(qo)_2$	Elemental analyses.		35

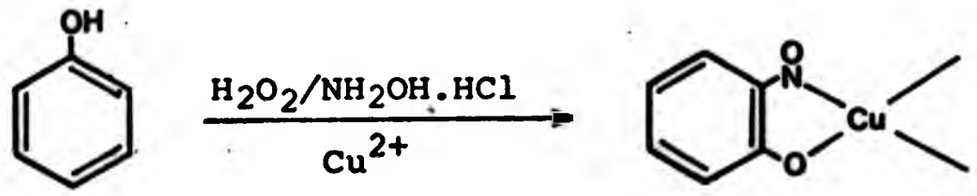
The nitrosation method involves the nitrosation of a phenol, using sodium or potassium nitrite and glacial acetic acid, in the presence of a transition metal salt (Reaction 4). This method was first reported by Cronheim[21]



Reaction 4

and later modified by Charalambous et. al.[22], to prepare a number of copper(II), nickel(II), iron(III) and cobalt(III) complexes.

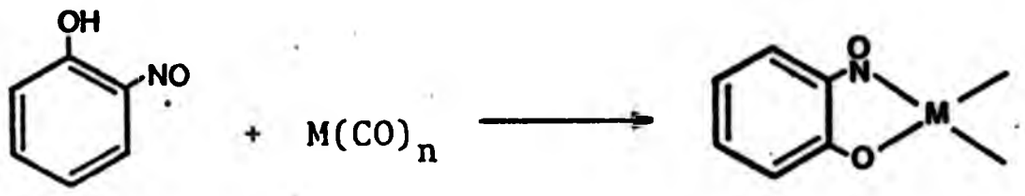
The Baudisch method involves the oxidative action of hydrogen peroxide and hydroxylamine hydrochloride on a phenol in the presence of a copper(II) salt (Reaction 5).



Reaction 5

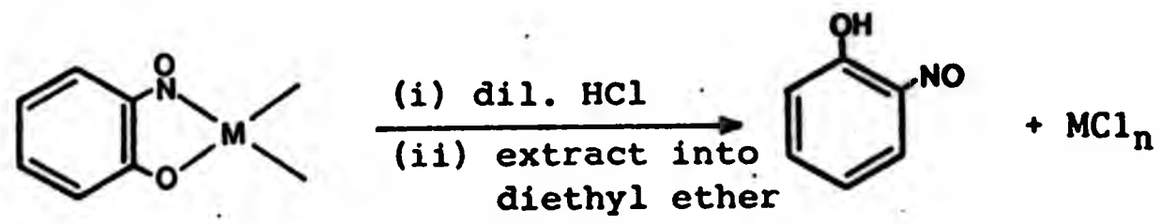
However no analytical and limited preparative data were presented and the work must be treated with some scepticism.[23-25]

Metal complexes of 2-nitrosophenols and their derivatives may be obtained from the reaction of the ligand with a metal carbonyl (Reaction 6). The development of this method is currently receiving attention[26-28] (see also Chapter 4).



Reaction 6

In some cases the free ligand has been obtained by the acidification of a solution or suspension of the metal complex and extraction into a suitable solvent (Reaction 7), thus revealing the position of nitrosation.

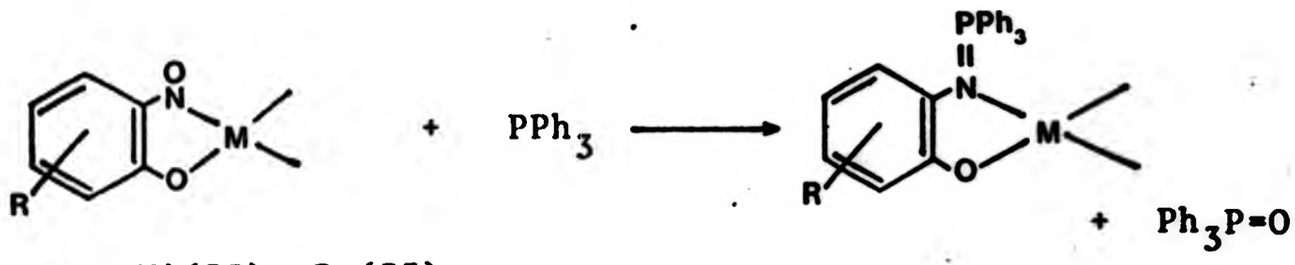


Reaction 7

Many metal complexes of 2-nitrosophenols have been employed for analytical purposes and are still widely used in this context.[29-31] A number have found use in the paint and dye industry; e.g the sulphonated derivatives of the iron(III) complexes derived from 1-nitroso-2-naphthol and 2-nitroso-1-naphthol, have found extensive use in the dye industry.[32] In addition metal complexes derived from

2-nitrosophenols have considerable synthetic potential.[33-35]

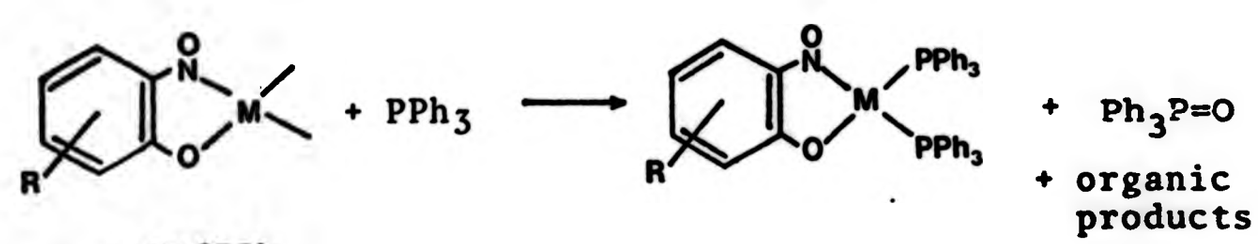
Charalambous and his coworkers[34] have studied the interaction of triphenylphosphine with various copper(II), nickel(II), zinc(II), iron(II) and iron(III) complexes of 2-nitrosophenols and their derivatives. Nickel(II) and zinc(II) complexes produced an iminophosphorane complex (Reaction 8). However when a copper(II) complex was used, reduction of the metal occurred with the formation of a



M = Ni(II), Zn(II)

Reaction 8

triphenylphosphine adduct and a dihydroxyphenazine (Reaction 9). If an iron(III) complex is used, a phenazine is again formed, however no trace of a triphenylphosphine adduct is detected. In addition general routes to phenoxazines,



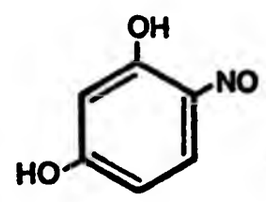
M = Cu(II)

Reaction 9

phenoxazinones and substituted phenoxazinones have been established - see Section 3.1.[36]

1.2 The mono- and di-nitrosation of resorcinol.

The nitrosation of resorcinol may lead to either mono and/or dinitroso derivatives. The nature of the products depends of the ring substituents and the reaction conditions used. For example resorcinol gives 5-hydroxy-2-nitrosophenol (7) and 2,4-dinitrosoresorcinol (8). These compounds will be abbreviated as mnrH and $dnrH_2$



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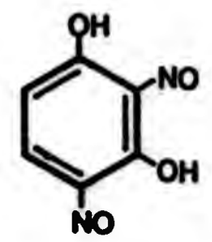
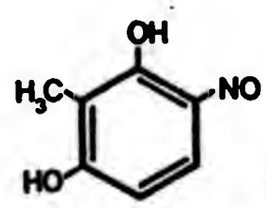


(8)

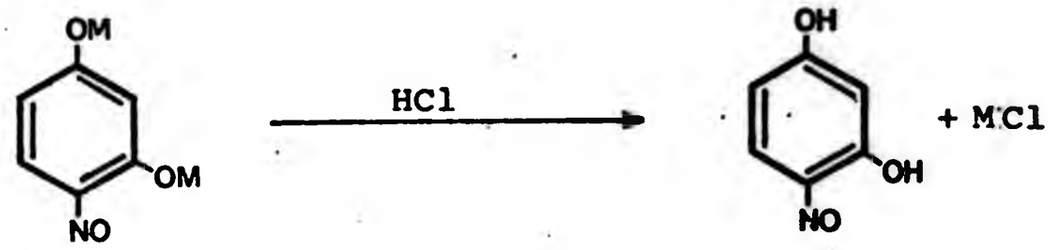
respectively. In the case of 2-methylresorcinol only the mononitroso- derivative, 5-hydroxy-6-methyl-2-nitrosophenol (9) [6-MemnrH] has so far been isolated.



(9)

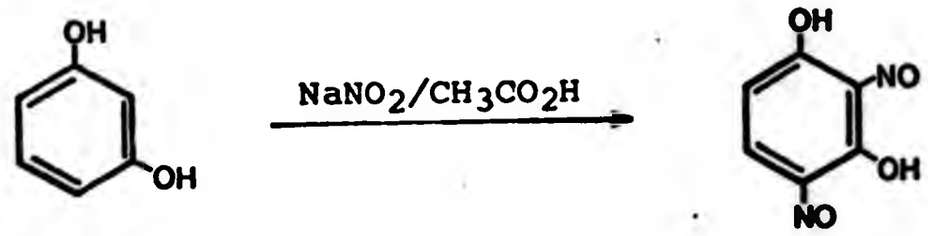
The mononitrosation of resorcinol is achieved by the action of amyl nitrite on resorcinol in alkaline ethanol at ca. -10 ^{o}C.[36] The reaction leads to a disodium or

dipotassium salt of 5-hydroxy-2-nitrosophenol, which on acidification gives the free nitroso compound (Reaction 11).



Reaction 11

If the reaction is carried out at, or above ambient temperature, dinitrosation is achieved. Dinitrosation also results if resorcinol is treated with a mixture of sodium nitrite and glacial acetic acid (Reaction 12).[37]



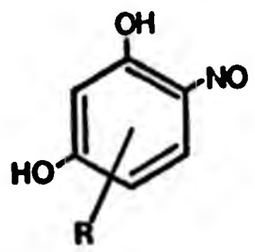
Reaction 12

Both the mono- and di-nitrosoresorcinols show tautomeric behaviour and readily form metal complexes.[38-40] These aspects have been examined during this study and are discussed in the following sections.

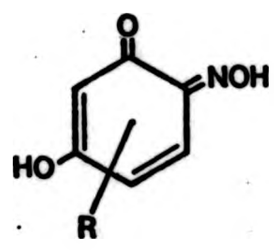
1.3 Structural studies of 5-hydroxy-2-nitrosophenol (mnrH) and 5-hydroxy-6-methyl-2-nitrosophenol (6-MemnrH)

As described in Section 1.1, 2-nitrosophenols exhibit a complex tautomeric equilibrium that is solvent dependent and involves quinoneoximic and nitrosophenolic tautomers (Scheme 1). Several X-ray crystallographic studies have indicated that in the solid state 2-nitrosophenols are primarily quinoneoximic in character.

In the case of 5-hydroxy-2-nitrosphenol (mnrH) or 5-hydroxy-6-methyl-2-nitrosophenol (6-MemnrH), analogous behaviour is expected involving the nitrosophenolic tautomer (10a) and the quinoneoximic tautomer (10b). In addition a

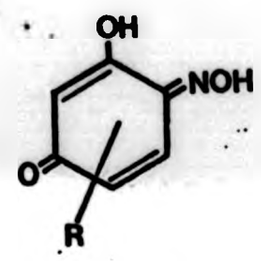


(10a)



(10b)

contribution from the 1,4-benzoquinonemonooxime tautomer(11) is also possible. In order to investigate this tautomeric behaviour, the i.r., n.m.r. and mass spectra of 5-hydroxy-



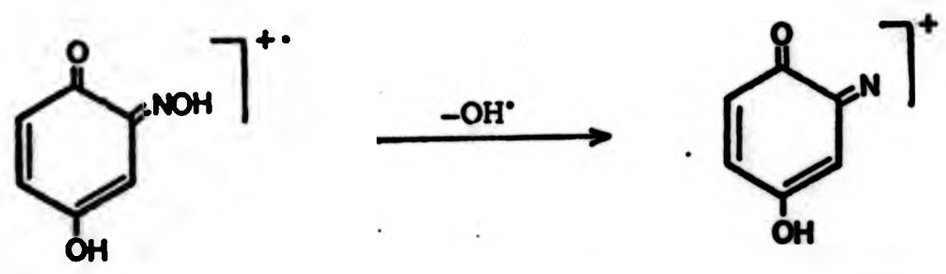
(11)

-2-nitrosophenol and 5-hydroxy-6-methyl-2-nitrosophenol have been investigated.

a) Mass spectra.

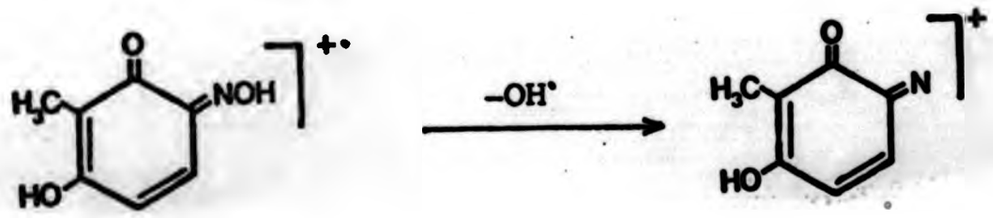
The mass spectra of mnrH and 6-MemnrH are illustrated in Figures 4 and 5 respectively. Both show intense molecular ions which correspond to the base peaks. For each compound the spectra were independent of temperature suggesting either an absence of a tautomeric equilibrium between the unionised molecules or a low enthalpy change for the isomerisation in the vapour state.

For each compound the molecular ion fragments by loss of $OH^{\bullet}$. This loss is metastable supported and can be accounted for in terms of a quinoneoximic molecular ion (Schemes 2 and 3)



m/e 139 m/e 122

Scheme 2



m/e 153 m/e 136

Scheme 3

Figure 4 Mass spectrum of mnrH

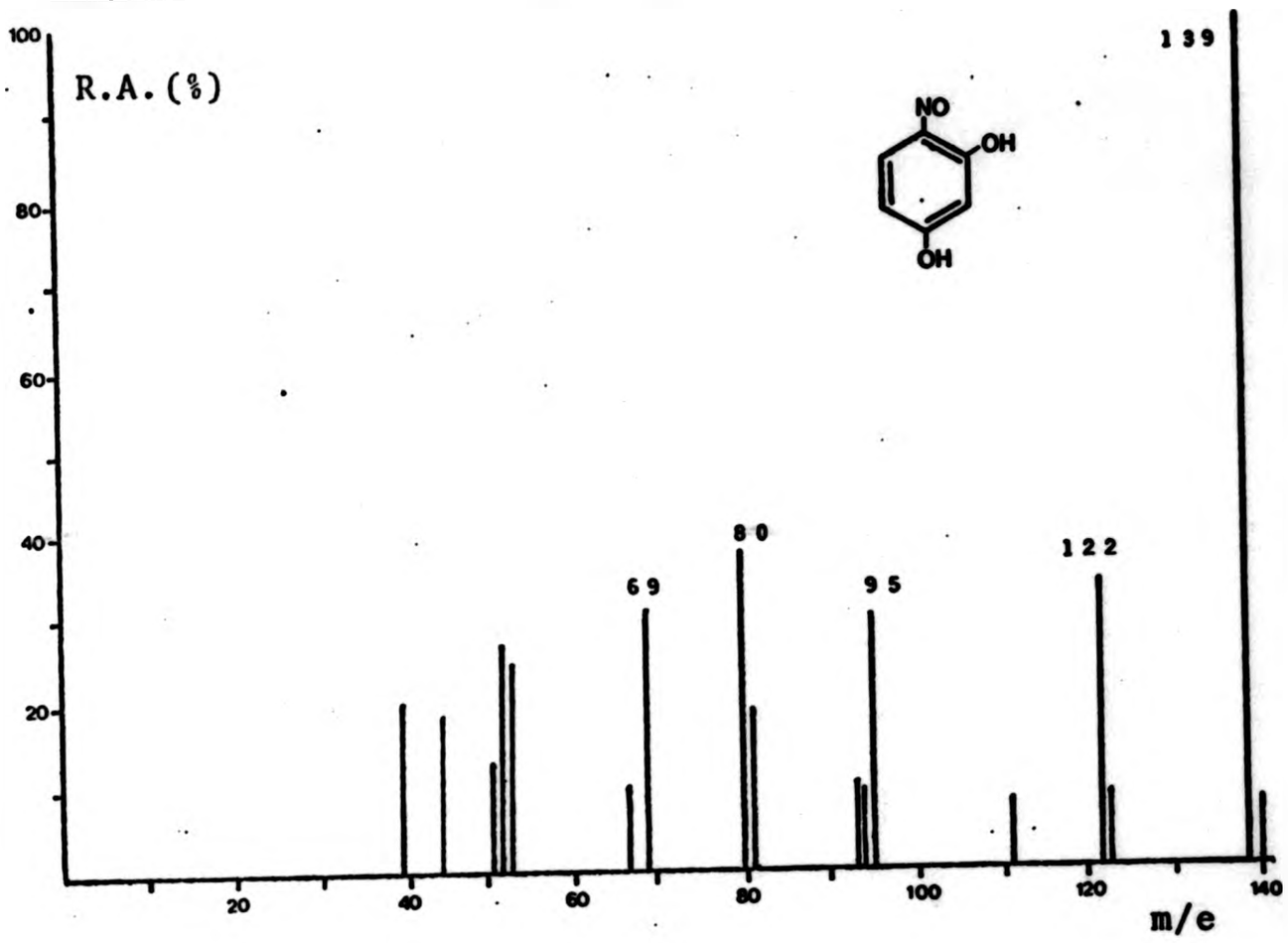
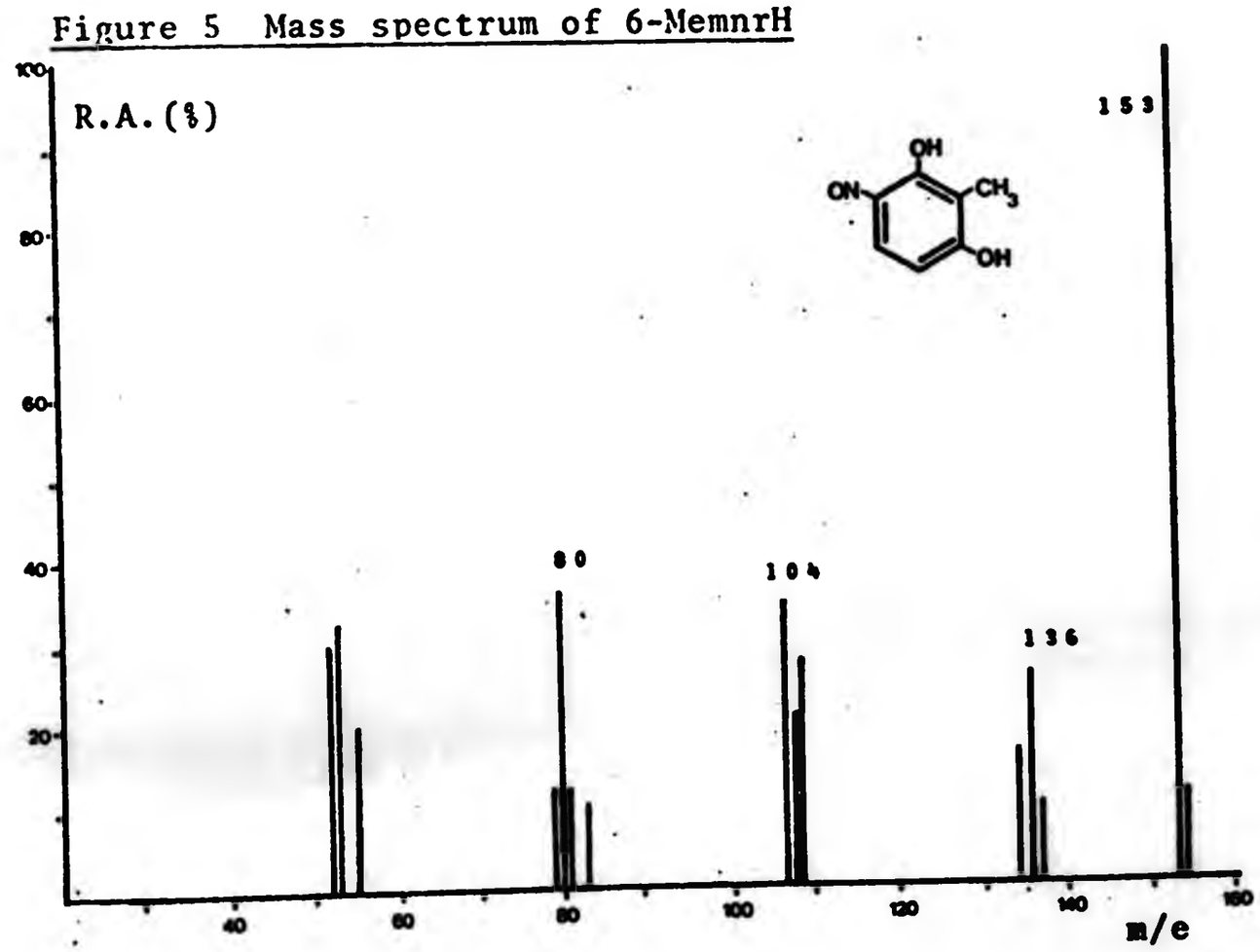
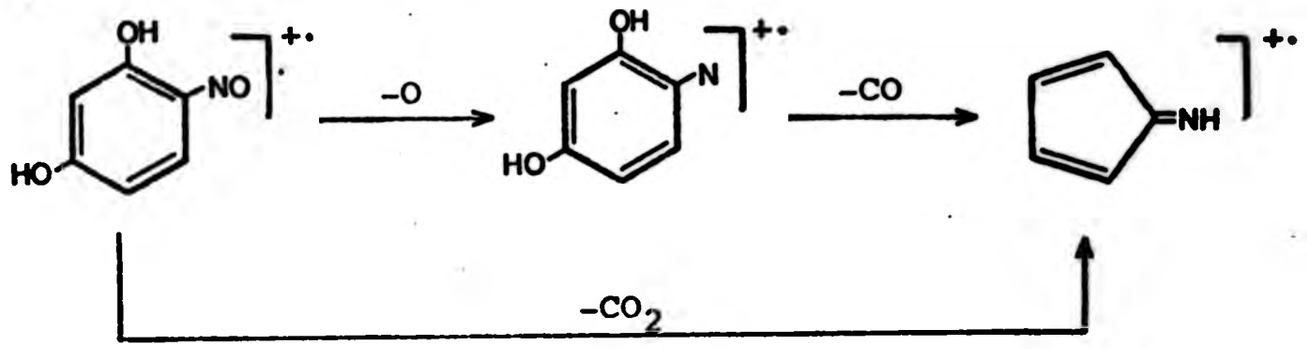


Figure 5 Mass spectrum of 6-MemnrH



This suggestion is in accord with the readiness of the molecular ions of various oximes to fragment by loss of $OH^{\bullet}$.

The spectra of both compounds contain ions that correspond to the loss of O and CO_2 from the molecular ion and are metastable supported (Scheme 4). These fragmentations



Scheme 4

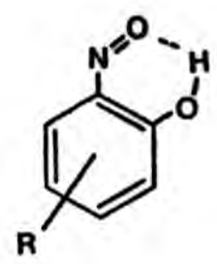
can be rationalised in terms of the nitrosophenolic structure (11b). However nitroso compounds usually fragment by facile loss of NO . In accord with the spectrum of 5-methoxy-2-nitrosophenol, mnrH and 6-MemnrH do not show loss of NO, a feature which is present in the spectra of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol.[41]

b) N.m.r. spectra

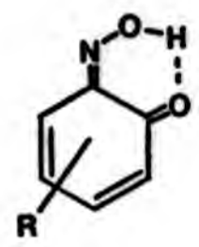
i) ^1H n.m.r.

The ^1H n.m.r and i.r. spectra of nitrosophenols, nitrosonaphthols and their derivatives have been investigated by several workers.[44-46] They proposed that these compounds exhibit a solvent dependent equilibrium with the oxime tautomer predominating. For both the oxime and nitroso

tautomers, a chelated, intramolecularly hydrogen bonded structure was proposed (12a) and (12b).

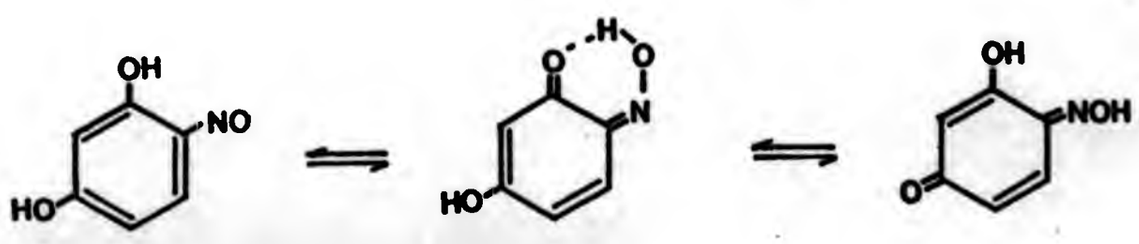


(12a)



(12b)

The ^1H n.m.r. spectra of 5-hydroxy-2-nitroso-phenol and 5-hydroxy-6-methyl-2-nitrosophenol are given in Figures 6 and 7. The spectrum of mnrH shows three aromatic protons at 5.7 p.p.m., 6.2 p.p.m. and 7.5 p.p.m.. The latter two protons split each other with a coupling constant of approximately 10 Hz. There are two exchangeable protons at 11.4 p.p.m. and 13.8 p.p.m.. There are several tautomeric structures available to 5-hydroxy-2-nitrosophenol, for example (13a), (13b) and (13c). From the ^1H n.m.r. evidence



(13a) (13b) (13c)

Figure 6. ^{1}H n.m.r. spectrum of mnrH

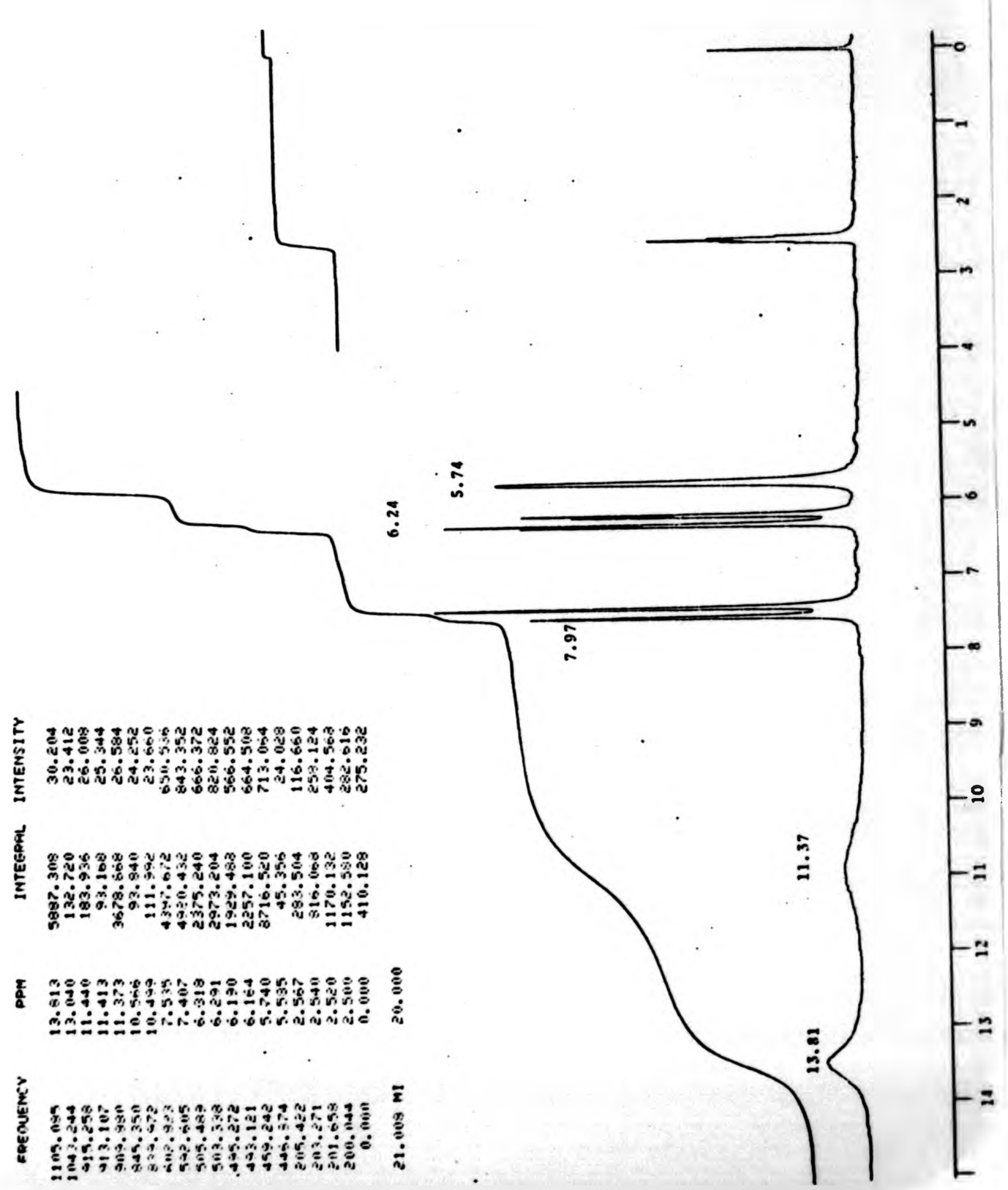
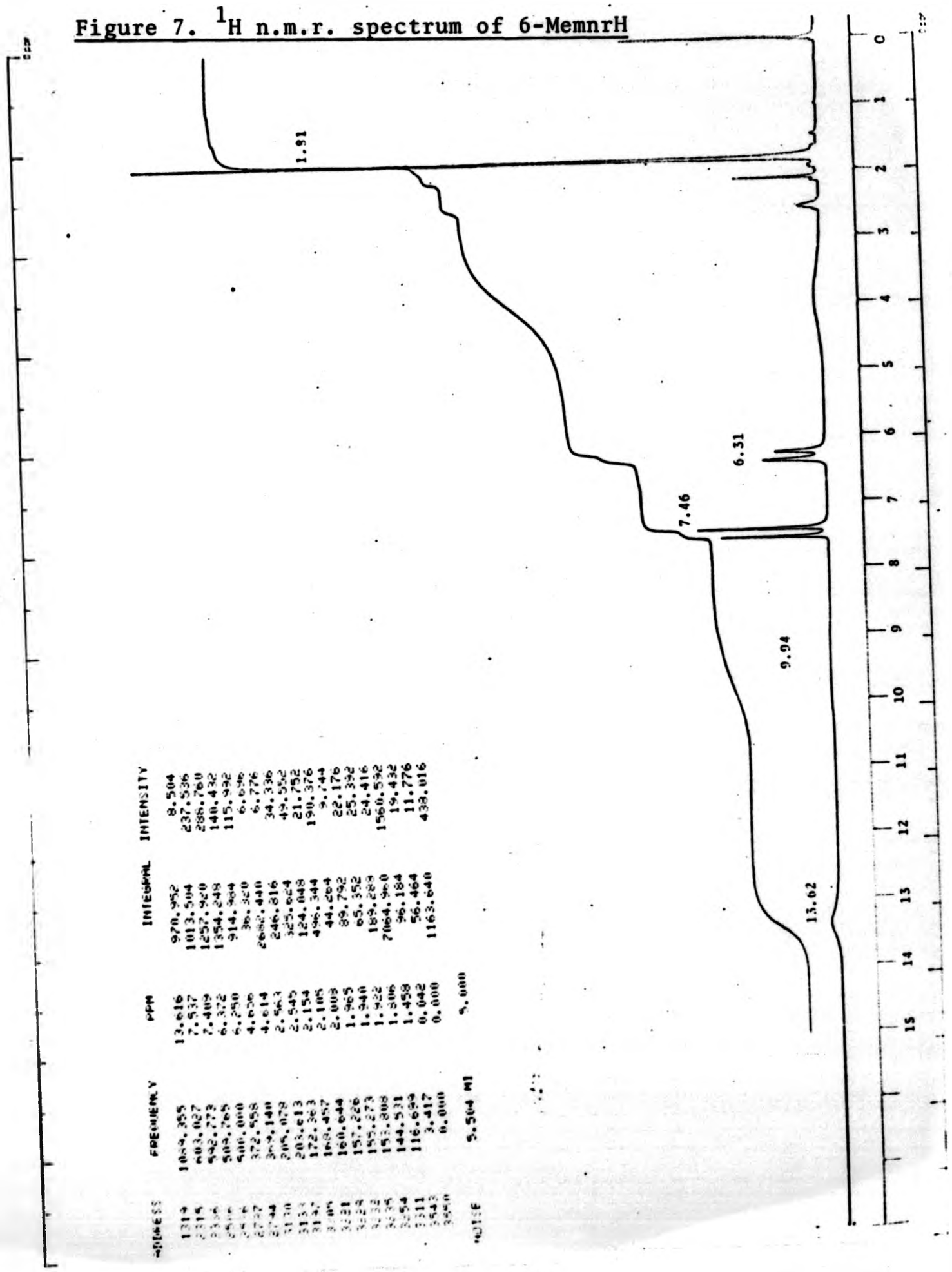
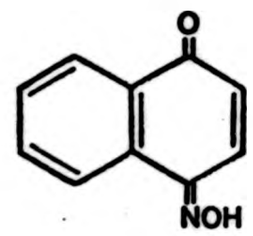


Figure 7. ^{1}H n.m.r. spectrum of 6-MemnrH



tautomer (13a) may be excluded since in this structure both exchangeable protons are hydroxylic and would be expected to have similar chemical shifts. Of the two remaining tautomers, (13b) is thought to be the most likely structure since it is able to form an intramolecular hydrogen bond between the oximic proton and the adjacent quinonic oxygen atom.
The peak at 13.8 p.p.m. disappears on shaking with D_2O and is assigned to the oximic proton. This value compares with a value of 13.5 p.p.m. observed for the analogous proton in 1,4-naphthoquinone-4-oxime[47] (14). The remaining exchangeable



(14)

proton at 11.4 p.p.m. can therefore be only due to the hydroxylic proton.

The ^1H n.m.r. of 6-MemnrH (Figure 7) also shows two exchangeable protons at 13.6 p.p.m. and 9.9 p.p.m. which are assigned to the oximic and hydroxylic protons respectively. In addition two coupled aromatic protons (J = 10 Hz) appear at 6.3 p.p.m. and 7.5 p.p.m., and the methyl group at 1.8 p.p.m.. These observations are similar to that those made for mnrH, and are consistent with an intramolecularly hydrogen bonded molecule in solution.

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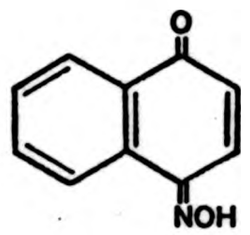

(14)

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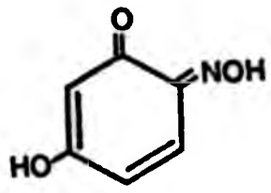
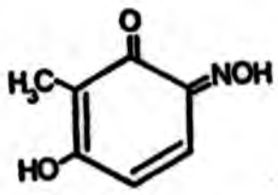
ii) ^{13}C N.m.r.

The ^{13}C n.m.r. of mnrH and 6-MemnrH have been examined and the results are presented in Table 2. There is no

Compound	Broad band proton decoupled (p.p.m.)	Single frequency off resonance decoupled (ppm)
 mnrH	105.6 122.8 128.8 146.4 163.6 184.6	105.9(s) 123.0(d) 127.3(d) 146.6(s) 163.9(s) 183.8(s)
 6-MemnrH	7.5 115.0 122.0 135.0 146.4 161.9 189.1	7.5(q) 115.0(s) 122.1(d) 131.0(d) 146.0(s) 160.0(s) 189.3(s)

Key: s=singlet, d=doublet, q=quartet.

Table 2 ^{13}C n.m.r. spectra of mnrH and 6-MemnrH in CD_3OD.

evidence of a tautomeric mixture in methanol and the spectra have been assigned on the basis of a quinoneoximic structure.

The broad band proton decoupled spectrum of mnrH and 6-Memnrh show six and seven carbon sites respectively. In the case of 6-MemnrH, the methyl and two of the aromatic carbon atoms may be assigned on the evidence provided by the off-resonance decoupled spectrum in which the methyl signal is expanded to a quartet, and each singly protonated aromatic carbon atom to a doublet. All other signals remain unsplit. These remaining signals comprising the oximic, quinonic, hydroxylic and methyl-substituted carbon atoms were assigned by comparison of shift data for similar compounds. Thus the signal at 189.1 p.p.m. is assigned to the quinonic carbon atom which compares with a value of 187 p.p.m. in 1,4-benzoquinone.[48] The signal at 161.9 p.p.m. is assigned to the oximic carbon atom and compares with a value of 159.4 p.p.m. for the oximic carbon atom in cyclohexanonemonooxime.[49] The remaining unassigned upfield signal at 146.4 p.p.m. is therefore due to the hydroxylic carbon atom. The methyl-substituted carbon atom which is unaffected by off-resonance decoupling is at 115.0 p.p.m.

The ^{13}C n.m.r. of mnrH was assigned similarly and the results are given in Table 2.

1.4 The nature of the complexes derived from mononitroso- resorcinols and dinitrosoresorcinols.

As noted in the previous section, mononitroso- and dinitrosoresorcinols exhibit a tautomeric equilibrium involving nitrosophenolic and quinonoximic tautomers.

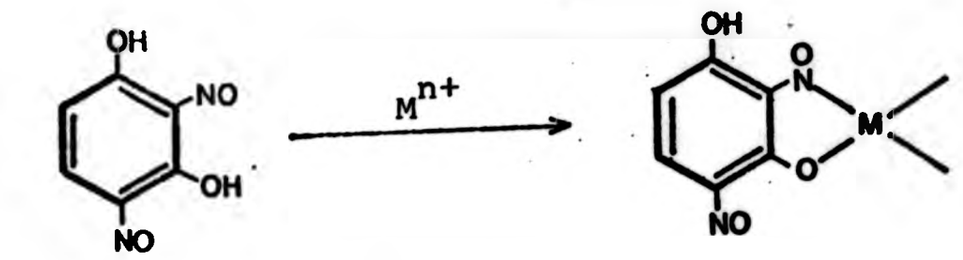
The chelate compounds formed by replacing the acidic hydrogen in 5-hydroxy-2-nitrosophenol (mnrH) and 5-hydroxy-6-methyl-2-nitrosophenol (6-MemnrH) by a metal can be represented in valence bond terms as involving resonance between structures (15a) and (15b). Such complexes

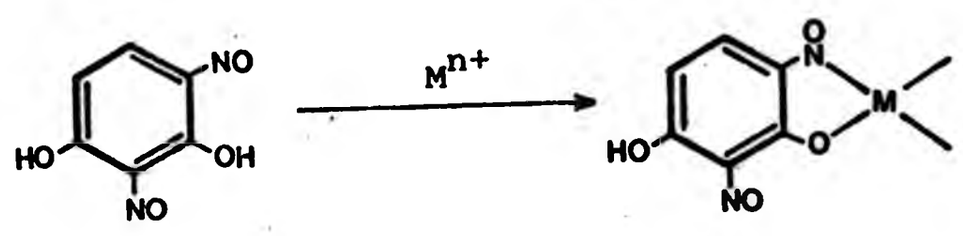
R=H, CH_3

(15a) (15b)

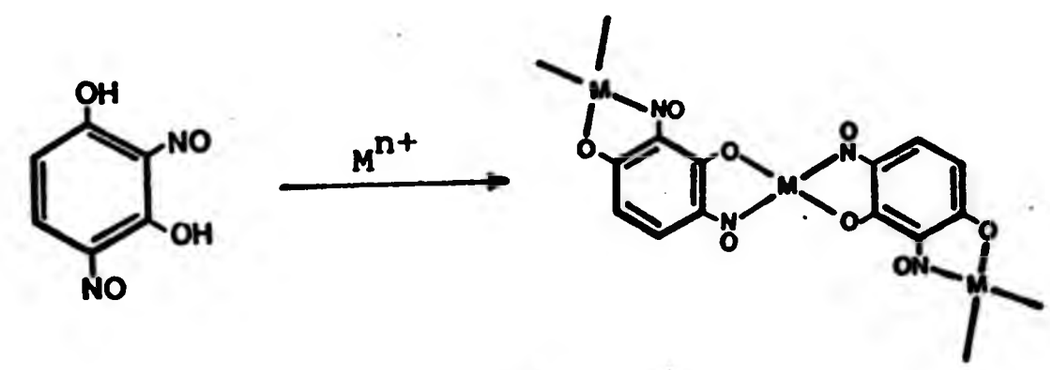
have been used for the quantitative determination of cobalt, copper, nickel and iron[50], however their properties and structure have not been investigated systematically.

2,4-Dinitrosoresorcinol may lose one acidic hydrogen to give, for example with a divalent metal, complexes of type $M(dnrH)_2$ containing the monoanion $dnrH^-$ (Reaction 13). However no complexes of this type have as yet been isolated. Alternatively 2,4-dinitrosoresorcinol may lose both acidic hydrogens to form a coordination polymer containing the catenating dianion dnr^{2-} (Reaction 14).



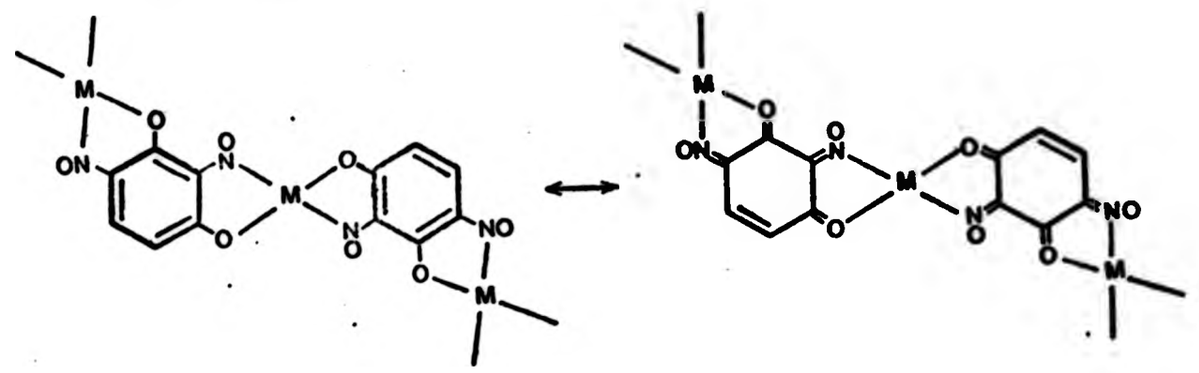


Reaction 13



Reaction 14

The structure of such a coordination polymer may be represented in valence bond terms as a resonance hybrid of structures (16a) and (16b). Although some of these compounds have found uses as dyes[51] and analytical reagents



(16a) (16b)

the formation and study of their properties and structure as so far received limited attention.[38-40]

1.5 A study of the complexing behaviour of 5-hydroxy-2-nitrosophenol and 5-hydroxy-6-methyl-2-nitrosophenol towards copper(II) and iron(II)

When 5-hydroxy-2-nitrosophenol (2 mol. equiv.) and copper(II) chloride (1 mol. equiv.) were mixed in aqueous ethanol a red-brown, non-crystalline, diamagnetic copper compound resulted. A similar product was formed when 5-hydroxy-6-methyl-2-nitrosophenol was used. The diamagnetism of the compounds suggested that they are either copper(I)complexes or copper(II) complexes which have subnormal magnetic moments.[52] The presence of absorbtions in the i.r. spectrum assignable to νOH, and elemental analysis data suggested a formulation such as shown in Figure 6 for the compounds. Further

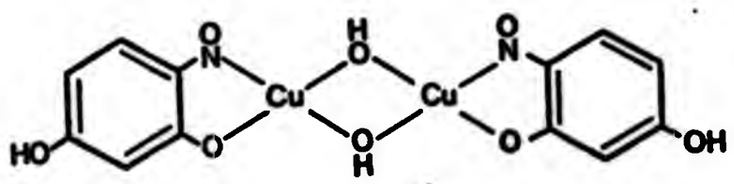


Figure 6

evidence for the suggested formulation is provided by the inertness of the complexes towards pyridine.

Compounds with hydroxy or alkoxy bridges are well known and often show subnormal magnetic moments. For example the dinuclear carboxylato-bridged copper(II) compound

in which there is significant metal-metal interaction leading to a value of $\mu_{eff.}$ of 1.4 B.M. per copper atom at 25 °C (Figure 7)[53]. Another example is the roof shaped cation in di-μ-hydroxy-tetrakis(cyclohexylamino)dicopper(II) perchlorate. (Figure 8)[54]

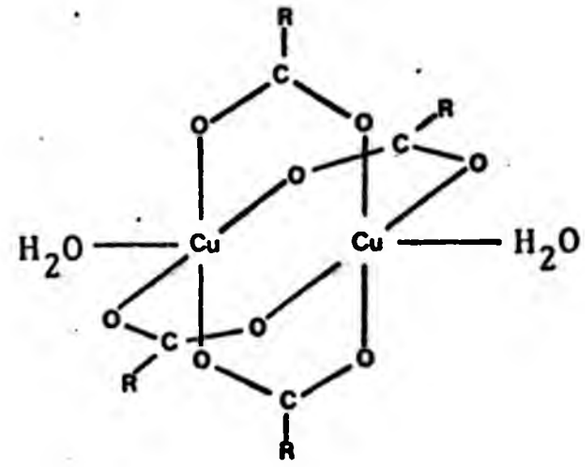
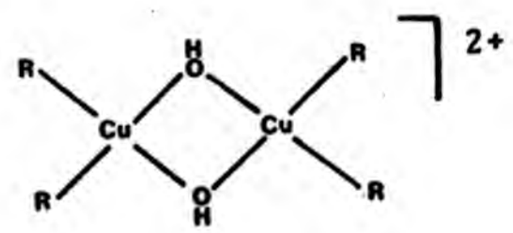


Figure 7



R = cyclohexylamine

Figure 8

The magnetic properties of $[Cu(mnr)OH]_2$ and $[Cu(6\text{-}Memnr)OH]_2$ may be interpreted as interaction (magnetic coupling) of the nominally paramagnetic copper atoms via the bridging hydroxy groups. The mechanism of magnetic coupling has been described previously[55] in terms of overlap of the d orbitals of the metal ions with the s

and p orbitals of the bridging hydroxy groups.

In order to try and obtain the copper(II) bischelate of mnrH and 6-MemnrH the reaction was carried out in a solution buffered to pH 9. This method also gave the hydroxy-bridged compounds. The bischelates were finally prepared in the form of the pyridine adducts, $Cu(mnr)_2.py$ and $Cu(6\text{-}Memnr)_2.py$, by carrying out the reaction using pyridine as solvent. These dark brown non-crystalline solids were characterised by elemental analysis and room temperature magnetic susceptibility measurements. The latter results (ca. 1.7B.M.) are slightly subnormal for magnetically dilute copper(II), and are probably indicative of association in the solid state.

When iron(II) ammonium sulphate (1 mol. equiv.) was treated with 5-hydroxy-2-nitrosophenol (2 mol. equiv.) in aqueous ethanol, a green compound soluble in water, acetone and methanol and insoluble in chloroform and light petrol was formed. Elemental analysis indicated a ratio of three ligand molecules per iron atom suggesting oxidation of iron(II) to iron(III) and formation of an iron(III) trischelate. The compound showed loss of three water molecules per metal atom at approximately 200 ^{o}C, but its involatility precluded a mass spectrometric investigation.

A ^{1}H n.m.r. study of the complex in acetone indicated that it was paramagnetic and this observation was supported by a variable temperature magnetic susceptibility study(Table 3). This showed that the magnetic moment was temperature independent. The value of $\mu_{eff.}$ (2.8 B.M.) at 20 ^{o}C is indicative of low spin iron(III) sites in a distorted

Table 3. Variable temperature magnetic susceptibility measurements on tris(5-hydroxy--1,2-benzoquinone-2-oximato)iron(III)-trihydrate

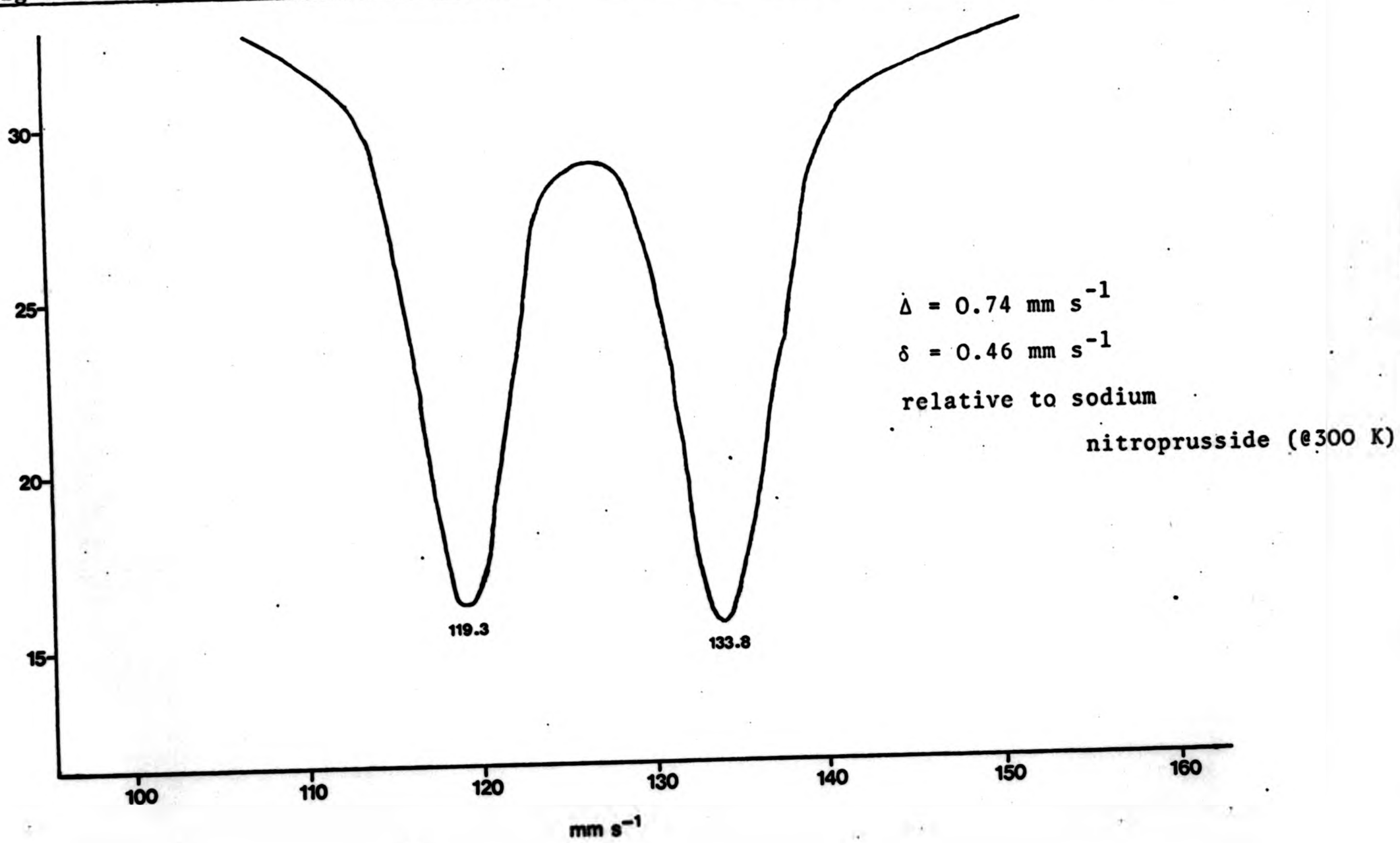
T(K)	363.7	333.7	363.3	292.3	273.1	243.1	213.8	193.3	157.3	123.7
$10^6 \chi_A$	2898	2980	3116	3305	3738	4072	4830	5508	6462	7791
$\mu_{eff.}$(B.M.)	2.90	2.82	2.75	2.54	2.86	2.82	2.87	2.84	2.81	2.77

octahedral crystal field.[56] This proposal is supported by the Mössbauer parameters obtained at room temperature (Figure 9). The value of $\mu_{eff.}$ obtained is consistent with other iron(III) trischelates derived from quinoneoxime type ligands (Table 4)[57]

Compound	Formulation	$\mu_{eff.}$(BM)
1-Nitroso-2-naphthol	$Fe(1\text{-}nqo)_3$	2.21
2-Nitroso-1-naphthol	$Fe(2\text{-}nqo)_3$	2.46
5-Methoxy-2-nitrosophenol	$Fe(5\text{-}MeOqo)_3$	2.11
5-Methyl-2-nitrosophenol	$Fe(5\text{-}Meqo)_3$	2.31
4,5-Dimethyl-2-nitrosophenol	$Fe(4,5Me_2qo)_3$	2.41
Phenthrene-9,10-quinone-monooxime	$Fe(qo)_3$	2.38

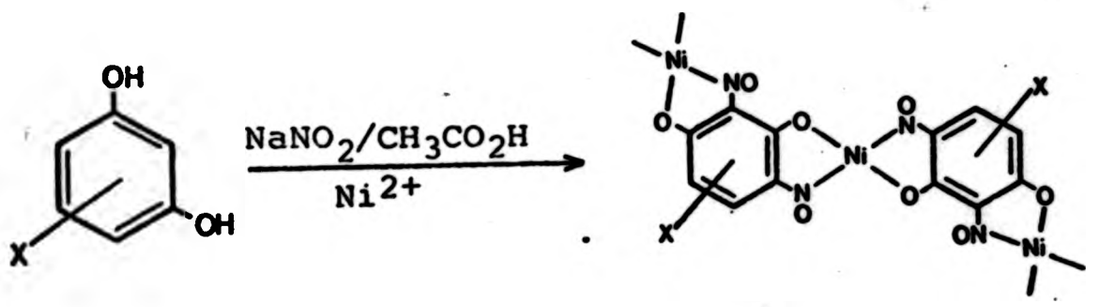
Table 4. Room temperature magnetic moments of iron trischelates derived from quinoneoxime ligands

Figure 9 Mössbauer spectrum of tris(5-hydroxy-1,2-benzoquinone-2-oximato)iron(III)-trihydrate



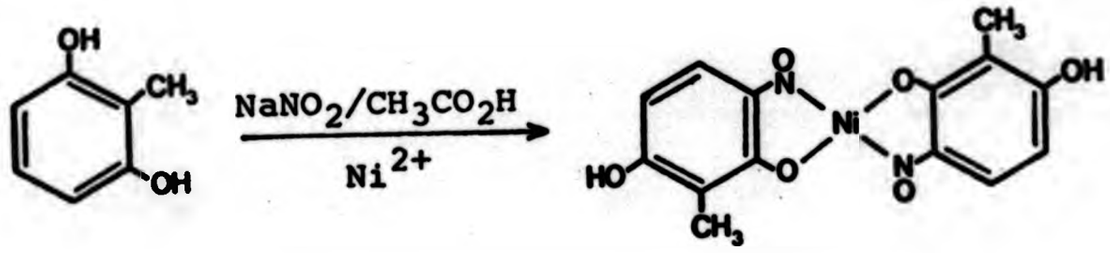
1.6 A study of the complexing behaviour of 2,4-dinitroso resorcinol and its derivatives towards nickel(II) and copper(II)

When resorcinol (1 mol.equiv.) was dinitrosated in the presence of nickel(II) chloride (1 mol. equiv.) a brown, non-crystalline, polymeric complex formulated as $Ni(dnr).H_2O$ was isolated. The analogous complexes $Ni(X\text{-}dnr).2H_2O$ (X = 6-Cl,6-ethyl, 5-methyl) were formed when substituted resorcinols were dinitrosated in the presence of a nickel(II) salt (Reaction 5)[37]. In contrast, nitrosation



Reaction 5

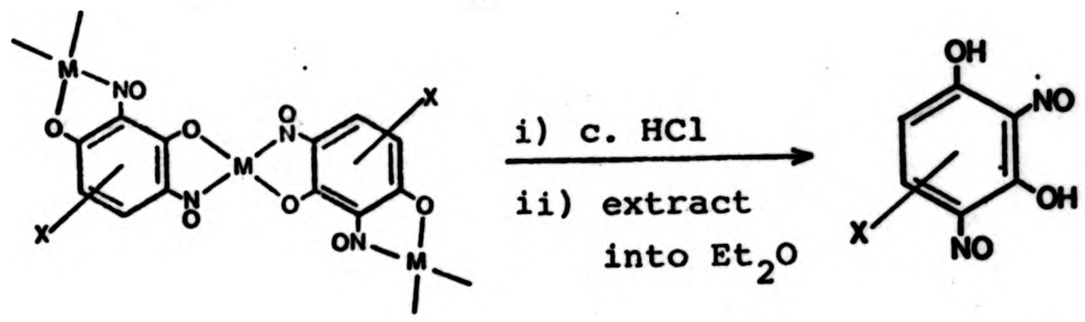
of 2-methylresorcinol in the presence of nickel(II) chloride led to mononitrosation and formation of the complex $Ni(2\text{-}Memnr)_2.4H_2O$ (Reaction 6). Attempts to dinitrosate



Reaction 6

2-methylresorcinol using amyl nitrite also failed.

The formulation of the complexes was established by elemental analysis and i.r.spectroscopy. In all cases the position of nitrosation was determined by acidification of the complex and characterising the liberated, protonated ligand (Reaction 7).



Reaction 7

The complexes Ni(X-dnr).$2H_2O$ (X = H,6-ethyl, 5-methyl) were insoluble in acetone, chloroform, diethyl ether and ethanol but dissolved in refluxing pyridine to give 1:2 adducts. Thermogravimetric analysis on all the hydrates and the pyridine adduct Ni(6-Etdnr).2py (Table 5) showed

Compound	Loss of adduct (^{o}C)	Weight loss(mg)		Decomp. (^{o}C)
		Found	Calc.	
Ni(dnr).H_2O	165	24	28	235
Ni(6-Etdnr).$2H_2O$	155	28	24	260
Ni(6-Etdnr).2py	180	56	57	260

Table 5. Thermogravimetric analysis data.

that water or pyridine was lost between 150 ^{o}C and 180 ^{o}C. to give Ni(X-dnr) which decomposed between 235 ^{o}C and 280 ^{o}C.

Room temperature magnetic susceptibilities for the complexes Ni(X-dnr).$2H_2O$ and Ni(6-Etdnr).2py were measured and the calculated magnetic moments are given in Table 6. The room temperature magnetic moments are close

Compound	$\mu_{eff.}$ (B.M.)
Ni(dnr).$2H_2O$	2.88
Ni(6-Etdnr).$2H_2O$	2.94
Ni(5-Mednr).$2H_2O$	2.90
Ni(6-Etdnr).2py	2.95

Table 6. Room temperature magnetic moments of the complexes Ni(X-dnr).$2H_2O$ and Ni(6-ETdnr).2py

to the lower limit of the range expected for magnetically dilute nickel(II) in an approximately octahedral field.[56]

The results of a variable temperature study on Ni(5-Mednr).$2H_2O$ and Ni(6-Etdnr).$2H_2O$ are presented in Table 7. The values of magnetic susceptibility have been corrected for diamagnetism. The magnetic susceptibilities of both complexes studied are temperature dependant and the large negative Weiss constants (ca. -90 K) suggest antiferromagnetic interaction through the bridging X-dnr^{2-} ligand (see 16a and 16b)

The dinitrosation of resorcinol and its derivatives in the presence of copper(II) chloride gave metal complexes analogous to those obtained with nickel(II) chloride. Thus the complexes listed in Table 8 were obtained by this method. The room temperature magnetic moments obtained were

Table 7. Variable temperature measurements on $Ni(5\text{-Mednr}).2H_2O$ and $Ni(6\text{-Etdnr}).2H_2O$

$Ni(5\text{-Mednr}).2H_2O$

T(K)	314.2	297.7	273.1	246.2	216.7	187.2	155.3	128.2	98.8	83.2
$10^6\chi_A$	3381	3536	3624	3942	4333	4780	5327	6033	7116	7827
μ_{eff}(B.M.)	2.92	2.90	2.82	2.79	2.74	2.68	2.57	2.49	2.37	2.28

$Ni(6\text{-Etdnr}).2H_2O$

T(K)	297.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8	91.2
$10^6\chi_A$	3655	3906	4236	4623	5164	5713	6474	7555	7193
μ_{eff}(B.M.)	2.94	2.92	2.89	2.83	2.78	2.67	2.58	2.45	2.39

subnormal indicating a similar type of structure to that proposed for the nickel(II) complexes (16).

Ligand	Formulation of product	μ_{eff}(B.M.)
Resorcinol	Cu(dnr).H_2O	1.0
	Cu(dnr).py	1.3
4-Ethylresorcinol	Cu(6-Etdnr).H_2O	1.4
	Cu(6-Etdnr).py	1.6
5-Methylresorcinol	Cu(5-Mednr).H_2O	1.3

Table 8.

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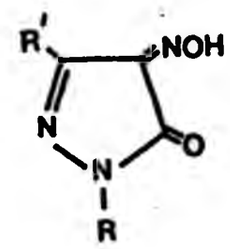
CHAPTER 2

PYRAZOL-5-ONE OXIMES AND THEIR METAL COMPLEXES.

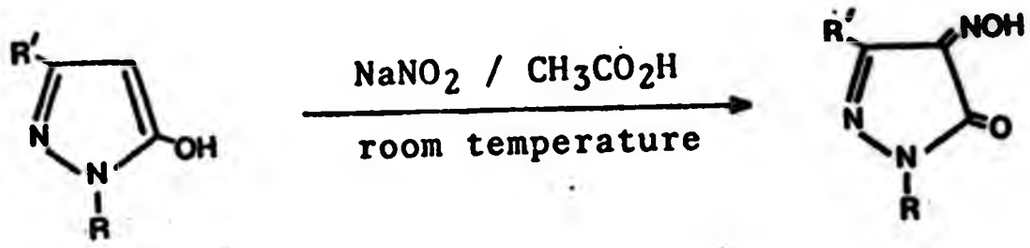
2.1 Introduction.

Pyrazol-5-one oximes[1] (1) are comparable in certain respects to monooximes of 1,2-benzoquinones. Because of the synthetic importance of the latter and of their metal complexes, a systematic study of pyrazol-5-one oximes has been undertaken.



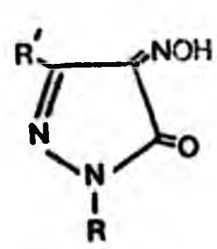
(1)

Pyrazol-5-one oximes may be prepared by the nitrosation of 5-hydroxypyrazoles (Reaction 1). Their

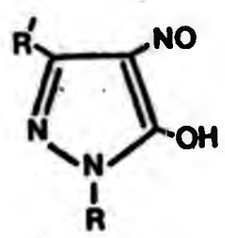


Reaction 1

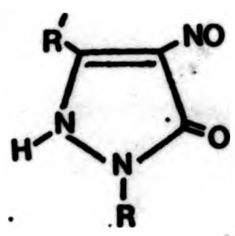
chemistry has received limited attention but it has been suggested that they can exhibit a complex tautomeric behaviour involving oximic (2a) and nitroso (2b and 2c) structures. They react with metals to form chelates which



(2a)

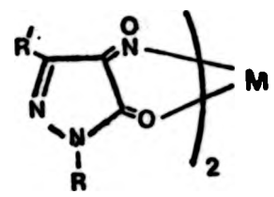


(2b)



(2c)

have been assigned a quinoneoximic structure[2-6] (3). Although



(3)

these structural proposals are reasonable, they lack experimental evidence. As a consequence, a methodical study of the metal complexes has been undertaken. This work comprises the study of their structure and an investigation of the synthesis, properties and structure of the metal chelates derived from the oximes. An investigation of the reactions of the oximes and their complexes with iron pentacarbonyl and triphenylphosphine is also reported.

2.2 Spectral studies of pyrazol-5-one oximes

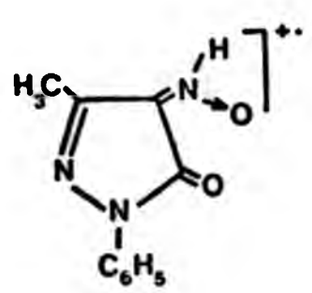
In order to gain some understanding of the structure of pyrazol-5-one oximes and in particular their tautomeric behaviour, the i.r., n.m.r., u.v. and mass spectra of 3-methyl-4-oxime-1H-pyrazol-4,5-dione [(1), R=H, R'=CH_3] and 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione [(1),

$R=C_6H_5$, $R'=CH_3$] were investigated. In this thesis these oximes will be abbreviated as poH and PpoH respectively.

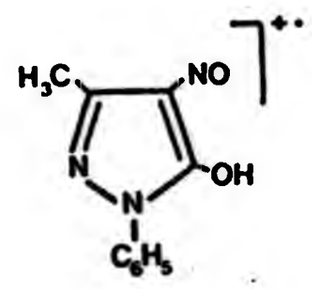
a) Mass spectra

The mass spectra of poH and PpoH are illustrated in Figures 1 and 2. Both compounds show fairly intense molecular ions at m/e 127 and 203 respectively.

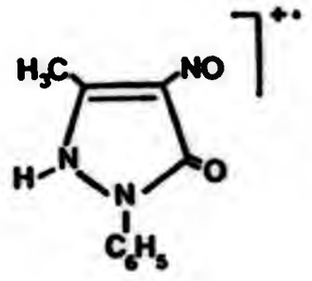
In the case of PpoH the fragmentation of the molecular ion involves loss of O, CO and $HCO^{\bullet}$. These observations can be accounted for in terms of the nitrone



(4a)

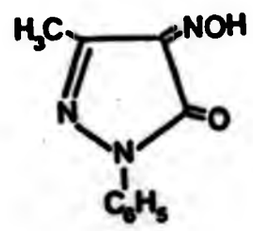


(4b)



(4c)

(4a) or nitroso (4b and 4c) molecular ion structures (Schemes 1 and 2). The absence of any fragmentations of the molecular ion involving loss of $OH^{\bullet}$ suggests that the



(4d)

oximic structure (4d) is not significant in the vapour

Figure 1. Mass spectrum of poH

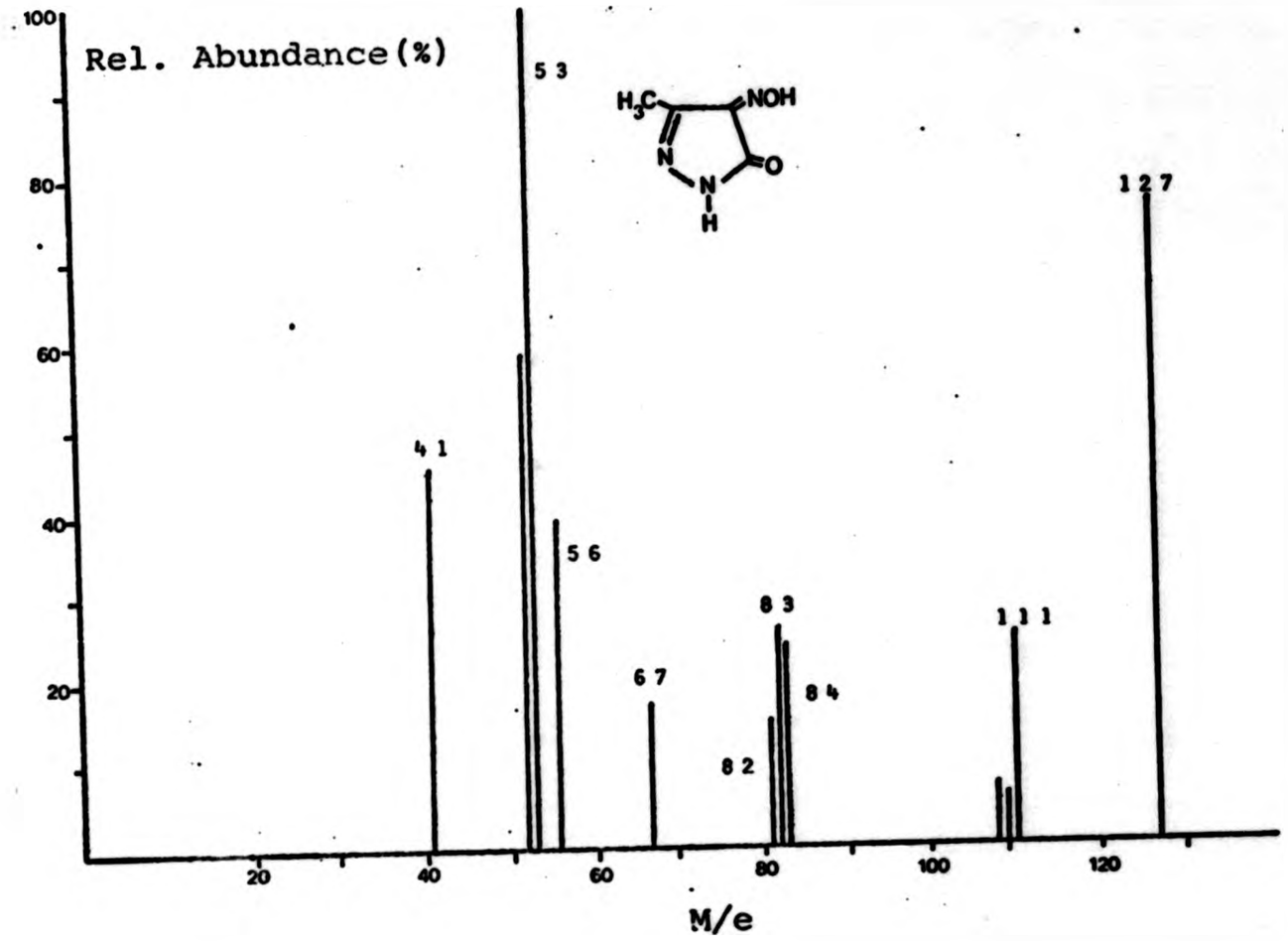
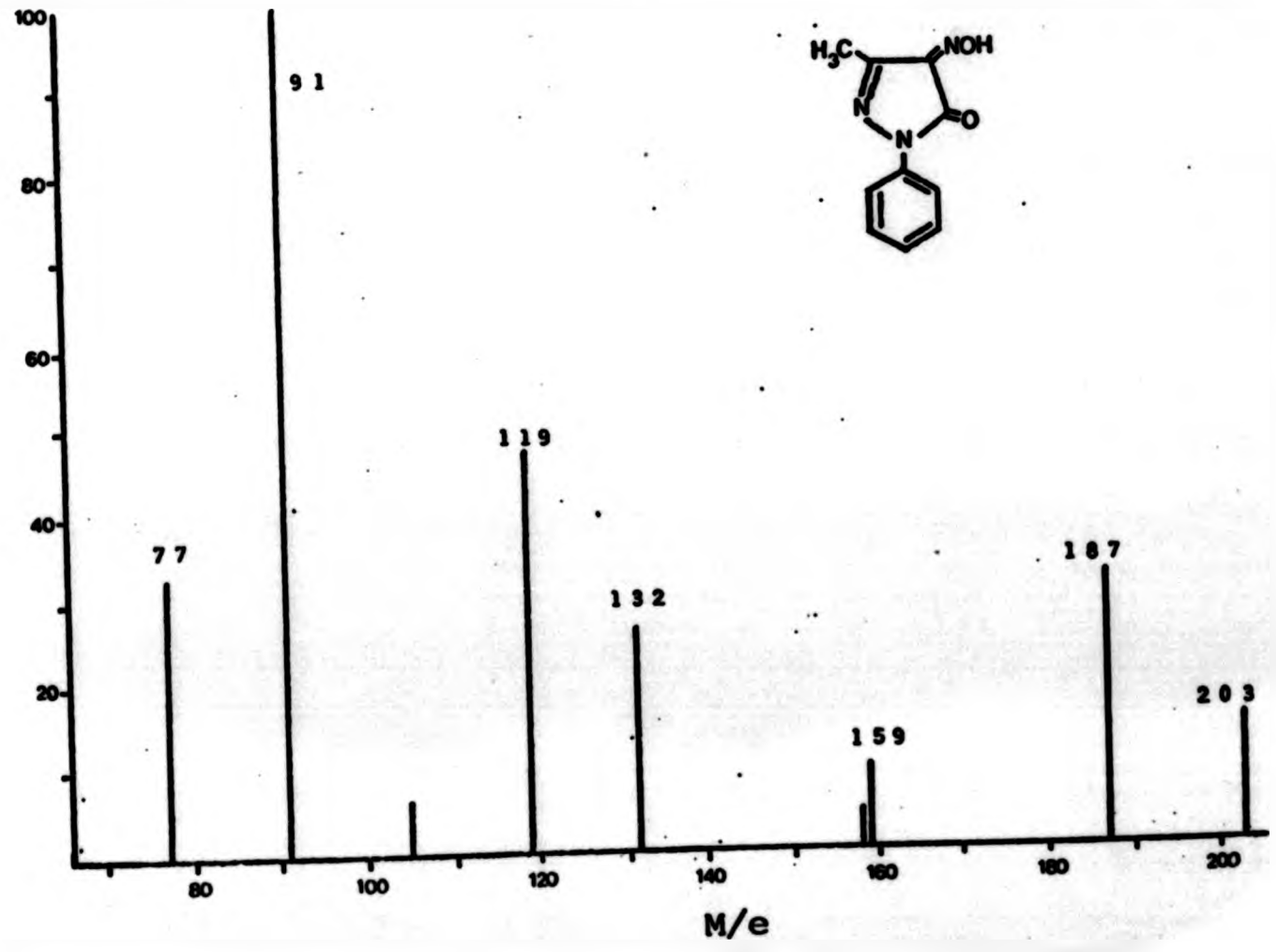
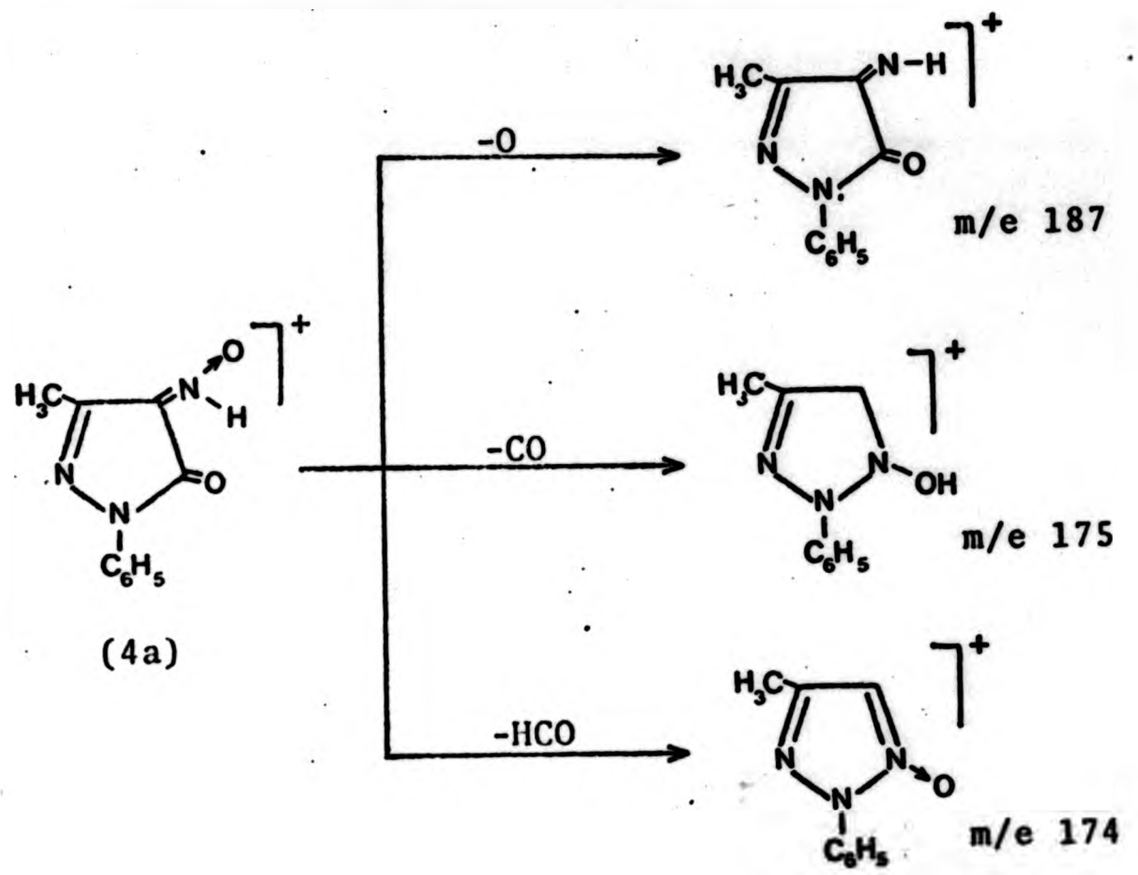


Figure 2. Mass spectrum of PpoH

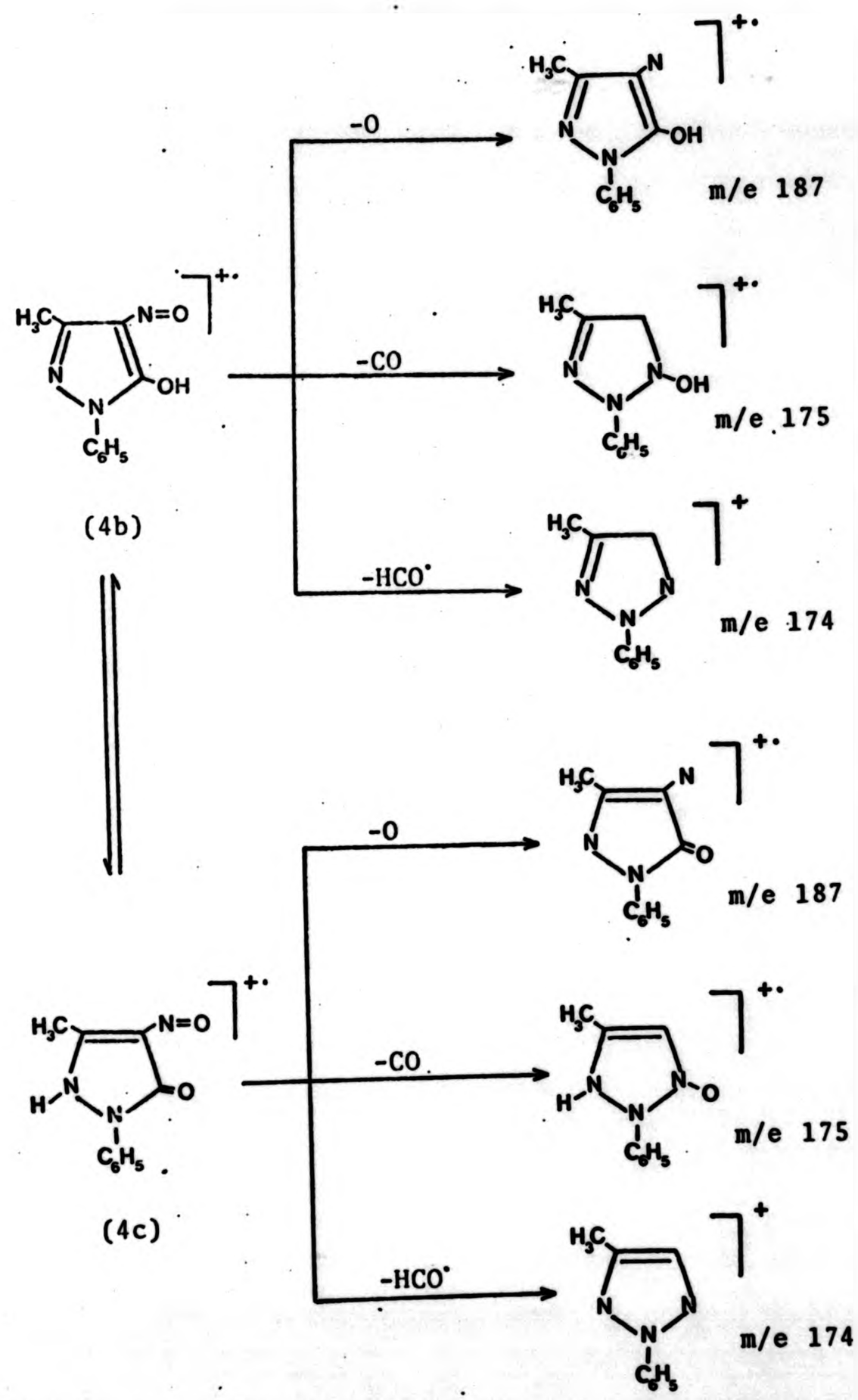




(4a)

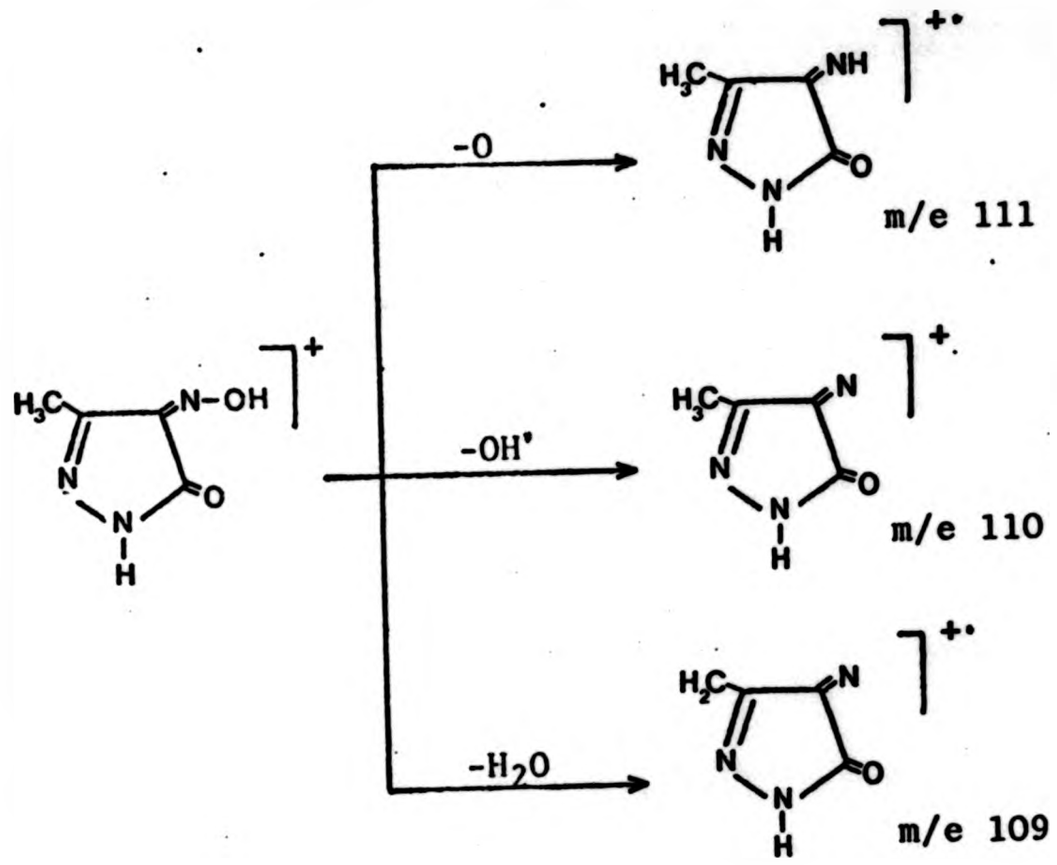
Scheme 1

phase. The losses of CO and HCO· from the molecular ion of PpoH is indicative of a phenolic type structure as they are analogous to reactions shown by the molecular ions of simple phenols.[7]



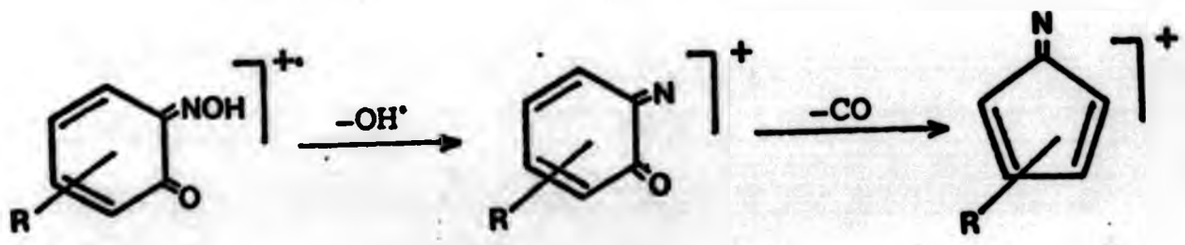
Scheme 2

The molecular ion of poH also shows loss of O and $HCO^{\bullet}$ but in addition losses of $OH^{\bullet}$ and H_2O are observed. The latter suggests some contribution from the oximic structure (Scheme 3).



Scheme 3

The fragmentation behaviour of poH and PpoH contrasts with that of 1,2-benzoquinone monooximes whose molecular ions fragment mainly by consecutive losses of $OH^{\bullet}$ and CO[8] (Scheme 4; see also Section 1.3). It should



Scheme 4

be noted that nitroso compounds give molecular ions that fragment by facile loss of NO[9]. This feature is absent from the spectra of poH and PpoH.

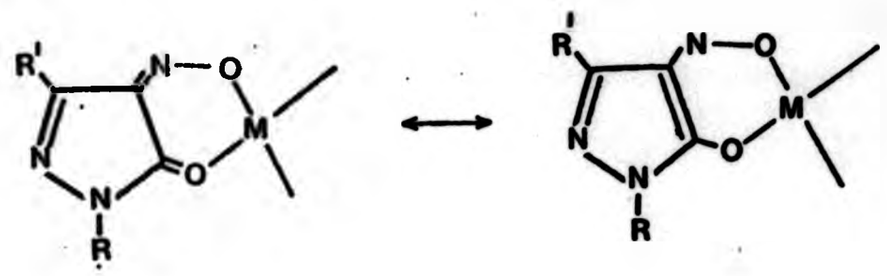
The molecular ions of poH and PpoH undergo ring fission to give their respective base peaks (Schemes 5 and 6).

Scheme 5

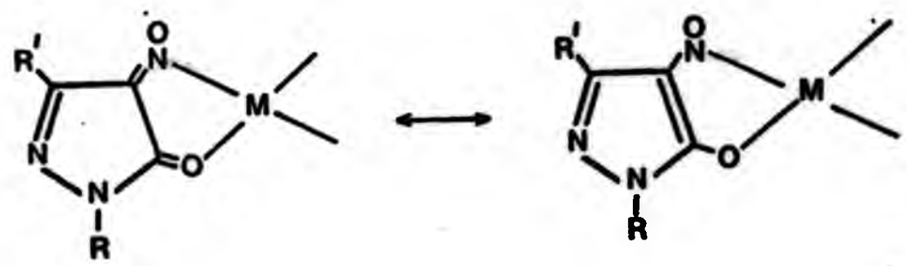
Scheme 6

b) Infra red spectroscopy

In valence bond terms the metal chelates derived from poH and PpoH may be represented as involving resonance between structures (5a) and (5b). The contributions of structures (5a) and (5b) can, in principle, be observed from the i.r. spectra. If the oxime structure (5a) is considered, chelation should decrease the double bond character of the C=N and C=O bonds, thereby resulting in a



(5a) (5b)

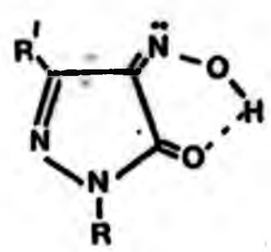


(5c) (5d)

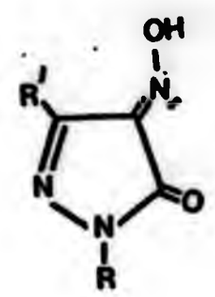
lowering of the frequency of the appropriate i.r. bands. A similar argument applies to the nitroso structure (5b), however the lowering of the frequency of the appropriate band should be less. The problem of observing the relative contributions of each canonical form is therefore one of assigning various bands in the i.r. spectrum.

Assignments and the interpretation of the spectra of the compounds will be based on the change in the $\nu C{=}O$ absorbtion as this can be identified with more certainty than for example $\nu C{=}N$ or $\nu O{-}H$ bands. Therefore the discussion will be limited to the region 1400-1800 cm^{-1}.

For either poH or PpoH in an intramolecularly bonded system (6), $\nu C{=}O$ is lower compared to $\nu C{=}O$ in an intermolecularly bonded system (7). This is a result of the reduction in bond order of C=O (an increase in bond length)



(6)



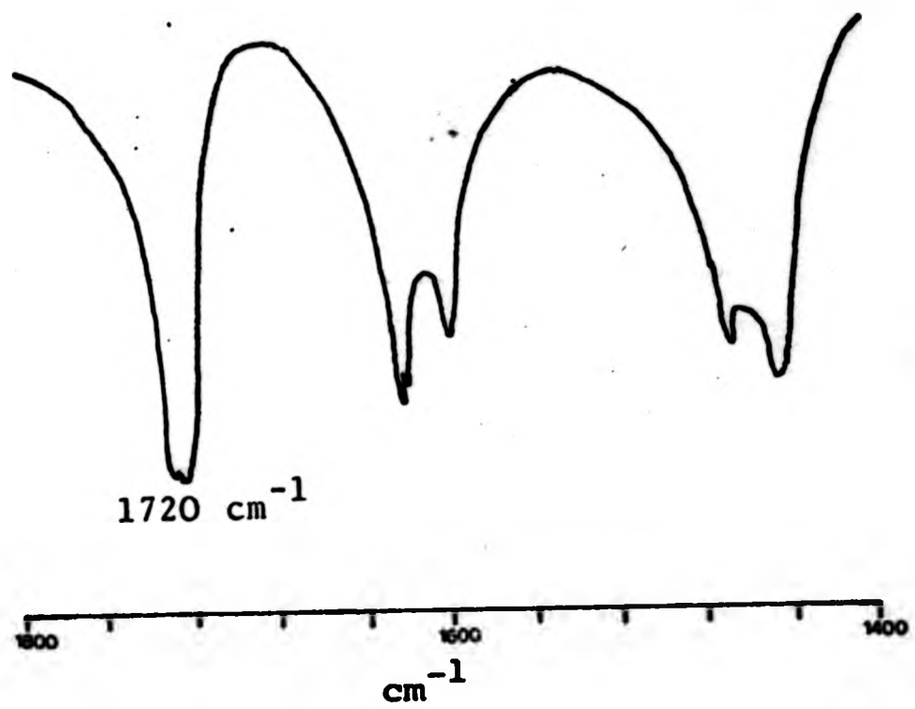
(7)

caused by an intramolecular hydrogen bond. Therefore if the ligand is intramolecularly hydrogen bonded a relatively small drop in νC=O is expected upon complexation. A large reduction in νC=O would indicate that the ligand is intermolecularly hydrogen bonded, i.e. the anti isomer (7). A comparison of the spectra of the ligands and that of the corresponding iron(II) complexes in the region 1400 - 1800 cm^{-1} are given in Figures 2 and 3. The very high values of νC=O in the free ligands (~1725 cm^{-1}) indicates the structures of the molecules are predominantly quinoneoximic and are not intramolecularly hydrogen bonded. This observation is further supported by the solution i.r. spectrum of PpoH in chloroform which shows no change in νC=O compared to the spectrum recorded as a KBr disc. If intermolecular hydrogen bonding was significant it would be expected that chloroform would disrupt it and cause a shift in νC=O.

A similar observation is made in the i.r. spectrum of 1,2-naphthoquinone-2-oxime which has the anti oxime structure (8) and in which νC=O shifts from 1668 to

Figure 2. Comparitive i.r. spectra of poH and its iron(II) complex

a) Free ligand (poH)



b) Iron(II) complex $[Fe(po)_2.H_2O]$

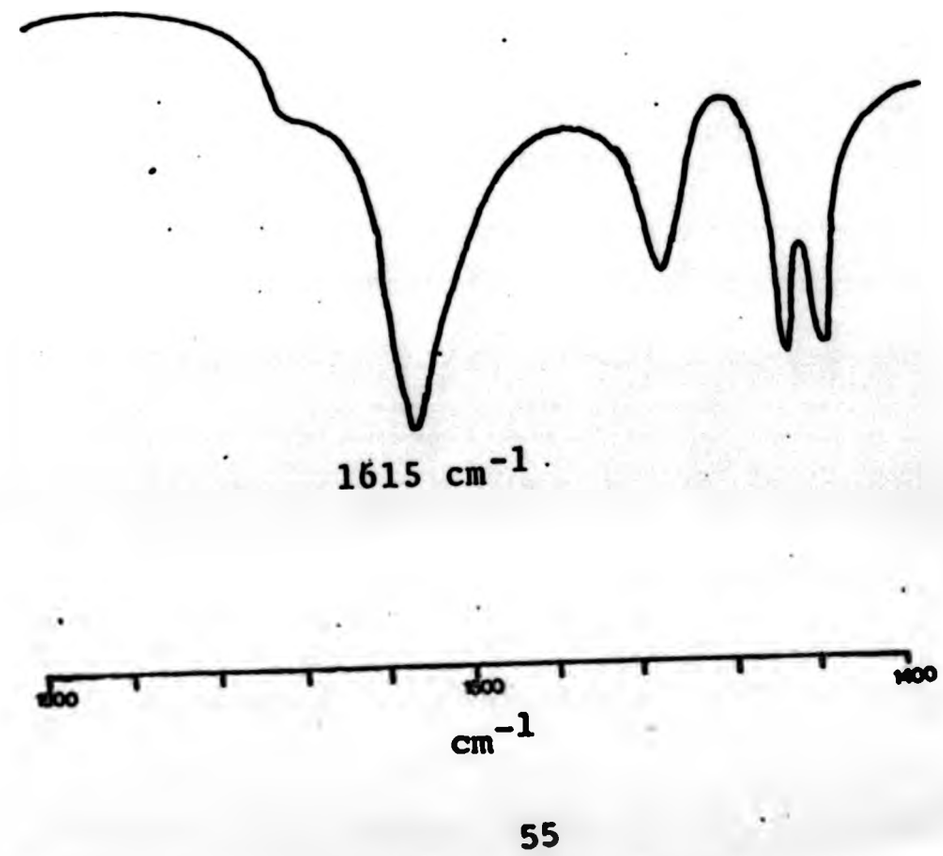
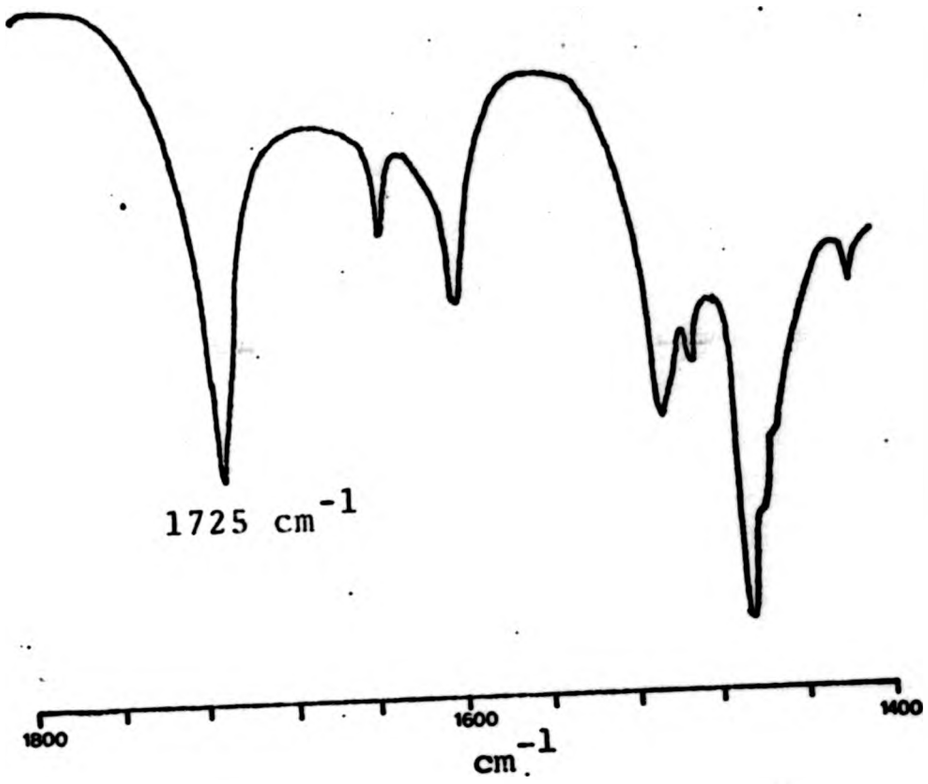
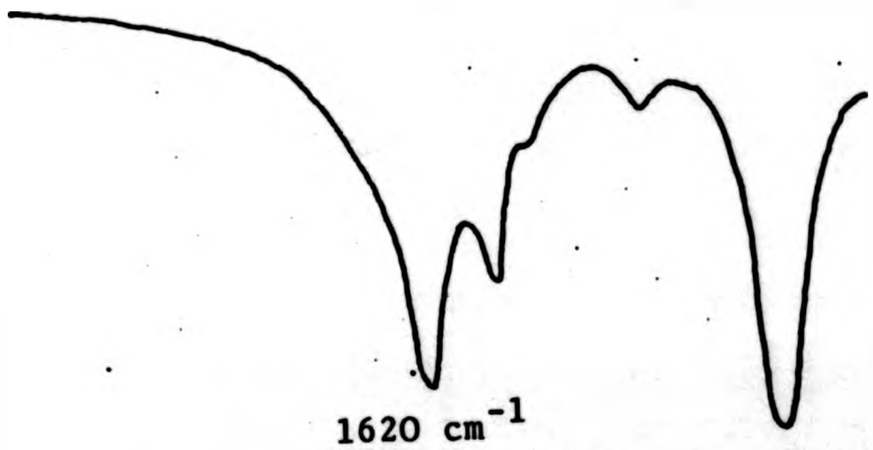


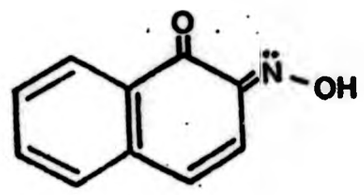
Figure 3. Comparitive i.r. spectra of PpoH and its iron(II) complex

a) Free ligand (PpoH)



b) Iron(II) complex $[Fe(Ppo)_2.H_2O]$

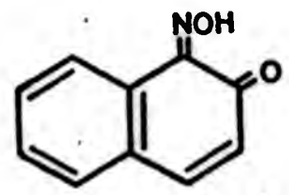




(8)

$1612\ cm^{-1}$ upon complexation with iron(II).

In contrast 1,2-naphthoquinone-1-oxime (9) shows a drop in νC=O from 1618 to only 1608 cm^{-1} on



(9)

complexation, indicating an intramolecular hydrogen bond.[10,11] This differs with 5-methoxy-2-nitrosophenol, which has been shown by X-ray studies to have the anti oxime form in the solid state, and which, on complexation, shows a shift in νC=O from 1660 to 1605 cm^{-1}.[12-14]

c) Ultra-violet/visible spectra

The quantitative estimation of a nitrosophenol-quinoneoxime equilibrium mixture has been performed for several compounds using u.v./visible spectroscopy.[15-17] The technique involves observing a band at 750 nm described as that due to the C-N=O group, establishing an 'average'

molar extinction coefficient ($\varepsilon_{max.}$), then calculating the percentage of the nitrosophenol form from the value of the observed extinction coefficient at 750 nm and $\varepsilon_{max.}$[18]. This system has many errors and can only be used as a guide.

The u.v./visible spectra of poH and PpoH did not show a band at 750 nm and so no conclusions could be made about the state of the equilibrium.

Anderson et. al.[15] suggested that the position of the equilibrium was solvent dependent and that the quinoneoxime form predominated in 1,4-dioxan, chloroform and ethanol solution. However the spectra of poH and PpoH were identical when recorded in carbon tetrachloride and methanol. This suggests that in solution, poH and PpoH exist in the oxime form since no band ascribable to C-N=O (750 nm) was observed.

Nuclear Magnetic Resonance Spectra

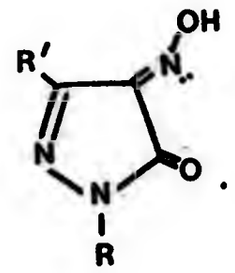
i) ^{1}H n.m.r.

The ^{1}H n.m.r. and i.r. spectra of compounds of type (1) [R=C_6H_5, p-$CH_3C_6H_4$, p-$NO_2C_6H_4$, CH_3; R'=H, CH_3 C_6H_5, p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$] have been investigated by Hänsel[19]. He proposed that the oximes exist as syn-[Z](10a) and anti-[E](10b) isomers in solution, and that the percentage contribution of each isomer in this mixture could be changed by solvent choice or heating (Table 1)

Table 1. Relative proportions of the "E/Z" isomers in pyrazol-5-one oximes of type (1) and the shift in νC=O upon chelation.

R	R'	% contribution of equilibrium mixture		νC=O free ligand in $CHCl_3$ (cm^{-1})	νC=O on chelation in $CHCl_3$ (cm^{-1})
		in $CDCl_3$	in d^6DMSO		
C_6H_5	H	100 "E"		1735	1670
C_6H_5	CH_3	13 E:87 Z	64 E:36 Z	1735	1665
$4\text{-}CH_3C_6H_4$	CH_3			1730	1665
$4\text{-}NO_2C_6H_4$	CH_3	15 E:85 Z	61 E:39 Z	1710(in $CHCl_3$)	
C_6H_5	C_6H_5				1665
C_6H_5	$4\text{-}OCH_3C_6H_4$	100 Z	100 Z		1665
C_6H_5	$4\text{-}NO_2C_6H_4$		100 Z		
CH_3	C_6H_5				1675
CH_3	CH_3	12 E:88 Z	65 E:35 Z	1730	1675

(10a)



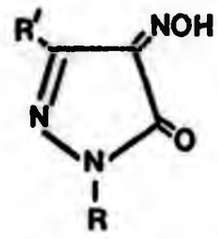
(10b)

Hänsel concluded that the E form predominated when steric repulsions between the substituent on C3 and the N-OH group are absent. When these steric repulsions are present the Z isomer predominates with an intramolecular hydrogen bond.

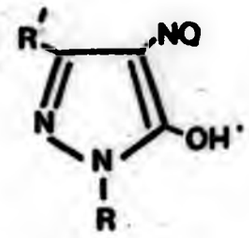
The ^{1}H n.m.r. spectra of poH and PpoH are in agreement with those reported previously.[19] Both compounds show one exchangeable proton at ∿11.3 p.p.m. assignable to the oximic -OH, and a signal at ∿2.3 p.p.m. corresponding to three protons and assignable as the methyl group. In the case of PpoH there is a complex multiplet centred at 7.5 p.p.m. arising from the five aromatic protons; whereas in poH the single N-H proton is found at 6.2 p.p.m.

ii) ^{13}C n.m.r.

Hänsel proposed that pyrazol-5-one oximes existed as E and Z isomers in solution. The possibility that a tautomeric mixture made up of quinoneoxime(11a) or nitrosophenol(11b) forms was not mentioned. Consequently the ^{13}C n.m.r. spectra of poH and PpoH were examined to



(11a)

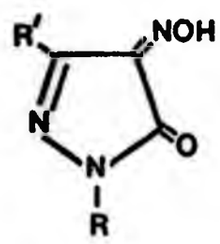


(11b)

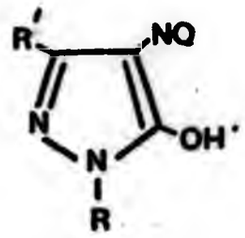
see whether pyrazol-5-one oximes in solution exist as tautomers or geometrical isomers. The ^{13}C spectrum of poH is given in Figure 3. The eight signals observed excludes the possibility of geometrical isomerism since it would not be expected that the E and Z isomers would produce radically different ^{13}C signals. The eight signals are ascribable to the four carbon atoms per tautomer. The two methyl signals at approximately 12 p.p.m. and 17 p.p.m. (identified by single frequency off resonance irradiation which expands them to quartets) were used to estimate the percentage contribution of each tautomer on an intensity and integrated basis.† Assuming that the signal furthest downfield (163.5 p.p.m.) is due to C=O (oxime tautomer)

---

†Normally the peaks in a ^{13}C spectrum cannot be integrated meaningfully. This is a manifestation of the Nuclear Overhauser Effect and the variable relaxation times of the moeities involved. However if the radio frequency is pulsed with sufficient delay (in this case 300 seconds), enough time is allowed for the nuclei to relax and the spectrum may be integrated to obtain quantitative information.



(11a)



(11b)

see whether pyrazol-5-one oximes in solution exist as tautomers or geometrical isomers. The ^{13}C spectrum of poH is given in Figure 3. The eight signals observed excludes the possibility of geometrical isomerism since it would not be expected that the E and Z isomers would produce radically different ^{13}C signals. The eight signals are ascribable to the four carbon atoms per tautomer. The two methyl signals at approximately 12 p.p.m. and 17 p.p.m. (identified by single frequency off resonance irradiation which expands them to quartets) were used to estimate the percentage contribution of each tautomer on an intensity and integrated basis.† Assuming that the signal furthest downfield (163.5 p.p.m.) is due to C=O (oxime tautomer)

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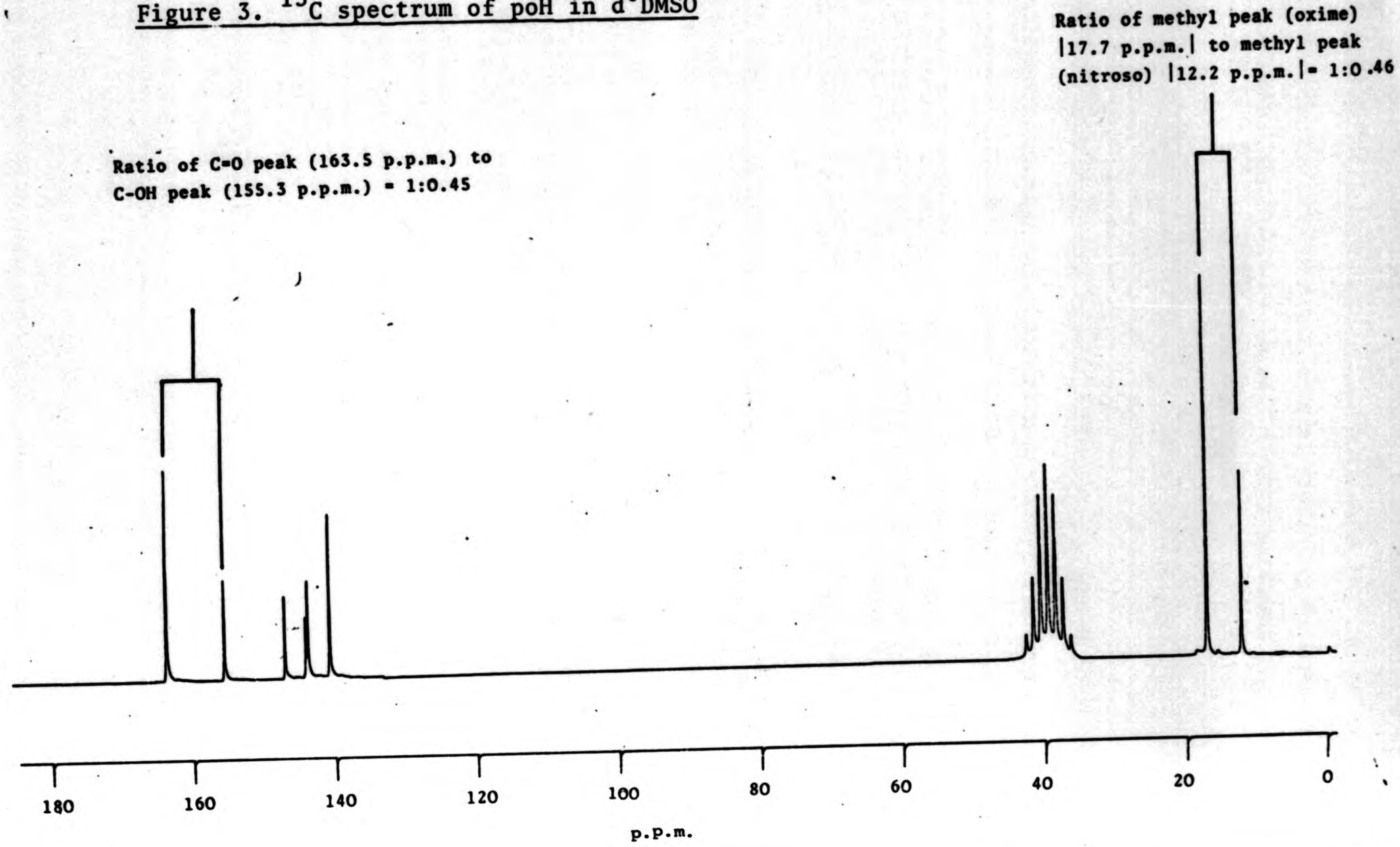
†Normally the peaks in a ^{13}C spectrum cannot be integrated meaningfully. This is a manifestation of the Nuclear Overhauser Effect and the variable relaxation times of the moeities involved. However if the radio frequency is pulsed with sufficient delay (in this case 300 seconds), enough time is allowed for the nuclei to relax and the spectrum may be integrated to obtain quantitative information.

Figure 3. ^{13}C spectrum of poH in d^6DMSO



and that the next signal upfield (155.3 p.p.m.) is due to C-OH (nitroso tautomer) a ratio of 1:0.45 was calculated. The relative areas of the methyl signals at 17 p.p.m. and 12 p.p.m. were calculated as 1:0.46. Thus the peak at 17.1 p.p.m. was assigned as that of the methyl group in the oximic tautomer, and the peak at 12.2 p.p.m. that due to the methyl group in the nitroso tautomer. Therefore the percentage contribution of each tautomer in solution was calculated on the basis of the areas under the methyl peaks. The results are given in Table 2. Using the same principle

Table 2. Relative proportions of oxime and nitroso tautomers in the ^{13}C spectrum of poH at 310, 350 and 375K in d^6DMSO.

T(K)	% oxime	% nitroso	[K]
310	69	31	2.2
350	65	35	1.9
375	64	36	1.8

[K] calculated for nitroso $\rightleftharpoons$ oxime

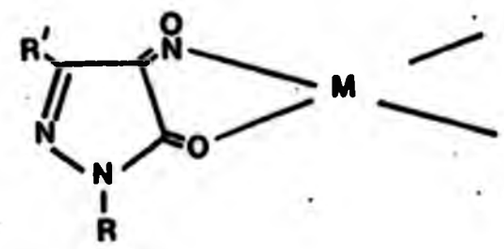
as that applied to poH the methyl peaks in PpoH were assigned. The percentage contribution of oxime lay between 60% and 67% in d^6DMSO at 310 K. In $CDCl_3$, 75% oxime was observed

In the case of PpoH the relative contributions of each tautomer are in agreement with that observed by Hänsel in d^6DMSO at room temperature (64% "E" isomer, 36% "Z" isomer). However he described the equilibrium in terms of geometrical isomers and this is open to question. The results obtained in the case of poH show that the oxime is the predominant tautomer and that the equilibrium is temperature dependent.

The overall conclusion to this study of tautomerism in the pyrazol-5-one oxime series, indicates that in solution the oxime form predominates and that it is probably the E isomer. Similarly, in the solid phase the E-isomer predominates. The mass spectrometric behaviour of poH and PpoH show that in the gas phase their fragmentation patterns may be rationalised more in terms of the nitroso or nitrone tautomers.

2.3 Metal chelates of pyrazol-5-one oximes - Synthesis, Properties and Structure of Iron(II) Complexes.

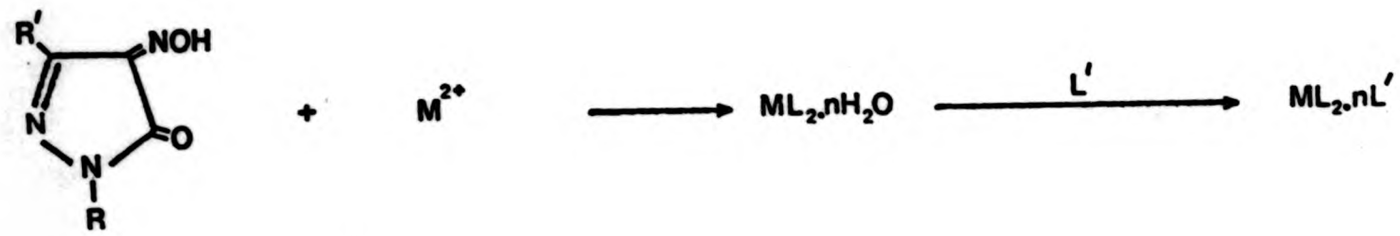
Metal complexes derived from pyrazol-5-one oximes have been reported and studied earlier.[2-6] Hovorka and Sucha carried out an extensive study of the Cu(II), Ni(II), Mn(II), Zn(II) and Cd(II) complexes derived from ligands of type (1) [R=H, C_6H_5, p-$NO_2C_6H_4$, p-ClC_6H_4, 2,4-$(NO_2)_2C_6H_3$; R'=H, CH_3, C_6H_5]. The chelates were prepared by the direct reaction of the ligand with a metal salt in aqueous ethanol. Adducts were prepared by the addition of small quantities of pyridine or ammonia to the reaction mixture (Table 2). The suggested formulation(12) was based on measurements of elemental analysis, room temperature magnetic susceptibilities (Table 3), and thermal gravimetric studies(Table 4). The thermal behaviour of the



(12)

complexes and their adducts showed that the ammonia adducts lost ammonia at a higher temperature than the pyridine adducts or the hydrated complex lost pyridine or water respectively. Hovorka and Sucha concluded that whereas ammonia was coordinated to the central metal atom, water and pyridine were present as solvent of crystallisation.

Table 3. Metal complexes derived from substituted 4-oxime-1H-pyrazole-4,5-diones.



R	R'	M(II) in $ML_2.nH_2O$		$ML_2.nL'$ (L'= NH_3, pyridine)	
				n	
		M	n	NH_3	pyridine
H	H	Cu	-	3 or 4	-
H	H	Ni	2	-	2
H	CH_3	Cu	2	-	2
H	CH_3	Ni	1 or 2	-	2
H	CH_3	Mn	0 or 2	-	2
H	CH_3	Zn	2	-	-
H	CH_3	Cd	2	2	-
H	CH_3	Mg	2	-	-

Table 3. continued.

R	R'	M(II) in $ML_2.nH_2O$		$ML_2.nL'$ (L'= NH_3, pyridine)	
				n	
		M	n	NH_3	pyridine
H	C_6H_5	Cu	2	1	-
H	C_6H_5	Ni	1	2	2
H	C_6H_5	Mn	0	-	2
H	C_6H_5	Mg	2	-	-
H	C_6H_5	Zn	2	-	-
H	C_6H_5	Cd	2	-	-
C_6H_5	H	Cu	2	2	2
C_6H_5	H	Ni	0 or 2	-	2
C_6H_5	H	Mn	0 or 2	-	2
C_6H_5	H	Zn	2	-	-
C_6H_5	H	Cd	2	-	-
C_6H_5	H	Mg	2	-	-
$p\text{-}NO_2C_6H_4$	CH_3	Cu	2	2	-
$P\text{-}NO_2C_6H_4$	CH_3	Ni	0 or 2	-	2
$p\text{-}NO_2C_6H_4$	CH_3	Mn	0	-	-

Table 3. continued.

R	R'	M(II) in $ML_2.nH_2O$		$ML_2.nL'$ (L'= NH_3, pyridine)	
				n	
		M	n	NH_3	pyridine
$p\text{-}NO_2C_6H_4$	CH_3	Zn	0	-	-
$p\text{-}NO_2C_6H_4$	CH_3	Cd	2	-	-
$p\text{-}NO_2C_6H_4$	CH_3	Mg	2	-	-
$p\text{-}ClC_6H_4$	CH_3	Cu	2	-	-
$p\text{-}ClC_6H_4$	CH_3	Ni	2	-	-
$p\text{-}ClC_6H_4$	CH_3	Mn	2	-	-
$p\text{-}ClC_6H_4$	CH_3	Zn	2	-	-
$p\text{-}ClC_6H_4$	CH_3	Cd	2	-	-
$p\text{-}ClC_6H_4$	CH_3	Mg	2	-	-
$2,4(NO_2)_2C_6H_3$	CH_3	Cu	2	2 and 3	-
$2,4(NO_2)_2C_6H_3$	CH_3	Ni	-	2 and 4	-
C_6H_5	C_6H_5	Cu	2	2	-
C_6H_5	C_6H_5	Mn	0	-	-
C_6H_5	C_6H_5	Mg	2	-	-
C_6H_5	C_6H_5	Zn	2	-	-
C_6H_5	C_6H_5	Cd	2	-	-

Table 3. continued.

R	R'	M(II) in $ML_2.nH_2O$		$ML_2.nL'$ (L'= NH_3, pyridine)	
				n	
		M	n	NH_3	pyridine
$p\text{-}NO_2C_6H_4$	C_6H_5	Cu	2	-	-
$p\text{-}NO_2C_6H_4$	C_6H_5	Ni	0	2 and 3	-
$p\text{-}NO_2C_6H_4$	C_6H_5	Mn	2	-	-
$p\text{-}NO_2C_6H_4$	C_6H_5	Zn	-	1 and 2	-
$p\text{-}NO_2C_6H_4$	C_6H_4	Cd	-	1 and 2	-

Table 4. Room temperature magnetic susceptibilities of Ni(II) and Mn(II) complexes of type $ML_2.nL'$ derived from pyrazol-5-one oximes.

R	R'	M^{n+}	$\mu_{eff.}$ (B.M.)			
			anhyd.	$2H_2O$	2py.	$2NH_3$
H	H	Ni	-	3.0	3.0	-
H	CH_3	Ni	-	3.0	3.1	-
H	C_6H_5	Ni	-	$2.8(1H_2O)$	3.1	3.0
C_6H_5	H	Ni	2.4	3.1	3.0	-
$p\text{-}NO_2C_6H_4$	H	Ni	2.4	3.1	3.0	3.0
C_6H_5	CH_3	Ni	2.5	3.1	-	-
H	CH_3	Mn	5.6	5.8	-	-
H	C_6H_5	Mn	5.6	-	5.8	-
C_6H_5	H	Mn	5.6	5.8	-	-

Table 4. Thermogravimetric data of metal complexes derived from pyrazol-5-one oximes of type $ML_2.nL'$

LH =

R	R'	M^{2+}	L'	Temp.of loss of adduct ^oC	Decomp. Temp ^oC
H	H	Cu	H_2O	90-110	240
H	H	Ni	H_2O	110	250
H	H	Cu	$3NH_3$	180-260	270
H	H	Ni	1py	200-210	280
C_6H_5	H	Cu	$2H_2O$	90-110	230
C_6H_5	H	Cu	$2NH_3$	190	220
C_6H_5	H	Cu	2py	170-180	230
C_6H_5	H	Ni	2py	190-220	330
H	CH_3	Cu	$2H_2O$	100-140	230
H	CH_3	Cu	2py	170-200	220
H	CH_3	Ni	$2H_2O$	190-210	280
H	CH_3	Ni	2py	210	270
H	CH_3	Zn	$2H_2O$	200-220	280
H	CH_3	Cd	$2H_2O$	180-210	290
H	CH_3	Mg	$2H_2O$	170-210	260
H	C_6H_5	Cu	NH_3	180-200	250
H	C_6H_5	Ni	H_2O	200	300
H	C_6H_5	Ni	2py	250-270	300
H	C_6H_5	Ni	$2NH_3$	200-25o	300
C_6H_5	CH_3	Cu	$2H_2O$	110-190	230
C_6H_5	CH_3	Ni	$2H_2O$	120-140	340

Table 4 continued

R	R'	M^{2+}	L'	Temp. of loss of adduct °C	Decomp. Temp. °C
$pNO_2C_6H_4$	CH_3	Cu	$1\frac{1}{2}H_2O$	90-110	270
$pNO_2C_6H_4$	CH_3	Ni	$2H_2O$	190-220	315
$pNO_2C_6H_4$	CH_3	Ni	2py	200-260	310
$pNO_2C_6H_4$	CH_3	Zn	$2H_2O$	220-260	310
$pNO_2C_6H_4$	CH_3	Cd	$2H_2O$	180-260	310
$pNO_2C_6H_4$	CH_3	Mg	$2H_2O$	170-260	290
C_6H_5	C_6H_5	Cu	$4H_2O$	90-110	210
C_6H_5	C_6H_5	Cu	NH_3	90-140	220
C_6H_5	C_6H_5	Cu	$2NH_3$	90-140	220

An investigation of the spectrophotometric properties of the complexes derived from pyrazol-5-one oximes has been carried out.[20-24] However these studies were limited to stability constant determinations and the complexes were not generally isolated.

In this study the reaction of poH and PpoH with iron(II) and iron(III) salts under various conditions has been examined. The reaction of the hydrated complexes with pyridine has also been investigated.

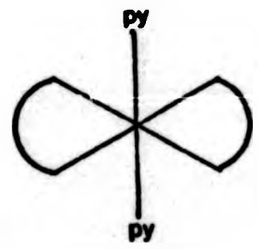
The reaction of iron(II) ammonium sulphate with PpoH in aqueous ethanol gave a turquoise complex of stoichiometry $Fe(Ppo)_2.H_2O$. In contrast poH failed to react with iron(II) ammonium sulphate under similar or forcing conditions. However the preparation of the iron(II) complex of poH, formulated as $Fe(po)_2.H_2O$, was achieved by the reaction of the oxime with iron pentacarbonyl (see following section).

The interaction of poH or PpoH with iron(III) ammonium sulphate did not result in complex formation. This lack of reaction is not clearly understood, but significantly, no trischelates of pyrazol-5-one oximes have been reported in the literature and attempts to obtain the cobalt(III) complex of PpoH failed.[25]

In order to obtain some understanding of the structure of the complexes, the magnetic properties of $Fe(po)_2.H_2O$, $Fe(Ppo)_2.H_2O$ and their corresponding bispyridine adducts have been investigated. The room temperature magnetic moments of all the complexes lay between 5.2 B.M. and

5.4 B.M.. The results of a variable temperature study on $Fe(Ppo)_2.H_2O$ and $Fe(Ppo)_2.2py$ are presented in Table 6. The values of magnetic susceptibility have been corrected for diamagnetism and magnetic moments calculated from $\mu_{eff.} = 2.83(\chi_A T)^{\frac{1}{2}}$. The susceptibilities of the complexes subjected to measurement at variable temperature were independent of field strength used. The susceptibility of both the hydrate and the pyridine adduct follows the Curie-Weiss law, $\chi = C/(T-\theta)$, throughout the whole temperature range measured (124-363 K).

The magnetic susceptibility of $Fe(Ppo)_2.2py$ is independent of temperature, suggesting that the metal ion is in a magnetically dilute environment. The observed room temperature magnetic moment of 5.2 B.M. is in accord



(13)

with high spin iron(II) in an octahedral environment, e.g.(13).

The magnetic susceptibility of $Fe(Ppo)_2.H_2O$ is temperature dependent and suggests antiferromagnetic behaviour. This is most likely to be caused by association between neighbouring molecules (Figure 3).[27,28]

Table 6. Variable temperature magnetic susceptibility measurements on $Fe(Ppo)_2.H_2O$ and $Fe(Ppo)_2.2py$

$Fe(Ppo)_2.H_2O$

T(K)	363.0	333.5	303.5	273.1	243.1	213.4	183.8	153.3	123.9
$10^6\chi_A$	10443	11202	11383	12032	12789	13481	14437	14920	16367
$\mu_{eff.}$(B.M.)	5.51	5.47	5.26	5.13	4.99	4.80	4.61	4.28	4.03

$Fe(Ppo)_2.2py$

T(K)	363.2	334.9	302.9	273.1	243.1	212.9	183.9	152.7	124.1
$10^6\chi_A$	10399	11402	12515	13431	15650	17870	20688	24645	30768
$\mu_{eff.}$(B.M.)	5.50	5.53	5.51	5.42	5.52	5.52	5.52	5.49	5.53

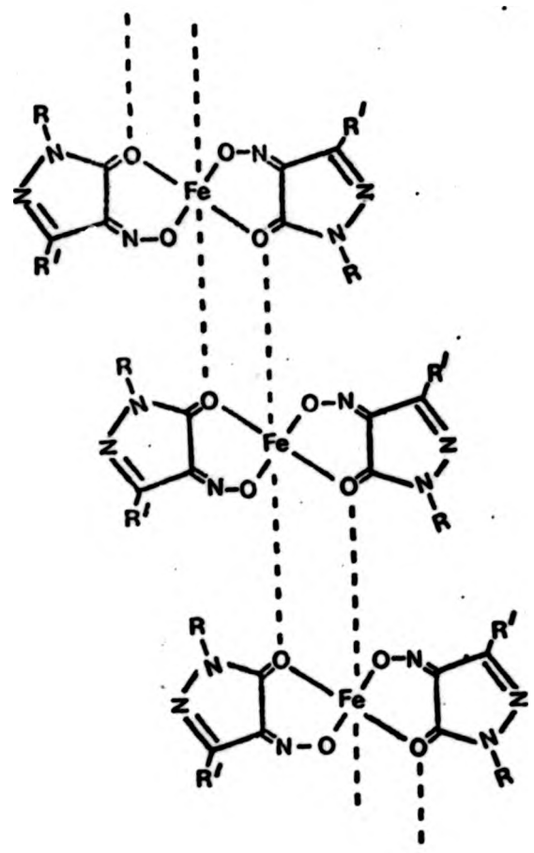


Figure 3

The Mössbauer spectra of $Fe(Ppo)_2.H_2O$ and $Fe(Ppo)_2.2py$ are illustrated in Figures 4 and 5 respectively. The parameters obtained for each complex at 77 K and 300 K are identical. They are in accord with high spin iron(II)[29-32] species and support the structural proposals already made.

The magnetic behaviour of $Fe(Ppo)_2.H_2O$ and $Fe(Ppo)_2.2py$ is fundamentally different to that observed for the analogous bischelates $Fe(qo)_2.nL$ (L=O or 2)[33,34] [qoH = 1,2-benzoquionone monooxime or 1,2-naphthoquinone monooxime]. These complexes have magnetic moments consistent with low spin iron(II), e.g. $Fe(qo)_2.2py$ is diamagnetic[27], which is evidence of the high ligand field exerted by the qo^- anion. The high spin characteristics of the complexes derived from pyrazol-5-one oximes is indicative of the weak ligand field strength of po^- and Ppo^-.

Figure 4

Mössbauer spectrum of bis(3-methyl-1-phenyl-4-oximato-1H-pyrazole-4,5-dione)iron(II)-monohydrate

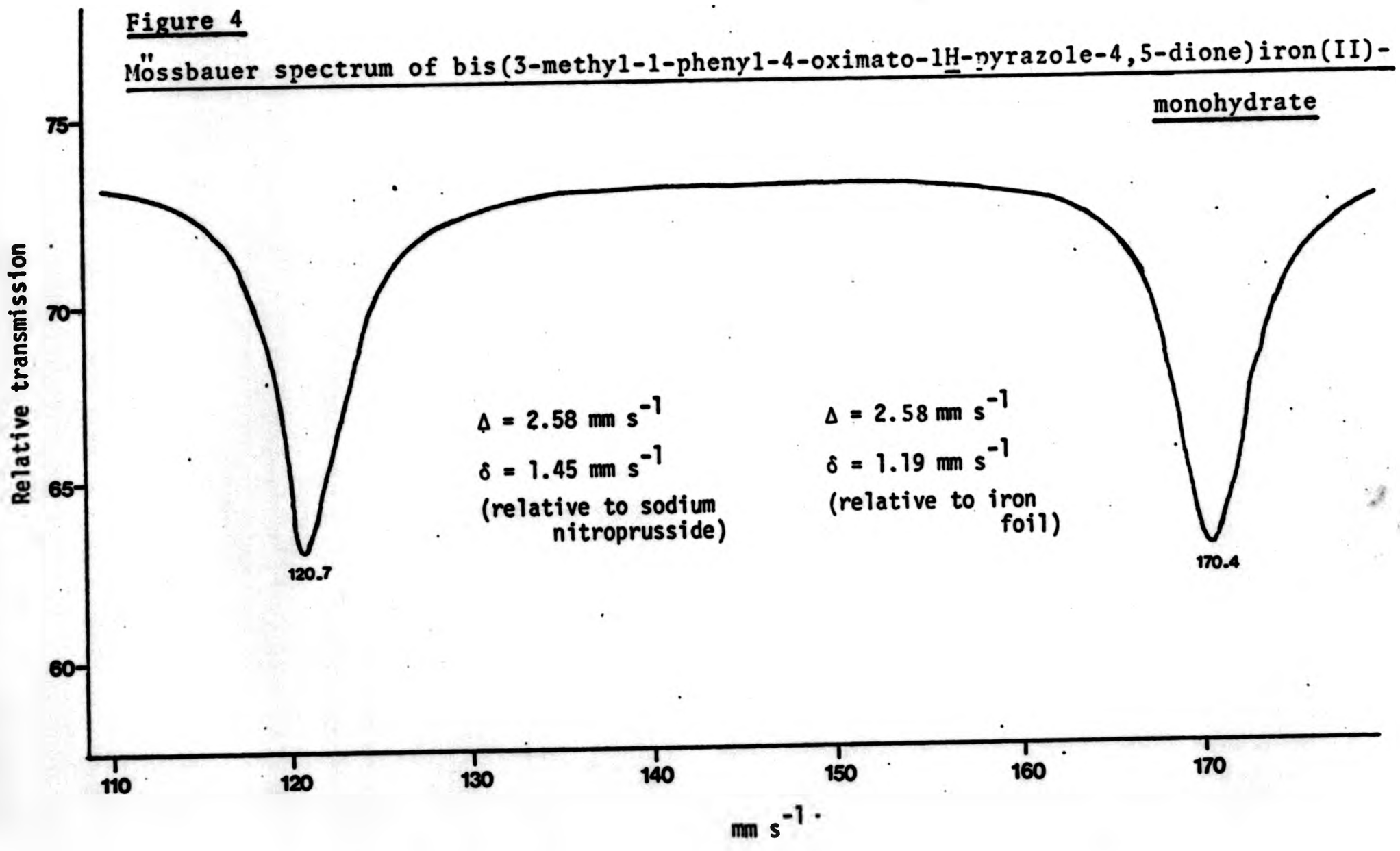
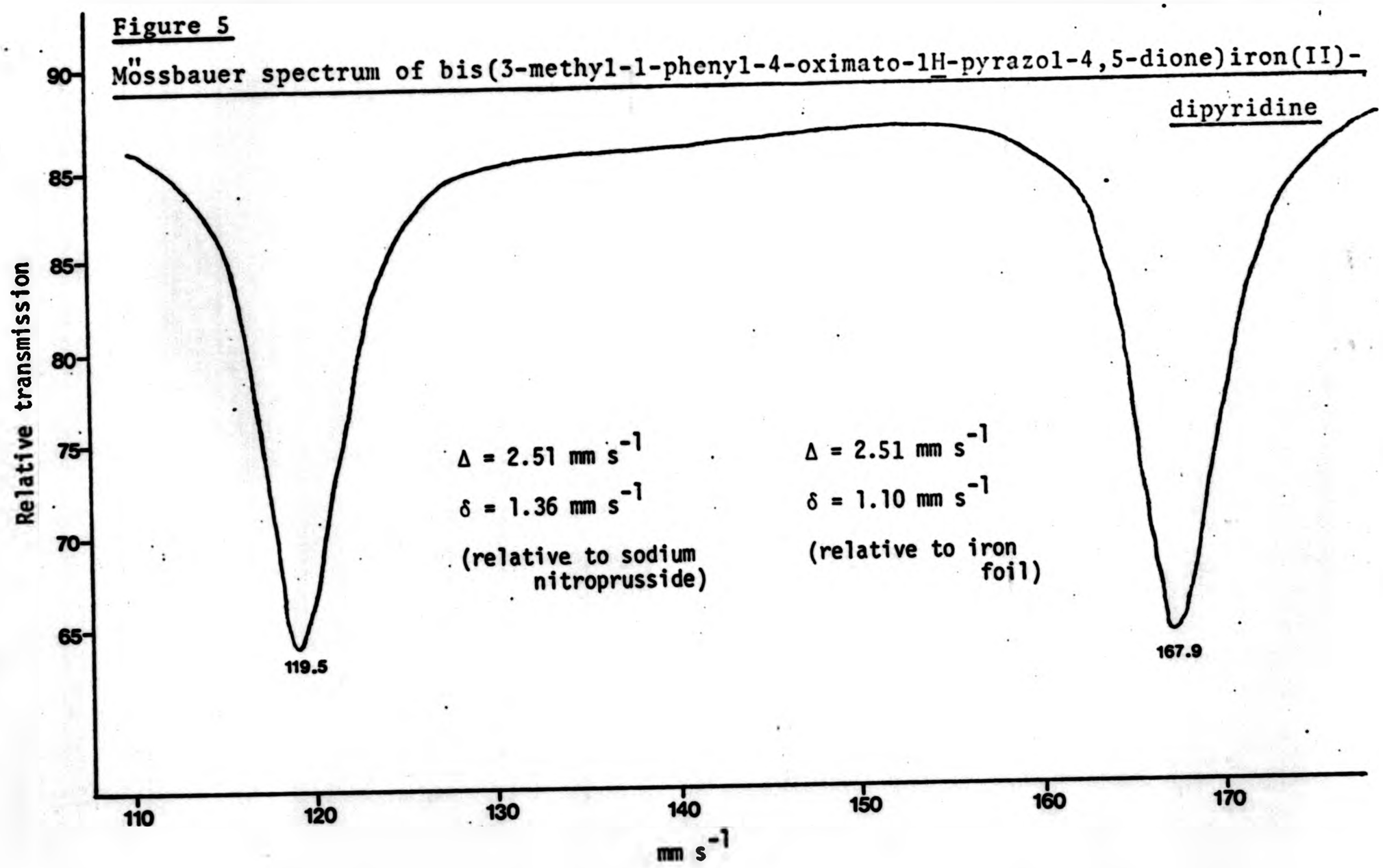
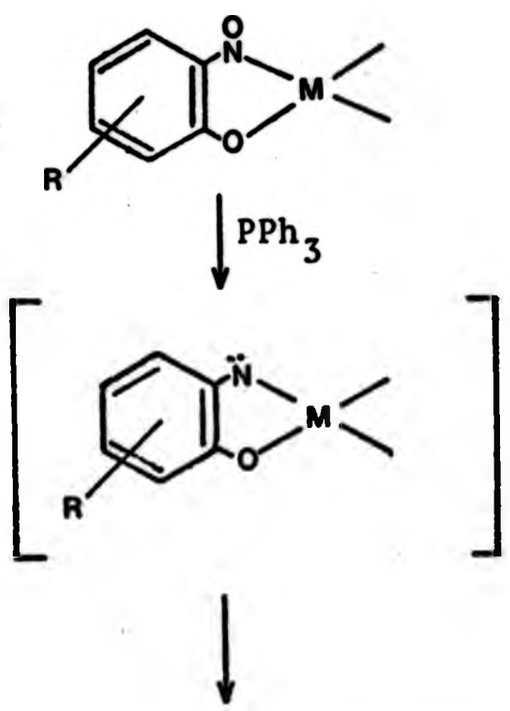


Figure 5

Mössbauer spectrum of bis(3-methyl-1-phenyl-4-oximato-1H-pyrazol-4,5-dione)iron(II)-dipyridine



Another difference is the behaviour of the complexes towards Lewis bases. For example metal complexes derived from qoH[35,36], are rapidly deoxygenated when treated with triphenylphosphine (Scheme 6), whereas complexes



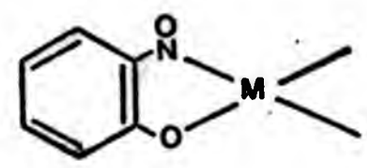
amines, iminophosphoranes, phenazines (see Chapter 1).

Scheme 6

derived from pyrazol-5-one oximes do not react with the phosphine.

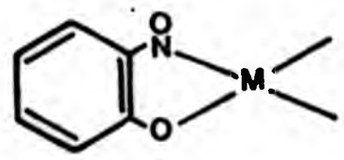
The different magnetic behaviour and chemical properties of metal complexes of pyrazol-5-one oximes compared with quinoneoxime complexes can be related to the electronic structure of the ligands involved and their respective mode of bonding to the metal. Previously[37-39] it has been shown, through extensive X-ray crystallographic

and other studies[40], that in quinoneoximic complexes the ligand bonds to the metal via the nitrogen atom of the NO group(14)

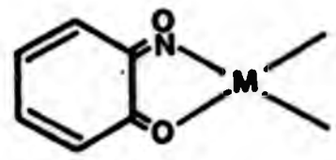


(14)

(see also Section 1.1).The reactivity of the complexes derived from qoH has been related to the lability of the NO oxygen towards deoxygenation in either the complexed quinoneoximic(15a) or nitrosophenolic(15b) structures. In

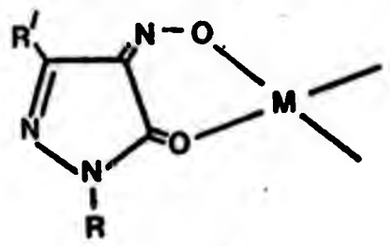


(15a)



(15b)

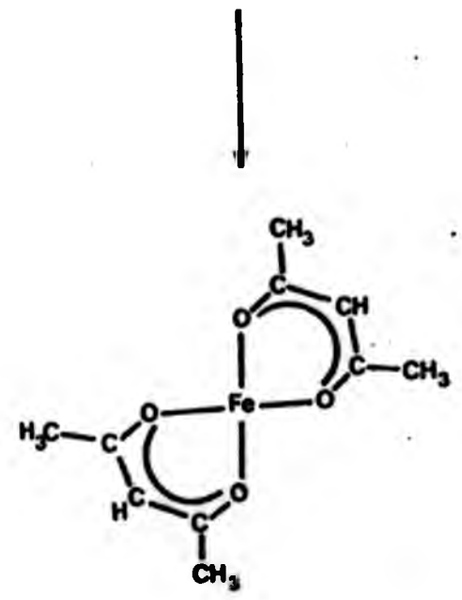
addition the high ligand field strength of qo^- has been attributed to its quinoneoxime character and the extended conjugation possible within its metal complexes. On such a basis it is reasonable to assume that the structure of the metal complexes of pyrazol-5-one oximes involves O-M bonding (16). Thus their stability towards deoxygenation can be accounted for in terms of the absence of labile



(16)

oxygen, and the low field strength in terms of the O_4 character of the ligand and the very limited conjugation within the chelate. Significantly other O_4 type complexes of iron(II) e.g. $Fe(acac)_2$ [41] [acacH = acetylacetone], are high spin (Reaction 2)

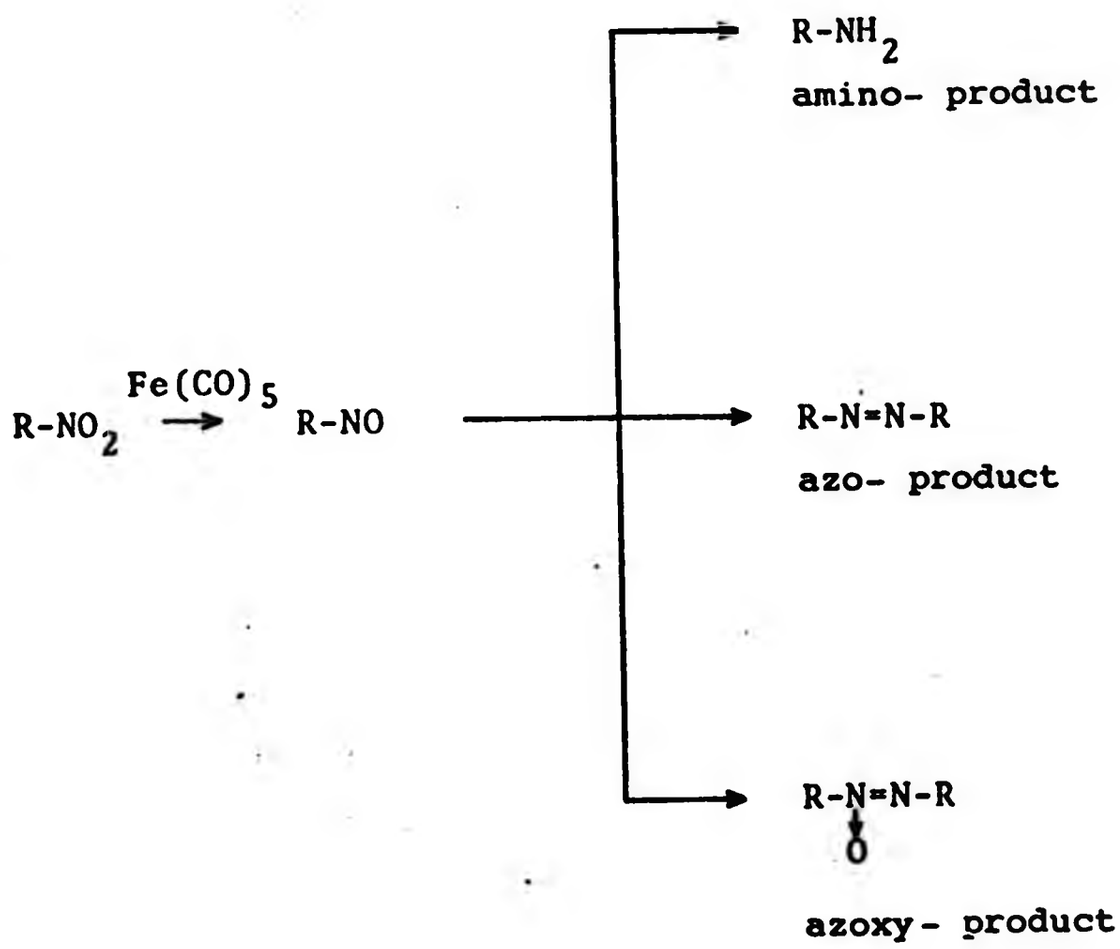
2 acacH + Fe^{2+}



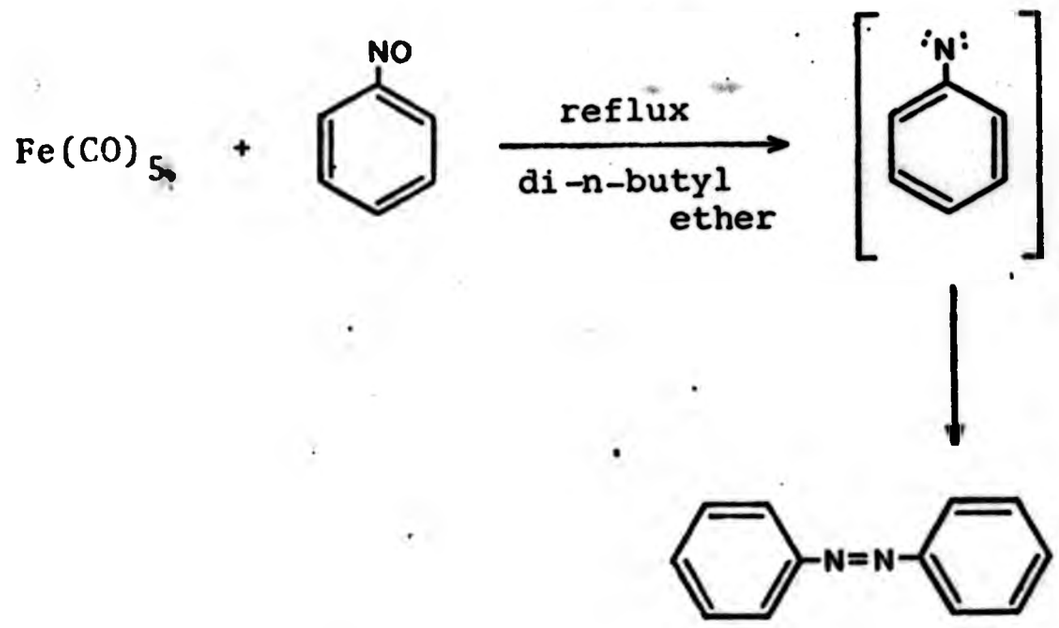
Reaction 2

2.4 The reaction of pyrazol-5-one oximes with iron pentacarbonyl.

The reactions of iron pentacarbonyl with several nitro-, nitroso- and oximino compounds have been previously described.[42-50] Nitro- and nitroso- compounds undergo deoxygenation to give products, the formulation of which is generally accounted for in terms of nitrene intermediates (Schemes 7 and 8).[51,52]

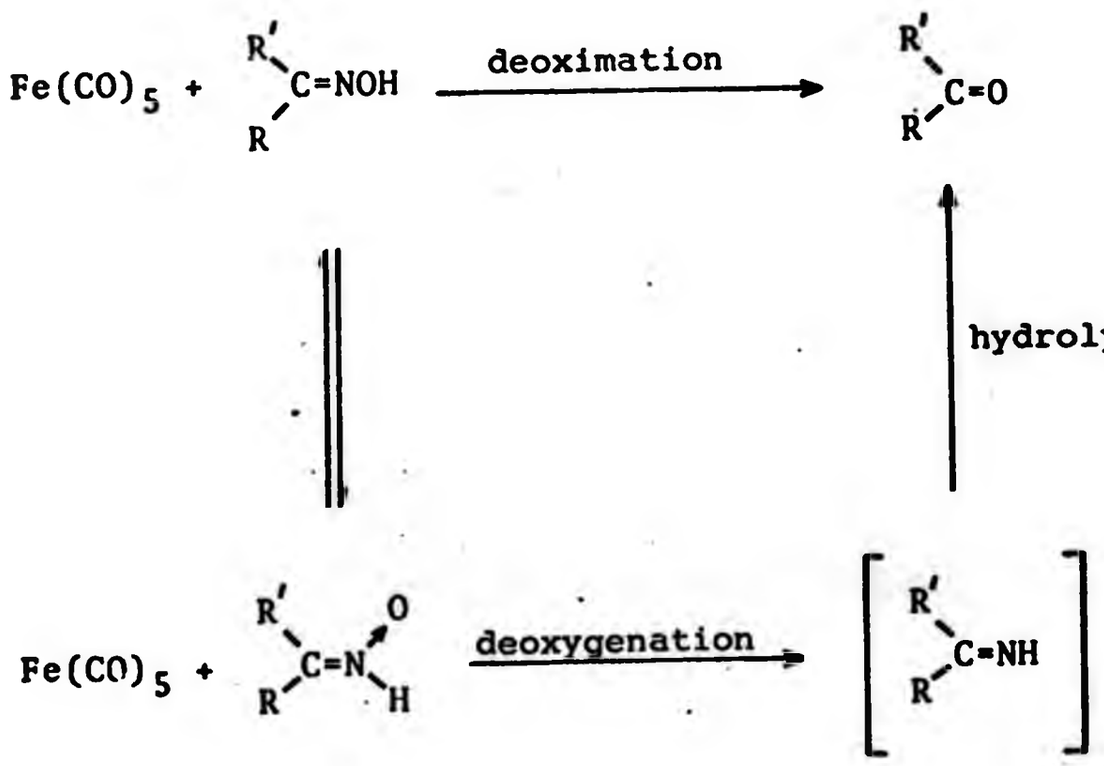


Scheme 7



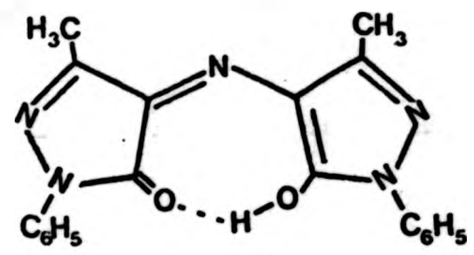
Scheme 8

For oximinocompounds, both deoxygenation and deoximation behaviour has been reported (Scheme 9)[44,53].



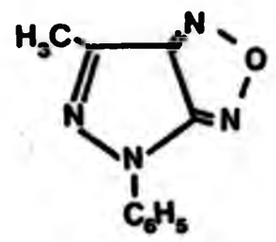
Scheme 9

3-Methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione (2 mol. equiv.) reacted with iron pentacarbonyl (1 mol. equiv.) in refluxing tetrahydrofuran to give mainly 2,4-dihydro-4-[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl) imino]-5-methyl-2-phenyl-3H-pyrazol-3-one (17). Minor



(17)

products included 1,2,5-oxadiazolo-[3,4-d]-6-methyl-4-phenyl-4H-pyrazole (18) and $Fe(Ppo)_2.nH_2O$. When excess

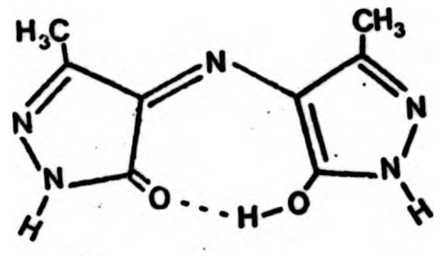


(18)

iron pentacarbonyl was used, the main product was again (17) but no trace of the bischelate was detected.

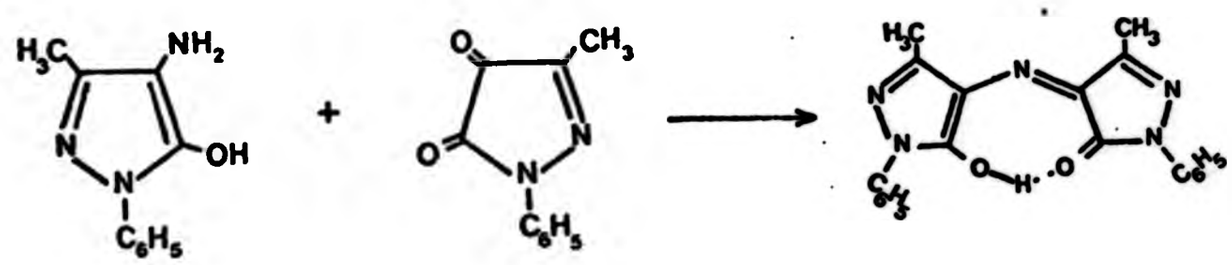
The reaction of 3-methyl-4-oxime-1H-pyrazol-4,5-dione with iron pentacarbonyl in a 2:1 mole ratio under similar conditions was slow. However when the ratio was 5:1 or above, the complex $Fe(po)_2.H_2O$ was isolated. Organic products included 2,4-dihydro-4-[(5-hydroxy

-3-methyl-1H-pyrazol-4-yl)imino]-5-methyl-3H-pyrazol-3-one (19) and small quantities of unreacted ligand.



(19)

Previously compound (17) was prepared by the condensation of 4-amino-5-hydroxy-3-methyl-1-phenyl-1H-pyrazole with 3-methyl-1-phenyl-1H-pyrazol-4,5-dione (Reaction 3)[54]. Further evidence for the structure assigned



Reaction 3

to (17) is now provided by studies of the C^{13} n.m.r.(Figure 6), i.r. spectra (Figure 7) and mass spectra.

The peaks in the ^{13}C spectrum of (17) due to the phenyl group may be readily assigned by comparison with those obtained for PpoH, and those obtained by Begtrup et. al. for 3-methyl-1-phenyl-1H-pyrazol-4,5-dione (Table 7)[55].

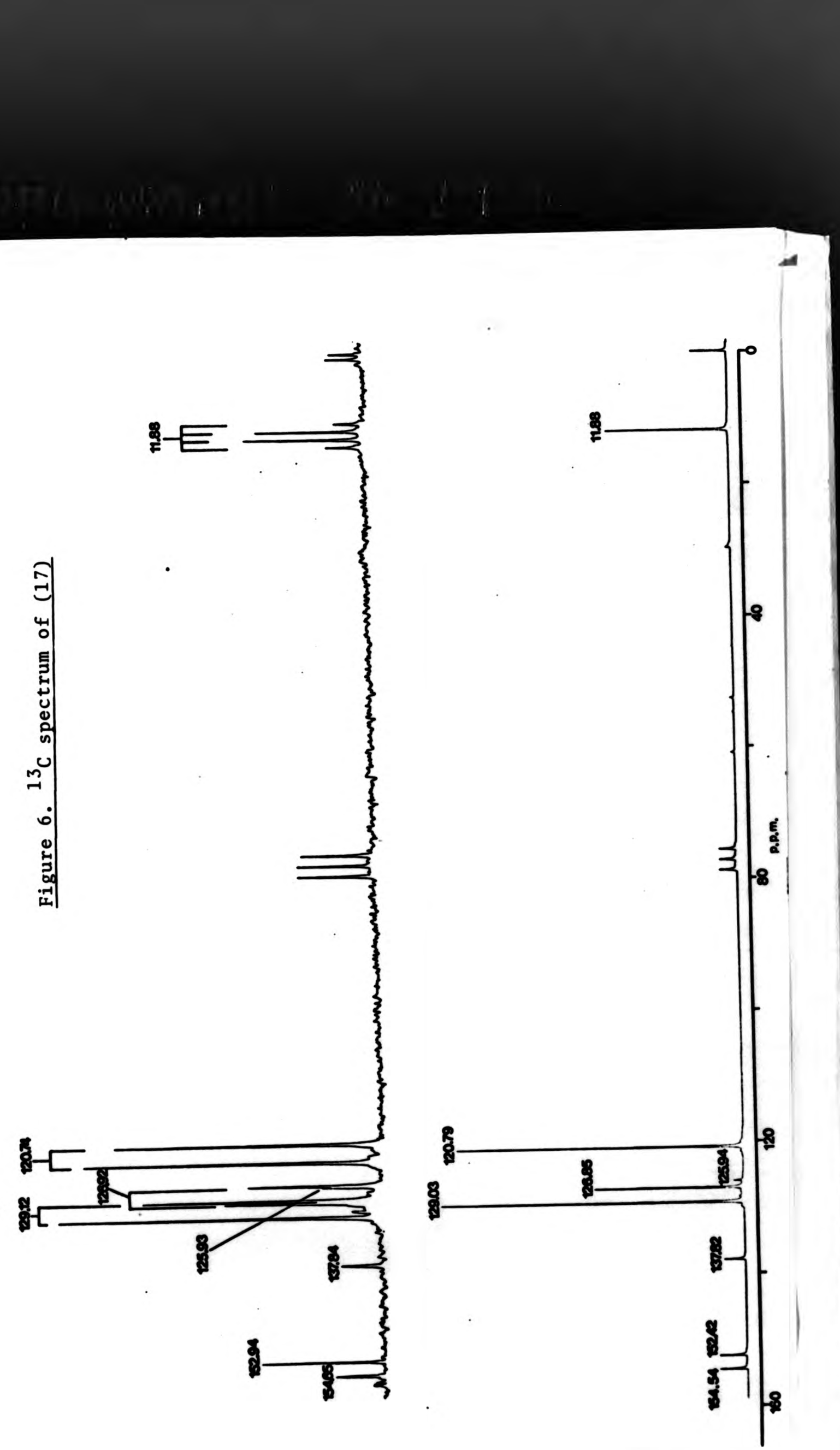
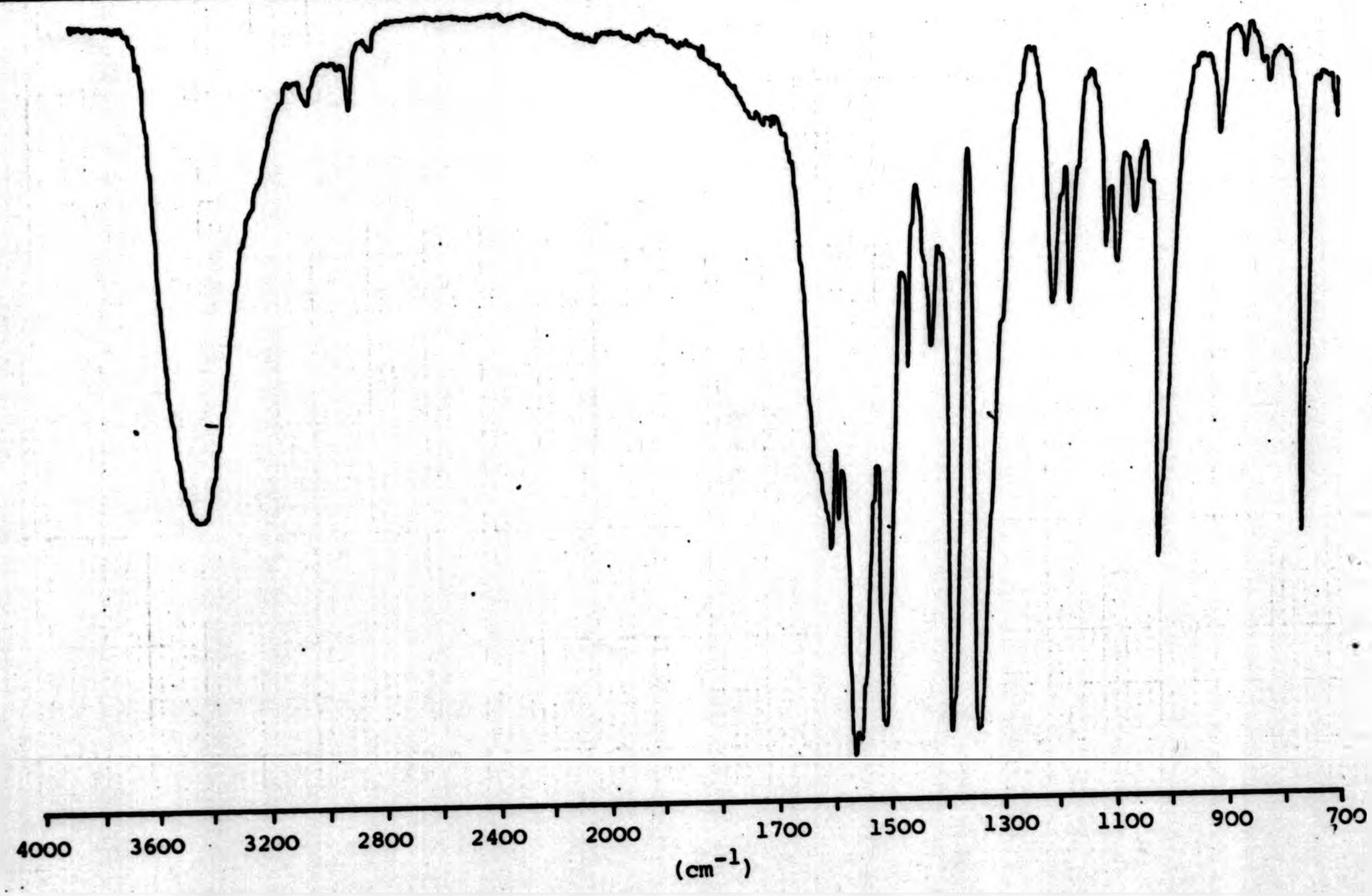


Figure 6. ^{13}C spectrum of (17)

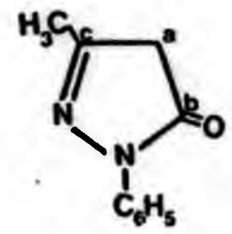
Figure 7. I.r spectrum of (17) (KBr disc)



Phenyl C atom	Chemical shift(p.p.m.)		
	(17)	PpoH	Begtrup et. al.[55]
ortho-	120.7	118.4	121.1
meta-	129.0	129.0	128.8
para-	126.9	124.9	126.7
Cl	137.8	138.1	137.2

Table 7

The remaining signals were assigned by comparison with those observed by Feeney et. al. for 3-methyl-1-phenyl-1H-pyrazol-5-one (Figure 8)[56]. It is reasonable to assume that

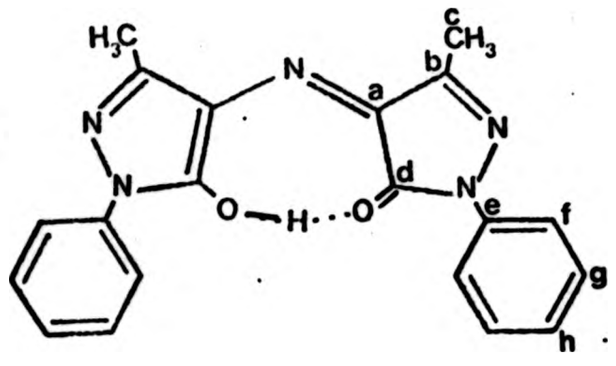


Shifts(p.p.m.)
a 150.5
b 157.5
c 90.5

Figure 8

(17) follows a similar pattern. Consequently all the signals obtained in the ^{13}C spectrum of (17) are assigned and tabulated in Figure 9.

The i.r. spectrum of (17) is presented in Figure 7. The molecule is stabilised by a strong, intramolecular hydrogen bond making up part of an eight membered ring. A sharp peak at 1560 cm^{-1} in the i.r. spectrum of (17) has been assigned to C=O stretch compared to 1725 cm^{-1} in PpoH. This large drop is due to the reduction in bond order of the carbonyl group and a consequent lengthening



Shifts (p.p.m.)

a 152.5
b 125.9
c 11.9
d 154.5
e 137.8
f 120.7
g 129.0
h 126.9

Figure 9

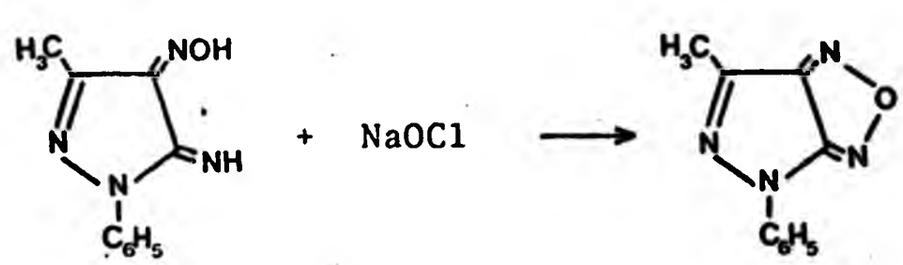
of the carbon-oxygen bond. The chelated proton appears in the ^{1}H n.m.r. spectrum at 16.7 p.p.m.. This extremely low value is indicative of the heavy deshielding experienced by the proton and is comparable to the intramolecular hydrogen bond in acetylacetone which appears at 16.2 p.p.m.[57]. The mass spectrum of (17) produced an intense molecular ion whose exact mass corresponded to the proposed molecular formula.

Compound (17) was resistant to acid hydrolysis, but was reduced by lithium aluminium hydride to the corresponding N,N'-bis-3-methyl-1-phenylpyrazole(20)-Reaction 4.

(20)

Reaction 4

Compound (18) was previously prepared by Mohr[58] by the oxidation of 5-imino-3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione with sodium hypochlorite (Reaction 5). Compound (18) was characterised by a



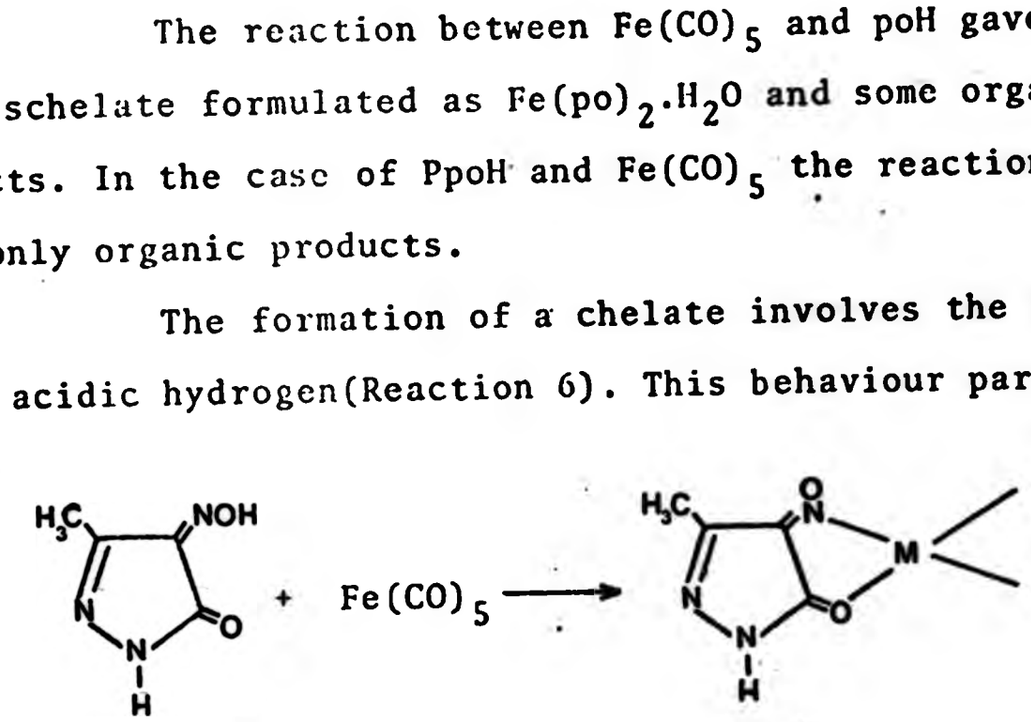
Reaction 5

comparative melting point and mass spectrometry.

Compound (19) is analogous to (17) and was characterised by ^1H n.m.r. and exact mass measurements. Compound (19) also possesses a strong intramolecular hydrogen bond, which appears at 16.7 p.p.m.in the ^1H n.m.r. and disappears upon shaking with D_2O. The mass spectrum of (19) shows an intense parent ion at m/e 207, the exact mass of which corresponds to the proposed molecular formula. The i.r. spectrum shows an intense absorbtion at 1545 cm^{-1} ascribable to C=O stretch and comparing with a value of 1720 cm^{-1} in the free ligand.

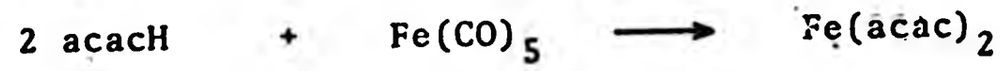
The reaction between $Fe(CO)_5$ and poH gave the bischelate formulated as $Fe(po)_2.H_2O$ and some organic products. In the case of PpoH and $Fe(CO)_5$ the reaction gave only organic products.

The formation of a chelate involves the loss of an acidic hydrogen(Reaction 6). This behaviour parallels



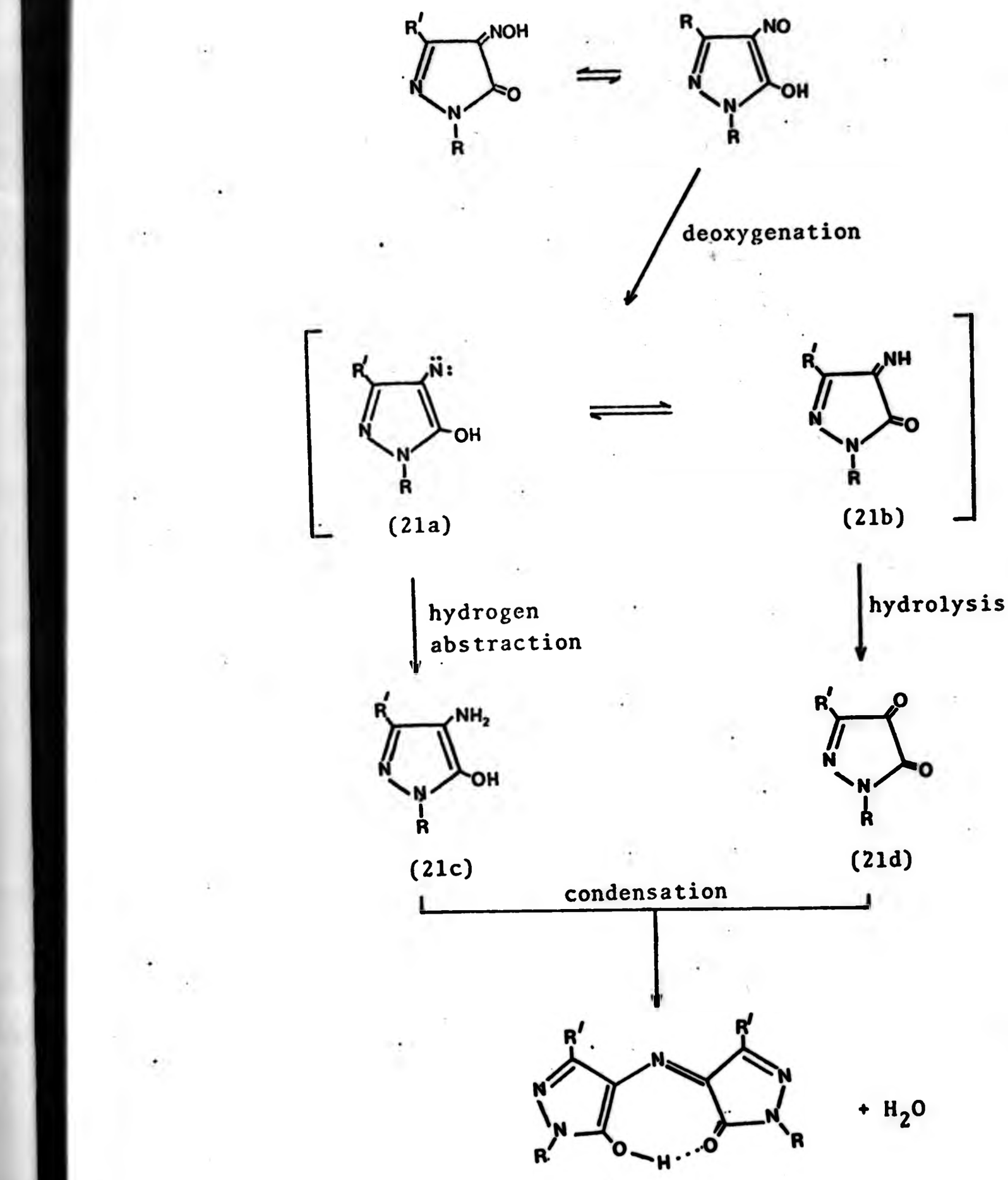
Reaction 6

that of other chelating ligands towards iron pentacarbonyl e.g. Reaction 7.[59-61]



Reaction 7

The formation of the organic products can be rationalised in terms of deoxygenation of the ligand as described in Scheme 10. Initial deoxygenation of the nitroso tautomer results in an intermediate species best described in terms of a nitrene (21a)-quinoneimine (21b) tautomeric mixture. The nitrene species can abstract hydrogen from the solvent to form the corresponding amino


deoxygenation
(21a)
(21b)
hydrogen abstraction
hydrolysis
(21c)
(21d)
condensation
+ H_2O

Scheme 10

compound (21c). The quinoneimine may simultaneously be hydrolysed to yield a dione (21d) which then condenses with the amine (21c) to yield the desired product.

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CHAPTER 3

THE INTERACTION OF 5-HYDROXY-2-NITROSOPHENOL AND 5-HYDROXY-6-METHYL-2-NITROSOPHENOL AND THEIR COPPER(II) COMPLEXES WITH TRIPHENYLPHOSPHINE.

3.1 Introduction

It is well known that trivalent phosphorus compounds deoxygenate aromatic nitro-[1-5] and nitroso-[6-8] compounds (Reaction 1). The ease with which this reaction takes place

$$PPh_3 + ZO_2 \text{ (or ZO)} \longrightarrow Ph_3P{=}O + [Z]$$

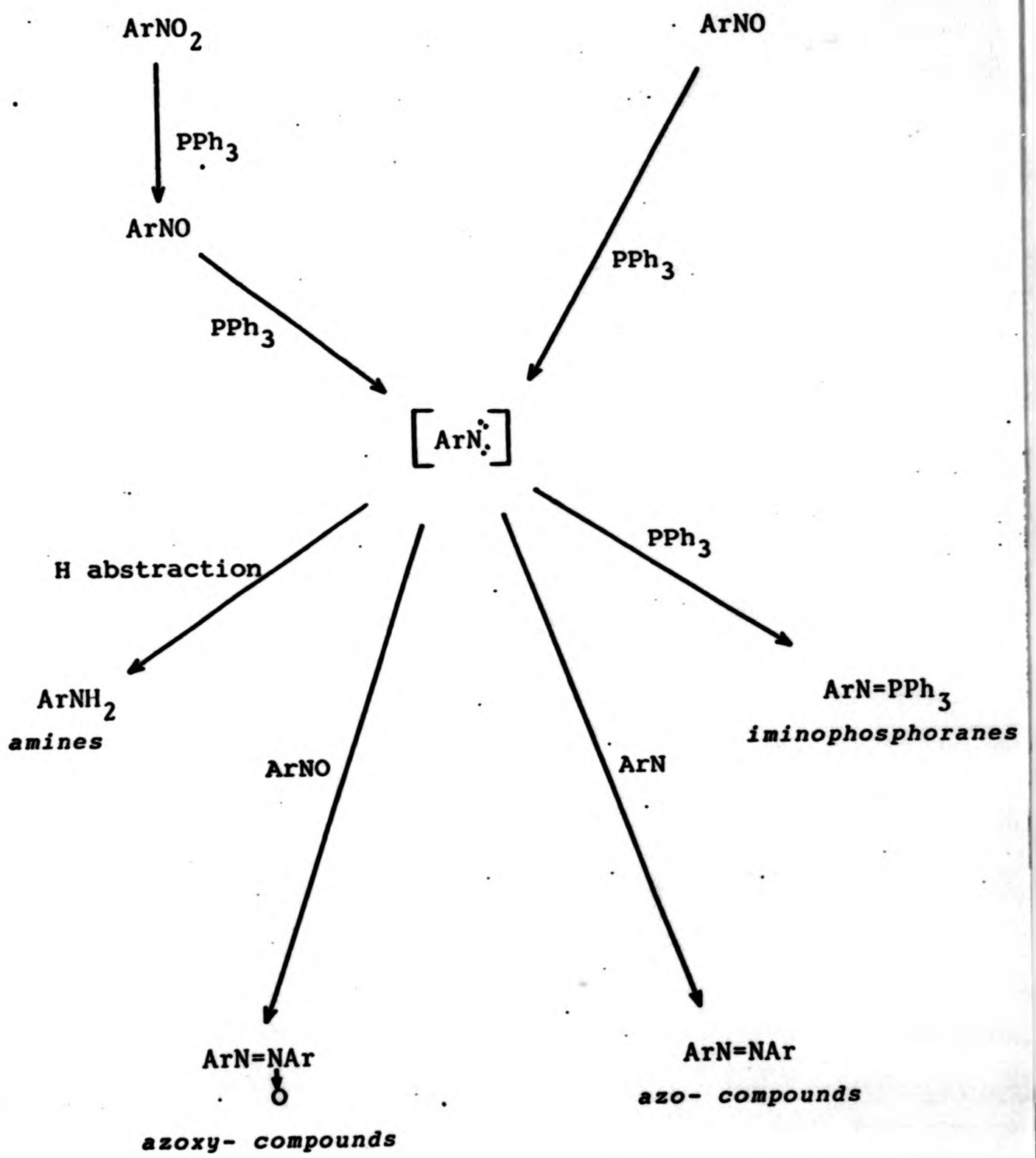
(Z=ArN)

Reaction 1

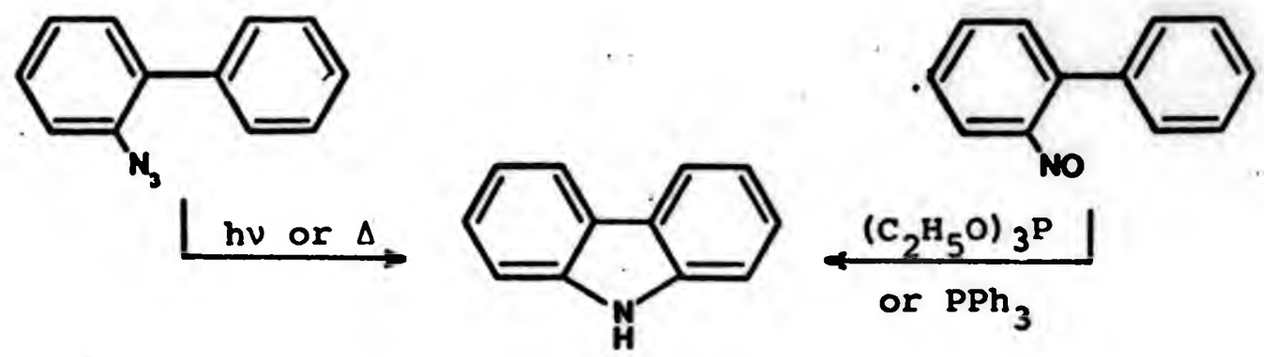
is attributed to the ability that phosphorus has to extend its valence shell to accommodate ten electrons and the great strength of the phosphorus-oxygen double bond.[9]

It has been suggested that the intermediate [Z] in Reaction 1 is a nitrene which may react further to give the type of compounds described in Scheme 1.

Support for the intermediacy of nitrenes has been provided by the comparison of the deoxygenation of aromatic nitro- and nitroso- compounds with the pyrolysis and photolysis of the corresponding azides (Scheme 2).[10]


ArNO2
PPh3
ArNO
PPh3
ArNO
PPh3
[ArN:]
H abstraction
ArNH2
amines
PPh3
ArN=PPh3
iminophosphoranes
ArNO
ArN
ArN=NAr
azoxy- compounds
ArN=NAr
azo- compounds

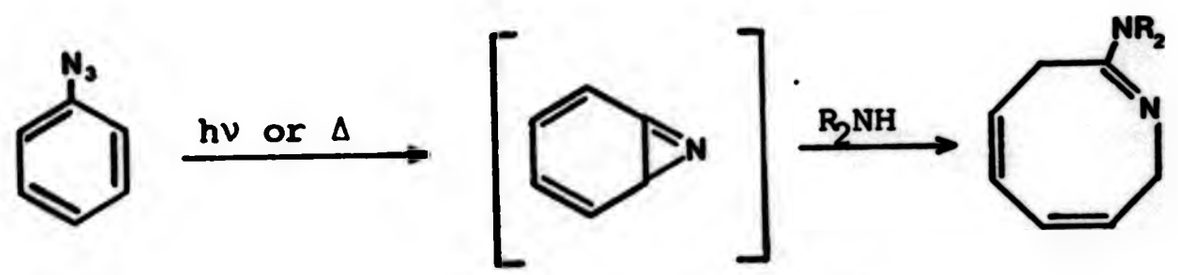
Scheme 1



Scheme 2

The common product, carbazole, suggested that both reactions proceeded via a common nitrene intermediate.

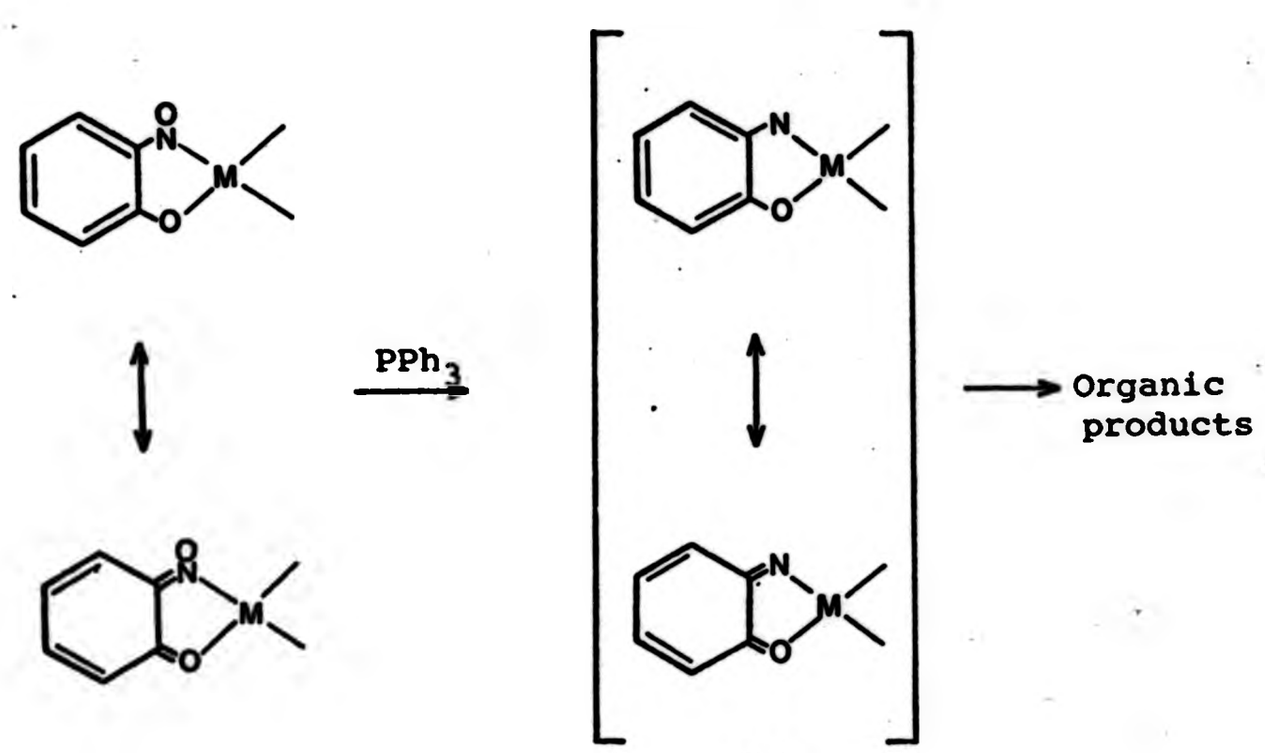
Further support for the intermediacy of the nitrene species is provided by the pyrolysis and photolysis of phenyl azides in amines[11]. These reactions proceed via nitrenes which undergo ring expansion in the presence of the amine to give derivatives of 2-amino-3-H-azepines (Reaction 2).



Reaction 2

The deoxygenation of metal complexes derived from 2-nitrosophenols and their derivatives was thought to provide a convenient method of trapping nitrene intermediates[12-14]. It was

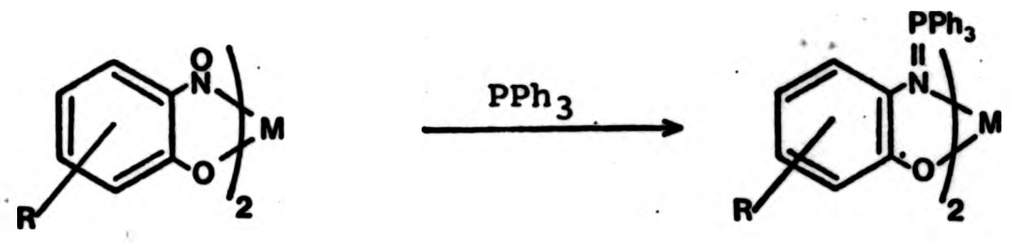
anticipated that such a species may be isolable as the more stable quinoneimine complex (5). However even though



(5)

no nitrene complexes were isolated, the nature of the products derived from the reactions were rationalised in terms of nitrene intermediates.[15]

The nature of the products formed is dependent on the metal used and its available oxidation states, and the character of the ligand. For example the zinc(II) and nickel(II) complexes derived from qoH (qoH = 2-nitrosophenol or a substituted 2-nitrosophenol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol) give iminophosphoranes (Scheme 3).

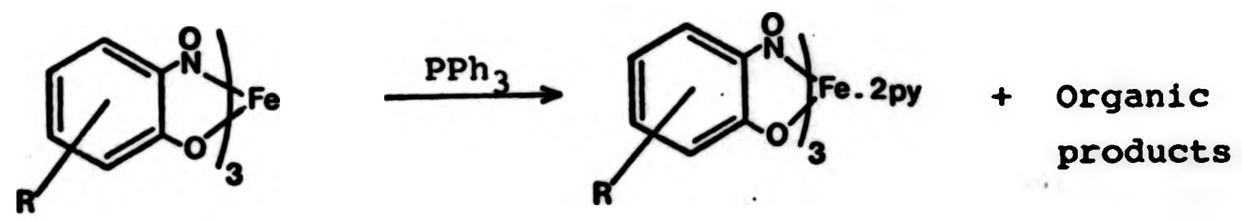


R = H, alkyl, alkoxy.

M = Ni(II), Zn(II).

Scheme 3

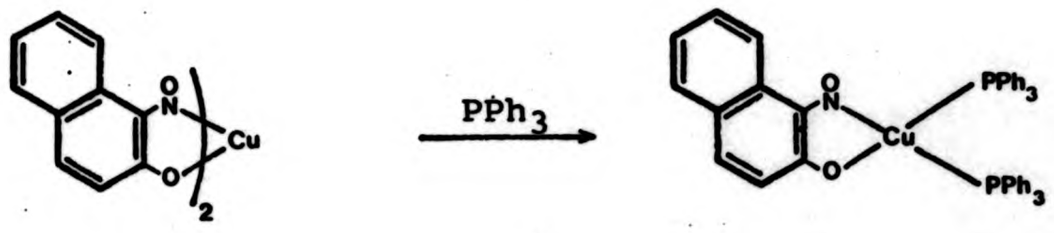
In contrast the copper(II) and iron(III) complexes derived from qoH, yield the respective copper(I) and iron(II) complexes and organic products, e.g. Schemes 4,5,6.[16]

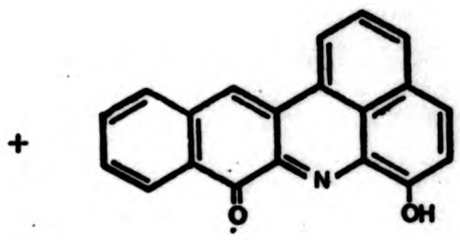


R = H, alkyl, alkoxy;

Scheme 4

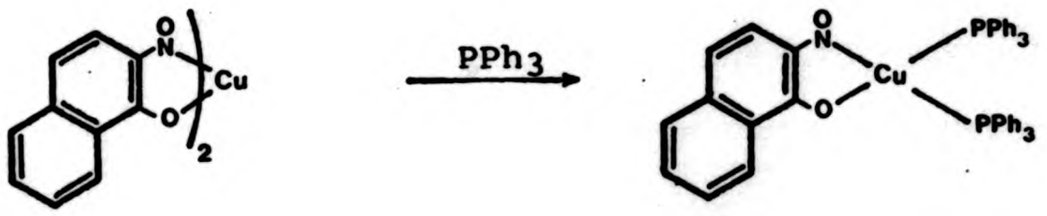
In these cases the nature of the organic products depends on the substitution pattern of the ligand. Thus whereas bis(1,2-naphthoquinone-1-oximato)copper(II) when treated with triphenylphosphine gives 1,2-naphthoquinone-1-oximatobis-(triphenylphosphine)copper(I) and organic products (Scheme 5); the isomeric complex bis(1,2-naphthoquinone-2-oximato)copper (II) when reacted under similar conditions gives 1,2-naphtho-quinone-2-oximatobis(triphenylphosphine)copper(I) and a different set of organic products (Scheme 6)[17].

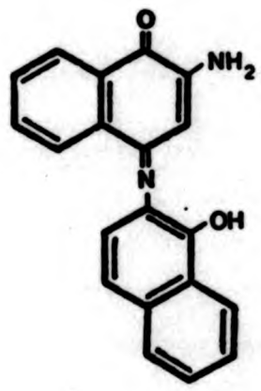




+ + Other organic products.

Scheme 5



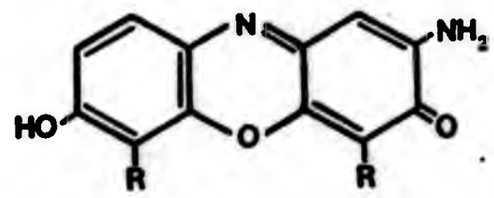


+ + Other organic products.

Scheme 6

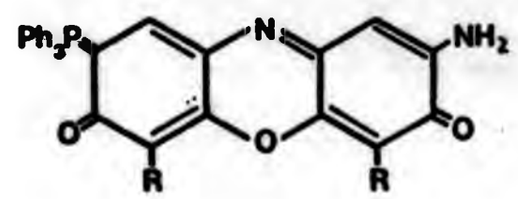
3.2 A study of the interaction of $Cu(mnr)_2.py$, $Cu(6\text{-}Memnr)_2.py$ mnrH and 6-MemnrH with triphenylphosphine.

When bis(5-hydroxy-1,2-benzoquinone-2-oximato) copper(II)-monohydrate (1 mol. equiv.) and triphenylphosphine (5 mol. equiv.) were heated under reflux in pyridine (150 cm^3) a multiple component mixture resulted. Upon separation using column chromatography, five fractions were obtained. The fractions obtained, in increasing polarity of eluting solvent gave triphenylphosphine, triphenylphosphine oxide, 2-amino-7-hydroxy -3H-phenoxazine-3-one (Compound A)(Figure 1,R=H), 2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (Compound B)(Figure 2,R=H). A black intractable mass remained on top of the chromatography column.



R = H, CH_3

Figure 1 Compound A



R = H, CH_3

Figure 2 Compound B

The reaction of bis(5-hydroxy-6-methyl-1,2-benzoquinone-2-oximato)copper(II)-monohydrate (1 mol. equiv.) with triphenylphosphine (5 mol. equiv.) in refluxing pyridine produced the analogous compounds, 2-amino-7-hydroxy-4,6-dimethyl-3H-phenoxazine-3-one (Figure 1,R=CH_3) and 2-amino-4,6-dimethyl-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (Figure 2,R=CH_3).

These products were also obtained when 5-hydroxy-2-nitrosophenol and 5-hydroxy-6-methyl-2-nitroso-phenol were reacted with triphenylphosphine in a 1:5 mole ratio using either pyridine or chloroform as solvent.

A feature of note of all the phenoxazinones was their extreme insolubility and very high extinction coefficients (Table 1).

Compound	λ_{max}[nm] (ϵ[$m^2 mol^{-1}$])
Compound A, R=H	203(79.3), 233(93.4), 455(71.5)
Compound B, R=H	228(2641), 265(1720), 527(1429)
Compound A, R=CH_3	194(85.6), 221(104.1), 454(71.0)
Compound B, R=CH_3	220(1940), 264(1709), 501(1289)

Table 1. Extinction coefficients of Compounds A and B in methanol.

Compounds A (R=H or CH_3) were reddish-pink on the silica column but were eluted by toluene as yellow solutions and crystallised from pyridine as yellow cubes. Compounds B(R=H or CH_3) were fluorescent red and crystallised from pyridine/light petrol(80-100 fraction) as very dark red cubes.

Compound A(R=H) was characterised by microanalysis, and using spectral methods. The i.r. spectrum of A(R=H) showed bands at 3460 cm^{-1} and 3360 cm^{-1} assignable to νN-H. Its ^{1}H n.m.r spectrum in d^{6}DMSO (Figure 3) showed five aromatic protons plus two exchangeable peaks comprising one and two protons and assigned as the OH and NH_2 groups respectively. These results suggest a structure as shown in Figure 1. Further evidence is provided by the mass spectrum of A(R=H) which shows loss of CO from the parent ion m/e 228.

The high insolubility of compound B(R=H) presented considerable characterisation problems. The i.r. spectrum of B(R=H) showed the presence of OH and NH groups and microanalysis indicated a phosphorus containing compound. Fourrier transform ^{1}H n.m.r. provided no structural backbone information but indicated at least two and possibly three exchangeable protons. ^{13}C n.m.r. was precluded by its high insolubility.

In order to obtain a more soluble product the acetylation of compound B(R=H) was attempted. Stirring in the cold with acetic anhydride and precipitation into water yielded a solid which was also highly insoluble. However recrystallisation from pyridine gave a red product (C). The mass spectrum of C (Figure 4) showed a parent ion at m/e 530 of exact mass 530.1426. This corresponded to the molecular formula $C_{32}H_{23}N_4O_4P$ and indicated monoacetylation which was comfirmed by elemental analysis. A ^{31}P n.m.r. study on C in dimethyl sulphoxide required sixty hours of machine time

ADDRESS	FREQUENCY	PPM	INTEGRAL	INTENSITY
1204	840.332	10.504	2922.496	294.912
1207	618.856	7.733	2251.264	119.808
1474	612.792	7.659	2332.672	683.008
1479	610.824	7.635	6523.904	1055.744
1480	604.320	7.562	8240.640	1886.208
1484	602.050	7.525	7197.696	833.536
1488	556.152	6.951	1186.304	398.848
1748	553.710	6.921	2413.568	664.064
1749	547.333	6.854	1830.576	718.336
1800	546.336	6.829	4840.448	1827.840
1810	540.113	6.751	7820.800	759.296
1812	516.113	6.451	4697.600	2009.600
1813	502.200	6.353	4570.624	2052.096
1814	505.371	6.317	15133.696	2576.384
2336	265.136	3.314	5070.336	1633.792
2511	204.101	2.551	10227.712	3239.424
2515	202.145	2.526	16800.256	4907.008
2519	200.683	2.508	9305.088	3736.064
2522	194.730	2.434	4418.048	1819.136
2525	194.777	2.459	6329.344	611.328
2727	98.632	1.232	1695.744	448.512
2730	60.058	0.750	4276.224	1373.248
2731	3.417	0.042	108838.400	65891.328
2814	0.000	0.000	8214.016	1841.664
2815	3.417 -	0.042		
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Figure 3. ^{1}H n.m.r of Compound A(R=H) in d^{6}DMSO

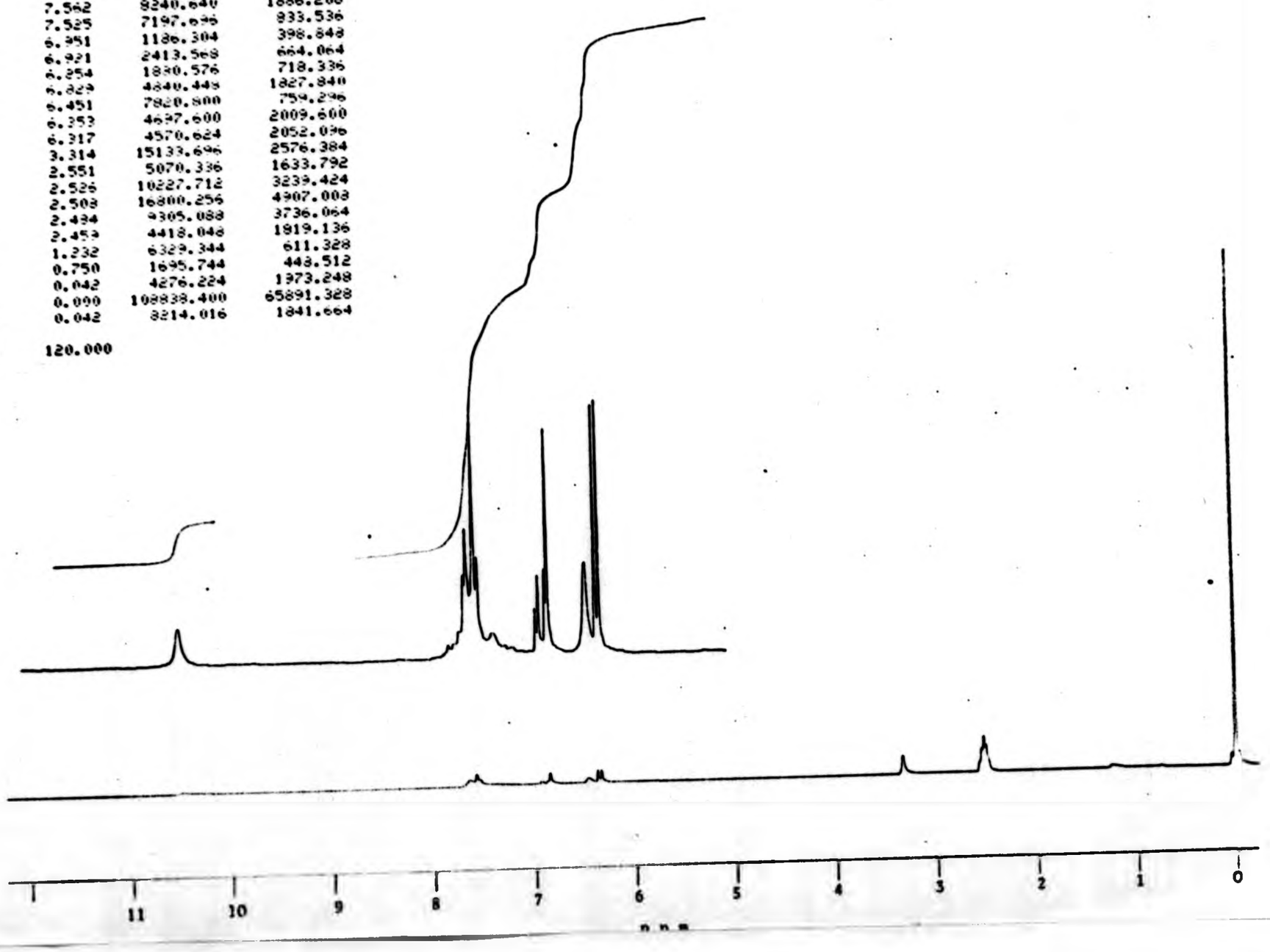
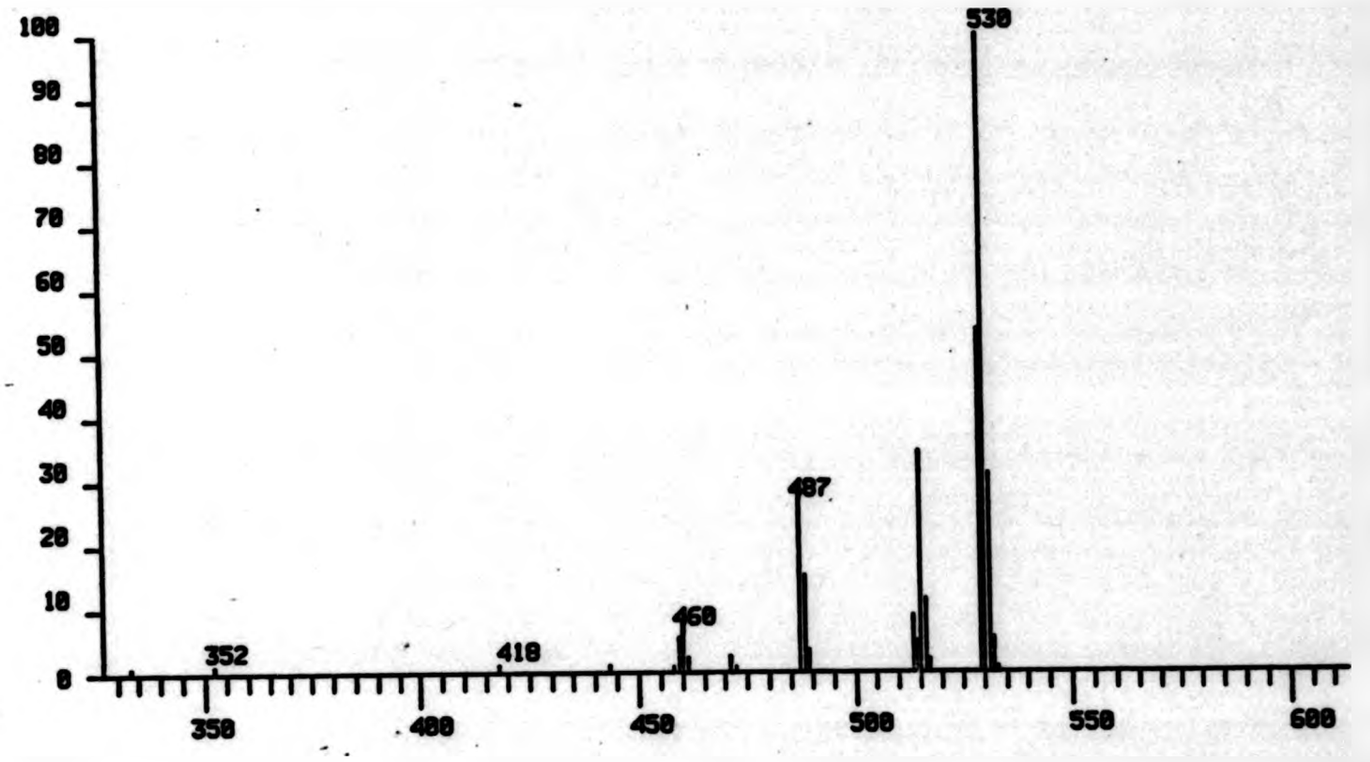
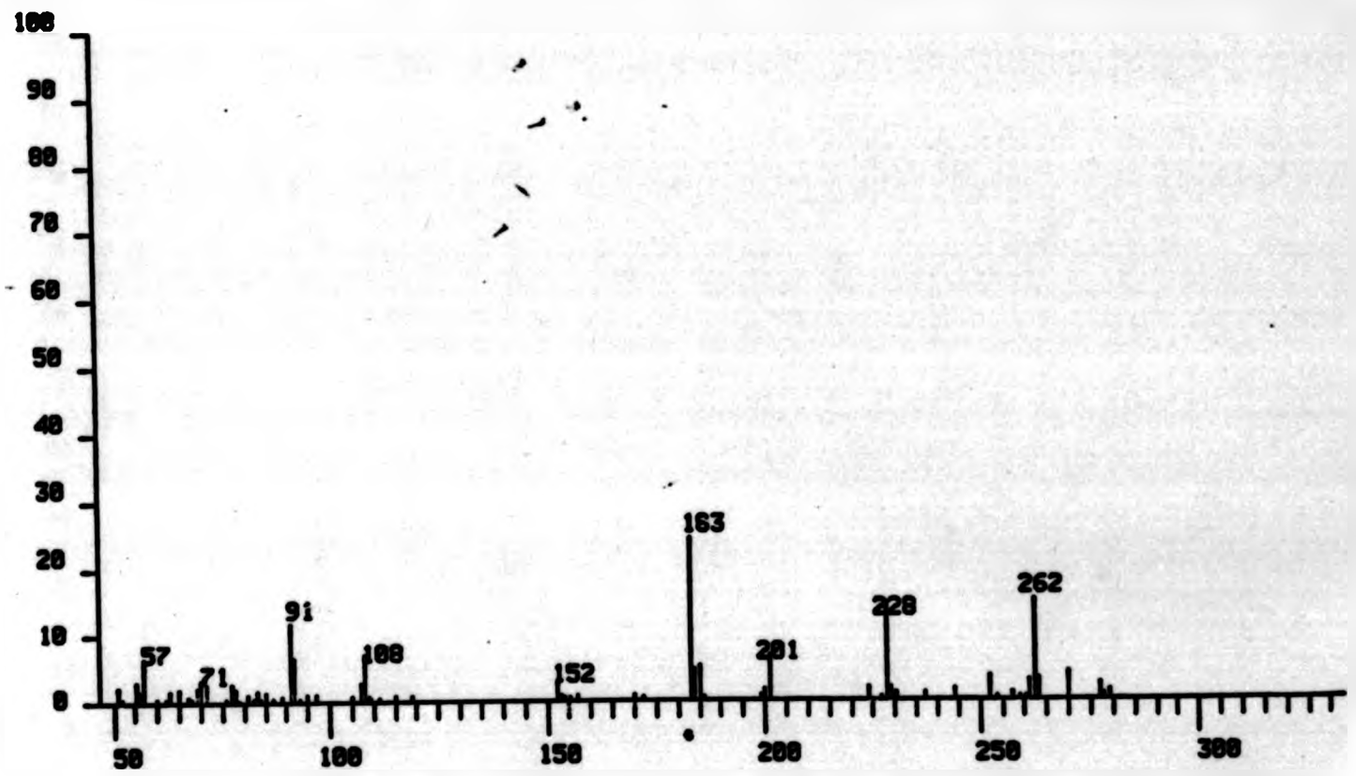
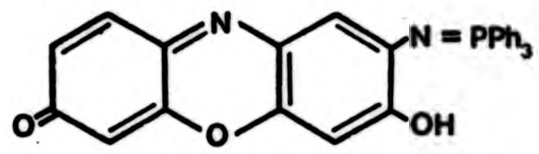


Figure 4. Mass spectrum of Compound C

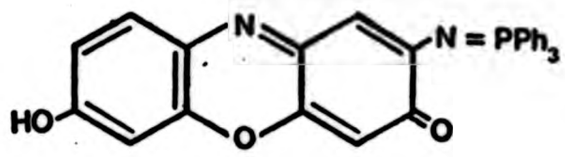




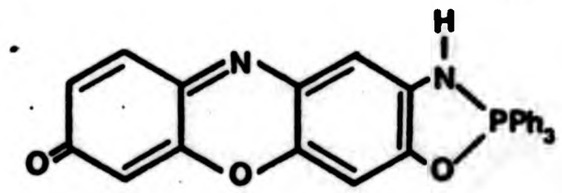
and produced only a weak signal at 21.2 p.p.m. (Figure 5). However this provided no useful information as values of chemical shift for the ^{31}P nucleus range from +200 p.p.m. to -200 p.p.m.[18] At this stage three structural possibilities for Compound C included (1), (2) and (3).



(1)

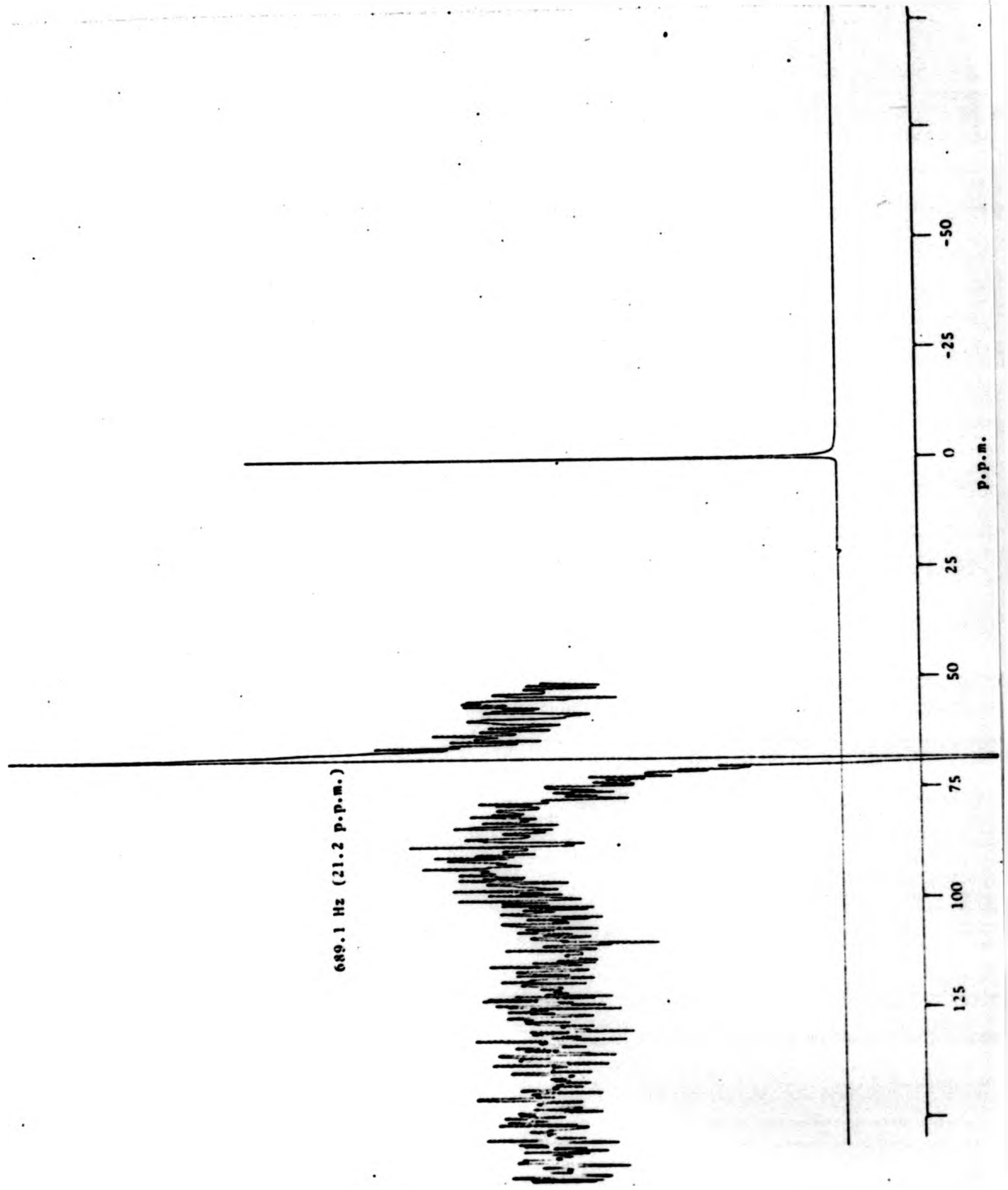


(2)

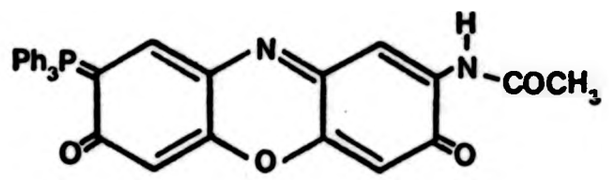


(3)

Figure 5. ^{31}P spectrum of Compound C



As the spectral methods employed did not lead to a structural formulation for compound C, it was decided to undertake an X-ray crystallographic study. Suitable crystals were grown from pyridine/light petrol(80-100 fraction). This study revealed that compound C was 2-N-acetyl-8-(triphenyl-phosphoranylidene)-3H,7H-phenoxazine-3,7-dione (4). Details



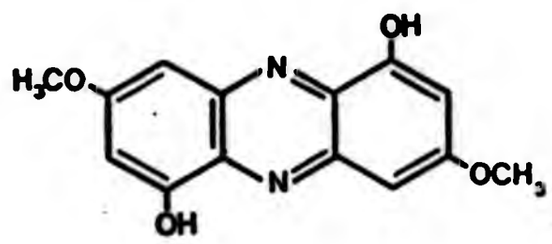
(4)

of this investigation are given in Chapter 4.

The characterisation of compounds A and B ($R=CH_3$) was achieved by elemental analysis, i.r. and u.v. spectroscopy, and by analogy to compounds A and B (R=H).

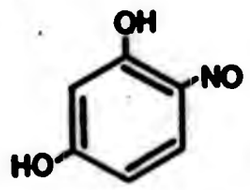
3.3 A reinvestigation of the reaction of 5-methoxy-2-nitrosophenol and its copper(II) complex with triphenylphosphine.

The formation of phenoxazinones in the mononitrosoresorcinol/triphenylphosphine system discussed in the previous section raised some doubts about the formulation of the main organic product of the 5-methoxy-2-nitroso-phenol/triphenylphosphine system.[19] It had been claimed that the product was 1,6-dihydroxy-3,8-dimethoxyphenazine(5). Therefore

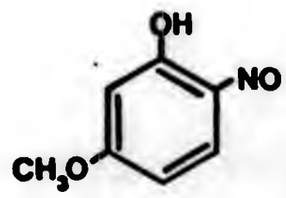


(5)

it is surprising that although the substitution patterns of the respective ligands are identical (6) and (7), the former

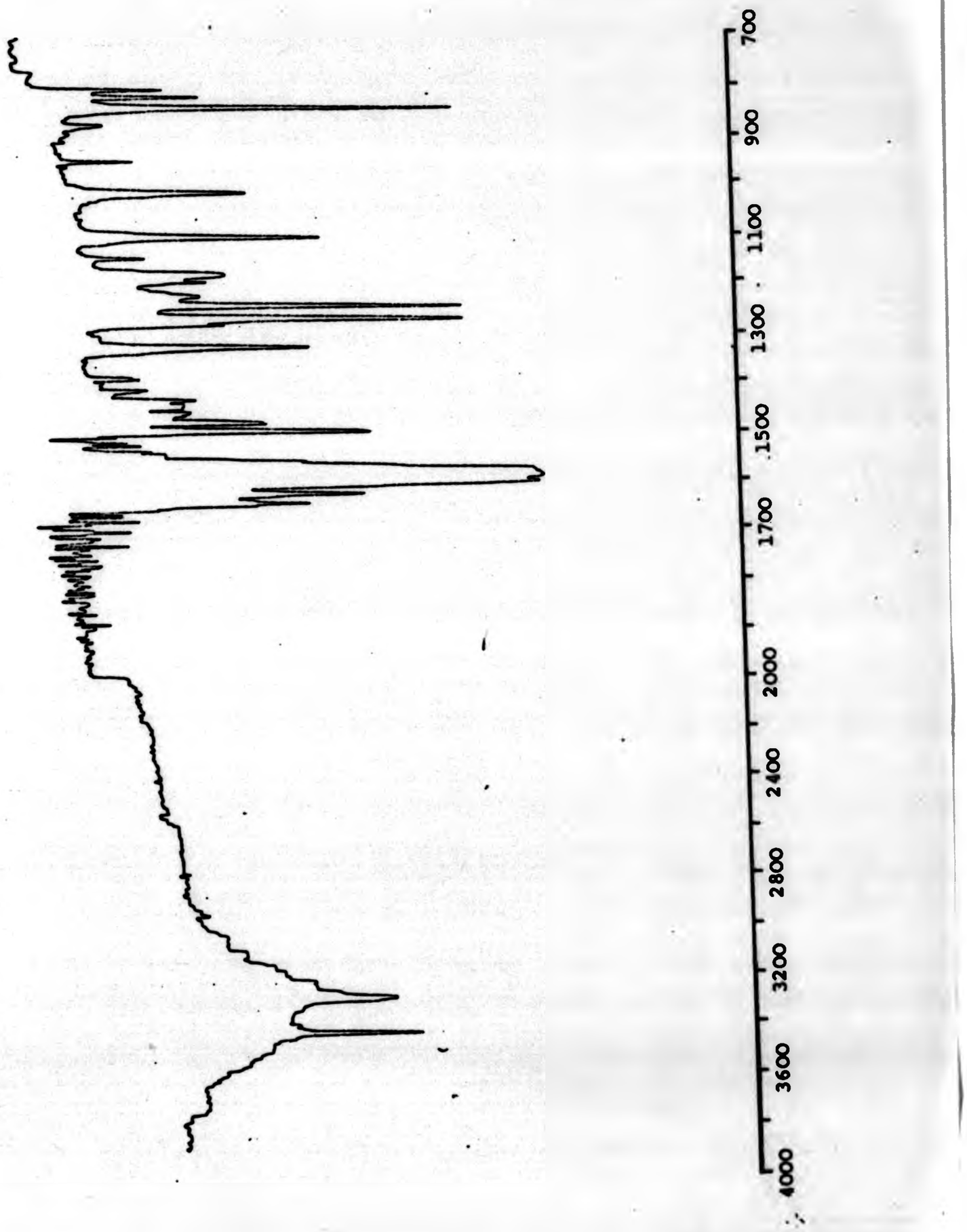


(6)



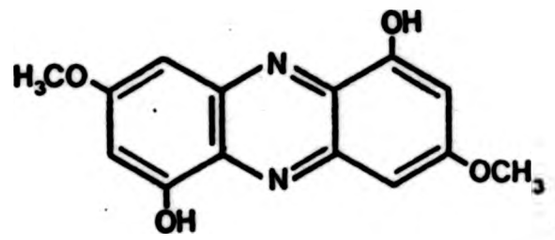
(7)

Figure 6. I.r. spectrum of D (KBr disc)



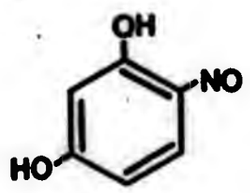
3.3 A reinvestigation of the reaction of 5-methoxy-2-nitrosophenol and its copper(II) complex with triphenylphosphine.

The formation of phenoxazinones in the mononitrosoresorcinol/triphenylphosphine system discussed in the previous section raised some doubts about the formulation of the main organic product of the 5-methoxy-2-nitroso-phenol/triphenylphosphine system.[19] It had been claimed that the product was 1,6-dihydroxy-3,8-dimethoxyphenazine(5). Therefore

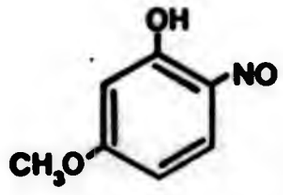


(5)

it is surprising that although the substitution patterns of the respective ligands are identical (6) and (7), the former



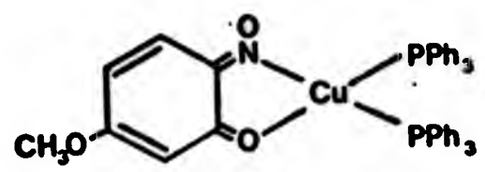
(6)



(7)

system produces exclusively phenoxazinones, while the latter produces phenazines as the major organic product. As a consequence it was decided to reinvestigate the reaction of 5-methoxy-2-nitrosophenol and its copper(II) complex with triphenylphosphine.

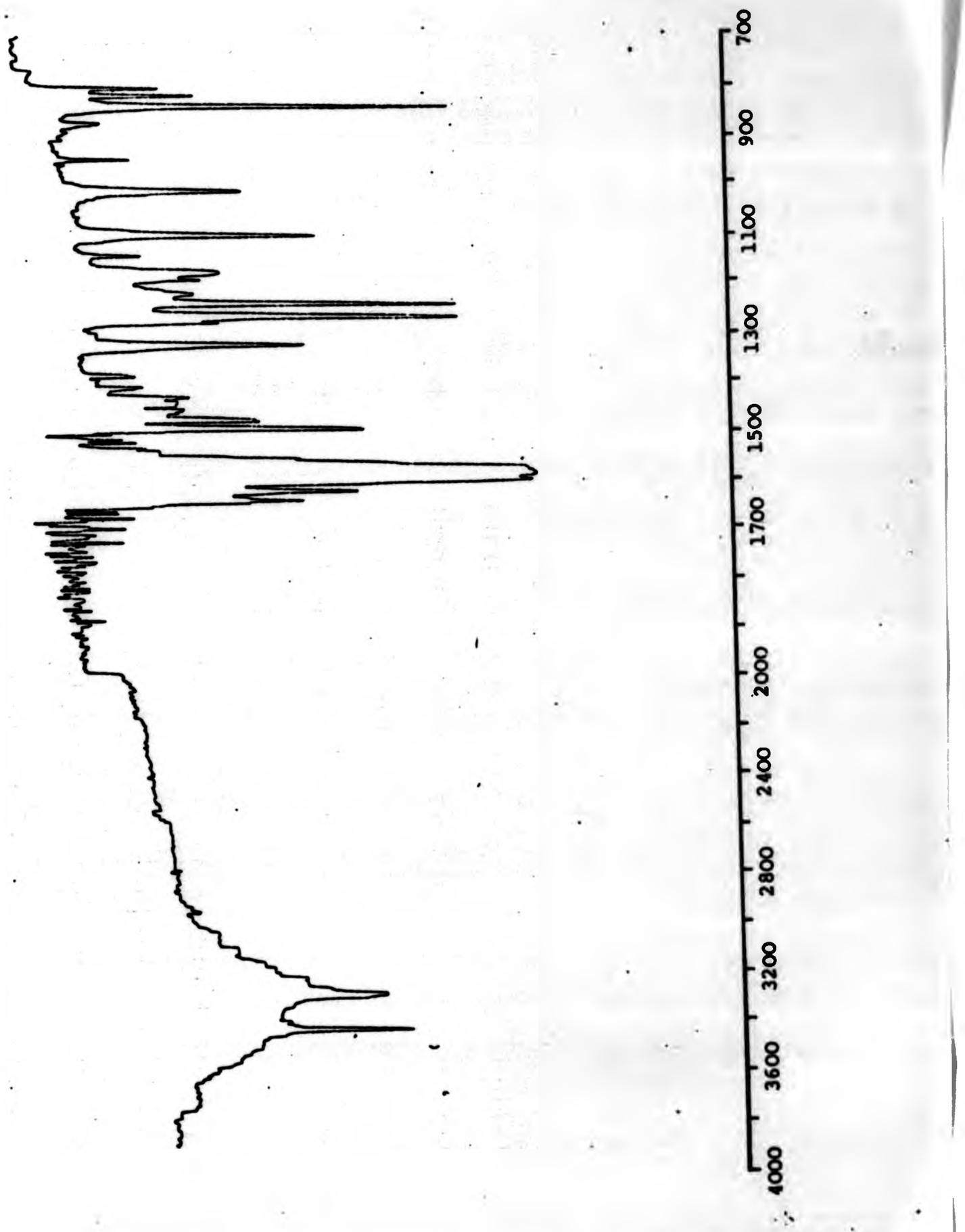
Bis(5-methoxy-1,2-benzoquinone-2-oximato) copper(II) (1 mol. equiv.) and triphenylphosphine (5 mol. equiv.) were heated under reflux in pyridine (150 cm^3) for six hours. Four main products were isolated by Soxhlet extraction. The metal containing product 5-methoxy-1,2-benzoquinone-2-oximatobis(triphenylphosphine)copper(I) (8)



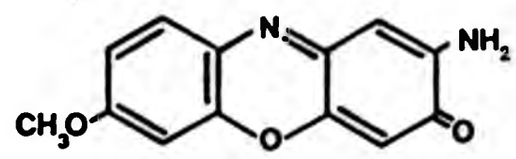
(8)

was extracted from the reaction mixture using diethyl ether. In addition triphenylphosphine and triphenylphosphine oxide were extracted by this process. The residue remaining in the Soxhlet thimble was re-extracted with pyridine to give an orange-red compound. This was recrystallised from pyridine as fine orange-red crystals (Compound D). Elemental analysis and exact mass measurements on the parent ion indicated a molecular formula of $C_{14}H_{12}N_2O_4$. The i.r. spectrum of D (Figure 6), shows bands at 3370 cm^{-1} and 3490 cm^{-1} assignable

Figure 6. I.r. spectrum of D (Kbr disc)



to νOH and νNH. The ^{1}H n.m.r. (Figure 7) showed three protons at 3.9 p.p.m. assignable to the methoxy group, five aromatic protons between 6.2 p.p.m. and 8.1 p.p.m., and two exchangeable protons at 6.8 p.p.m. assigned to the amino group. As a consequence of this reinvestigation it is concluded that compound D is 2-amino-7-methoxy-3H-phenoxazine-3-one (9)

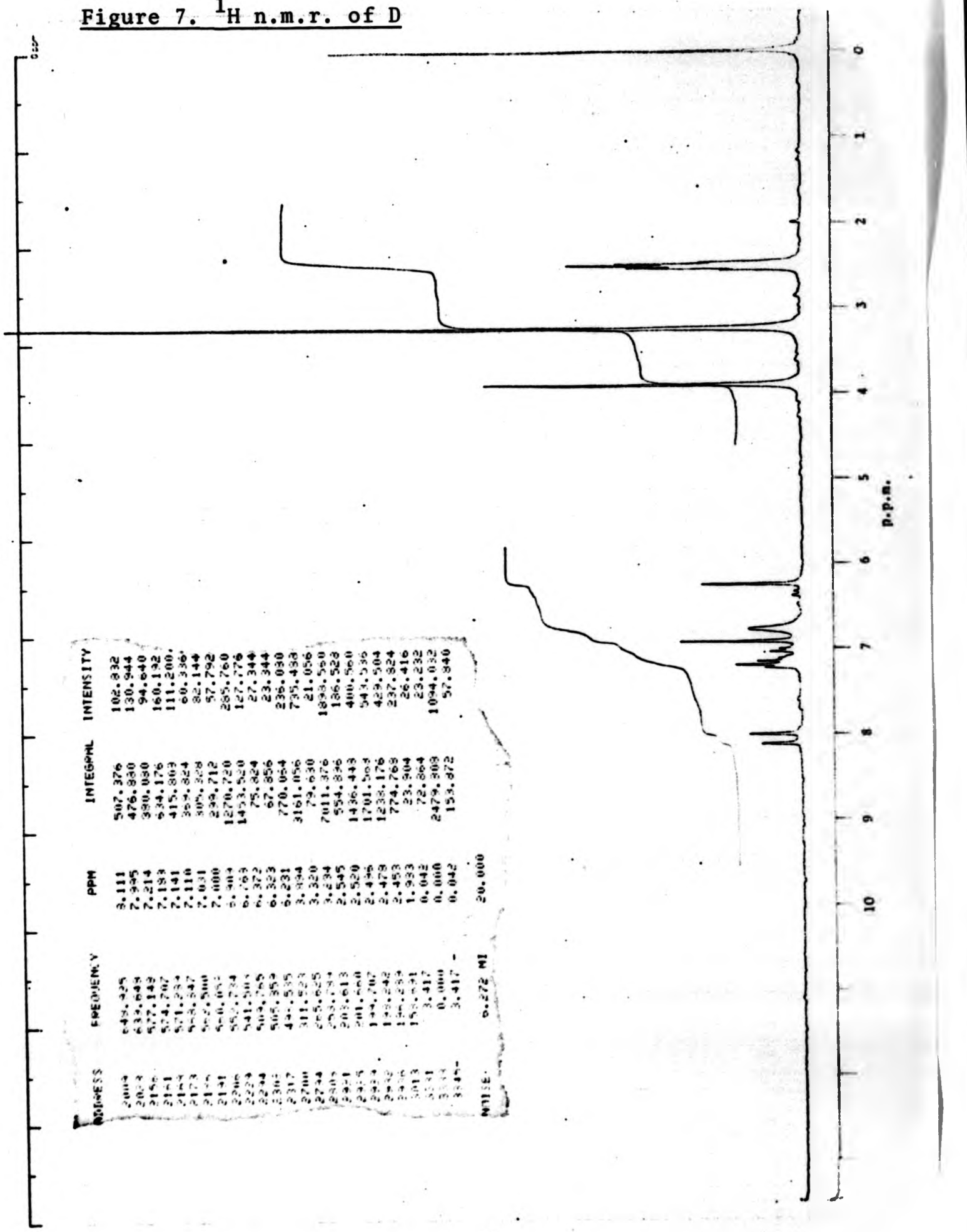


(9)

and not the phenazine as previously formulated.

It is of interest that the reaction of triphenylphosphine with 5-methoxy-2-nitrosophenol in a 5:1 mole ratio also gave the phenoxazinone D.

Figure 7. ^{1}H n.m.r. of D



3.4 A kinetic investigation of the reaction of bis(5-hydroxy-1.2-benzoquinone-2-oximato)copper(II)-monopyridine with triphenylphosphine in methanol at 25°C.

Before the kinetic investigation was commenced the u.v./visible spectra of bis(5-hydroxy-1,2-benzoquinone-2-oximato)copper(II)-monopyridine; 2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione and 2-amino-7-hydroxy-3H-phenoxazine-3-one were obtained. Standard solutions were made up and the results presented in Table 2.

Compound	$\lambda_{max.}$ (nm)	$\varepsilon(m^2mol^{-1})$
Bis(5-hydroxy-1,2-benzoquinone-2-oximato)copper(II)-monopyridine	215	6.0×10^{-3}
	354	5.6×10^{-3}
	458	2.7×10^{-2}
2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione	228	2641
	265	1720
	527	1429
2-amino-7-hydroxy-3H-phenoxazine-3-one	203	79.3
	233	93.4
	455	71.5

Table 3

The reaction was studied using a 1:4 mole ratio of complex to triphenylphosphine in methanol at 25 °C. The reaction was monitored by recording the decrease in

absorbance at 354 nm as a result of the consumption of the copper bischelate. The reaction was considered complete after 160 hours. In a typical reaction a methanolic solution of triphenylphosphine (9.24×10^{-4} mol dm^{-3}) was added to a methanolic solution of the copper complex (2.25×10^{-4} mol dm^{-3}). The spectrum obtained is shown in Figure 8.

A plot of $\ln(A_t - A_\infty)$ against time for the decrease in absorbance at 354 nm is given in Figure 9. The linearity of this plot after 400 minutes reaction time indicates a first order reaction with respect to the copper complex. However the portion of the graph preceeding 400 minutes does not appear to follow the first order rate law expression. An explanation of this non-linearity is that the overall reaction takes place in two discrete steps, the second step of which is first order with respect to the complex.

However assuming that this is the case, it is not valid to process the data from the early part of the reaction, i.e. that preceeding 400 minutes, using the value of A_∞ (0.709) measured after leaving the reaction mixture for one week. It was therefore proposed that as a useful approximation, to draw the best straight line through the data points following 400 minutes and that where the earlier points started to deviate from this line, that value of $\ln(A_t - A_\infty)$ could be used to calculate a 'new' value of A_∞ . This new value (A_∞') could then be used to reprocess the earlier data.

A plot of $(A_t - A_\infty')$ against time was then drawn (Figure 10) and the gradients of the tangents to the curve at various times measured. This gives a measure of the

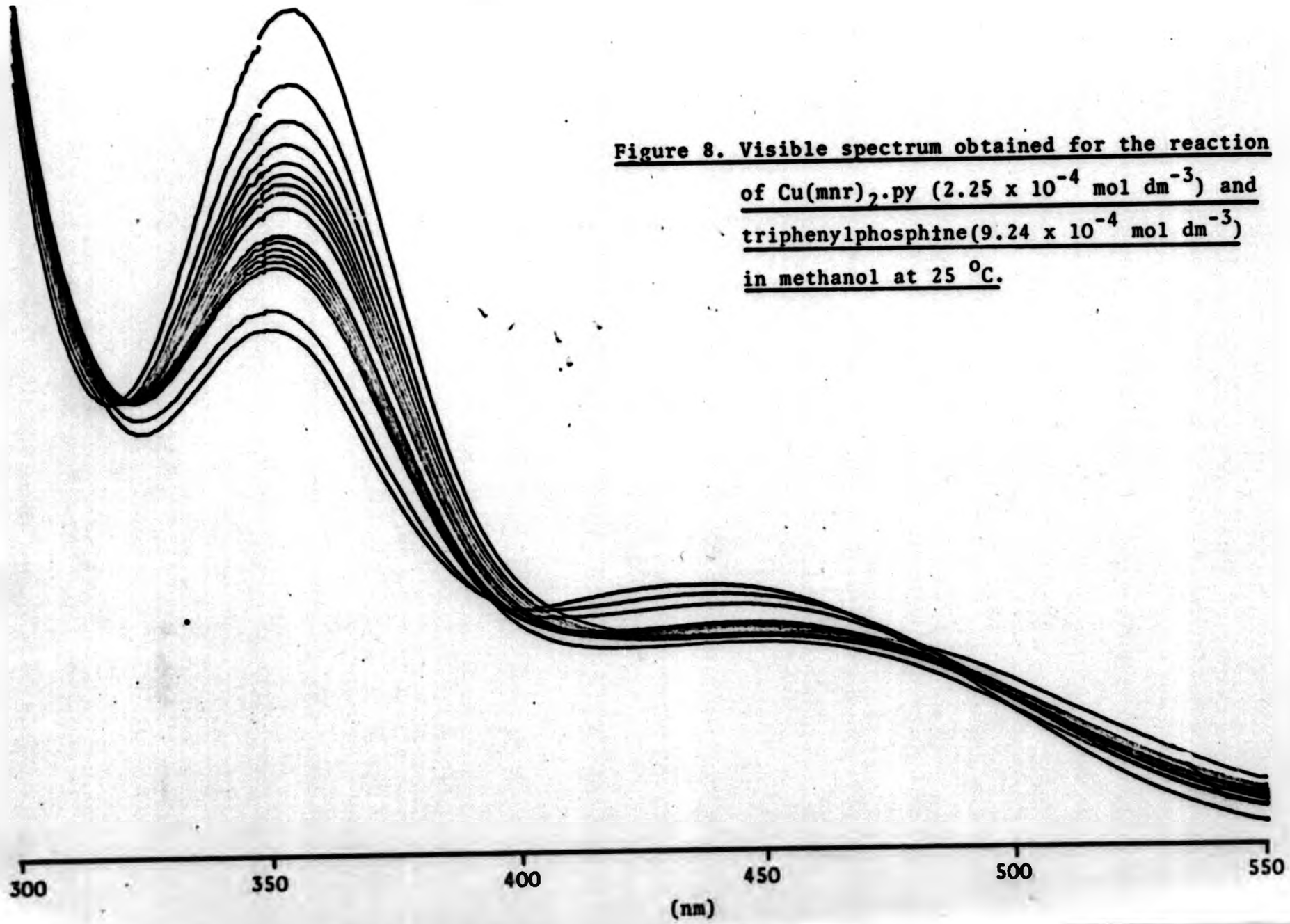


Figure 8. Visible spectrum obtained for the reaction of $Cu(mnr)_2.py$ (2.25×10^{-4} mol dm^{-3}) and triphenylphosphine (9.24×10^{-4} mol dm^{-3}) in methanol at 25 °C.

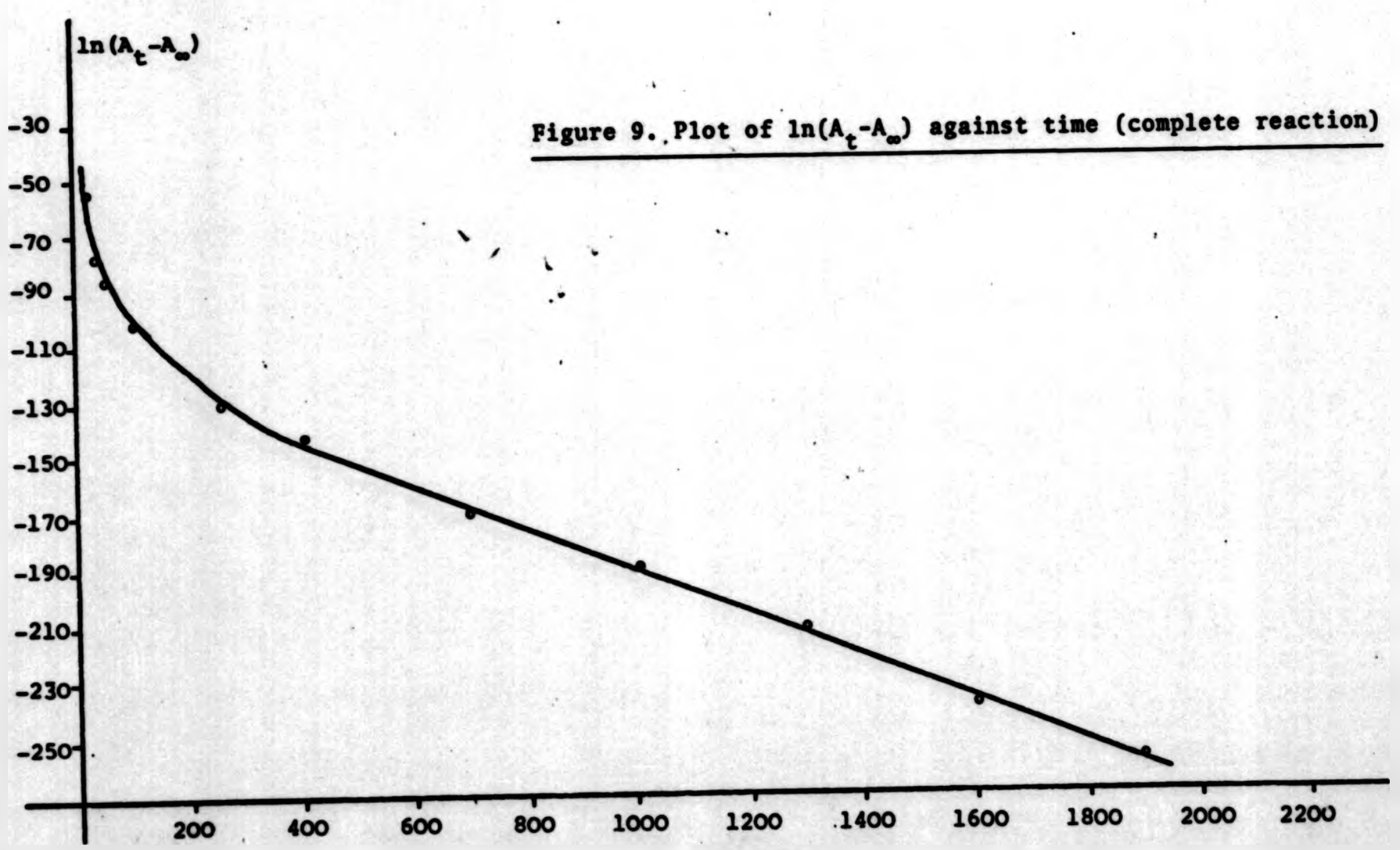


Figure 9. Plot of $\ln(A_t - A_\infty)$ against time (complete reaction)

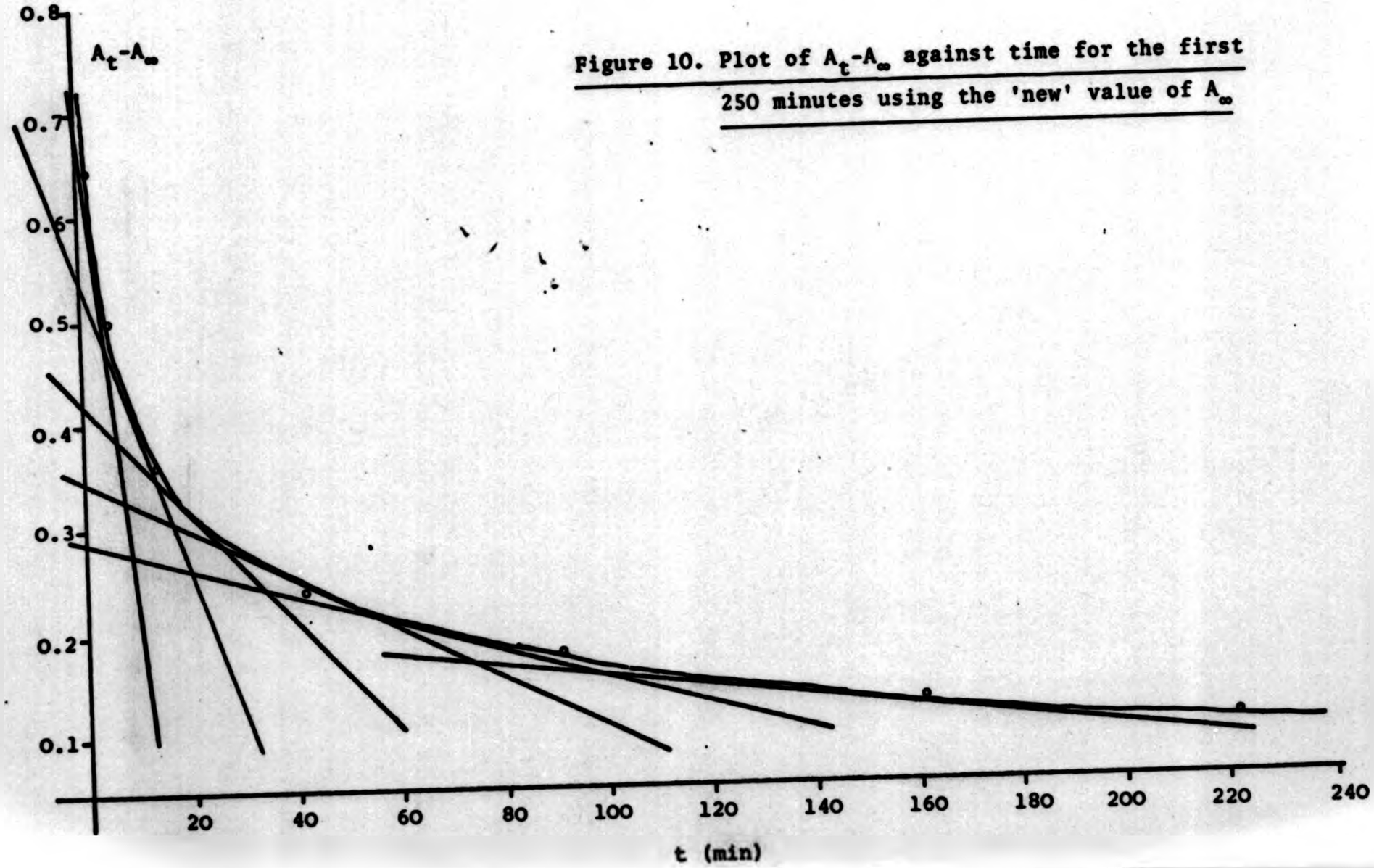


Figure 10. Plot of A_t-A_∞ against time for the first 250 minutes using the 'new' value of A_∞

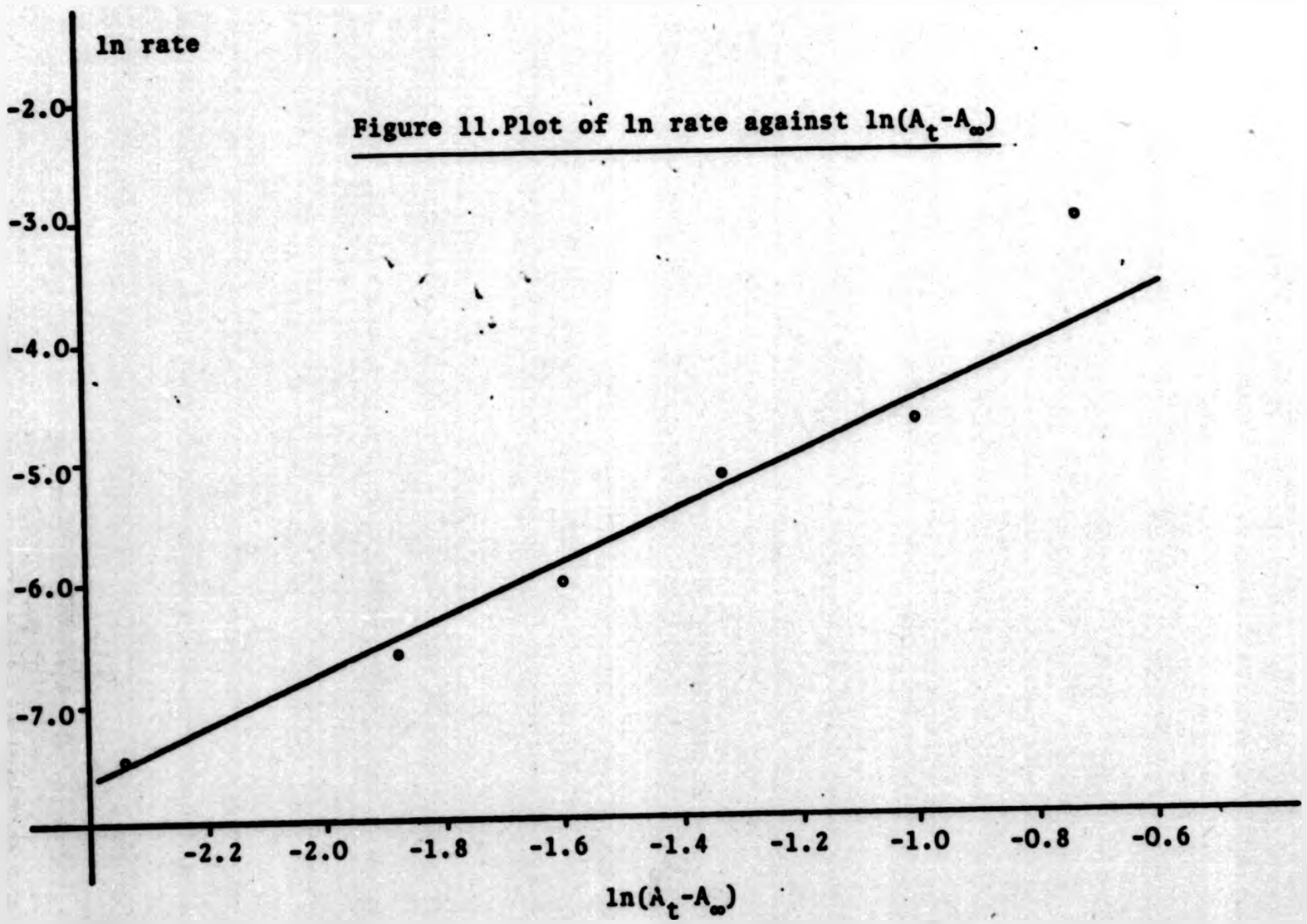
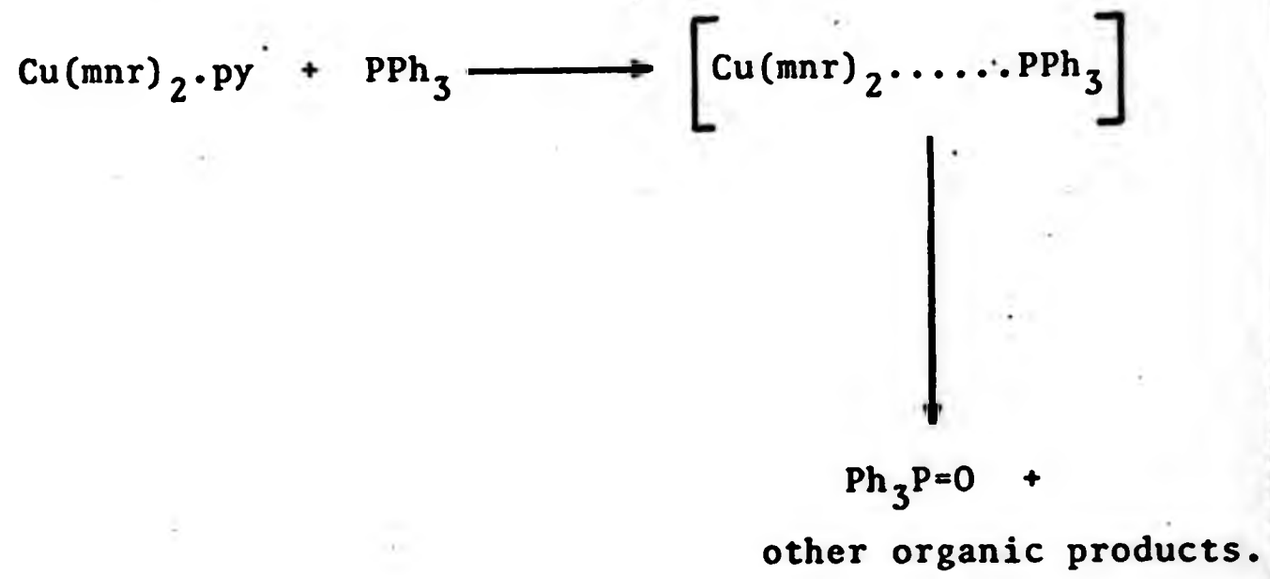


Figure 11.Plot of ln rate against $\ln(A_t-A_\infty)$

rate of reaction at various times. A plot of ln(rate) against $\ln(A_t - A_\infty')$ was then drawn (Figure 11) and found to be linear with a slope of approximately 2. This indicated that the early part of the reaction approached second order kinetics.

The tentative conclusions that may be drawn from this study suggest a mechanism as depicted in Scheme 7.

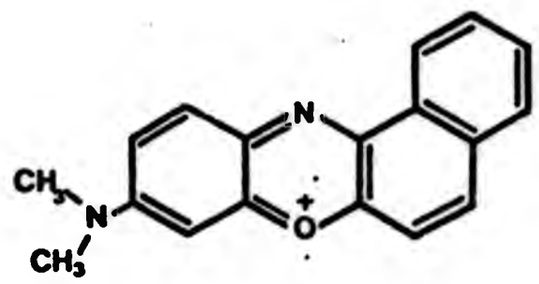


Scheme 7

Initially adduct formation between one molecule of triphenylphosphine and one molecule of metal complex proceeds via a second order reaction. This species then decomposes unimolecularly to give triphenylphosphine and the other organic products. These aspects are examined in the following section.

3.5 Discussion

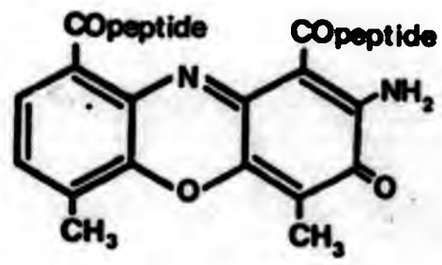
Phenoxazines and phenoxazinones are important and useful heterocyclic compounds. They have found uses as biological stains and dyes, e.g. Meldola's Blue (10)[20], orcein



(10)

and litmus[21], and have considerable chemotherapeutic activity. Pharmacolgically they have been used as nervous system depressants, sedatives, antiepileptics, tranquilisers and anti-cancer agents.[22-27]

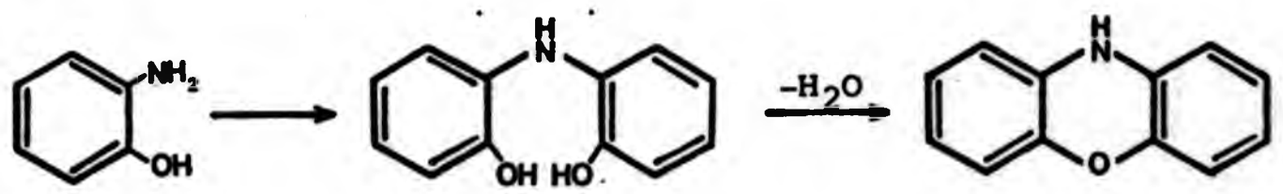
There are a large number of naturally occurring phenoxazinones existing mainly as derivatives of 2-amino-3H-phenoxazine-3-ones. The actinomycins (11) represent an



(11)

interesting group of antibiotics containing this nucleus bound through peptide links to pentapeptide side chains.[28-30] The various actinomycins differ only in the amino acid sequence of the peptide chains. These compounds have about the same antibiotic activity as the penicillin series but their unusual toxicity caused by their ability to block the synthesis of protein by binding to DNA, has precluded their wider chemotherapeutic application.[25] However much effort has been spent in chemically modifying the molecular structure in order to reduce its toxicity. So far these efforts have been unsuccessful.[31]

The classical method of preparation of the phenoxazine nucleus consists of the pyrolytic condensation of 2-aminophenols with catechols[32] (Reaction 3). They have also

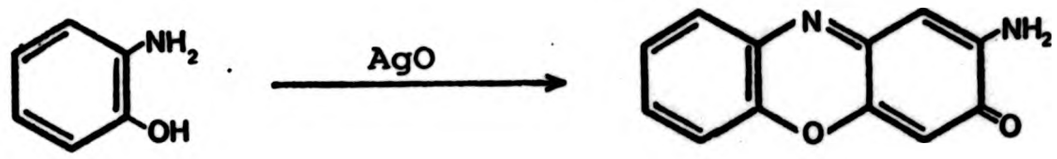


(12)

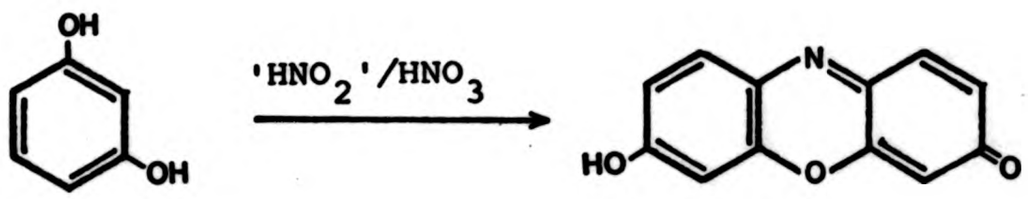
Reaction 3

been obtained by the oxidation of 2-aminophenols by iodine.[33] Both of these reactions proceed via the intermediate, 2,2'-dihydroxydiphenylamine (12).

Phenoxazinones have been obtained from the oxidative action of silver oxide on 2-aminophenols (Reaction 4),[34] and interestingly by treating resorcinol with nitric acid adulterated with nitrous acid (Reaction 5).[35]

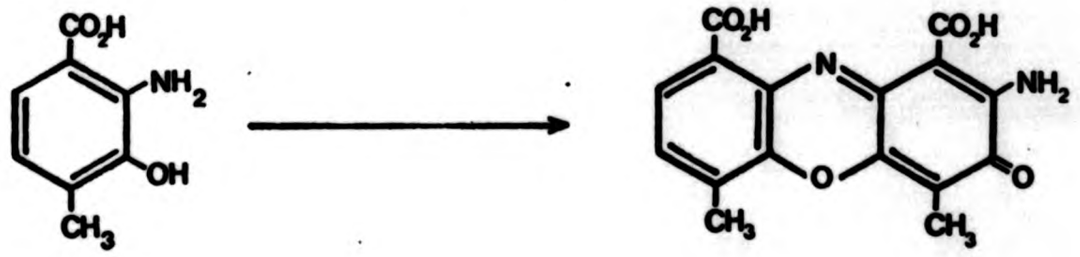


Reaction 4



Reaction 5

Certain phenoxazinones such as those of the actinomycin series are naturally occurring and are produced by certain strains of *Streptomyces*. For example the actinomycin chromophore (13) may be synthesised enzymatically by the action of *Streptomyces antibioticus* on 4-methyl-3-hydroxyanthranilic acid (Reaction 6)[36]. Chemical synthesis



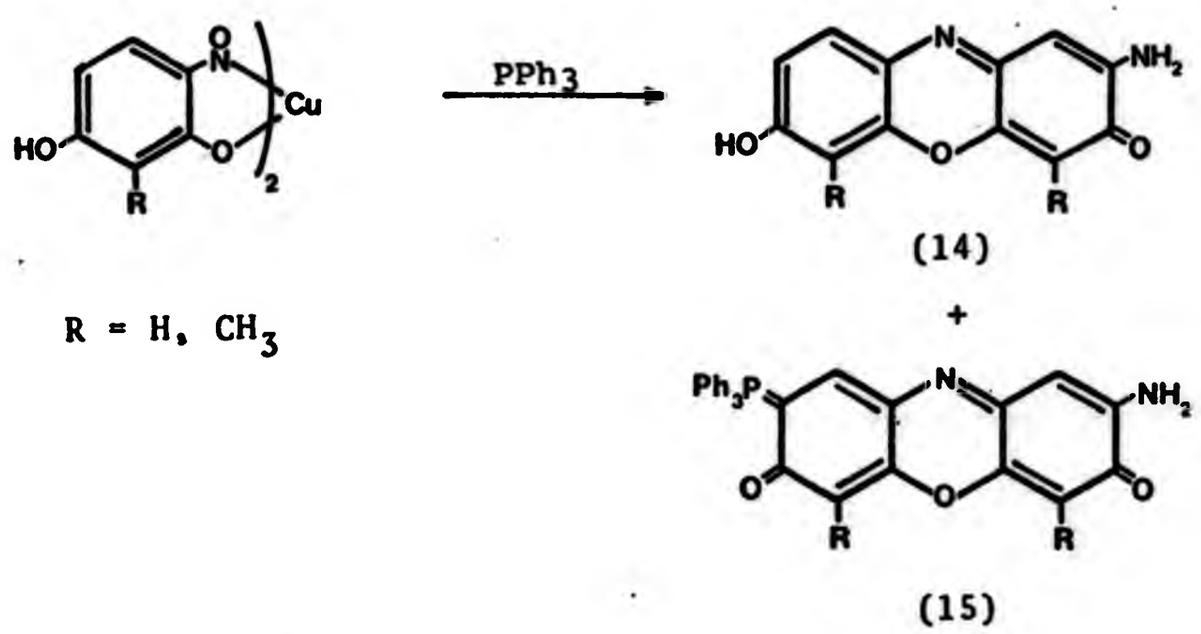
(13)

Reaction 6

of this compound involves a multi-stage reaction scheme starting from p-toluic acid and inevitably leads to poor yields.[37]

The reaction of the copper(II) complexes derived from 5-hydroxy-2-nitrosophenol and 5-hydroxy-6-methyl-2-nitrosophenol with triphenylphosphine provides a convenient route to analogues of the actinomycin chromophore.

The reaction of these readily available compounds produces a mixture of the phenoxazinones (14) and (15) (Reaction 7). The yields obtained (10-20%) are low but



R = H, CH_3

(14)

+

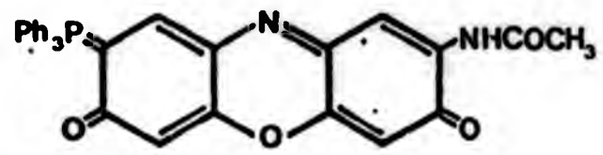
(15)

Reaction 7

no effort has been made to optimise them. However compound (14, R=H) has been obtained in high yield (~65%) by heating 5-hydroxy-2-nitrosophenol under reflux in pyridine.

Compound (15, R=H or CH_3) contains a nominally phosphorus(V) atom which is substituted directly into the phenoxazinone ring. Compounds of this type have not been

previously reported in the literature, and an X-ray structure determination of its N-acetyl derivative (16) has revealed

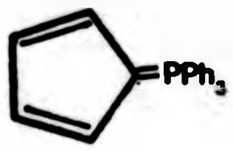


(16)

considerable ylid character (see Chapter 4).

Ylids of the type $R_3\overset{+}{P}-\bar{C}R'_2$ e.g. R= alkyl or aryl, R'=H, alkyl, are well known and documented. However ylids which bond directly into a cyclic system (exocyclic ylids) are relatively few, for example the adducts obtained from the reaction of 1,4-benzoquinone with triphenylphosphine (Reaction 8)[38], and those based on the cyclopentadiene system (13)[39]

Reaction 8

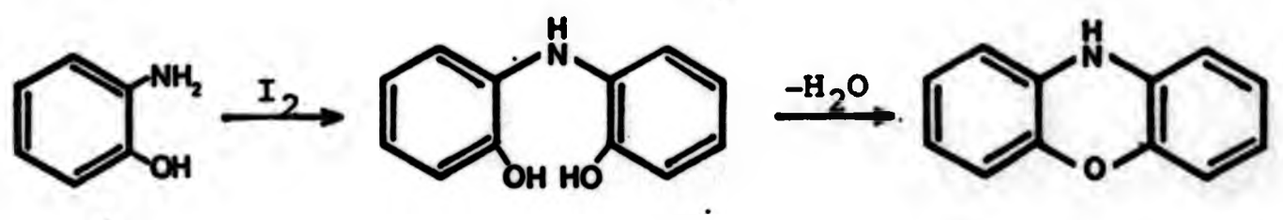


(17)

3.6 A mechanistic appraisal of the triphenylphosphine/ 5-hydroxy-2-nitrosophenol system

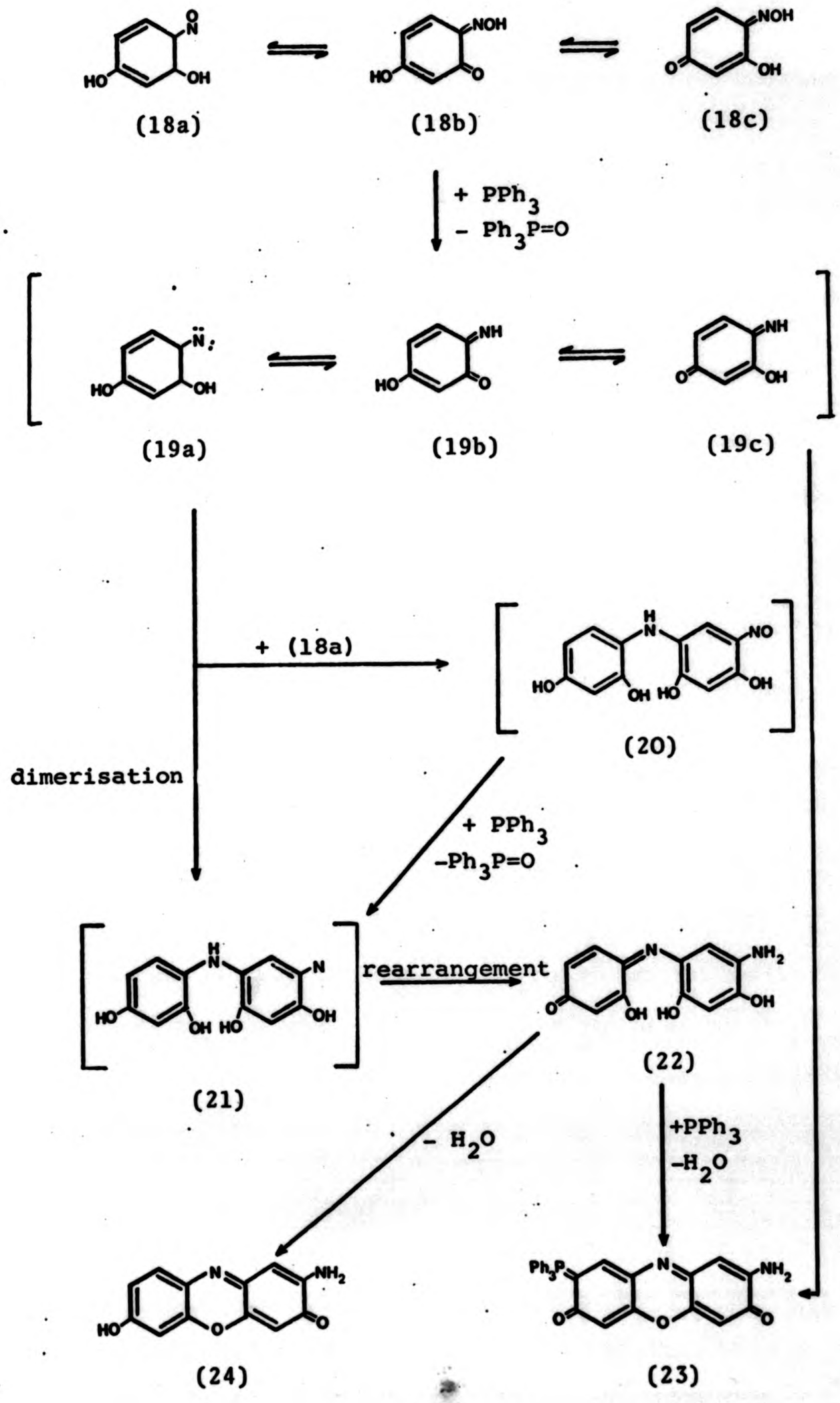
The formation of 2-amino-7-hydroxy-3H-phenoxazine-3-one and 2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione from the reaction of 5-hydroxy-2-nitrosophenol with triphenylphosphine can be rationalised as depicted in Scheme 8.

Initially, deoxygenation of the nitrosophenol (18a) produces the quinoneimine/nitrene species (19a-c). These intermediates may either dimerise to give (21) or, more probably, attack one of its precursors to yield (20),which on deoxygenation by triphenylphosphine will also give (21). Compound (21) then undergoes rearrangement to give (22), which upon condensation gives 2-amino-7-hydroxy-3H-phenoxazine-3-one (24). Compounds of type (22) have isolated and proposed as intermediates in the synthesis of phenoxazines by the pyrolysis of 2-aminophenols in the presence of iodine.[33] (Reaction 9) - see also Section 3.5.



Reaction 9

The phenoxazinone ylid (25) does not derive from the action of triphenylphosphine on the phenoxazinone(24)

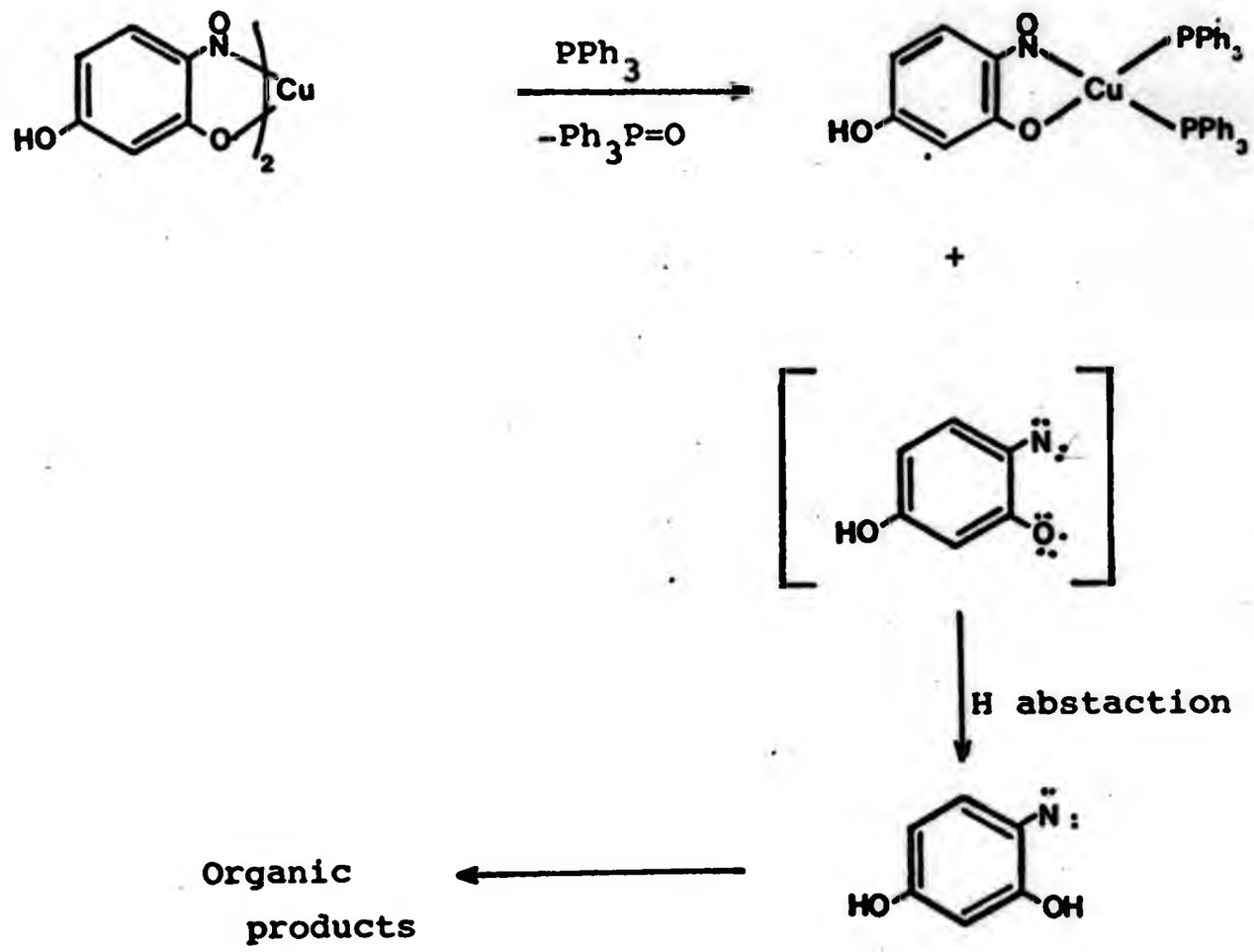

(18a)
(18b)
(18c)
+ PPh3
- Ph3P=O
(19a)
(19b)
(19c)
+ (18a)
dimerisation
(20)
+ PPh3
-Ph3P=O
(21)
rearrangement
(22)
- H2O
+PPh3
-H2O
(24)
(23)

Scheme 8

since both the compounds are isolated from the reaction of triphenylphosphine with 5-hydroxy-2-nitrosophenol. This was confirmed by a control experiment which established the inertness of (24) towards triphenylphosphine. In this experiment no reaction was observed when 2-amino-7-hydroxy-3H-phenoxazine-one was heated under reflux with triphenylphosphine for several hours.

Previously[38] it has been observed that 1,4-benzoquinone reacts with triphenylphosphine to give an ylid (Reaction 8). By analogy it is suggested that the corresponding ylid (23) is formed through a reaction involving attack of triphenylphosphine on the 1,4-benzoquinonemonoimine species (19c) or an intermediate with similar quinonemonoimine character, for example (22). Corroborating evidence for such a mechanism is provided by the composition of the organic products isolated from the reaction of triphenylphosphine with 5-methoxy-2-nitrosophenol (see Section 3.3). In this reaction no phosphorus containing heterocyclic ylid is isolated. It is proposed that in the case of 5-methoxy-2-nitrosophenol the presence of the methoxy group in the 5- position precludes the formation of an intermediate having a 1,4-benzoquinone-monoimine structure such as (19c) or (22).

The reaction between 5-hydroxy-1,2-benzoquinone-2-oximato)copper(II)-monopyridine and triphenylphosphine may be rationalised by assuming initial formation of a triphenylphosphine adduct (Reaction 11)[16]. Subsequent decomposition of this adduct via an internal redox reaction, followed by hydrogen abstraction leads to the nitrosophenol (18a) which affords the products via routes analogous to those suggested in Scheme 8.



Reaction 11.

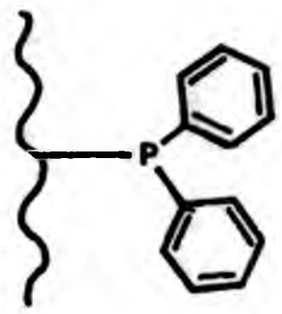
In order to gain some further insight into the mechanism of the above reactions involving triphenylphosphine and the copper(II) bischelates, it was decided to synthesise reagents which were anchored to insoluble polymer supports and to repeat the reactions using them.

3.7 The use of insoluble polymer supports in the reaction between triphenylphosphine and the copper(II) complexes derived from nitrosoresorcinols.

The use of polymeric reagents in organic syntheses dates to the mid-1930's.[40] However pioneering work by Merrifield on peptide synthesis established polymer supported techniques as an invaluable tool to the synthetic organic chemist.[41] Polymer bound reagents have found uses as catalysts , metal recovery agents , and as important reactants in various organic syntheses.

In this study it was decided to form polymer bound reagents involving a styrene - (2%)divinylbenzene backbone to which were attached the reactive groups.

The first method involved attachment of the triphenylphosphine reagent onto the backbone (Figure 11).



insoluble polymer backbone

Figure 11

The second method used a poly-4-vinylpyridine support to which bis(5-hydroxy-1,2-benzoquinone-2-oximato)copper(II) was attached (Figure 12). The third method involved the synthesis of an insoluble support incorporating the nitrosoresorcinol

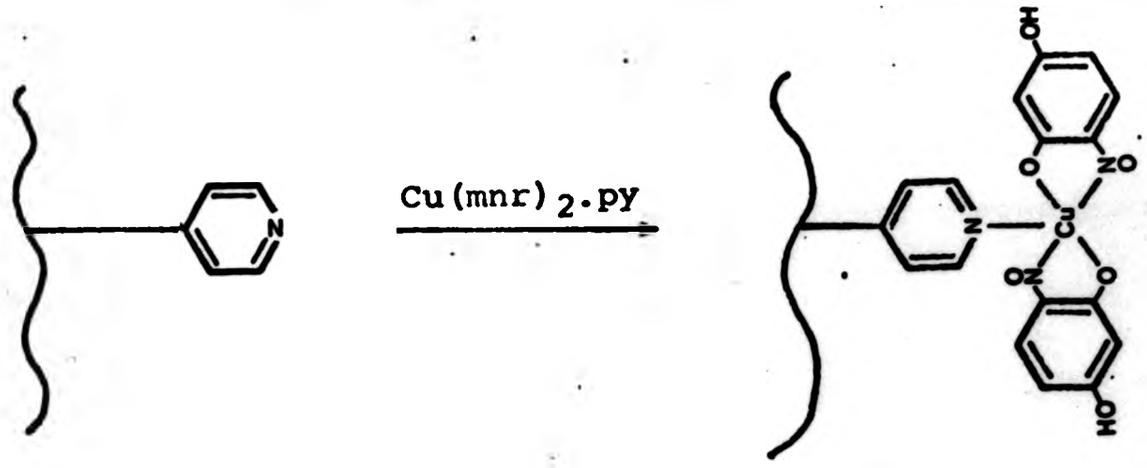


Figure 12

moeity, which upon addition of a solution of a copper(II) salt formed a copper(II) complex (Figure 13). The last method

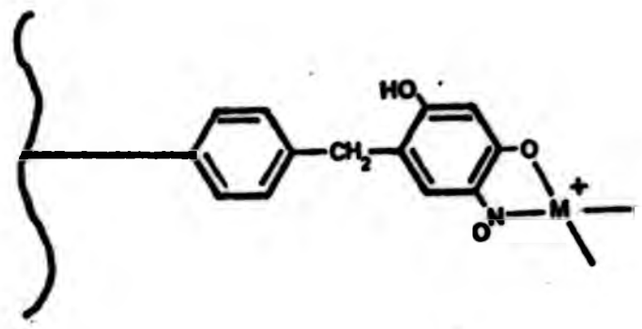


Figure 13

involved the esterification of the 5-hydroxy group of bis(5-hydroxy-1,2-benzoquinone-2-oximato)copper(II) with an acid chloride functional group attached to the polymer (Figure 14).

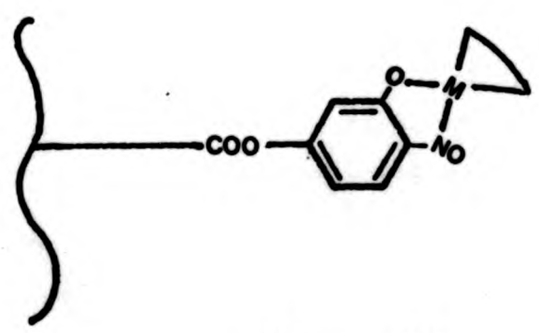


Figure 14

The deoxygenative reactions involving triphenylphosphine investigated in this thesis involve the formation of

triphenylphosphine as one of the main organic products. This substance causes considerable problems in the separation of the organic mixtures that result from these reactions. Even minute quantities of triphenylphosphine oxide can contaminate the mass spectra of the organic products. Using an insoluble polymer bound triphenylphosphine reagent, the work-up of the mixture is expected to be simplified.

The redox nature of the reactions involving triphenylphosphine and the copper bischelates is thought to proceed via the shedding of a ligand as a nitrene or nitrene radical which may then attack a precursor to give the organic products. Although in the polymer bound system described above, shedding of the ligand is feasible, attack of the nitrene intermediate on the precursor is precluded since the rest of the molecule is covalently bonded to the polymer support.

Evidence of attachment of the metal complexes to the polymer support was provided by i.r. studies and microanalysis . In addition a considerable change in colour was observed when the complex (dark brown) was attached to the polymer(light tan).

However although the synthesis and modification of the polymer supports were carried out successfully, no reaction involving the polymer supported materials was detected. This may be due to a dilution effect on the polymer support which could be rectified by increasing the concentration of the reagent on the support. Alternatively any products formed could be trapped within the support by adsorption and therefore would not be detected.

The lack of reactivity of the polymeric reagents is difficult to rationalise and this area merits further attention.

The experimental details of the synthesis of the polymer supports are given in the Appendix.

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CHAPTER 4

THE CRYSTAL STRUCTURE OF 2-N-ACETYL-(8-TRIPHENYLPHOSPHORANYLIDENE)-PHENOXAZINE-3,7-DIONE

CRYSTAL DATA. $C_{32}H_{23}N_2O_4P.C_5H_5N$, M = 609.62, triclinic space group $C\bar{1}$, a = 12.848(5), b = 29.165(5), c = 8.417(4) Å, α = 90.52(2), β = 98.76(3), γ = 89.97(3)°, U = 3117.03 Å^3, Z = 4, D_c = 1.299g cm^{-1}, $F(000)$ = 1272, Mo K_α radiation (λ = 0.71069 Å), (Mo K_α) = 0.94cm^{-3}. Dimensions for the standard space group $P\bar{1}$ are a = 15.994(5), b = 8.413(5), c = 12.860(4) Å, α = 98.76(2), β = 113.84(3), γ = 85.95(3)°.

A Phillips PW1100 four-circle diffractometer with a θ-2θ scan was used for data collection. Reflections with $3.0 < \theta < 25.0°$ were examined. A constant scan speed of 0.05 s^{-1} and a scan width of 0.80° were used, with a background measuring time equal to half the scan time. Three standard reflections were measured every two hours during data collection and showed no significant variation in intensity. The intensities were calculated from the peak and background measurements with a program written for the PW1100 diffractometer[1]. The variance of the intensity I was calculated as $[\{ \sigma_c(I) \}^2 + (0.04\ I)^2]^{\frac{1}{2}}$, where $\{ \sigma_c(I) \}^2$ is the variance due to counting statistics and the term in I^2 was introduced to allow for other

sources of error[2]. I and $\sigma(I)$ were corrected for Lorentz and polarisation factors. Absorbtion corrections were not applied and would be expected to be insignificant for this molecule. The final data set consisted of 5803 independant reflections of which only 1285 were considered to be observed with $I > 3\sigma(I)$ and used in the refinement.

4.1 Summary of the work done leading up to the X-ray diffraction studies.

The precursor to the compound under consideration was obtained as a fraction from the chromatographic column. Low resolution mass spectrometric investigation indicated its relative molecular mass to be 488. A ^{13}C n.m.r. study was precluded by its extreme insolubility. A ^{31}P n.m.r was available but after 50000 pulses only a weak peak at 21.2 p.p.m. was observed. A ^{1}H n.m.r. indicated that the compound contained at least two exchangeable protons but no backbone structural detail was forthcoming.

In order to improve the solubility characteristics and thereby gain more structural information, the compound was treated with acetic anhydride. Mono-acetylation was achieved as revealed by an increase in relative molecular mass of 42 mass units to 530. However very little improvement in solubility was achieved. High resolution mass spectrometric studies indicated the parent ion to have a precise mass of 530.1426 corresponding to a molecular formula $C_{32}H_{23}N_2O_4P$. This information suggested the following possibilities (Figure 1).

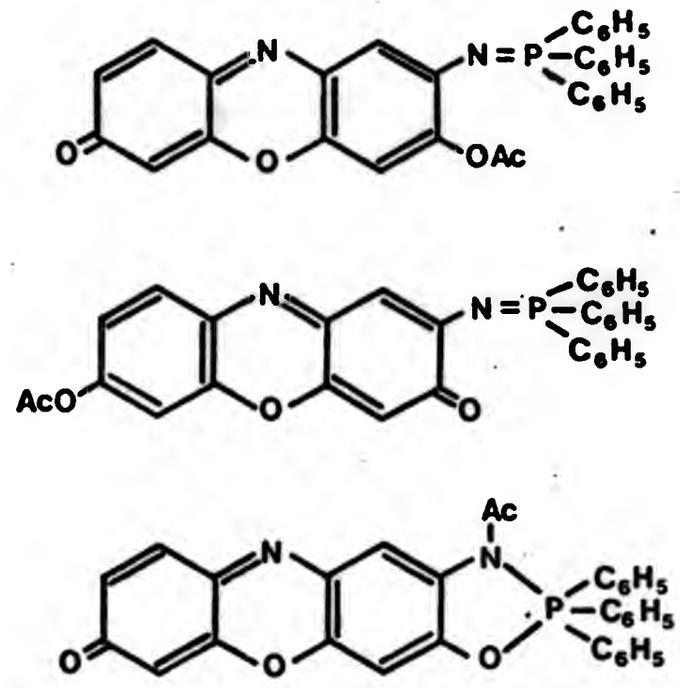


Figure 1

Recrystallisation of the mono-acetylated derivative from pyridine/light petrol(80-100 fraction) gave suitable crystals for a total structure determination by X-ray diffraction.

4.2 Structure solution and refinement

X-rays are scattered by electrons and hence the higher the atomic number of the atom involved, the greater the scatter (diffraction). The object of the study is to obtain the electron density (ρ) at any point x,y,z in the unit cell using:

$$\rho(x,y,z) = \frac{1}{V}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} |F_{hkl}| \exp\left(-2\pi i[hx + ky + lz]\right)$$

However F_{hkl}, the structure factor for the hkl reflection is specified by an amplitude and a phase angle. It can

thus be split into a structure factor amplitude $|F|$ and a term involving the phase angle. The larger the structure factor magnitude the greater the effect on the estimated phase (i.e. those relationships chosen to represent the basis for statistical phasing). For this reason the contributions of atomic scattering and thermal motion factors must be removed from the structure factor amplitudes. This may be achieved by calculating a normalised structure factor:

$$|E_{hkl}| = |F_{hkl}| / \left[\varepsilon \sum^{N} f^2\right]^{\frac{1}{2}} \exp\left(- \langle B \rangle \sin^2\theta/\lambda^2\right)$$

$\langle B \rangle$ is the average isotropic temperature factor of the structure and ε is a factor to account for the symmetry dependence of certain reflections. In cases where the average thermal motion is not isotropic the value of $\langle B \rangle$ may be replaced by overall anisotropic temperature factors[3].

Attempts to use the standard statistical centrosymmetric program in the SHELX 76 package of programs[4] to solve the structure using terms in $E > 1.2$ failed to reveal any chemically reasonable fragments of the molecule. The E-maps produced displayed either a series of sheets of 'chicken-wire' patterns of interlocking six-membered rings, or an infinite chain of fused, six-membered rings interlocking with a second, slightly displaced chain.

The E-maps produced by the more powerful tangent refinement method, where starting sets of phases were chosen by hand, produced similar results to those obtained previously. An analysis of the statistical

relationships between the *E*-values and sin $(\theta)/\lambda$ supported the assumption that the structure was $C\bar{1}$ and not $C1$.

A detailed analysis of the Patterson function was then carried out in the hope of obtaining some information about the structure which could be used to start the direct methods procedure.

4.3 The Patterson Function

A crystal structure analysis is carried out on the basis of the intensities arising in the diffraction of an X-ray beam by a crystal. The measured intensities are treated by a mathematical transformation into amplitudes, and then by a a Fourrier transformation to give the distribution of the electron density in the crystal. However the Fourrier transformation requires not only the magnitude of the amplitude but also their phases. No method is available to observe these phases experimentally. Hence any crystal structure analsis is a problem for which only half the data for solution is available. This constitutes the so-called 'phase problem of X-ray crystallography. The Patterson function or vector space map must be regarded as the most powerful attack on the phase problem.

The Patterson function is a convolution of the electron expression (see above), in which the structure factor F_{hkl} is replaced by the scalar quantity $|F_{hkl}|^2$:

$$P(u,v,w) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \exp[-2\pi i(hu + kv + lw)]$$

the $P(u,v,w)$ is independant of the structure factor phase,

and provides, instead of the electron density distribution in the unit cell, the vector distribution between elements of electron density. Therefore for a structure containing N atoms in the unit cell, there are N^2 maxima in the Patterson function. For instance, in the two atom structure (Figure 2) the Patterson function will contain vectors from atom 1 to atom 2, atom 2 to atom 1, atom 1 to atom 1 and atom 2 to atom 2.

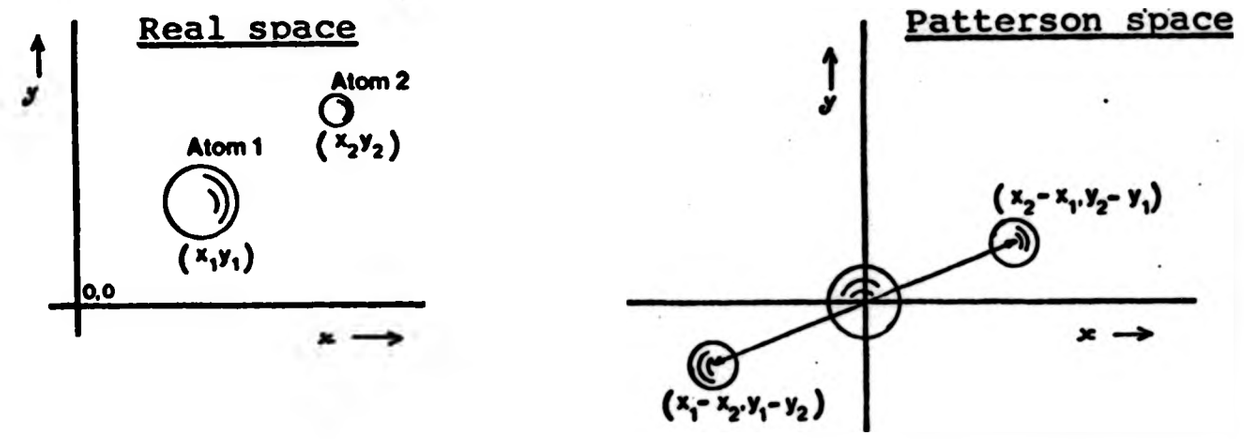


Figure 2. Diagrammatic representation of a two atom molecule in real and Patterson space.

The plot of $P(u,v,w)$ will show only three maxima since the last two vectors are of zero length and will appear at the origin. The other peaks are displaced from the cell origin by their interatomic vectors. The Patterson function therefore contains complete information about the structure.

In the case of a six-membered ring the Patterson function is as straightforward. The equivalent positions for the space group cI are:

(i) x,y,z

(ii) -x,-y,-z

(iii) $\frac{1}{2}+x, \frac{1}{2}+y, z$

(iv) $\frac{1}{2}-x, \frac{1}{2}-y, -z$

Therefore the vectors produced for one atom are;

(a) $2x,2y,2z$

(b) $\frac{1}{2}-2x,\frac{1}{2}-2y,-2z$

and the vectors produced between two differant atoms;

(c) $x_1-x_2,\ y_1-y_2,\ z_1-z_2$

(d) $x_1+x_2,\ y_1+y_2,\ z_1+z_2$

(e) $\frac{1}{2}+(x_1-x_2),\frac{1}{2}+(y_1-y_2),z_1-z_2$

(f) $\frac{1}{2}+(x_1+x_2),\frac{1}{2}+(y_1+y_2),z_1+z_2$

For the short intramolecular vectors of type (c) a Patterson function of one six-membered ring produces a pattern as shown in Figure 3.

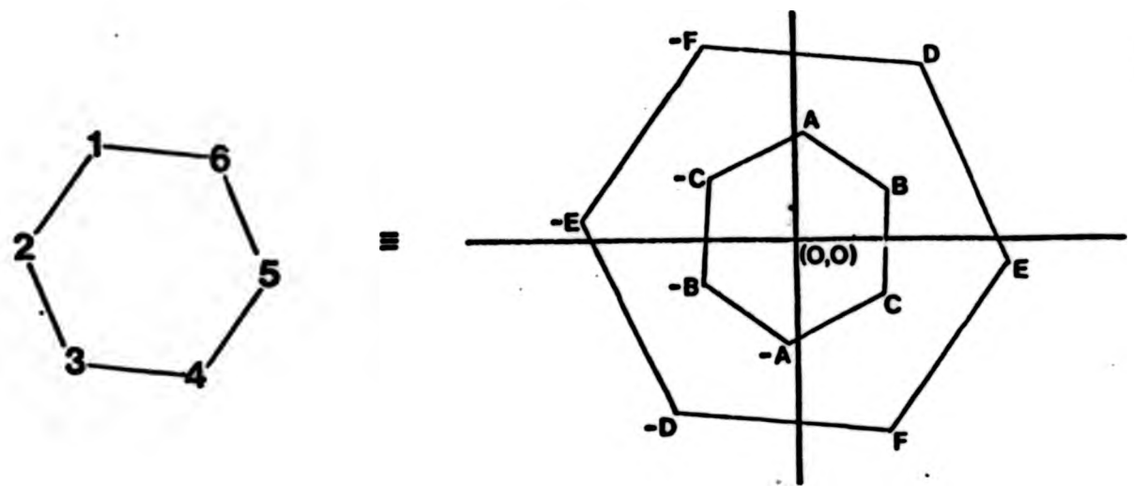
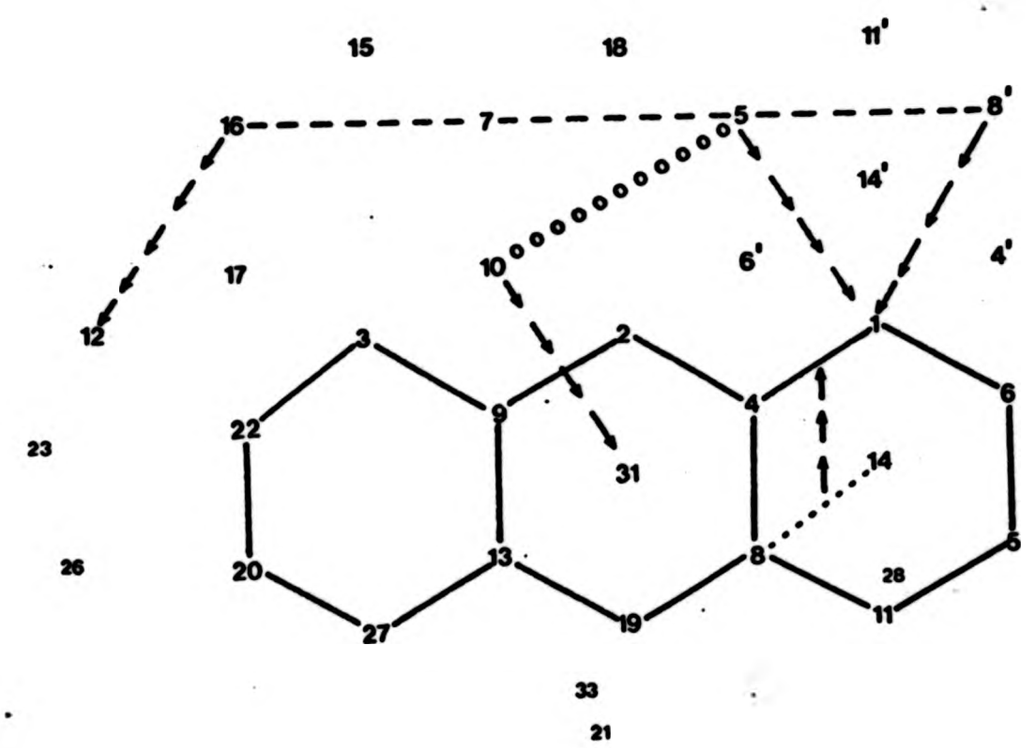


Figure 3

Where peaks A,B,C (and -A,-B,-C) result from *ortho-* vectors such as x_1-x_6, y_1-y_6 and z_1-z_6, and peaks D,E,F (and -D,-E, -F) result from *meta-* vectors such as x_1-x_5, y_1-y_5 and z_1-z_5. A similar pattern is produced from vectors of type (d). By identifying these vectors a set of simultaneous equations can be built up to solve for the (x,y,z) coordinates.

The particular molecule under study was thought to contain a linear set of fused six-membered rings (see

Figure 1). If this were so, identification of the vectors would be almost impossible as a result of overlap. However, the vector overlap does give the orientation of the ring system and possibly the origin of the molecule in the unit cell. From the vector map for this compound the orientation was readily deduced from the pattern of vectors (Figure 4)



------ *ortho* vector

---- *meta* vector(x3)-giving orientation of the molecule

ooooo *para* vector

Figure 4. Patterson figure (x_m-x_n) vectors

By matching an x_1-x_2, y_1-y_2, z_1-z_2 vector with the corresponding x_1+x_2, y_1+y_2, z_1+z_2 vector it should be possible to solve for the pair of atoms (x_1,y_1,z_1) and (x_2,y_2,z_2) by the method of simultaneous equations, however the origin of the molecule could not be found.

Attempts to use the orientation obtained from the Patterson map either by putting the solution into the direct methods package of programs or by systematically moving the coordinates obtained throughout the unit cell to obtain low *R*-factors, also failed.

The Patterson vectors did imply that there were up to five fused rings in the molecule or that there were atoms arranged in such a manner as to give rise to vectors corresponding to five fused rings.

At this stage Dr Ernst Egert of the University Chemical Laboratory, Cambridge, made available a newer version of the SHELX program which generates multisolution phases by 'magic integers'[5] and uses figures of merit to order the possible solutions by a combination of the NQEST routine[7] and *R*α.[8] A run using this program, with 250 *E* values, calculated nine possible solutions, the third of which - using 22 of the highest 27 peaks - showed five, six-membered rings [NQEST = -0.446, $R(\alpha)$ = 0.087].

These twenty two atom positions were recycled into a tangent expansion routine that indicated four of the positions to be unreal. In addition the position of a triphenylphosphine moiety was revealed.

A Fourrier map based on thirty three new atoms generated all the non-hydrogen atoms in the molecule, including a pyridine molecule present as solvent of

crystallisation. Isotropic refinement using all the available data resulted in a *R*-value of 0.188. Analysis of the isotropic temperature values and a knowledge of the chemical origin of the molecule, plus the spectroscopic data available, allowed an assignment of all the atoms comprising the molecule.

The structure was then refined by a full-matrix least-squares method with the heteroatoms (P,N,O) anisotropic. The hydrogen atoms of the phenoxazine ring system were included at calculated positions 'riding' on their respective carbon atoms with the interatomic distance fixed at 1.08 Å. As a result of the low data to parameter ratio, the three phenyl rings at the phosphorous atom were refined as rigid bodies with the carbon-carbon distance fixed at 1.395 Å.

The final *R*-value was 0.0821 and R_w = 0.0764.

where $R_w = (\Sigma_w |F_{obs.}| - |F_{calc.}|^2 \Sigma_w |F_{obs.}|^2)^{\frac{1}{2}}$

with $\omega = 1/\sigma^2|F|$.

A final differance synthesis showed up the position of the N-H hydrogen atom. No other significant features were revealed in this map. Neutral atom scattering factors were used.[9]

An ORTEP 2[10] diagram of the final structure is given in Figure 5.

4.4 Difficulties involved in structure solution

The problem with statistical methods of structure solution is that they are as likely not to work as they are to succeed (hence the term statistical). It is therefore difficult to try and explain why this particular structure

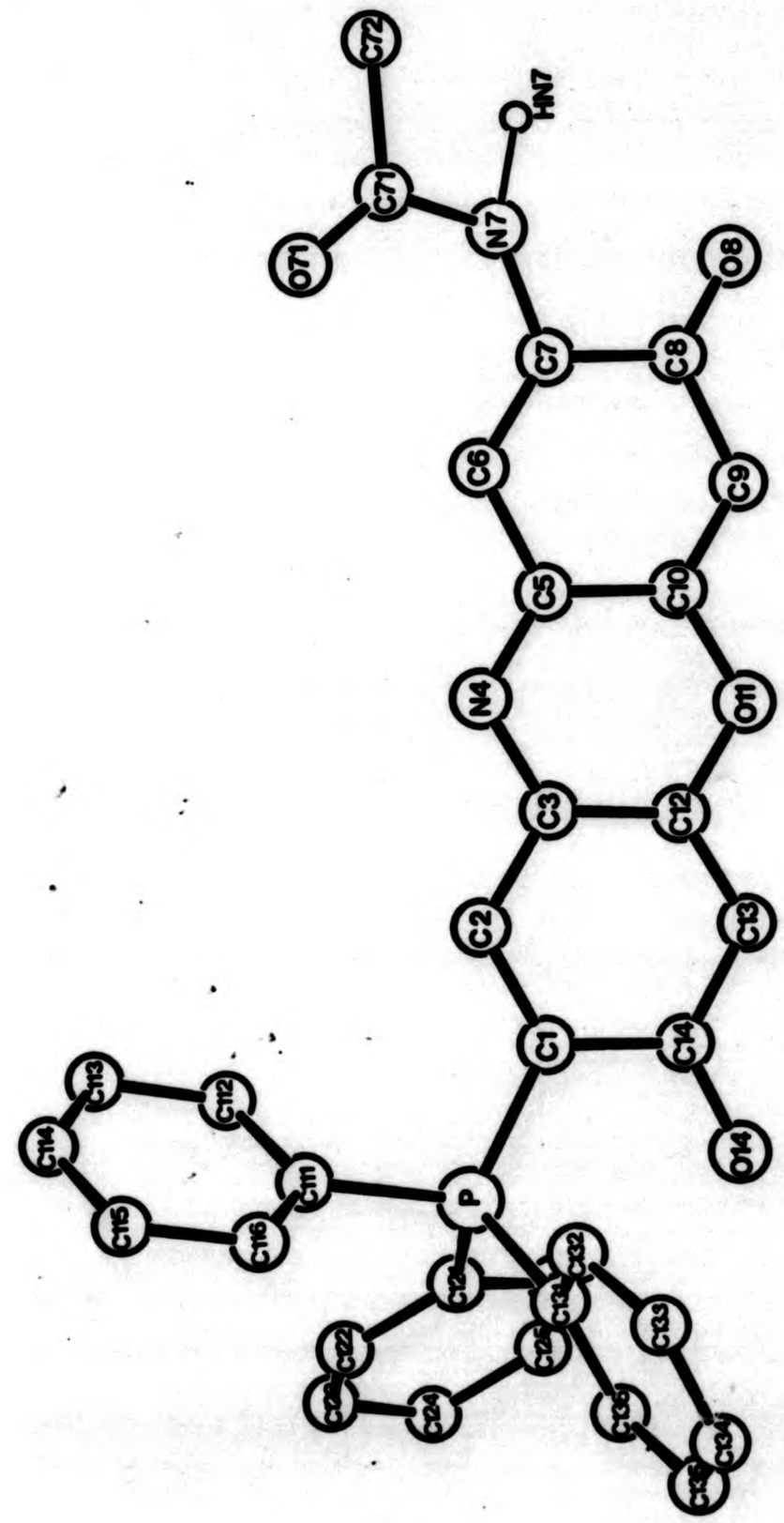


Figure 5 ORTEP2 diagram of 2-N-acetyl-8-(triphenylphosphoranylidene)-phenoxazine-3,7-dione

was so time-consuming to solve. Statistical methods of structure solution tend to have difficulties with large, flat, light-atom molecules. Although this molecule is by no means flat overall, a large part of the phenoxazinone ring is (see Table 3b).

The stereoscopic view of the unit cell (Figure 6) shows that the molecules tend to pack head-to-tail giving an extended flatness to a large part of the unit cell.

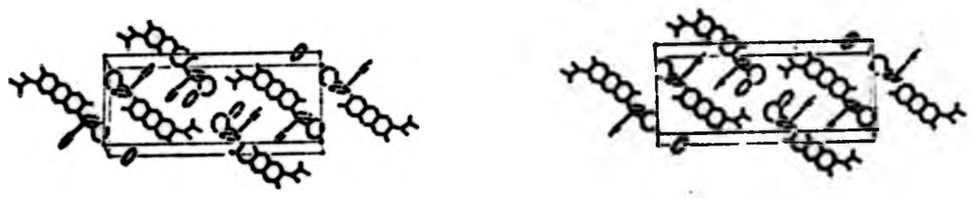


Figure 6 Stereoscopic view of the unit cell.

This extended flat system is shown in the Patterson map (Figure 4) in which a pseudo fourth ring is being built up beyond the third ring. Such a method of packing may have contributed to the difficulties encountered in solution and refinement.

4.5 Results

The folowing tables contain:

Table 1. Atomic coordinates for the molecule,

Table 2. Molecular geometry (bond lengths and angles) for the molecule,

Table 3a. Atoms defining certain planes and the equations of those planes,

Table 3b. Deviations from those planes,

Table 3c. Angles between those planes.

Table 1

Atomic coordinates for 2-N-acetyl-8-(triphenylphosphoranylidene)-phenoxazine-3,7-dione. Isotropic Temperature factors ($x10^3$ Å^2) with estimated standard deviation values in parentheses.

ATOM	x	y	z	U_{iso}
a) Non-hydrogen atoms				
P(1)	0.3532(3)	0.8839(1)	0.2045(5)	*
C(111)	0.2861(7)	0.9301(3)	0.2889(10)	34(3)
C(112)	0.3408	0.9651	0.3802	42(4)
C(113)	0.2857	1.0010	0.4392	65(5)
C(114)	0.1760	1.0021	0.4068	70(5)
C(115)	0.1213	0.9671	0.3155	66(5)
C(116)	0.1763	0.9311	0.2566	60(5)
C(121)	0.3944(6)	0.9024(3)	0.0233(9)	35(3)
C(122)	0.3855	0.9480	-0.0258	49(4)
C(123)	0.4284	0.9619	-0.1601	59(4)
C(124)	0.4803	0.9302	-0.2455	69(4)
C(125)	0.4892	0.8847	-0.1964	62(4)
C(126)	0.4463	0.8707	-0.0621	54(4)
C(131)	0.2578(5)	0.8394(2)	0.1618(14)	36(3)
C(132)	0.2169	0.8202	0.2906	68(4)
C(133)	0.1386	0.7867	0.2624	75(4)
C(134)	0.1012	0.7724	0.1056	76(4)
C(135)	0.1420	0.7916	-0.0232	80(4)
C(136)	0.2203	0.8251	0.0050	65(4)
C(1)	0.4633(10)	0.8609(4)	0.3333(16)	33(3)
C(2)	0.4668(10)	0.8161(4)	0.3915(16)	38(4)

* Anisotropic thermal parameters ($x10^3$ Å^2)

C(3)	05577(10)	0.8006(4)	0.4932(16)	31(3)
N(4)	0.5567(9)	0.7568(4)	0.5523(14)	*
C(5)	0.6415(12)	0.7439(5)	0.6498(19)	44(4)
C(6)	0.6452(11)	0.6984(4)	0.7182(17)	42(4)
C(7)	0.7327(11)	0.6863(5)	0.8241(17)	35(3)
C(8)	0.8209(12)	0.7166(5)	0.8770(19)	48(4)
C(9)	0.8160(11)	0.7616(4)	0.8016(17)	42(4)
C(10)	0.7303(11)	0.7735(4)	0.6974(17)	36(4)
O(11)	0.7310(7)	0.8169(3)	0.6303(12)	*
C(12)	0.6444(11)	0.8304(4)	0.5296(17)	38(4)
C(13)	0.6458(10)	0.8730(4)	0.4679(16)	35(3)
C(14)	0.5577(11)	0.8911(5)	0.3642(18)	40(4)
O(14)	0.5524(7)	0.9311(3)	0.3073(11)	*
O(8)	0.8940(7)	0.7051(3)	0.9785(13)	*
N(7)	0.7506(8)	0.6425(4)	0.8933(4)	*
C(71)	0.6965(14)	0.6030(6)	0.8552(22)	66(5)
O(71)	0.6134(9)	0.6020(3)	0.7632(15	*
C(72)	0.7464(12)	0.5588(5)	0.9343(19)	64(4)
N(1py)	-0.0991(16)	0.0656(6)	0.1892(33)	*
C(1py)	-0.0081(17)	0.0800(7)	0.1278(26)	103(7)
C(2py)	0.0546(16)	0.1134(7)	0.2091(26)	103(7)
C(3py)	0.0246(19)	0.1333(7)	0.3406(29)	125(8)
C(4py)	-0.0682(22)	0.1213(9)	0.3887(34)	172(11)
C(5py)	-0.1338(24)	0.0889(9)	0.3099(34)	152(12)

b) Hydrogen atoms (common U_{iso} = 0.149(13) $Å^2$)

H(112)	0.4257	0.9642	0.4052
H(113)	0.3280	1.0281	0.5099
H(114)	0.1333	1.0300	0.4525

H(115)	0.0363	0.9679	0.2905
H(116)	0.1340	0.9041	0.1859
H(122)	0.3454	0.9725	0.0403
H(123)	0.4215	0.9972	-0.1981
H(124)	0.5135	0.9410	-0.3495
H(125)	0.5293	0.8601	-0.2625
H(126)	0.4532	0.8354	-0.0241
H(132)	0.2460	0.8313	0.4120
H(133)	0.1070	0.7719	0.3621
H(134)	0.0405	0.7465	0.0838
H(135)	0.1130	0.7805	-0.1446
H(136)	0.2519	0.8399	-0.0947
H(2)	0.4007	0.7934	0.3579
H(6)	0.5810	0.6745	0.6866
H(9)	0.8810	0.7853	0.8292
H(13)	0.7156	0.8938	0.4979
H(1py)	0.011	0.0648	0.0185
H(2py)	0.1265	0.1237	0.1674
H(3py)	0.0759	0.1580	0.4096
H(4py)	-0.0922	0.1397	0.4889
H(5py)	-0.2089	0.0814	0.3465
HN7	0.8081	0.6172	0.9747

Atom	*U(11)*	*U(22)*	*U(33)*	*U(23)*	*U(13)*	*U(12)*
P(1)	35(2)	27(2)	48(3)	5(2)	11(2)	-2(1)
N(4)	50(8)	39(7)	45(8)	10(6)	5(7)	-4(6)
O(11)	31(6)	29(5)	85(8)	23(5)	-3(6)	-2(4)
O(14)	67(7)	22(5)	60(8)	26(5)	3(6)	4(4)
O(8)	56(7)	45(6)	92(9)	15(6)	-17(7)	10(5)

N(7)	61(9)	27(7)	48(9)	17(6)	0(7)	6(6)
O(71)	84(8)	45(6)	134(12)	28(7)	-39(9)	-25(6)
N(1py)	126(18)	95(14)	260(27)	43(17)	9(19)	-15(13)

Anisotropic values given in the form:

$$\exp\left[-2\pi^2\left(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\right)\right]$$

Table 2

Molecular geometry for 2-N-acetyl-8-(triphenylphosphoranylidene)-phenoxazine-3,7-dione with estimated standard deviation values in parentheses.

a.) Bond lengths (Å)

P(1)-C(11)	1.799(9)		
P(1)-C(121)	1.778(9)		
P(1)-C(131)	1.781(8)		
P(1)-C(1)	1.780(13)		
C(1)-C(2)	1.396(18)	C(2)-C(3)	1.416(17)
C(3)-N(4)	1.376(17)	C(3)-C(12)	1.408(18)
N(4)-C(5)	1.316(18)	C(5)-C(6)	1.451(19)
C(6)-C(7)	1.372(18)	C(7)-N(7)	1.413(17)
N(7)-HN(7)	1.189	N(7)-C(71)	1.356(20)
C(71)-O(71)	1.220(20)	C(71)-C(72)	1.548(23)
C(7)-C(8)	1.451(19)	C(8)-O(8)	1.219(17)
C(8)-C(9)	1.461(20)	C(9)-C(10)	1.346(18)
C(10)-O(11)	1.390(16)	O(11)-C(12)	1.353(16)
C(12)-C(13)	1.352(18)	C(13)-C(14)	1.424(18)
C(14)-O(14)	1.264(16)	C(14)-C(1)	1.490(18)
N(1py)-C(1py)	1.414(33)		
C(1py)-C(2py)	1.374(28)		
C(2py)-C(3py)	1.352(33)		
C(3py)-C(4py)	1.363(38)		
C(4py)-C(5py)	1.365(38)		
C(5py)-N(1py)	1.347(39)		

b) Bond angles (^{o})

C(111)-P(1)-C(121)	109.2(4)
C(131)-P(1)-C(111)	105.4(4)
C(131)-P(1)-C(121)	109.9(5)
C(1)-P(1)-C(111)	115.3(5)
C(1)-P(1)-C(121)	109.2(6)
C(1)-P(1)-C(131)	107.7(5)

Mean = 109.5

C(2)-C(1)-P(1)	123.5(9)
C(14)-C(1)-P(1)	115.6(9)
C(14)-C(1)-C(2)	120.7(11)
C(3)-C(2)-C(1)	119.8(11)
N(4)-C(3)-C(2)	118.0(11)
C(12)-C(3)-N(4)	123.1(11)
C(12)-C(3)-C(2)	118.9(12)
C(5)-N(4)-C(3)	116.3(11)
C(6)-C(5)-N(4)	119.2(12)
C(10)-C(5)-N(4)	123.2(13)
C(10)-C(5)-C(6)	117.6(12)
C(7)-C(6)-C(5)	118.3(12
C(8)-C(7)-C(6)	124.3(12)
N(7)-C(7)-C(6)	124.9(12)
N(7)-C(7)-C(8)	110.7(11)
C(71)-N(7)-C(7)	128.7(12)

N(N7)-N(7)-C(71)	81.8
H(N7)-N(7)-C(7)	148.6
O(71)-C(71)-N(7)	122.3(15)
C(72)-C(71)-N(7)	116.3(13)
C(72)-C(71)-O(71)	121.5(15)
C(9)-C(8)-C(7)	115.8(12)
O(8)-C(8)-C(7)	121.7(13)
O(8)-C(8)-C(9)	122.4(13)
C(10)-C(9)-C(8)	119.8(12)
C(9)-C(10)-C(5)	124.1(13)
O(11)-C(10)-C(5)	119.2(11)
O(11)-C(10)-C(9)	116.7(12)
C(12)-O(11)-C(10)	118.0(10)
O(11)-C(12)-C(3)	120.2(11)
C(13)-C(12)-C(3)	122.7(12)
C(13)-C(12)-O(11)	117.1(12)
C(14)-C(13)-C(12)	121.8(12)
C(13)-C(14)-C(1)	115.7(12)
O(14)-C(14)-C(1)	119.1(11)
O(14)-C(14)-C(13)	125.0(12)
P(1)-C(111)-C(112)	121.9(7)
P(1)-C(111)-C(116)	118.1(6)
P(1)-C(121)-C(122)	122.0(7)
P(1)-C(121)-C(126)	117.7(7)

P(1)-C(131)-C(132)	117.9(8)
P(1)-C(131)-C(136)	122.0(8)
C(5py)-N(1py)-C(1py)	120.8(20)
C(2py)-C(1py)-N(1py)	119.0(21)
C(3py)-C(2py)-C(1py)	119.1(21)
C(4py)-C(3py)-C(2py)	120.3(21)
C(5py)-C(4py)-C(3py)	122.6(27)
C(4py)-C(5py)-N(1py)	117.2(27)

NOTE The three phenyl rings attached to the phosphorous atom were constrained to be rigid with internal angles of 120° and bond lengths equal to 1.395 Å.

Table 3

Least-squares plane for 2-N-acetyl-8-(triphenylphosphoranylidene)-phenoxazin-3,7-dione. Estimated standard deviation values in parentheses.

a) The atoms defining the planes and the equations of the planes are given by pX + qY + rZ = s where X?Y and Z are expressed as orthogonal coordinates.

Plane No.	Atoms defining plane	p	q	r	s
				$\times(10^4)$	
1	C(111), C(112), C(113) C(114), C(115), C(116)	-0470	-5158	8554	-12.7623
2	C(121), C(122), C(123) C(124), C(125), C(126)	8633	2135	4573	9.5721
3	C(131), C(132), C(133) C(134), C(135), C(136)	-7012	7123	0297	15.1592
4	C(1), C(2), C(3) C(12), C(13), C(14)	-3582	3567	8628	8.2609
5	C(3), N(4), C(5) C(10), O(11), C(12)	-4041	3575	8433	7.8948
6	C(5), C(6), C(7) C(8), C(9), C(10)	14397	3521	8262	7.3720
7	C(7), N(7), C(71) O(71), C(72), H(N7)	-5047	1874	8427	3.6064
8	C(1), C(2), C(3) N(4), C(5), C(6) C(7), C(8), C(9) C(10), O(11), C(12) C(13), C(14), O(14) O(8)	-4141	3525	8392	7.6996

b) Deviations from the plane (Å)

Atom \ Plane No.	4	5	6	7	8
P(1)	0.020	0.198	0.397	-0.362	0.203
C(1)	0.035	0.135	0.268	-0.456	0.122
C(2)	-0.020	0.67	0.198	-0.307	0.058
C(3)	-0.008	0.016	0.093	-0.400	-0.008
N(4)	-0.018	-0.005	0.071	-0.202	-0.024
C(5)	0.031	-0.016	0.009	-0.262	-0.050
C(6)	0.040	-0.021	-0.001	-0.046	-0.051
C(7)	0.141	0.017	-0.015	-0.062	-0.028
C(8)	0.282	0.106	0.022	-0.240	0.041
C(9)	0.225	0.065	-0.014	-0.498	-0.004
C(10)	0.214	0.025	-0.002	-0.484	-0.029
O(11)	0.073	-0.014	-0.038	-0.739	-0.072
C(12)	0.020	-0.006	0.022	-0.684	-0.049
C(13)	-0.004	-0.019	0.011	-0.909	-0.066
O(14)	0.005	0.066	0.152	-0.990	0.030
O(8)	0.446	0.216	0.085	-0.169	0.138
N(7)	0.085	-0.060	-0.104	0.053	-0.105
C(71)	-0.256	-0.369	-0.376	0.012	-0.398
O(71)	-0.417	-0.472	-0.428	0.024	-0.484
C(72)	-0.443	-0.595	-0.630	-0.061	-0.628
N(N7)	0.060	-0.129	-0.206	0.035	-0.1809

c) Angles between planes (^{o})

Plane	1	2	3	4	5	6	7	8
1		76	108	55	56	57	50	56
2			116	81	83	86	91	84
3				58	56	54	59	56
4					3	5	13	3
5						2	11	1
6							10	2
7								11
8								

4.6 Discussion

A perspective view of the molecule is shown in Figure 5 with the crystallographic numbering system used. The I.U.P.A.C. numbering system is given at the end of the chapter.

Significant bond lengths are given in Figure 7. and bond angles in Figure 8.

The molecule consists of a very slightly puckered, but essentially planar, phenoxazinone nucleus, with a triphenylphosphine moeity attached at C(1). The amino group at C(7) has been mono-acetylated.

The phenoxazinone nucleus

Several crystal structures of phenazines[11], phenoxazines[12], phenothiazines[12,13], and phenoxazinones[14], have been reported. (Table 4)

In the molecule under discussion, alternation of single and double bonds over the phenoxazinone ring system is that expected for the Kekulé formula given in Figure 9.

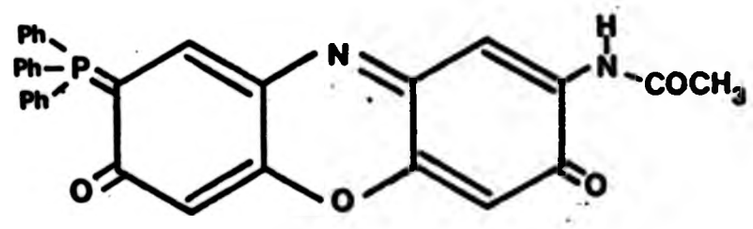


Figure 9

Figure 7Bond lengths

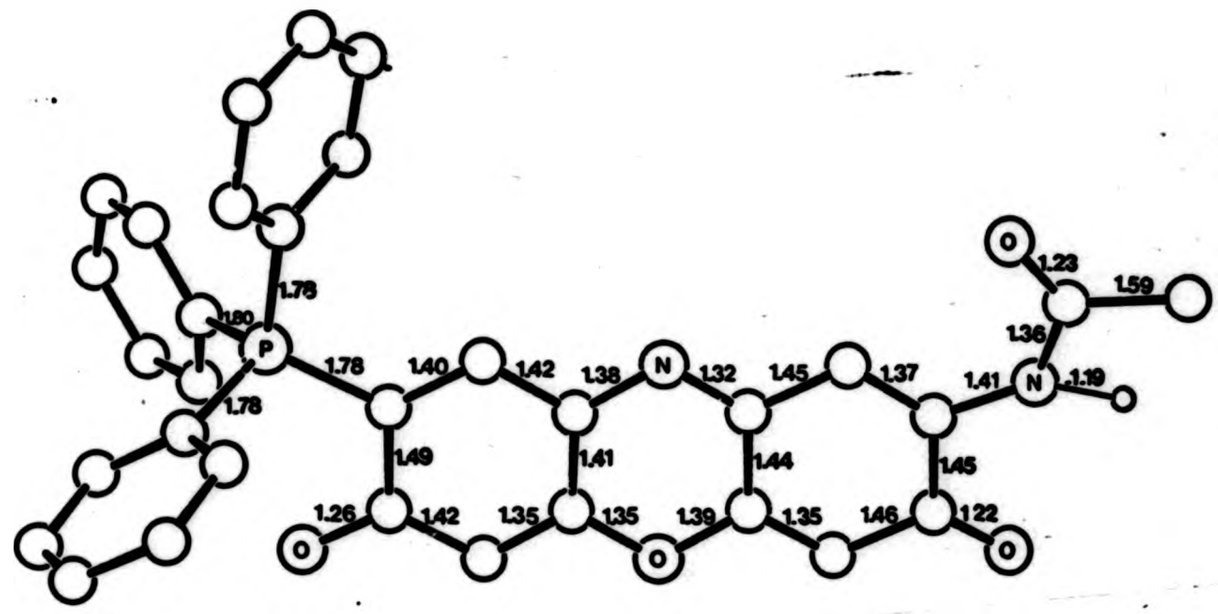
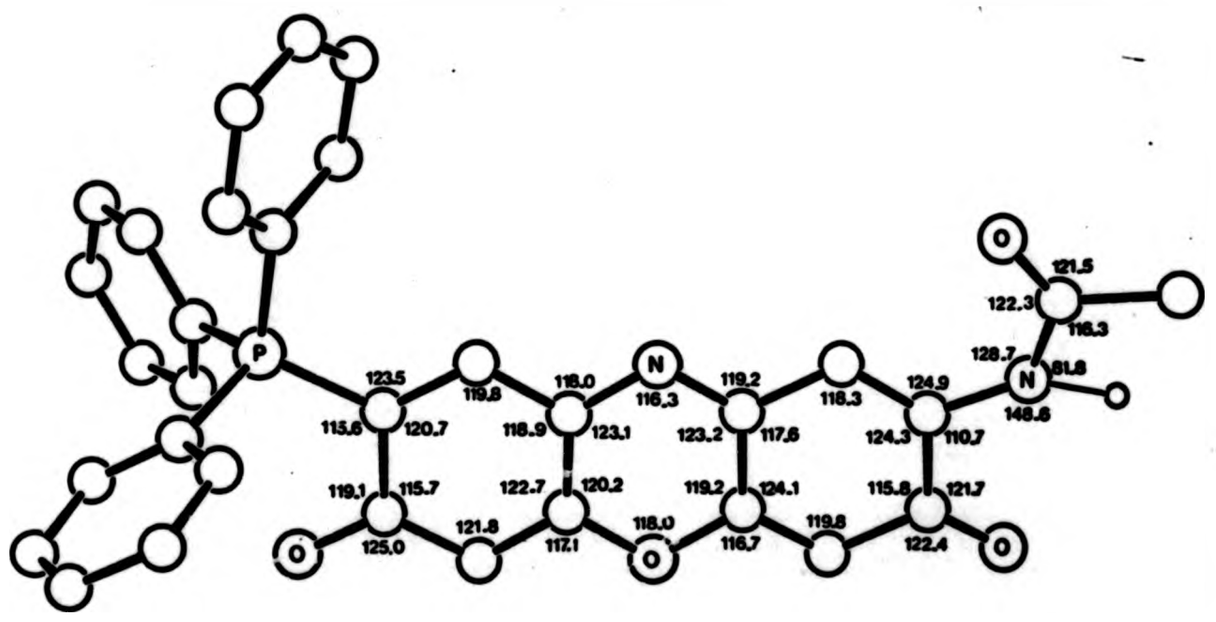


Figure 8 Bond angles



Mean angle at phosphorous = 109.5°

Table 4. Relevant bond lengths in phenazines, phenothiazines, phenoxazines and phenoxazinones. (crystallographic numbering system)

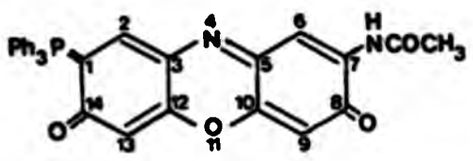
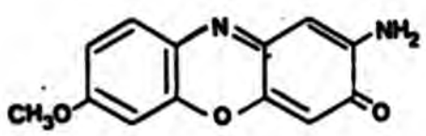
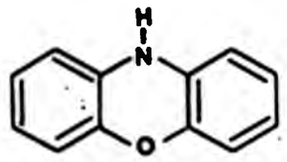
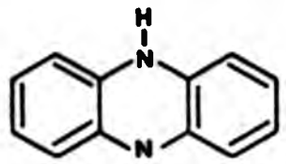
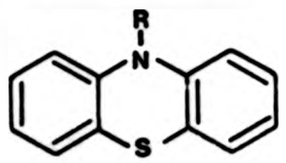
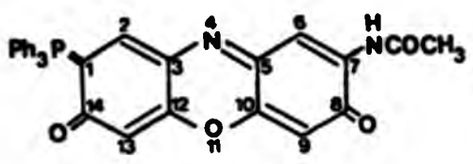
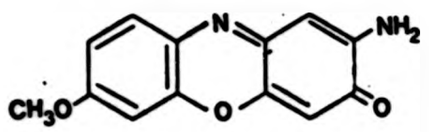
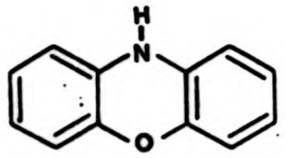
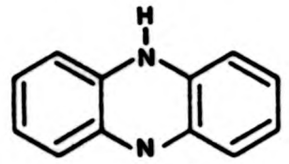
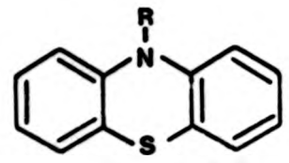
Compound	Bond lengths (Å)						Ref.
	C8-O8	C10-O11	O11-C-2	C14-O14	C3-N3	N4-C5	
	1.219(17)	1.390(16)	1.353(16)	1.264(16)	1.376(17)	1.316(18)	This work
	1.238(8)	1.376(7)	1.373(3)	-	1.373(7)	1.315(7)	14
	-	1.34(1)	1.35(1)	-	-	-	12
	-	-	-	-	1.342(9)	1.345(9)	11
 R = $CH_2C_6H_5$	-	-	-	-	1.406(3)	1.412(3)	12,13

Table 4. Relevant bond lengths in phenazines, phenothiazines, phenoxazines and phenoxazinones. (crystallographic numbering system)

Compound	Bond lengths (Å)						Ref.
	C8-O8	C10-O11	O11-C-2	C14-O14	C3-N3	N4-C5	
	1.219(17)	1.390(16)	1.353(16)	1.264(16)	1.376(17)	1.316(18)	This work
	1.238(8)	1.376(7)	1.373(3)	-	1.373(7)	1.315(7)	14
	-	1.34(1)	1.35(1)	-	-	-	12
	-	-	-	-	1.342(9)	1.345(9)	11
 R = $CH_2C_6H_5$	-	-	-.	-	1.406(3)	1.412(3)	12,13

The molecule under study is very similar to that prepared by Buckley *et.al.*[14,15], and Shutie (see section 3. Chapter 3.) 2-Amino-7-methoxy-3H-phenoxazine-3-one (Figure 10) was prepared by, in the former case, the action of diaminoethane on the copper(II) complex of 5-methoxy-2-nitrosophenol; and in the latter case, the reaction of 5-methoxy-2-nitrosophenol with triphenylphosphine.

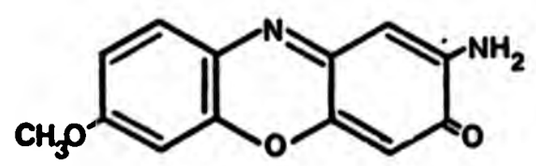


Figure 10

Relevant bond lengths and angles of the two molecules are compared in Table 5. C-C single bond lengths range from 1.424(18) Å to 1.451(19) Å for the molecule under discussion compared with 1.430(9) Å to 1.487(8) Å for 2-amino7-methoxy-3H-phenoxazine-3-one. C=C double bonds range from 1.352(18) Å to 1.372(18) Å for the former molecule to 1.334(8) Å to 1.390(8) Å for the latter.

Within the phenoxazinone ring of the molecule under discussion, bond lengths involving C(14) and C(1) are lengthened [C(14)-C(1) 1.490(18) Å; C(14)-O(14) 1.264(16) Å] relative to that expected for C-C single bond (1.54 Å)[16] or a quinoidal carbonyl (1.218Å)[17]. In addition C(2)-C(3) is much longer (1.416(17) Å) than that expected for the C=C double bond shown in the Kekulé structure (Figure 9).

Table 5. Comparison of molecular geometry between 2-N-acetyl-8-(triphenylphosphoranylidene-phenoxazine-3,7-dione (I) and 2-amino-7-methoxy-3H-phenoxazine-3-one (II)

Bond lengths(Å)

	(I)	(II)
C1-C2	1.396	1.364
C2-C3	1.416	1.420
C3-N4	1.376	1.373
C3-C12	1.408	1.390
N4-C5	1.316	1.315
C5-C6	1.451	1.430
C6-C7	1.372	1.347
C7-N7	1.413	1.358
C7-C8	1.451	1.487
C8-O8	1.219	1.238
C8-C9	1.461	1.450
C9-C10	1.346	1.334
C10-O11	1.390	1.376
O11-C12	1.353	1.373
C12-C13	1.352	1.389
C13-C14	1.424	1.384
C14-O14	1.264	1.369
C14-C1	1.490	1.397

Bond angles(°)

	(I)	(II)
C1-C2-C3	119.8	121.3
N4-C3-C2	118.0	120.0
C12-C3-N4	123.1	123.3
C12-C3-C2	118.9	116.6
C5-N4-C3	116.3	116.8
C6-C5-N4	119.2	121.0
C10-C5-N4	123.2	123.0
C10-C5-C6	117.6	116.0
C7-C6-C5	118.3	122.5
C8-C7-C6	124.3	120.6
N7-C7-C6	124.9	124.1
N7-C7-C8	110.7	115.4
C9-C8-C7	115.8	117.2
O8-C8-C7	121.7	120.2
O8-C8-C9	122.4	122.6
C10-C9-C8	119.8	120.0
C9-C10-C5	124.1	123.8
O11-C10-C5	119.2	118.8
O11-C10-C9	116.7	118.2
C12-O11-C10	118.0	118.9
O11-C12-C3	120.2	119.9
C13-C12-C3	122.7	123.2
C13-C12-O11	117.1	116.9
C14-C13-C12	121.8	117.9
C13-C14-C1	115.7	120.9
O14-C14-C1	119.1	114.2
O14-C14-C13	125.0	124.9

A reason for this lengthening of interatomic distances may be due to the presence of the triphenylphosphine group. It is highly likely that the molecule exists with considerable ylid character (Figure 11).

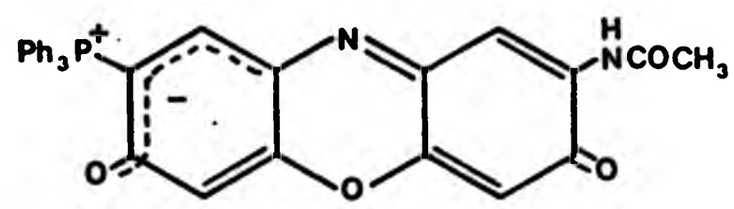


Figure 11

With this kind of the structure the negative charge is delocalised over atoms O(14), C(14), C(1) and C(2), i.e. those atoms involved in bond lengthening.

The endocyclic bond angles of the phenoxazinone ring range from 115.3(5)^{o} to 124.3(12)^{o}. This compares with the bond angles of the molecules in Table 2, which do not deviate significantly from the value expected, 120^{o}. Such a range of bond angles may be a result of the slight puckering of the ring system. Table 3b gives the deviation of every atom from certain specified planes. Plane 8 denotes the whole phenoxazinone ring. The extent of the puckering is shown in the sequence C(6)-C(7)-C(8)-C(9)-C(10)-O(11)-C(12)-C(13). Deviations from this plane (Å) are C(6),-0.051; C(7),-0.028; C(8),0.041; C(9),-0.004; C(10),-0.029; O(11),-0.072; C(12),-0.049; C(13),-0.066. There are no intramolecular contacts of significance.

The triphenylphosphine group

The most interesting feature of this molecule is the P-C bond at C(10). As explained in the previous section, lengthening of certain bond lengths within the phenoxazinone nucleus may indicate that the molecule has partial ylid character wiht the negative charge delocalised over four or five atoms. The stability of the compound depends on the delocalisation of this negative charge in the dipolar form, and to the electron withdrawing characteristics of the rest of the molecule.

P-C bond lengths within the triphenylphosphine part of the molecule are similar to those obtained in triphenylphosphine and other triphenylphosphonium ylids (Table 6.)

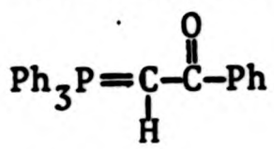
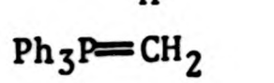
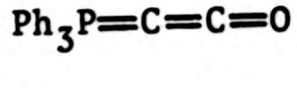
C-C bond lengths within the phenyl rings were 1.395 Å which compares with the interatomic distance of 1.398 Å in benzene[18].

The molecule triphenylphosphonium cyclopentadienylide[19] (Figure 12) which is thought to exist

(A) (B)

Figure 12 Mesomeric forms of triphenylphosphonium cyclopentadienylide

Table 6. P-C bond lengths and angles for P-phenyl group.

Compound	Mean P-C bond length(Å)	Mean angle at P(°)	Reference
Subject molecule	1.79(9)	109.5(4)	This study
	1.805(2)	109.5(1)	[19]
See Fig.5.18.	1.809(10)	108.2	[28]
	1.74	108.7(13)	[26]
	1.823	105.0	[22]
	1.805	107.3	[20]
	1.85	103.0	[21]

with 16% contribution of (A) and 84% of (B), has a P-C (ring) bond length of 1.718(2) Å. This much shorter than the P-C bond length (1.780(13) Å) found in the subject molecule. The shortness of the bond length is attributed to dπ-pπ overlap of the involving the unshared electrons of the carbon atom and the d orbitals of the phosphorous atom.

Among the shortest P-C distances reported are those of 1.648(7) Å for the triphenylphosphoranylidene-keten[20], (Figure 13).

$Ph_3P{=}C{=}C{=}O$

Figure 13

However such a compound is an extreme example, the ylid carbon atom being joined to only two other atoms - the formal hybridisation lying somewhere between sp and sp^2.

Perhaps the best example of an sp^2 ylid showing considerable P-C double bond character is methylenetriphosphorane[22], (Figure 14).

$Ph_3P{=}CH_2$

Figure 14.

The P-C distance in this molecule is 1.661(8) Å. This is much longer than the single bond distance in tertiary phosphines (1.85 Å), and close to the value obtained by Pauling[23] as the sum of the covalent radii of carbon and

phosphorus. The conclusion made is that methylenetriphenylphosphorane is best described as a carbanion (formally $PPh_3^+-CH_2^-$) although not in the extreme form.

The reaction of tri-p-tolylphosphine and methylacetylenedicarboxylate yields a product formulated as in Figure 15.[24]

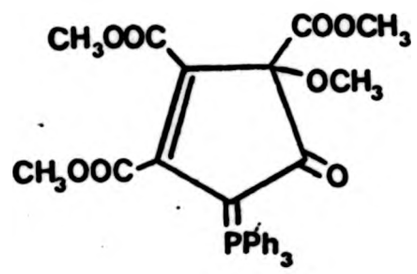


Figure 15

This molecule contains a P-C distance of 1.728(8) Å. The authors claim that within the molecule there is evidence that the phosphorous-carbon bond takes part in a conjugated system with a carbonyl group such as that proposed by Stephens[25,26] (Figure 16)

Figure 16

The reaction of triphenylphosphine with benzotrifuroxan[27] gives a variety of products including

iminophosphoranes and two compounds as shown in Figures 17[28] and 18.[29]

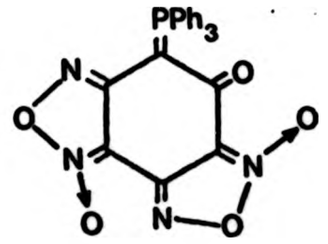


Figure 17

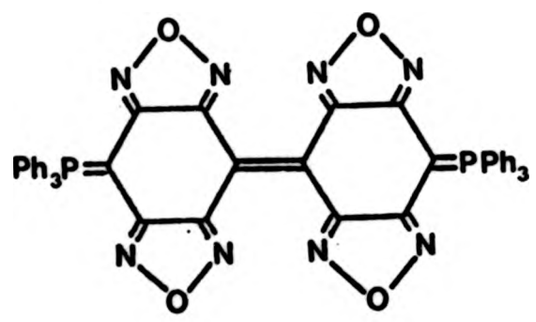
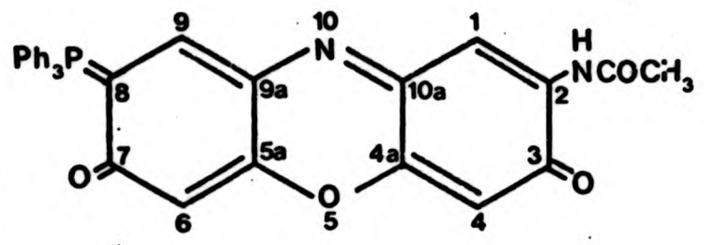


Figure 18

The crystal structures of these compounds show P-C bond lengths of 1.770(2) Å and 1.708(1.4) Å respectively. These are too long to be considered as double bonds, but the second molecule does possess some double bond character.

At present there is no reported structure having a phosphorous atom bonded nominally as P=C in any type of ring. From a comparative study of several significant structures it is not possible to describe the molecule discussed in this chapter as either an ylene or an ylid. It is better thought of as an intermediate structure with contribution from both mesomeric forms (see Figures 9 and 11)

Figure 19 I.U.P.A.C. numbering system for 2-N-acetyl-8-(triphenylphosphoranylidene)-phenoxazine-3,7-dione.



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CHAPTER 5

5.1 General

The reagents and solvents used were generally of 'Analar' grade and were used without further purification.

The kinetic experiments were carried out using 'Spectrosol' methanol which was used as supplied.

Iron pentacarbonyl was distilled under vacuum at room temperature immediately prior to use.

Macroreticular polymer supports were kindly supplied gratis by Rohm & Haas and Zerolit

Nitrogen was dried by passing it through a column packed with phosphorus pentoxide and then filtered through glass wool.

Silica gel adsorbent used in the chromatography columns was of 70 - 230 mesh and supplied by B.D.H. Chemicals Limited. Pre-coated silica gel plates of 0.25 mm. thickness were used for thin layer chromatography purposes. Large preparative plates were made up at The Polytechnic of North London. Solvent systems for thin layer chromatography were either chloroform or toluene/ethylacetate(5:2).

5.2 Analytical techniques.

Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical services of The Polytechnic of North London.

Phosphorus analyses were kindly carried out by Bill Stoten of Johnson Mathey Limited.

Metal analyses were carried out by atomic absorbtion spectroscopy on a Pye Unicam SP9 machine at the Polytechnic of North London. Wet oxidation was achieved by heating a small amount(ca. 0.1 g) of the material in concentrated nitric acid(10 cm^3), plus a few drops of 100 volume hydrogen peroxide.

5.3 Physical Techniques

Infra red spectroscopy.

Infra red spectra over the region 700-4000 cm^{-1} were recorded on a Pye Unicam SP2000 and SP4-200 microdisc spectrophotometer. The spectra were recorded as Nujol mulls or as a KBr disc.

Electronic spectroscopy

Ultra violet and visible spectra in the region 200-900 nm were recorded on a Pye Unicam SP1800 double beam spectrophotometer or a Varian DMS 90 programmable spectrophotometer.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (n.m.r.) spectra were obtained using a Perkin Elmer R12B 60MHz spectrometer (^1H), Bruker WP80 80MHz Fourrier Transform spectrometer (^1H and ^{13}C),at the Polytechnic of North London, and a 140 MHz instrument (^1H) at the Physico-Chemical Measurements Unit at Harwell. Tetramethylsilane was used as the standard reference.

Mass Spectrometry

Routine mass spectra were recorded using a Hitachi-Perkin Elmer RMS4 single focussing instrument. High resolution and precise mass measurements were obtained on an A.E.I. MS9 double focussing spectrometer at the Polytechnic of North London. Additional spectra were obtained on an A.E.I. MS50 instrument via the Physico-Chemical Measurements Unit at Harwell.

^{57}Fe Mössbauer Spectra

Mössbauer spectra were obtained by kind permission of Dr. Desmond Cunningham at University College Galway.

Thermogravimetric Analysis

Thermogravimetric analysis (T.G.A.) were obtained using a Stanton thermobalance. A constant downward flow of nitrogen was maintained in the oven. A linear rise of temperature of 100 ^{o}C or 50 ^{o}C hour^{-1} was used.

Magnetic Susceptibility Measurements.

Room temperature magnetic moments were determined usind a Guoy balance with a permanent magnet of 0.36T flux density. Variable temperature measurements were determined on a Newport Instruments' Guoy balance at flux density 0.345, 0.545, 0.638 and 0.708T. The temperature recording device was calibrated using $CuSO_4.5H_2O$ and the sample tubes calibrated using mercury tetrathiocyanocobaltate(II).

Different batches of the same compound gave results that were in agreement within experimental error. The values of the diamagnetic corrections used in the calculations are given in Table 1.[1]

Table 1. Diamagnetic corrections of the metal complexes investigated by variable temperature magnetic work.

Compound	$10^6 \chi_{dia.}$
Tris(5-hydroxy-1,2-benzoquinone-2-oximato)iron(III)-trihydrate.	-176
Bis(3-methyl-4-oximato-1-phenyl-1H-pyrazol-4,5-dione)iron(II)-monohydrate.	-136
Bis(3-methyl-4-oximato-1-phenyl-1H-pyrazol-4,5-dione)iron(II)-monopyridine.	-220
6-Ethyl-1,2,3,4-benzoquinone-2,4-dioximatonickel(II)-dihydrate.	-83
6-Ethyl-1,2,3,4-benzoquinone-2,4-dioximatonickel(II)-monopyridine	-119

5.4 Reactions

The mononitrosation of resorcinol using amyl nitrite.

Sodium hydroxide (17.1 g, 1.4 mol. equiv.) was dissolved in dry ethanol (350 cm^3) and the solution cooled to -5 ^oC. Resorcinol (33.0 g, 1 mol. equiv.) was added and the solution vigourously stirred. Amyl nitrite (39 g, 1.1 mol. equiv) was added and the reaction mixture was allowed to reach room temperature over a period of two hours. A red solid precipitated from the reaction mixture and was filtered at the pump. The solid was dried at 0.1 mm/20 and then redissolved in ethanol (300 cm^3). The solution was filtered and light petrol (500 cm^3) added. Red bissodium 4-nitrosoresorcinolate trihydrate (39.4 g, 55%), (Found: C, 29.8; H, 3.9; N, 5.2%, Calc. for $C_6H_9Na_2NO_6$: C, 30.4; H, 3.8; N, 5.9%), m.p.34-6 ^oC, was filtered at the pump, washed with light petrol (40-60 fraction) and dried at 0.1 mm./20 ^oC.

If the above procedure was carried out using potassium hydroxide (23.9 g, 1.4 mol.equiv), red-brown, bispotassium-4-nitrosoresorcinolate (28.4 g, 44%), (Found; C, 32.8; H, 1.4; N, 6.1%, Calc. for $C_6H_3K_2NO_3$: C, 33.5; H, 1.4; N, 6.5%) was formed.

The dinitrosation of resorcinol.

Sodium nitrite (10 g) in water (50 cm^3) was added to a stirred solution of resorcinol (18 g) in alcohol (200 cm^3). Glacial acetic acid (5 cm^3) was added portionwise and the reaction mixture stirred for one hour. Dark brown

2,4-dinitrosoresorcinol (15.1 g, 55%) (Found; C, 43.1; H, 2.6; N, 16.1%,·Calc. for $C_6H_4N_2O_4$: C, 42.9; H, 2.4; N. 16.7%), m.p. 166-7 °C, lit.[2] 168 °C, was filtered at the pump, washed with water (5 x 100 cm^3), acetone (5 x 100 cm^3) and diethyl ether (5 x 100 cm^3), and dried at 0.1 mm/30°C.

If the reaction with amyl nitrite was carried out at or above ambient temperature 2,4-dinitrosoresorcinol was again formed.

The interaction of bissodium 4-nitrosoresorcinolate with hydrochloric acid.

Bissodium 4-nitrosoresorcinolate (25 g, 1 mol. equiv.) was dissolved in water (50 cm^3). Hydrochloric acid (5 mol dm^{-3}, 150 cm^3) was added to the solution with vigorous stirring. 4-Nitrosoresorcinol (12.8 g, 87%), (Found; C, 50.9; H, 3.8; N, 9.9%, Calc. for $C_6H_5NO_2$: C, 51.8, H, 3.6: N, 10.1%) precipitated from solution, was filtered at the pump, washed with water (5 x 100 cm^3), and dried at 0.1 mm/30 °C.

The same product was obtained when the acidification was carried out on bispotassium 4-nitrosoresorcinolate.

The nitrosation of resorcinol and its derivatives using sodium nitrite and acetic acid in the presence of nickel(II) chloride.

The resorcinol (ca. 6 g, 1 mol. equiv.) was dissolved in ethanol (100 cm^3) and added to a solution of

nickel(II) chloride (1 mol. equiv.), acetic acid (20 cm^3), and sodium acetate (20 g) in water (150 cm^3). Sodium nitrite (20 g) in water (50 cm^3) was then added in one portion. After one week the product was filtered off, washed by decantation with water and ethanol, and dried at 0.1 mm/50 ^oC. Analytical details are given below.

Phenol	Formula	Analyses				
			C	H	N	Ni
Resorcinol	Ni(dnr).$2H_2O$	F	27.9	1.7	10.8	21.4
		R	27.6	1.6	10.7	22.4
4-Ethylresorcinol	Ni(6-Etdnr).$2H_2O$	F	32.9	3.2	9.4	20.7
		R	33.3	3.5	9.7	20.3
5-Methylresorcinol	Ni(5-Medn r).$2H_2O$	F	30.2	2.4	10.9	22.8
		R	30.6	2.9	10.2	21.3

F=Found, R=Requires

<u>The interaction of (6-ethyl-1,2,3,4-benzoquinone-2,4-dioximato)nickel(II)-dihydrate with pyridine.</u>

6-Ethyl-1,2,3,4-benzoquinone-2,4-dioximato nickel(II)-dihydrate (3.0 g 1.mol.equiv.) was heated in pyridine (100 cm^3) at 100 ^oC. for one hour. The reaction mixture was filtered hot, and the filtrate evaporated to dryness at 0.1 mm/60 ^oC. The dark brown residue of <u>6-ethyl-1,2,3,4-benzoquinone-2,4-dioximato)nickel(II)-dipyridine</u> (3.1 g, 73%), (Found: C, 52.6; H, 4.0; Ni, 14.2; N, 13.8%, $C_{18}H_{16}NiN_2O_4$ requires : C, 52.7; H, 3.9; Ni, 14.3; N, 13.6%) was washed with ethanol and diethyl ether (2 x 100 cm^3) and dried at 0.1 mm/50 ^oC.

The interaction of 6-ethyl-1,2,3,4-benzoquinone-2,4-dioximatonickel(II)-dihydrate with aqueous hydrochloric acid.

Concentrated hydrochloric acid (10 cm^3) was added to a stirred solution of 6-ethyl-1,2,3,4-benzoquinone-2,4-dioximatonickel(II)-dihydrate (3.1 g) in water (50 cm^3). The mixture was stirred for one hour. 6-Ethyl-2,4-dinitrosoresorcinol monohydrate (1.91 g, 81%) (Found, C, 44.4: H, 4.4; N, 12.7%, $C_8H_{10}N_2O_5$ requires : C, 44.7, H, 4.6; N, 13.0%), m.p. 150-2 dec., was filtered at the pump, washed with dilute hydrochloric acid (2 x 100 cm^3) and water (2 x 100 cm^3) and dried at 0.1 mm/30 ^oC.

The nitrosation of 2-methylresorcinol using sodium nitrite and acetic acid.

2-Methylresorcinol (4.4 g, 1 mol. equiv.) was dissolved in water (150 cm^3). Sodium nitrite (9.0 g) in water (100 cm^3) was added with vigorous stirring. Glacial acetic acid (10 cm^3) was added and the reaction mixture stirred for one hour. A dark yellow solid precipitated from the mixture, was filtered at the pump and dried at 0.1 mm/ 20 ^oC. This yellow solid crystallised from toluene as yellow plates of 2-methyl-4-nitrosoresorcinol (4.8 g, 88%), (Found, C, 54.9; H, 5.8; N, 9.3%, $C_7H_7NO_3$ requires ; C, 54.9 H, 4.6: N, 9.1%) m.p. 146-8 ^oC.

The interaction of 4-nitroso-1,3-benzenediol with copper(II) acetate in aqueous ethanol.

4-Nitrosoresorcinol (3.2 g, 2 mol. equiv.) was dissolved in ethanol (100 cm^3). Copper(II) acetate dihydrate (2.5 g, 1 mol. equiv.) in water (100 cm^3) was added and the mixture stirred for two hours. Red-brown di-μ-hydroxy-bis(5-hydroxy-1,2-benzoquinone-2-oximato)dicopper (II),(2.4 g, 48%), (Found: C, 32.1; H, 1.9; Cu, 28.4; N, 6.1%, $C_{12}H_{10}Cu_2N_2O_8$ requires: C, 33.0; H, 2.3; Cu, 29.1; N, 6.4%) was filtered at the pump, washed with water (5 x 100 cm^3), acetone (5 x 100 cm^3) and diethyl ether (5 x 100 cm^3), and dried at 0.1 mm/30 ^oC.

When the above reaction was repeated in a buffered (pH 9) reaction mixture, the same product was formed.

The interaction of di-μ-hydroxy-bis(5-hydroxy-1,2-benzoquinone-2-oximato)dicopper(II) with pyridine

Di-μ-hydroxy-bis(5-hydroxy-1,2-benzoquinone-2-oximato)dicopper(II) (1.5 g) was heated under reflux in pyridine (100 cm^3) for twelve hours. Diethyl ether (200 cm^3) was added to the reaction mixture after cooling, which was then filtered. Di-μ-hydroxy-bis(5-hydroxy-1,2-benzoquinone-2-oximato)dicopper(II) (1.4 g, 93% recovery) was washed with diethyl ether and dried at 0.1 mm./30 ^oC.

The interaction of 4-nitrosoresorcinol or 2-methyl-4-nitroso-resorcinol with copper(II) acetate in pyridine.

4-Nitrosoresorcinol (5.0 g, 2.1 mol. equiv.) and copper(II) acetate dihydrate (3.6 g, 1 mol. equiv.) were stirred in pyridine for twelve hours. Brown, bis(5-hydroxy-1.2-benzoquinone-2-oximato)copper(II)-monopyridine (2.8 g, 37%), (Found: C, 48.1; H, 2.8; Cu, 14.8; N, 2.8%, $C_{17}H_{13}CuN_3O_6$ requires: C, 48.7; H, 3.1; Cu, 15.2; N, 3.1%) was filtered at the pump and washed with a 10% v/v solution of pyridine in diethyl ether (3 x 30 cm^3) and dried at 0.1 mm/2) ^oC.

When the above procedure was repeated using 2-methyl-4-nitrosoresorcinol (4.3 g, 2.1 mol. equiv.) and copper(II) acetate (2.9 g, 1 mol. equiv.), red-brown, bis(5-hydroxy-6-methyl-1.2-benzoquinone-2-oximato)copper(II)-monopyridine (1.9g, 30%), (Found: C, 50.9; H, 3.7; Cu, 13.8; N, 9.1%, $C_{19}H_{17}CuN_3O_6$ requires: C, 51.1; H, 3.8; Cu, 14.2; N, 9.4% was formed.

The interaction of 4-nitroso-1,3-benzenediol with iron (II) ammonium sulphate in aqueous alcohol.

4-Nitroso-1,3-benzenediol (2.5 g, 2 mol.equiv.) was dissolved in alcohol (50 cm^3). Iron(II) ammonium sulphate (3.5 g, 2 mol. equiv.) in water (50 cm^3) was added to the alcoholic solution with vigourous stirring. Chloroform (20 cm^3) was added to the reaction mixture which was then stirred for twelve hours. Green tris(5-hydroxy-1,2-benzo-quinone-2-oximato)iron(III) trihydrate (1.7 g, 54%), (Found: C, 40.6; H, 3.1; Fe, 10.3; N, 8.5%, $C_{18}H_{18}FeN_3O_{12}$ requires: C, 41.2; H, 3.4; Fe, 10.7; N, 8.0%) was filtered off at the pump, washed with chloroform and dried at 0.1 mm/30 ^oC.

Preparation of 3-methyl-4-oxime-1H-pyrazol-4,5-dione(poH) and 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione(PpoH)

3-Methyl-1H-pyrazol-5-one* (10 g) was stirred in water at room temperature. Glacial acetic acid (15 cm^3) was added followed by sodium nitrite (15 g). Yellow 3-methyl 4-oxime-1H-pyrazol-4,5-dione (9.5 g, 73%) was filtered at the pump and washed with water (5 x 200 cm^3). The yellow solid crystallised from water as needles of the hemihydrate, (Found: C,35.6; H,3.6; N,30.1%; Calc. for $C_4H_6N_3O_4$: C,35.2; H,4.3; N, 30.9%) m.p. 225-6 °C.

3-Methyl-1-phenyl-1H-pyrazol-5-one* (15 g) was treated with sodium nitrite and glacial acetic acid as described above. Orange, 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione (13.3 g, 76%) crystallised from water as long needles of the monohydrate. (Found: C,55.1; H,4.9; N,20.0%; Calc. for $C_{10}H_{11}N_3O_3$: C,54.3; H,5.0; N,19.0%) m.p. 163- 5 °C.

*Prepared as described by Fitton and Smalley[3]

Interaction of 3-methyl-4-oxime-1H-pyrazol-4,5-dione and 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione with copper(II) chloride and nickel(II) chloride.

The procedure was carried out as described by Hovorka and Sucha[4] . Pyridine adducts were prepared by warming the hydrated complex in pyridine, filtering the warm solution, and then precipating the pyridine adduct by

dropwise addition of the filtrate into a large volume of diethyl ether containing a few drops of pyridine. The yields obtained are given below.

3-Methyl-4-oxime-1H-pyrazol-4,5-dione (poH)

Formula	% yield	Formula	% yield
$Cu(po)_2.2H_2O$	42	$Cu(po)_2.2py$	88
$Ni(po)_2.2H_2O$	57	$Ni(po)_2.2py$	65

3-Methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione (PpoH)

Formula	% yield	Formula	% yield
$Cu(Ppo)_2.2H_2O$	76	$Cu(Ppo)_2.2py$	71
$Ni(Ppo)_2.2H_2O$	64	$Ni(Ppo)_2.2py$	64

Interaction of 3-methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione with iron(II) ammonium sulphate

3-Methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione (2.0 g,2 mol. equiv.) and iron(II) ammonium sulphate (1.9 g,1 mol. equiv.) were stirred in an ethanol/water (2:1) mixture (120 cm^3), for one hour. Turquoise bis(3-methyl-1-phenyl-4-oximato-1H-pyrazol-4,5-dione)iron(II)-monohydrate (1.4 g,59%), (Found: C,57.7; H,4.8; Fe, 11.3; N, 17.7%, $C_{20}H_{18}FeN_6O_5$ requires : C, 58.3; H, 4.8; Fe, 11.1, N, 18.1%) was filtered off at the pump, washed with water (2 x 100 cm^3) and ethanol (2 x 100 cm^3)

Interaction of 3-methyl-4-oxime-1H-pyrazol-4,5-dione with iron(II) ammonium sulphate.

3-Methyl-oxime-1H-pyrazol-4,5-dione (4.0 g, 2 mol. equiv.) and iron(II) ammonium sulphate (6.1 g, 1 mol.

equiv.) were heated under reflux in an alcohol/water mixture (150 cm^3) for four hours. The solution was cooled. 3-Methyl-4-oxime-1H-pyrazol-4,5-dione (3.5 g, 88% recovery) was filtered off unreacted (identified by i.r.).

Attempted reaction of 3-methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione and 3-methyl-4-oxime-1H-pyrazol-4,5-dione with iron(III) ammonium sulphate.

3-Methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione (4.0 g,3 mol. equiv.) and iron(III) ammonium sulphate (3.2 g, 1 mol. equiv.) were heated under reflux in water (150 cm^3) for two hours. The reaction mixture was cooled and the ligand (3.4 g, 85% recovery) was filtered off at the pump.

3-Methyl-4-oxime-1H-pyrazol-4,5-dione was recovered in 89% yield when treated with iron(III) ammonium sulphate as described above.

The ligands were also recovered unreacted when the above procedure was carried out in a buffered (pH 9) solution.

Interaction of 3-methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione with iron pentacarbonyl.

3-Methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione (2.1 g, 2 mol. equiv.) and iron pentacarbonyl (1.0 g, 1 mol. equiv.) were heated under reflux for twelve hours under nitrogen in freshly distilled (over $LiAlH_4$)

tetrahydrofuran (100 cm^3). Evaporation of the solution gave a dark brown solid (2.31 g) (Found: C, 53.8; H,4.1; Fe, 6.6; N, 19.4%) which was shown by t.l.c. to be a mixture of at least four components. A portion of the brown solid (0.92 g) was separated on a silica gel chromatography column. Toluene eluted on orange-red solid which crystallised from light petrol (60-80°C fraction) as red needles of 2,4-dihydro-4-[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-1-phenyl-pyrazol-3-one (0.41g 66%), m.p. 185-7 °C (lit.[5] 183 °C), (Found: C,67.1; H,5.1; N,18.7%, Calc. for $C_{20}H_{17}N_5O_2$: C,66.8; H,4.8; N,19.5%). ν_{max}(KBr) C=O, 1570 cm^{-1}; $\lambda_{max}(CH_3OH)$, 206 nm (ε=1541 m^2mol^{-1}); 240 nm (ε=1377 $m^2 mol^{-1}$); 351 nm (ε=636 m^2mol^{-1}); 444 nm (ε=925 m^2mol^{-1}). $\delta(CDCl_3)$: 2.32 p.p.m. (6H,singlet); 7.31-7.92 p.p.m. (10H, multiplet); 17.46 p.p.m. (1H, singlet,exchanged with D_2O). m/e 359 (P^+), Found 359.13717, Calc. for $C_{20}H_{17}N_5O_2$ 359.13822. Also obtained from the column (toluene) was a yellow solid which crystallised from acetone/light petrol (60-80°C fraction) as yellow prisms and was identified by its mass spectrum and melting point as 1,2,5-oxadiazolo [3,4-d]-6-methyl-4-phenyl-4H-pyrazole (0.04 g, 6%) m.p. 86-8 °C (lit.[6] 91°C). m/e 200 (P^+). Ethyl acetate eluted 3-methyl-1-phenyl-4-oxime-1H-pyrazol-4,5-dione (0.01 g) [identified by comparitive t.l.c. and i.r.]. Methanol eluted bis(3-methyl-1-phenyl-4-oximato-1H-pyrazol-4,5-dione)iron(II)-hydrate, (0.11 g,14%) [identified by i.r.]. A brown intractable solid remained on top of the column.

Interaction of 3-methyl-4-oxime-1H-pyrazol-4,5-dione with iron pentacarbonyl

3-Methyl-4-oxime-1H-pyrazol-4,5-dione (2.5 g, 1 mol. equiv.) and iron pentacarbonyl (19.4 g,5 mol. equiv.) were heated under reflux for twelve hours in freshly distilled (over $LiAlH_4$) tetrahydrofuran in a dry nitrogen atmosphere. The solution was filtered under anhydrous conditions to give to give dark green bis(3-methyl-4-oximato-1H-pyrazol-4,5-dione)iron(II)-monohydrate (1.5 g, 54%), (Found: C,29.9; H,2.8; Fe,17.1; N,25.9%, $C_8H_{10}FeN_5O_6$ requires: C,29.5; H,3.1; Fe,17.1; N,25.8%). The bischelate was washed with tetrahydrofuran and dried at 0.1 mm/30 °C. The washings were concentrated to 20 cm^3. Water (50 cm^3) was added and the solution filtered. The solid was washed with warm water (10 x 50 cm^3) to give 2,4-dihydro-4-[(5-hydroxy-3-methyl-1H-pyrazol-4-yl)imino]-5-methyl-3H-pyrazol-3-one (0.14 g,8%), (Found: C, 47.1; H, 4.9; N, 33.1%, $C_8H_9N_5O_2$ requires: C, 46.3; H, 4.3; N, 33.8%), m.p. 265-7°C sub. δ (d^6DMSO) : 2.15 p.p.m. (6H, singlet; 12.84 p.p.m. (2H, singlet); 16.68 p.p.m. (1H, singlet, exchanged with D_2O. m/e 207 (P^+), Found 207.0759, $C_8H_9N_5O_2$ requires 207.0756. The combined filtrate and washings were evaporated to dryness to give 3-methyl-4-oxime-1H-pyrazol-4,5-dione (0.24 g? 10% recovery).

Interaction of bis(3-methyl-4-oximato-1-phenyl-1H-pyrazol-4,5-dione)nickel(II)-dipyridine with triphenylphosphine.

Triphenylphosphine (0.6 g, 5 mol. equiv.) was added to a solution of bis(3-methyl-4-oximato-1-phenyl-1H-pyrazol-4,5-dione)nickel(II)-dipyridine in pyridine (50 cm^3) and the mixture heated under reflux for forty eight hours. The solution was cooled and diethyl ether (200 cm^3) added. Bis(3-methyl-4-oximato-1-phenyl-1H-pyrazol-4,5-dione) nickel(II)-dipyridine (0.5 g, 81% recovery) (identified by i.r.) was filtered at the pump and dried at 0.1 mm/2) ^{o}C.

When the above procedure was repeated using bis(3-methyl-4-oximato-1-pheny-1H-pyrazol-4,5-dione)copper (II)-dipyridine or bis(3-methyl-4-oximato-1-phenyl-1H-pyrazol-4,5-dione)iron(II)-dipyridine the unreacted complexes were recovered in 85% and 90% yield respectively.

The interaction of 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione and 3-methyl-4-oxime-1H-pyrazol-4,5-dione with triphenylphosphine in pyridine.

3-Methyl-4-oxime-1H-pyrazol-4,5-dione (1.6 g, 1 mol. equiv.) was heated under reflux in pyridine with triphenylphosphine (16.5 g, 5 mol. equiv.). The solution was cooled and water (100 cm^3) added. The mixture was filtered and the solid thoroughly washed with acetone. The solid remaining was identified by i.r. as 3-methyl-4-oxime-1H-pyrazol-4,5-dione (1.3 g, 81% recovery).

When the reaction was repeated using 3-methyl-4-oxime-1-phenyl-1H-pyrazol-4,5-dione, the ligand was recovered in 85% yield.

Interaction of bis(5-methoxy-1,2-benzoquinone-2-oximato) copper(II) with triphenylphosphine in pyridine.

Bis(5-methoxy-1,2-benzoquinone-2-oximato) copper(II) (2.8 g, 1 mol. equiv.) was dissolved in pyridine (80 cm^3). Triphenylphosphine (10.1 g, 5 mol. equiv.) was added and the reaction mixture heated under reflux for twelve hours. The reaction mixture was cooled and then evaporated to dryness. The resultant brown solid was Soxhlet extracted with diethyl ether (250 cm^3). The extract was concentrated to 20 cm^3 and filtered to give yellow, 5-methoxy-1,2-benzoquinone-2-oximatobis(triphenylphosphine)copper(I) (3.8 g, 66%), (Found: C, 69.1; H, 5.1; Cu, 8.6; N,2.2% , Calc. for $C_{43}H_{36}CuNO_3P_2$: C, 69.8; H, 4.9; Cu, 8.6; N, 1.9%), which was washed with diethyl ether (2 x 100 cm^3) and light petrol (2 x 100 cm^3) and dried at 0.1 mm/30 ^oC. The residue in the Soxhlet thimble was reextracted with ethyl acetate or pyridine (250 cm^3) to give a red solid (0.54 g). This solid crystallised from pyridine (30 cm^3) as red needles of 2-amino-7-methoxy-3H-phenoxazine-3-one (0.41 g, 37%),m.p.269 ^oC. (Found: C, 62.3; H, 5.0; N, 9.8%, Calc. for $C_{14}H_{12}N_2O_4$: C, 61.8; H, 4.4; N, 10.3%). Reextraction of the residue with methanol gave, bis(5-methoxy-1,2-benzoquinone-2-oximato) copper(II) (0.9 g , 33% recovery), (Found: C, 46.7; H, 4.0; Cu, 17.3; N, 6.9%, Calc. for $C_{14}H_{12}CuN_2O_6$: C, 45.7; H, 3.3; Cu, 17.3; N, 7.6%.

The ethereal filtrate was evaporated to dryness and chromatographed on a silica column. Light petrol (60-80 fraction) eluted triphenylphosphine (0.32 g)(identified

by comparative t.l.c. and i.r.). Toluene eluted more 5-methoxy-1,2-benzoquinone-2-oximatobis(triphenylphosphine) copper(II) (identified by comparative i.r.) and chloroform eluted triphenylphosphine oxide (2.6 g)(identified by comparative i.r.).

Interaction of 5-methoxy-2-nitrosophenol with triphenylphosphine in pyridine.

5-Methoxy-2-nitrosophenol (2.9 g, 1 mol. equiv.) was heated under reflux in pyridine (100 cm^3) with triphenylphosphine (24.8 g, 5 mol. equiv.) for twelve hours. The solution was cooled and then evaporated to dryness. The dark brown solid was extracted (Sohxlet) with light petrol (60-80 fraction). Evaporation of the extract yielded triphenylphosphine (21.8 g)(identified by comparative t.l.c. and i.r.). The residue in the Soxhlet thimble (5.5 g) was the redissolved in pyridine (50 cm^3) and silica (5.2 g) added. The impregnated silica was placed on a silica chromatography column. Toluene eluted more triphenylphosphine (0.4 g)(identified by comparative t.l.c. and i.r.) and 5-methoxy-2-nitrosophenol (0.9 g, 31% recovery). Ethyl acetate eluted triphenylphosphine oxide (2.7 g)(identified by comparative t.l.c. and i.r.), and 2-amino-7-methoxy-3H-phenoxazine-3-one (1.2 g, 52%)(identified by comparative t.l.c. and i.r.).

Interaction of 4-nitrosoresorcinol with triphenylphosphine in pyridine.

4-Nitrosoresorcinol (1.4 g, 1 mol. equiv.) was heated under reflux in pyridine (100 cm^3) with triphenylphosphine (12.7 g, 5 mol. equiv.) for twenty four hours. The reaction mixture was cooled and silica (9.2 g) added. The solvent was then evaporated off and a portion of the resulting solid (13.7 g) placed on a silica chromatography column. Toluene eluted triphenylphosphine (6.5 g)(identified by comparitive t.l.c. and i.r.). Chloroform eluted triphenylphosphine oxide (3.9 g)(identified by comparative t.l.c. and i.r.). A mixture of chloroform/diethyl ether (5:1) eluted 2-amino-7-hydroxy-3H-phenoxazine-3-one (0.16 g, 14%) (Found: C, 62.5; H, 3.4; N, 10.8%, $C_{12}H_8N_2O_3$ requires : C, 63.2; H, 3.5; N, 11.3%), $\nu_{max.}$(KBr) N-H, 3360 cm^{-1}, 3460 cm^{-1}, C=O, 1720 cm^{-1}; $\lambda_{max.}$(CH_3OH), 203 nm.(ε= 79.3 m^2mol^{-1}), 233 nm.(ε= 93.4 m^2mol^{-1}), 455 nm.(ε= 71.5 m^2mol^{-1}); δ(d^6DMSO), 6.32 p.p.m. (1H, singlet), 6.35 p.p.m. (1H,singlet), 6.45 p.p.m. (2H, singlet exchanged with D_2O), 6.87 p.p.m. (1H, multiplet). 7.60 p.p.m. (2H, multiplet), 10.50 p.p.m. (1H, singlet exchanged with D_2O). A mixture of ethyl acetate/ methanol (50:1) eluted 2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (0.29 g, 12%), (Found: C, 74.5; H, 5.0, N, 4.9; P, 6.0% $C_{30}H_{21}N_2O_3P$ requires: C, 73.8; H, 4.4; N, 5.7; P, 6.4%), $\nu_{max.}$(KBr) N-H 3315 cm^{-1}, 3460 cm^{-1}, C=O, 1735 cm^{-1}; confirmed by a single crystal X-ray structure determination on its N-acetyl derivative. Also eluted from the

column (methanol) were two fractions (0.1 g and 0.26 g) containing at least four unidentified substances.

Interaction of 2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione with acetic anhydride in pyridine.

2-Amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (0.11 g), was dissolved in pyridine and acetic anhydride (2 cm^3) added. The reaction mixture was stirred in the cold for twelve hours. The mixture was then filtered and the filtrate evaporated to dryness to give a red solid. The solid was redissolved in pyridine and silica (1.0 g) added. The impregnated silica was placed on the top short, narrow bore silica chromatography column and washed through with toluene for several minutes. Methanol eluted a red solid which crystallised from pyridine/light petrol(80-100 fraction) as red cubes of 2-N-acetyl-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (0.10 g, 84%) (Found: C, 73.1; H, 4.8; N, 5.3; P, 5.2%, $C_{32}H_{23}N_2O_4P$ requires: C, 72.5; H, 4.3; N, 5.3; P, 5.8%) $\nu_{max.}$(KBr) C=O 1735 cm^{-1} $\lambda_{max.}(CH_3OH)$, 228 nm.(ε=2641 m^2mol^{-1}), 265 nm.(ε=1720 m^2mol^{-1}), 527 nm.(ε=1429 m^2mol^{-1});$\delta^{31}P(d^6DMSO)$, 21.2 p.p.m., singlet; confirmed by X-ray diffraction, which was filtered in a Hirsch funnel, washed with light petrol (60-80 fraction) and dried at 0.1 mm/30 ^oC.

Interaction of bis(5-hydroxy-1,2-benzoquinone-2-oximato) copper(II)-monopyridine with triphenylphosphine in pyridine.

Bis(5-hydroxy-1,2-benzoquinone-2-oximato) copper(II)-monopyridine (0.5 g, 1 mol. equiv.) was heated under reflux in pyridine with triphenylphosphine (1.7 g. 5 mol.equiv) for twenty four hours. The reaction mixture was cooled and silica (3.5 g) added. A portion of the impregnated silica (5.2 g) was placed on a silica chromatography column. Toluene eluted triphenylphosphine (0.29 g)(identified by comparative t.l.c. and i.r.), A toluene/methanol (50:1) mixture eluted 2-amino-7-hydroxy-3H-phenoxazine-3-one (0.18 g, 25%)(identified by comparative t.l.c. and i.r.). Toluene/methanol (20:1) eluted 2-amino-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (0.21 g, 40%) identified by comparative t.l.c. and i.r.). Further elution gave triphenylphosphine oxide (0.18 g)(identified by comparative t.l.c. and i.r.), plus an unidentified blue substance (0.18 g) containing some triphenylphosphine oxide. Elution with pyridine gave a dark brown residue (0.11 g) with an ill-defined i.r.spectrum. An intractable black mass remained on top of the chromatography column.

Interaction of 2-amino-7-hydroxy-3H-phenoxazine-3-one with triphenylphosphine and triphenylphosphine oxide in pyridine.

2-Amino-7-hydroxy-3H-phenoxazine-3-one (0.10 g) was heated under reflux in pyridine (20 cm^3) with triphenylphosphine (0.55 g) for twelve hours. No reaction was detected

by t.l.c.. The reaction mixture was evaporated to dryness and then stirred with toluene. The solution was filtered and the solid remaining in the pre-weighed Hirsch funnel was thoroughly washed with toluene. The filtrate was collected and evaporated to dryness and dried at 0.1 mm/30 °C to give unreacted triphenylphosphine (0.51 g, 93% recovery)(identified by comparative t.l.c. and i.r.). The solid remaining in the Hirsch funnel was washed with light petrol (30-40 fraction) and dried at 0.1 mm/30 °C giving 2-amino-7-hydroxy-3H-phenoxazine-3-one (0.08 g, 80% recovery)(identified by comparative t.l.c. and i.r.).

When the reaction was repeated using triphenylphosphine oxide and 2-amino-7-hydroxy-3H-phenoxazine-3-one the reactants were recovered in 87% and 91% yield respectively.

The action of heat on 5-hydroxy-2-nitrosophenol in pyridine solution.

5-Hydroxy-2-nitrosophenol (6.4 g) was heated under reflux in pyridine for twelve hours. Upon cooling,silica (4.2 g) was added with stirring. The mixture was evaporated to dryness and a portion (9.1 g) placed on a silica chromatography column. Toluene eluted 5-hydroxy-2-nitrosophenol (1.5 g, 27% recovery)(identified by comparative t.l.c. and i.r.). Diethyl ether eluted 2-amino-7-hydroxy-3H-phenoxazine-3-one (2.9 g, 64%)(identified by comparative t.l.c. and i.r.).

The interaction of 5-hydroxy-6-methyl-2-nitrosophenol with triphenylphosphine in pyridine.

5-Hydroxy-6-methyl-2-nitrosophenol (2.0 g, 1 mol. equiv.) and triphenylphosphine (16.7 g, 5 mol. equiv.) were heated under reflux in pyridine (150 cm^3) for twenty four hours. The reaction mixture was cooled and then evaporated to dryness. A portion (15.2 g) was extracted (Soxhlet) with light petrol (80-100 fraction). The extract was evaporated to dryness to give triphenylphosphine (10.5 g)(identified by comparative t.l.c. and i.r.). A portion of the Soxhlet residue (4.4 g) was redissolved in pyridine and silica (3.8 g) added with stirring. This mixture was evaporated to dryness and a portion of the impregnated silica (5.4 g) placed on top of a silica column. Light petrol (60-80 fraction) eluted more triphenylphosphine (0.11 g)(identified by comparative t.l.c. and i.r.). Toluene/chloroform (1:1) eluted triphenylphosphine oxide (2.5 g)(identified by comparative t.l.c. and i.r.). Chloroform/ethyl acetate (2:1) eluted 2-amino-7-hydroxy-4,6-dimethyl-3H-phenoxazine-3-one (0.15 g, 12.1%), (Found: C, 64.7; H, 9.0; N, 10.0% ; $C_{14}H_{12}N_2O_3$ requires : C,65.5; H, 9.7; N, 10.9%) m.p. above 300 ^oC, $\nu_{max.}$(KBr) C=O 1725 cm^{-1}; $\lambda_{max.}(CH_3OH)$, 194 nm.(ε=85.6 m^2mol^{-1}), 221 nm. (ε=1720 m^2mol^{-1}), 454 nm. (ε=71.0 m^2mol^{-1}). Ethyl acetate eluted 2-amino-4,6-dimethyl-8-(triphenylphosphoranylidene)-3H,7H-phenoxazine-3,7-dione (0.22 g, 9%). (Found: C, 73.5; H, 4.1; N, 4.9%, $C_{32}H_{25}N_2O_3P$ requires: C,74.4; H, 4.8; N, 5.4%) m.p. above 300 ^oC; $\lambda_{max.}(CH_3OH)$, 220 nm. (ε=1940 m^2mol^{-1}), 264 nm.(ε=1709 m^2mol^{-1}), 501 nm.(ε= 1289

$m^2 mol^{-1}$). Methanol eluted a dark blue substance (0.35 g), with an ill-defined i.r.spectrum containing at least four unidentified substances.

5.5 References

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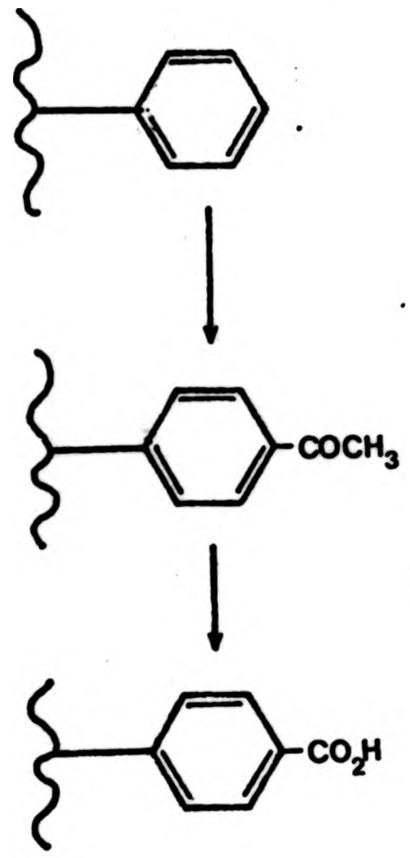
APPENDIX

The preparation of a polymer bound benzoic acid resin.

The polymer bound benzoic acid resin was prepared as described by Letsinger et. al.[1] and outlined in Scheme 1. The insoluble polymer support was a macroporous



(Found C,89.8; H,8.9%)

(Found C,83.8; H,7.8%)

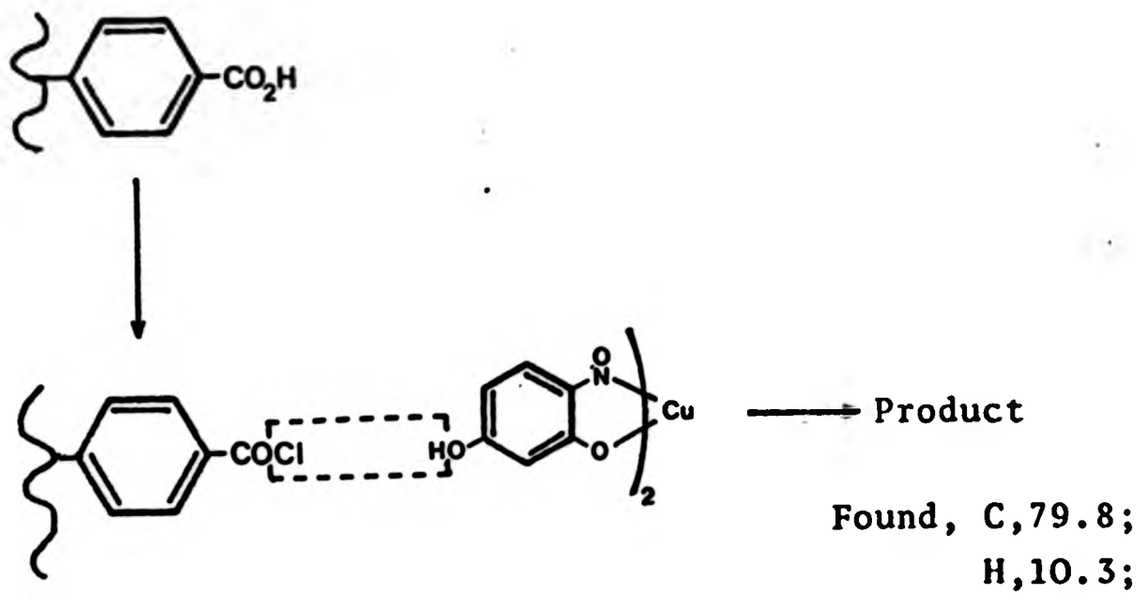
(Found C,66.2; H,5.5%)

Scheme 1

polystyrene cross-linked with 2% divinylbenzene. The degree of carboxylate functionalisation was determined to be between 1.0×10^{-3} and 1.4×10^{-3} equivalents of acid per gram by titration with a standard solution of sodium hydroxide.

1. R.L.Letsinger, *J. Amer. Chem. Soc.*, 1964, *86*, 5163.

The polymer bound benzoic acid resin was converted to the corresponding acid chloride resin by treatment with oxalyl chloride in pyridine immediately prior to esterification with the free hydroxyl group of the copper complex (Scheme 2)



Found, C,79.8;
H,10.3;
N,1.0%)

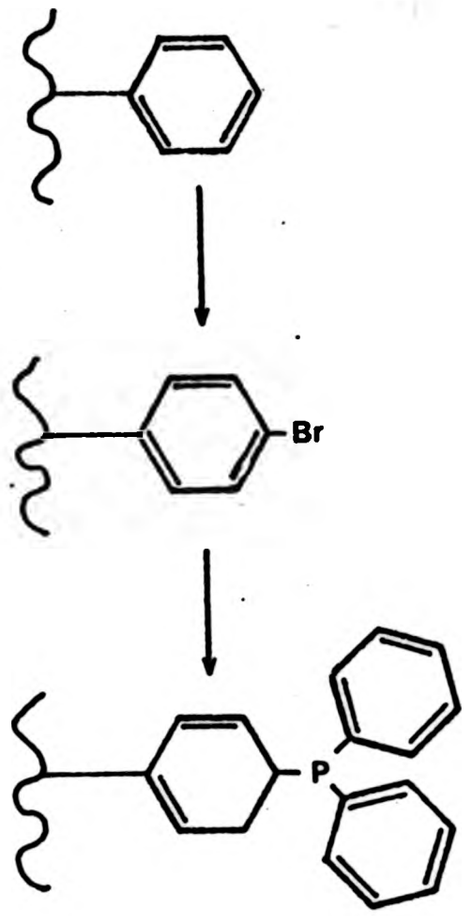
Scheme 2.

<u>The preparation of a polymer supported triphenylphosphine resin</u>

The preparation of this resin is outlined in Scheme 3 and involved a two step reaction.

<u>i) The bromination of macroporous polystyrene resin cross-linked with 2% divinylbenzene.</u>

A suspension of 2% cross-linked polystyrene (40 g) in nitromethane (250 cm^3) containing boron trifluoride



(Found C,42.2;
H,3.4:
P,12.9%)

Scheme 3

(25 g) was stirred at 25 °C in the dark. Bromine (120 g) was added dropwise while the temperature was maintained at 25 °C (external cooling required). The suspension was stirred overnight and the beads (63 g) filtered, washed with dichloromethane (5x200 cm^3) and methanol (5x200 cm^3) and dried at 30 °C/0.1 mm.

ii) <u>The reaction of chlorodiphenylphosphine with the brominated polystyrene resin</u>

The brominated polystyrene resin (18 g) was stirred in tetrahydrofuran (450 cm^3) under nitrogen for one hour. A solution of chlorodiphenylphosphine (40 g) in tetrahydrofuran (150 cm^3) was added followed by lithium wire (3.2 g)

The system was stirred overnight. Excess lithium was removed under nitrogen and the mixture refluxed for five hours. The light tan beads (21.2 g) were filtered at the pump, washed with dichloromethane (5x200 cm^3) and methanol (5x200 cm^3) and dried at 30 ^oC30.1 mm.

The preparation of a polymer supported pyridine resin.

Styrene (15 g), divinylbenzene (5 g), benzoyl peroxide (0.5 g) and a 0.5% aqueous solution of polyvinyl alcohol (30 cm^3) were heated at 50 ^oC for three hours with continuous stirring. The temperature was then raised to 70 ^oC for three hours. The beads were poured into a beaker and hydrochloric acid (0.1 mol dm^{-3}) (200 cm^3) was added. This suspension was filtered at the pump, washed with water(5x 200 cm^3) and dried at 60 ^oC/0.1 mm.

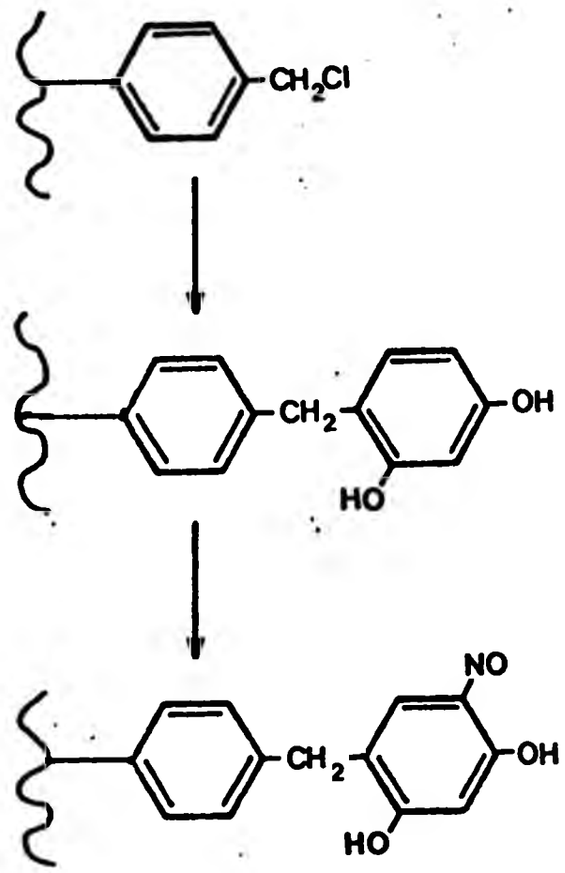
(As this is a suspension polymerisation the mesh size of the final product is dependent on the initial rate of stirring, e.g. the greater the rate of stirring, the smaller the bead size).

The preparation of a polymer supported nitrosoresorcinol resin

The preparation of the resin is outlined in Scheme 4. The reaction involves two steps.

i) The reaction of resorcinol with a chloromethylated styrene/divinylbenzene copolymer

The chloromethylated resin (50 g) was stirred



Scheme 4

in dioxan (200 cm^3) at room temperature. Resorcinol (45 g) and freshly fused zinc chloride (25 g) were added and the mixture heated at 100 ^oC for twelve hours. The product (55 g) was filtered at the pump, washed with methanol, 10% hydrochloric acid, water and methanol and dried at 30 ^oC/0.1 mm.

ii) <u>The reaction of the above product with nitrous acid</u>.

The resin (55 g) was added to a solution of sodium nitrite (22 g) in sodium hydroxide (1 mol dm^{-3}) (500 cm^3) with stirring. The mixture was cooled to 0 ^oC and sulphuric acid (5 mol dm^{-3}) (33 cm^3) added dropwise. The solution was stirred for a further two hours and the product (61 g) filtered at the pump, washed with water and methanol and dried at 30 ^oC/0.1 mm.

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Complexes of Nickel(II) with Mononitroso- and Dinitroso-resorcinols

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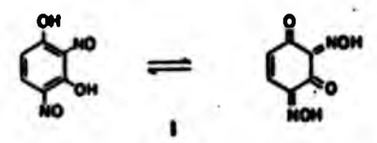
Polymeric complexes of the type Ni(X-dnr)·2L have been prepared, where X-dnrH$_2$ is 2,4-dinitroso-resorcinol, 6-ethyl-2,4-dinitrosoresorcinol, and 5-methyl-2,4-dinitrosoresorcinol and L is water or pyridine. The hydrated complexes have been obtained by nitrosation of resorcinol, 4-ethyl-resorcinol, and 5-methylresorcinol in the presence of nickel(II) chloride. Nitrosation of 2-methylresorcinol gives Ni(2-Memnr)·4H$_2$O (2-MemnrH = 2-methyl-4-nitrosoresorcinol). In the complexes Ni(X-dnr)·2H$_2$O magnetic susceptibility studies indicate antiferromagnetic interaction through the bridging X-dnr^{2-} ligand.

Introduction

2,4-Dinitrosoresorcinol (I) (dnrH$_2$) exhibits tautomerism and forms complexes with several metals [1–3]. With a divalent metal it could react to form a coordination polymer, containing the catenating dianion dnr^{2-}, which can be represented in valence-bond terms as a resonance hybrid of structures (IIa) and (IIb).



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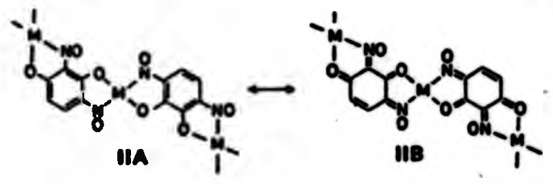

IIA IIB

2,4-Dinitrosoresorcinol could also react with a divalent metal by loss of one hydrogen to give complexes such as M(dnrH)$_2$, containing the monoanion dnrH$^-$. Complexes of 2,4-dinitrosoresorcinol with cobalt, iron, nickel and copper have been reported. Although some of these compounds have found use as dyes and analytical reagents they have not been fully characterised.

In this paper we describe the preparation, characterisation and report on magnetic studies of nickel(II) complexes derived from 2,4-dinitrosoresorcinol, 5-methyl-2,4-dinitrosoresorcinol (5-MednrH$_2$), 6-ethyl-2,4-dinitrosoresorcinol (6-EtdnrH$_2$) and 2-methyl-4-mononitrosoresorcinol (2-MemnrH). The

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TABLE I. Analytical and Magnetic Data for Ni(II) Complexes of Nitrosoresorcinols.

Phenol	Product		Yield (%)	Found (%)				Requires (%)				μ_{eff}, B.M. (ca. 295 K)
	Formula	No.		C	H	N	Ni	C	H	N	Ni	
Resorcinol	Ni(dnr)·2H$_2$O	1	85	27.9	1.7	10.8	21.4	27.6	1.6	10.7	22.4	2.88
4-Ethylresorcinol	Ni(6-Etdnr)·2H$_2$O	2	95	32.9	3.2	9.4	20.7	33.3	3.5	9.7	20.3	2.94
5-Methylresorcinol	Ni(5-Mednr)·2H$_2$O	3	95	30.2	2.4	10.9	22.8	30.6	2.9	10.2	21.3	2.90
2-Methylresorcinol	Ni(4-Memnr·H)$_2$·4H$_2$O	4	48	38.0	2.5	6.4	13.2	38.7	4.6	6.4	13.5	–
	Ni(6-Etdnr)·2py	5	77	52.6	4.0	13.8	14.2	52.7	3.9	13.6	14.3	2.95

TABLE II. Analytical and Other Data for Nitrosoresorcinols.

Compound	Yield (%)	Found (%)			Requires (%)			M.p. (t/°C)	^{1}H N.m.r. Spectra						Mass Spectrum P$^+$ (m/e)
		C	H	N	C	H	N								
2,4-Dinitrosoresorcinol monohydrate	68	38.4	3.3	15.1	38.7	3.2	15.1	166–7[b]	dec.	2.07	2.22	3.46	3.61		168
3-Ethyl-2,4-dinitrosoresorcinol monohydrate	81	44.4	4.4	12.7	44.7	4.6	13.0	150–2	dec.	2.33	8.79	8.90	9.0	7.40–7.75	196
5-Methyl-2,4-dinitrosoresorcinol monohydrate	75	41.8	3.6	13.9	42.0	4.0	14.0	130	dec.	3.60	7.88				182
2-Methyl-4-nitrosoresorcinol	60	54.9	5.8	9.3	54.9	4.6	9.1	146–8	dec.	2.4	2.58	3.57		7.41–7.56 8.21	153

[a] $(CH_3)_2SO$ solvent. [b] Lit., m.p. 168 °C dec. (Ref. 1).

investigation relates to our continuing studies of complexes derived from 2-nitrosophenols [4, 5].

Experimental

Preparation of the Complexes Ni(X-dmr)·2H$_2$O (X = H, 6-Et, and 5-Me) and Ni(2-Memr)$_2$·4H$_2$O by Nitrosation of Resorcinols

The resorcinol (*ca.* 6 g, 1 mol equiv) in ethanol (100 cm^3) was added to a solution of nickel(II) chloride (1 mol equiv) acetic acid (20 cm^3) and sodium acetate (20 g) in water (120 cm^3). Sodium nitrite (10 g) in water (60 cm^3) was then added in one portion with stirring. The mixture was stirred for one week and then *the product* was filtered off, washed thoroughly by stirring with water (3 × 100 cm^3) and ethanol (3 × 100 cm^3) for several hours and dried at 50 °C/0.1 mm (see Table I for analysis and other data).

Interaction of the Complex Ni(6-Etdmr)·2H$_2$O with Pyridine

The hydrated complex (*ca.* 3 g) was heated in pyridine (100 cm^3) at 100 °C for 1 h. The reaction mixture was filtered hot, the filtrate was evaporated to dryness at 60 °C/0.1 mm, and the resultant residue of *the pyridine adduct* was washed with ethanol and ether and dried at 100 °C/0.1 mm (see Table I for analysis of other data).

Interaction of the Complexes Ni(X-dmr)·2H$_2$O and Ni(2-Memr)$_2$·4H$_2$O with Aqueous Hydrochloric Acid

Concentrated hydrochloric acid (10 cm^3) was added to a well stirred suspension of the complex (*ca.* 3 g) in water (50 cm^3) and the mixture was stirred for 1 h. *The protonated ligand* was filtered off, washed with dilute hydrochloric acid and then with water and dried at 20 °C/0.1 mm (see Table II for analysis and other data).

Measurements

Thermogravimetric analysis data (Table III), magnetic susceptibility data, and electronic and mass spectra were obtained as described earlier [4, 5].

^{1}H n.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer 12B spectrometer using deuterated dimethylsulphoxide as solvent and tetramethylsilane as internal standard.

Results and Discussion

Bottei and McEachern [1] reported that the reaction of nickel acetate with 2,4-dinitrosoresorcinol in aqueous ethanol gave a product which they formu-

TABLE III. Thermogravimetric Analysis Data.

Compound[a]	Wt. of Sample (mg)	T/°C[b]	Weight Loss (mg)		Decomposition Temperature (°C) of Ni(X-dnr)[d]
			Found	Calc[c]	
1	206	165	24	28	235
2	191	155	28	24	260
5	149	180	56	57	260

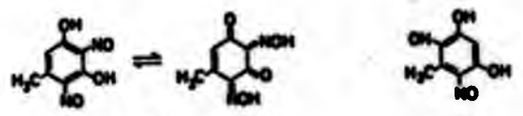
[a]Nos. from Table I. [b]Temperature of loss of water or pyridine. [b,d]Maxima on the rate of weight loss against temperature curve. [c]Calc. for 2 mol equiv of water or pyridine.

TABLE IV. Variable Temperature Magnetic Data for Ni(5-Medmr)·$2H_2O$ and Ni(6-Etdmr)·$2H_2O$.

Ni(5-Medmr)·$2H_2O$										
T/K	314.2	297.7	273.1	246.2	216.7	187.2	155.3	128.2	98.8	83.2
10^6 χ_A	3381	3536	3624	3942	4335	4780	5327	6033	7116	7827
μ_{eff}	2.92	2.90	2.82	2.79	274	2.68	2.57	2.49	2.37	2.28
$-\theta$/K	92									
Ni(6-Etdmr)·$2H_2O$										
T/K	297.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8	91.2	
10^6 χ_A	3655	3906	4236	4623	5164	5713	6474	7555	7193	
μ_{eff}	2.94	2.92	2.89	2.83	2.78	2.67	2.58	2.45	2.39	
$-\theta$/K	86									

lated as the polymeric complex Ni(dnr)·H_2O. In contrast, Hunter and Webb [2] reported that interaction of a nickel salt with 2,3-dinitrosoresorcinol in methanol followed by precipitation with diethyl ether, gave a complex which they formulated as Ni-(dnrH)$_2$·$4H_2O$. We have obtained a polymeric complex of formula Ni(dnr)·$2H_2O$ by nitrosation of resorcinol in the presence of nickel chloride. The analogous complexes Ni(5-Medmr)·$2H_2O$ and Ni(6-Etdmr)·$2H_2O$ have been obtained similarly by nitrosation of 5-methylresorcinol and 4-ethyl-resorcinol respectively. In contrast, nitrosation of 2-methyl-resorcinol in the presence of nickel chloride led to mononitrosation and formation of the complex Ni(2-Memnr)$_2$·$4H_2O$. Attempts to dinitrosate 2-methylresorcinol using acetic acid and sodium nitrite in aqueous media were unsuccessful. Nitrosation using amyl nitrite in ethanolic sodium hydroxide also gave the mononitroso derivative.

The formulation of the complexes was established by elemental analysis and i.r. spectroscopy. In each case the position of nitrosation was determined by acidifying the complex and characterizing the liberated protonated ligand (some properties of the protonated ligands are given in Table II). Thus the complex obtained by nitrosation of 2-methyl-resorcinol on treatment with aqueous hydrochloric acid gave 2-methyl-4-nitrosoresorcinol as indicated by elemental analysis, mass spectrometry, and by the proton n.m.r. spectrum which showed a quartet due to two non-equivalent ring protons in positions 5 and 6. The complex obtained from 4-ethylresorcinol on treatment with aqueous hydrochloric acid gave 6-ethyl-2,4-dinitrosoresorcinol monohydrate which was formulated on the basis of elemental analysis and of the mass spectrum which indicated a molecular weight of 196 for the anhydrous compound. The alternative formulation of the hydrated ligand as 6-ethyl-2,5-dinitrosoresorcinol is precluded because a requirement for the formation of a coordination polymer by chelation is that the nitroso and hydroxy groups are in ortho positions. In the case of the complex derived from 5-methylresorcinol analytical, n.m.r. and mass spectral data indicate that the protonated ligand is either 5-methyl-2,4-dinitrosoresorcinol (III) or 5-methyl-4,6-dinitrosoresorcinol (IV).



III IV

The complexes Ni(X-dnr)·$2H_2O$ (X = H, 6-Et, and 5-Me) were insoluble in common organic solvents but

dissolved in hot pyridine to give pyridine adducts as indicated by the isolation and characterisation of such an adduct when X = 6-Et. Thermogravimetric analysis (Table III) on all the hydrates and the pyridine adduct Ni(6-Etdnr)·2py showed that water or pyridine was lost between 150–180 °C to give Ni(X-dnr) which decomposed between 235–260 °C.

Magnetic susceptibilities for the complexes Ni(X-dnr)·$2H_2O$ and Ni(6-Etdnr)·2py were measured and the calculated magnetic moments are given in Table I. The room temperature moments are close to the low limit of the range (3.0–3.4 B.M.) expected for magnetically dilute nickel(II) in an approximately octahedral field. However, the decreasing magnetic moment with temperature (Table IV) and the negative Weiss constants (*ca.* −90 K) observed for two of the complexes subjected to measurements at variable temperature support antiferromagnetic interaction through the bridging X-dnr^{2-} ligand.

Acknowledgements

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Mass Spectrometric Studies of 2-Nitrosophenols

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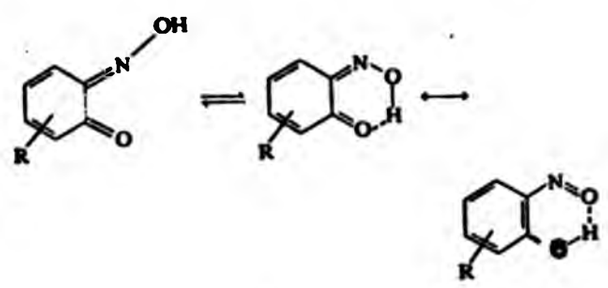
The mass spectra of 2-nitrosophenols are independent of the insertion temperature, suggesting that the compounds either do not exhibit tautomerism in the vapour phase or that the enthalpy of isomerization is low. However, their fragmentation patterns suggest tautomerism in the molecular ion.

INTRODUCTION

2-Nitrosophenols exist in two forms in the solid state which are essentially quinoneoximic in character as indicated by several X-ray crystallographic studies.[1,2] It has been suggested on the basis of infrared, nuclear magnetic resonance and ultraviolet spectroscopic studies, that 2-nitrosophenols in solution exhibit solvent dependent equilibria (Scheme 1) involving quinoneoximic and nitrosophenolic type species.[3]



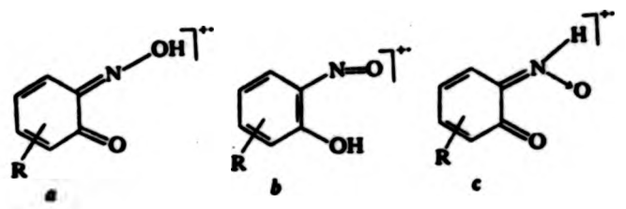
Scheme 1

Previously we reported on the mass spectra of metal complexes of 2-nitrosophenols,[4] and recently some aspects of the chemical ionization mass spectra of several 2-nitrosophenols have been discussed.[5] In this paper we report on the results of mass spectrometric studies which have been carried out in order to examine the structure of several 2-nitrosophenols in the vapour state.

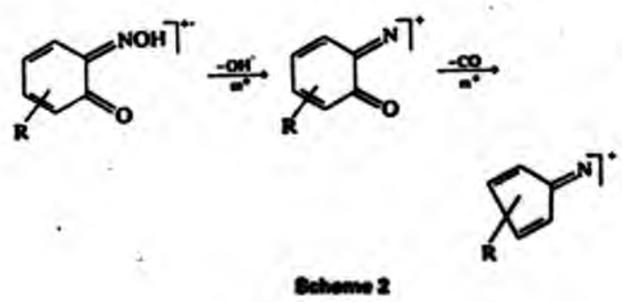
The compounds chosen were α-5-methoxy-2-nitrosophenol, β-5-methoxy-2-nitrosophenol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol and 4-dimethylamino-2-nitrosophenol.

RESULTS AND DISCUSSION

The mass spectra of both the α- and β- forms of 5-methoxy-2-nitrosophenol were recorded at various temperatures in the range 125–200 °C; in all cases the spectra obtained were very similar. One possible explanation is that in the vapour state these isomers have the same structure and do not exhibit a tautomeric equilibrium. However, an alternative explanation is that the enthalpy change for the isomerization is very low and hence the change of equilibrium constant over the temperature range examined is undetectable. The spectra of 1-nitroso-2-naphthol, 2-nitroso-1-naphthol and 4-dimethylamino-2-nitrosophenol were recorded at 150, 175 and 200 °C. For each compound the spectra obtained were found to be independent of temperature, indicating again the absence of tautomeric equilibria between unionized molecules or a low enthalpy change for the isomerization in the vapour state.



For each compound the molecular ion fragments mainly by consecutive losses of $OH^{\cdot}$ and CO. Both these reactions are metastable supported and can be accounted for in terms of a quinoneoximic molecular ion (Scheme 2). This suggestion is in accord with the readiness of the molecular ions of various types of oximes to fragment by loss of $OH^{\cdot}$.[6]



Scheme 2

The spectra of all the compounds exhibit ions corresponding to a loss of O or CO_2 from the molecular ion (Scheme 3). For the reactions involving the loss of O there are no corresponding metastable peaks, but mass analysed ion kinetic energy (MIKE) spectrometry gives evidence for such primary fragmentations in some cases. The loss of CO_2 from the molecular ion is metastable supported in the case of 1-

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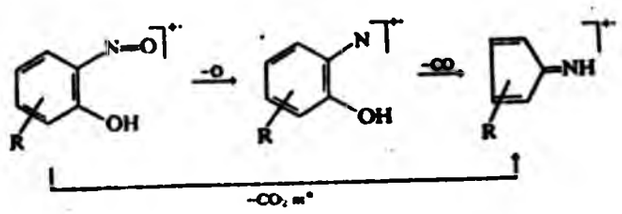
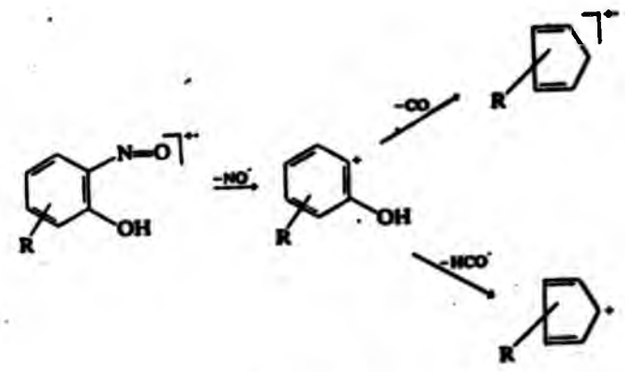


Scheme 3

nitroso-2-naphthol and 2-nitroso-1-naphthol. These reactions can be rationalized in terms of the nitrosophenolic structure *b*. The nitrosophenolic structure also provides a convenient rationalization for the loss of NO˙ from the molecular ion (Scheme 4).

Ions corresponding to $[M-NO]^+$ are present in the spectra of all compounds examined except that of 5-methoxy-2-nitrosophenol. However, all compounds show ions corresponding to $[M-58]^{+\cdot}$ and $[M-59]^+$, i.e. to loss of NO˙ and CO or NO˙ and HCO˙ respectively. The spectra of 5-methoxy-2-nitrosophenol and 4-dimethylamino-2-nitrosophenol also show ions corresponding to the loss of NO˙ and CH_3˙ from the molecular ion. In the case of 4-dimethylamino-2-nitrosophenol the ion $[M-58]^+$ arises through the initial loss of NO˙ followed by loss of CO as indicated by the presence of appropriate metastable peaks. The ions involved in this reaction sequence are fairly intense suggesting that for this compound the contribution of the nitrosophenolic structure *b* is relatively important. An alternative route to the ion $[M-58]^+$ involves initial loss of CO followed by loss of NO˙. Significantly, loss of CO is observed in all compounds and is metastable supported in the case of both the

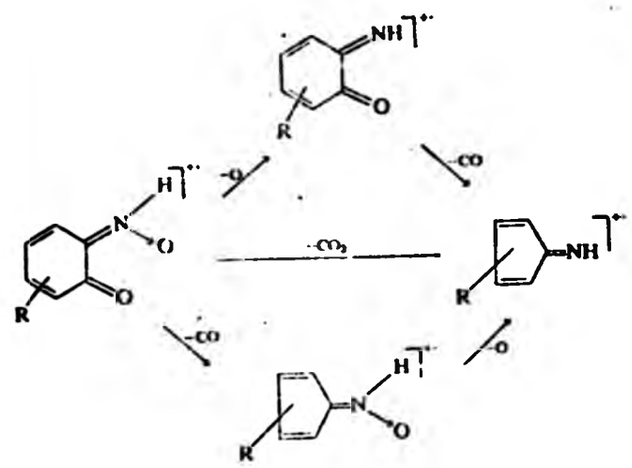


Scheme 4

Table 1. Mass spectra of 2-nitrosophenols

	5-Methoxy-2-nitrosophenol		1-Nitroso-2-naphthol		2-Nitroso-1-naphthol		4-Dimethylamino-2-nitrosophenol	
Ion assignment[a]	m/z[b]	%	m/z[c]	%	m/z[d]	%	m/z[e]	%
$[M]^{+\cdot}$	153	81	173	63	173	81	166	100
$[M-H]^+$	152	4	172	5	—	—	—	—
$[M-O]^{+\cdot}$	137	11	157	12	157	44	150	13
$[M-OH]^+$	136	100	156	48	156	100	149	82
$[M-H_2O]^{+\cdot}$	135	2	155	3	155	4	—	—
$[M-HCN]^{+\cdot}$	—	—	—	—	146	2	—	—
$[M-CO]^{+\cdot}$	125	4	145	16	145	2	—	—
$[M-HCO]^+$	124	5	—	—	—	—	137	3
$[M-NO]^+$	—	—	143	11	143	16	136	29
$[M-HNO]^{+\cdot}$	—	—	—	—	142	2	135	10
$[M-H_2NO]^+$	—	—	—	—	—	—	134	9
$[M-(CO+CH_3)]^+$	110	9	—	—	—	—	—	—
$[M-HCNO]^{+\cdot}$	—	—	130	2	130	58	—	—
$[M-CO_2]^{+\cdot}$	109	10	129	100	129	18	122	17
$[M-(HO+HCN)]^+$	—	—	—	—	—	—	122	6
$[M-HCO_2]^+$	108	18	128	70	128	59	121	9
$[M-(NO+CH_3)]^+$	108	18	—	—	—	—	121	10
$[M-(CO+H_2O)]^{+\cdot}$	107	5	127	21	127	11	—	—
$[M-(CH_2O+O)]^+$	106	12	—	—	—	—	—	—
$[M-2CO]^{+\cdot}$	—	—	117	16	—	—	—	—
$[M-(CO+NO)]^+$	—	—	115	58	115	75	108	37
$[M-(HCO+NO)]^{+\cdot}$	—	—	114	14	114	20	107	13
$[M-(H_2CO+HCO)]^+$	—	—	—	—	—	—	107	9
$[M-(H_2CO+NO)]^+$	—	—	113	10	113	11	106	7

[a] Ion assignment indicated by exact mass measurement.
[b] Also contains peaks at (% abundance in parentheses): 96 (5), 95 (16), 94 (8), 93 (15), 92 (5), 82 (4), 80 (14), 79 (12), 78 (2), 77 (4), 68 (4), 67 (7), 66 (6), 65 (13), 64 (7), 63 (8), 62 (4), 59 (2), 55 (3), 53 (4), 52 (12), 51 (8).
[c] Also contains peaks at (% abundance in parentheses): 103 (16), 102 (36), 101 (25), 100 (4), 90 (4), 89 (17), 88 (7), 87 (6), 85 (5), 78 (3), 77 (12), 76 (12), 75 (23), 74 (15), 73 (3), 65 (4), 63 (17), 62 (11), 61 (5), 52 (4), 51 (20).
[d] Also contains peaks at (% abundance in parentheses): 120 (6), 105 (4), 103 (16), 102 (58), 101 (30), 100 (3), 99 (2), 98 (3), 90 (3), 89 (19), 88 (10), 87 (9), 86 (6), 85 (9), 83 (13), 78 (4), 77 (18), 76 (21), 75 (28), 74 (21), 73 (4), 65 (9), 64.5 (4), 64 (9), 63 (24), 62 (13), 61 (7), 52 (6), 51 (27), 50 (32).
[e] Also contains peaks at (% abundance in parentheses): 106 (14), 94 (16), 93 (21), 92 (28), 82 (8), 80 (11), 79 (13), 78 (18), 77 (10), 76 (7), 72 (7), 69 (5), 68 (10), 67 (13), 66 (13), 65 (25), 64 (7), 63 (14), 62 (8), 61 (3), 55 (8), 54 (7), 53 (10), 52 (10), 51 (22).



Scheme 5

nitrosonaphthols. The initial loss of CO can be rationalized in terms of either structure *a* or structure *b*. The loss of CO, as well as the losses of O and CO_2 from the molecular ion can also be accounted for in terms of the nitrone structure *c* (Scheme 5).

EXPERIMENTAL

The nitrosophenols, with the exception of 4-dimethylamino-2-nitrosophenol, were obtained commercially. 4-dimethylamino-2-nitrosophenol was prepared by a previously reported method.[7] All compounds were purified chromatographically using silica gel coated plates and benzene as solvent. The α- and β-forms of 5-methoxy-2-nitrosophenol were obtained by recrystallization of the chromatographically purified commercial sample from benzene (green) and ethanol (yellow) respectively.

The mass spectra were obtained at 70 eV on AEI MS 9 and MS 50 instruments using the direct insertion probe. MIKE spectra were obtained using a VG Micromass ZAB reverse geometry mass spectrometer.

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