Studies of quinone monooximes derived from dihydroxynaphthalenes

A thesis submitted to London Metropolitan University in partial fulfillment of the requirements for the Degree of Master of Philosophy

By

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September 2007

Dedication

To my parents and my wife

Declaration

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

Mahmoud Mohamed Khozam

Abstract

This thesis is concerned with the nitrosation behaviour of 1,5-, 1,6- and 2,7-dihydroxynaphthalenes towards equimolar and excess sodium nitrite/acid. The direct and indirect methods of nitrosations have been used to prepare mono- and di-nitrosated products. Under all experimental conditions examined, only the mono-nitrosation products were isolated. No di-nitrosation products were observed even in the reaction involving excess sodium nitrite/acid. The direct nitrosation of 1,6-dihydroxynaphthalene afforded 6-hydroxy-1,2-naphthoquinone 2-oxime as the main product together with some 6-hydroxy-1,4-naphthoquinone 4-oxime as the 4-nitrosated compound, which were separated by using the chelating technique. For the 1,5- and 2,7-dihydroxynaphthalenes only one product resulted, 5-hydroxy-1,2-naphthoquinone 2-oxime and 7-hydroxy-1,2-naphthoquinone 1-oxime, respectively. In both cases no nitrosation at the 4-position occurred. The tendency of the dihydroxynaphthalenes investigated in this work to undergo only mono-nitrosation might reflect the deactivation of the naphthalene rings by the introduction of the CO and NO groups. In order to check this hypothesis compounds 5-hydroxy-, 6-hydroxy-1,2-naphthoquinone 2-oximes and 7-hydroxy-1,2-naphthoquinone 1-oxime were treated with excess sodium nitrite/acid, but in all cases no reaction was observed. All the new organic compounds of 1,2- and 1,4-oximes obtained from these studies were characterised by elemental analysis, IR and NMR spectroscopy, mass spectrometry and X-ray crystallography. The quinone oximic character of all 1,2-oximes was also supported by their acetylation behavior. The indirect nitrosation of the 1,6-dihydroxynaphthalene with sodium nitrite/acid in the presence of metal salts afforded the metal complexes of the 2-nitrosated compound as the main product together with some uncomplexed 4-nitrosated isomer. In contrast, nitrosation of 1,5- and 2,7-dihydroxynaphthalenes in the presence of metal salts gave only the metal complexes and no 4-nitrosated compounds were obtained.

During this study, a slightly modified procedure was used to prepare the uranium complexes. The method consists of reacting 6-hydroxy-1,2-naphthoquinone 2-oxime, 7-hydroxy-1,2-naphthoquinone 1-oxime or 6-hydroxy-1,4-naphthoquinone 4-oxime with uranyl nitrate hexahydrate in the presence of triethyl amine as base. The nickel, copper and uranium complexes were characterised by elemental analysis and IR spectroscopy. Nickel and copper were determined by atomic absorption spectrometry (AAS) while, uranium was determined by inductively coupled plasma mass spectrometry (ICP-MS).

Acknowledgement

I would like to thank my supervisor Professor John Charalambous for the valuable discussions throughout the work. I wish to express my deep appreciation and gratitude to Professor Brian Bointon - Head of Health and Human Science Department at London Metropolitan University and Dr. Trushar Adatia for their endless assistance and support to be able to submit my thesis. My sincere thanks to Dr. Khaddija O. Badahdah and Dr. Keith White for their continuous help and support and valuable discussions. I am very grateful to Prof. Abdullah Obaid, Prof. M. S. Makki, Prof. A. M. Asiri, Dr. K. Alfooty, Prof. Reda Abdel-Rahman, Prof. S. Basaif and Prof. Mamdouh Abdel-Moib of King Abdul-Aziz University, Chemistry department for their support and advice throughout the period of my studies. I am grateful to the analytical staff at the Chemistry department of London Metropolitan University and King Abdul-Aziz University for their help. My heartfelt appreciation and thanks to Dr. A. Bahajaj who spent precious time in reading the manuscript and valuable discussions. And lastly, I wish to express my sincere thanks to my parents, wife, brothers and sisters for their patience, support and encouragement.

Abbreviations

Am NO_2	Amyl nitrite
qoH	1,2-benzoquinone monooxime
1-qoH	1,2-benzoquinone 1-oxime
2-qoH	1,2-benzoquinone 2-oxime
5-RCONHqoH	5-acylamino-1,2-benzoquinone 2-oxime
5-PhNHqoH	5-phenylamino-1,2-benzoquinone 2-oxime
5-OH-2-nqoH	5-hydroxy-1,2-naphthoquinone 2-oxime
6-OH-2-nqoH	6-hydroxy-1,2-naphthoquinone 2-oxime
7-OH-1-nqoH	7-hydroxy-1,2-naphthoquinone 1-oxime
7-OH-2-nqoH	7-hydroxy-1,2-naphthoquinone 2-oxime
i.r.	Infra-red
n.m.r.	Nuclear magnetic resonance
m.p.	Melting point
t.l.c.	Thin layer chromatography
AAS	Atomic absorption spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
Ref.	Reference (s)
Cont.	Continue
h	Hour (s)
Fig.	Figure

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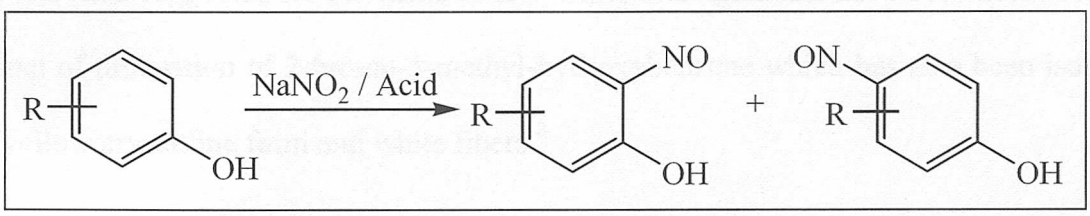
CHAPTER 1

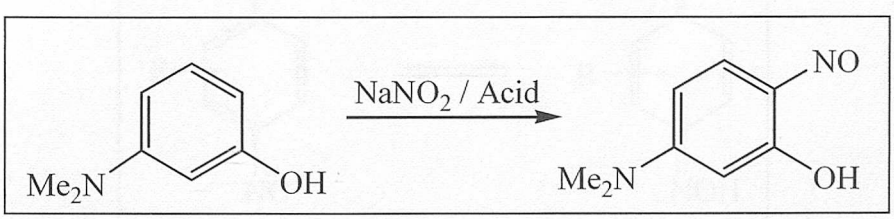
Introduction

1.1 Introduction

Nitrosation of aromatic compounds is difficult without the presence of strong activating groups attached to the aromatic ring, such as. hydroxy or amino. These groups are *ortho/para* directors. Nitrosation of hydroxybenzenes with sodium nitrite/acid can yield a mixture of 2-and 4-isomers (e.g. Reaction 1.1). In practice for most hydroxybenzenes the predominant product of this nitrosation is the 4-isomer and the 2-isomer is only formed in few cases, e.g. 3-(dimethylamino)hydroxybenzene (e.g. Reaction 1.2).[1-3] However, when the nitrosation is carried out in the presence of a transition metal salt the 2-nitrosated product is predominantly obtained in the form of its metal complex (e.g. Reaction 1.3).[4, 5]



Reaction 1.1



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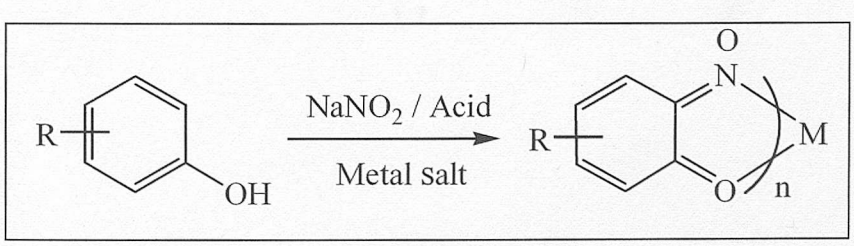
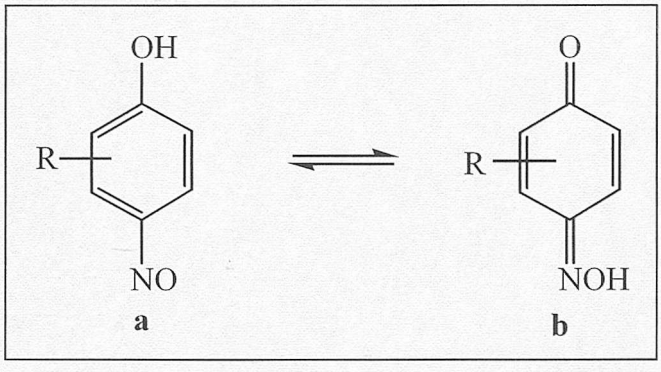
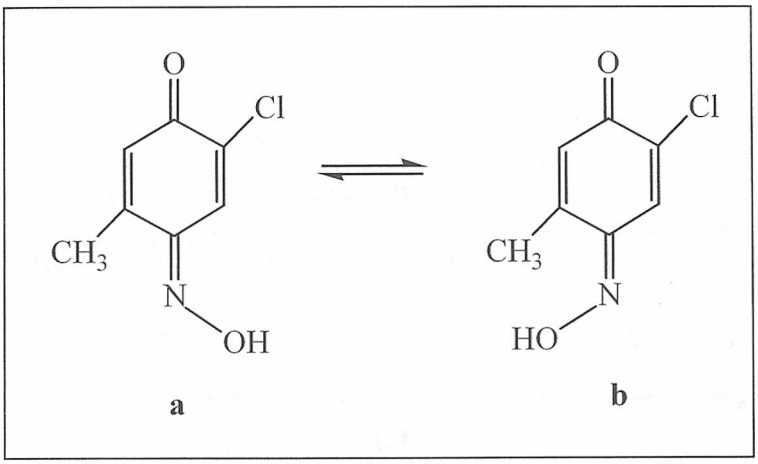


Reaction 1.3

The 4-isomer which obtained from reaction of hydroxybenzene and substituted hydroxybenzene with sodium nitrite/acid has been isolated in two forms.[6] One of these forms has been assigned a nitrosphenolic structure **1.1a**, and the other a quinone oximic structure **1.1b**. A tautomeric equilibrium between these forms was suggested to exist in the solution. Subsequent studies, however, have showed that both forms have quinone oximic structures in the solid state. Two forms were isolated, yellow crystals and white fibers, in the case of the 4-nitrosated product derived from the nitrosation of 2-chloro-5-methyl-hydroxybenzene.[7, 8] An X-ray crystallographic study of the yellow crystal revealed a quinone oximic with the OH of the NOH group *syn* to the chlorine **1.2a**.[7, 8] From chemical evidence and knowledge of the structure of the *syn* form, an *anti* quinone oximic structure **1.2b** has been suggested for the white fibers.[8] Similar assignments have been made for the product of nitrosation of 2-bromo-5-methyl-hydroxybenzene which has also been isolated in a yellow crystalline form and white fibers.[8]

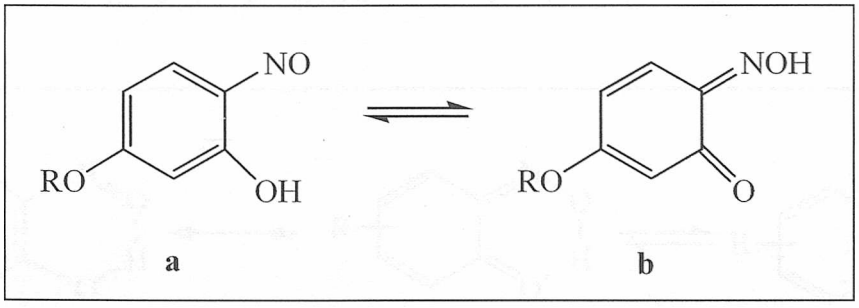


1.1

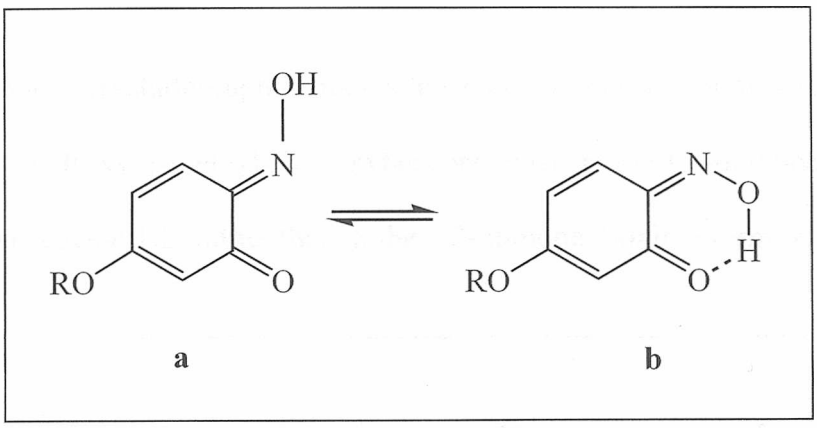


1.2

The 2-nitrosated products arising from the nitrosation of some hydroxybenzenes with sodium nitrite/acid have also been isolated in two forms. For instance, the product arising from the nitrosation of 3-methoxy-hydroxybenzene at the 2-position was obtained as green rectangular plates from benzene and as red needles from ethanol.[9] Initially the quinone oximic structure (**1.3b**, R = Me) has been assigned to the red α-form and the nitrosophenolic structure (**1.3a**, R = Me) to the green β-form. An X-ray crystallographic study of the α-form showed it have a quinone oximic structure with the OH of the NOH group *anti* to the CO group (**1.4a**, R = Me).[10]

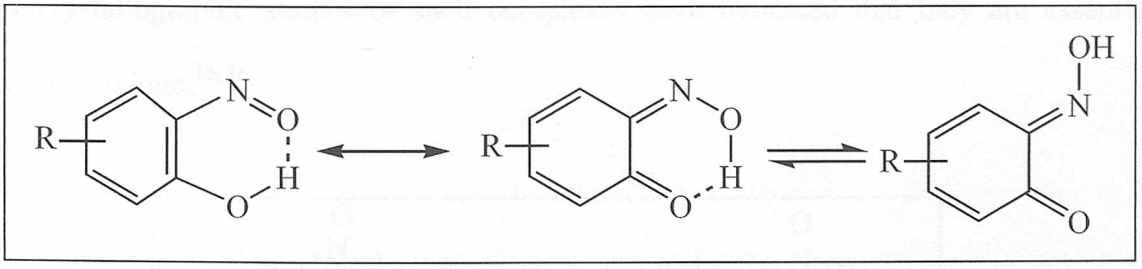


1.3



1.4

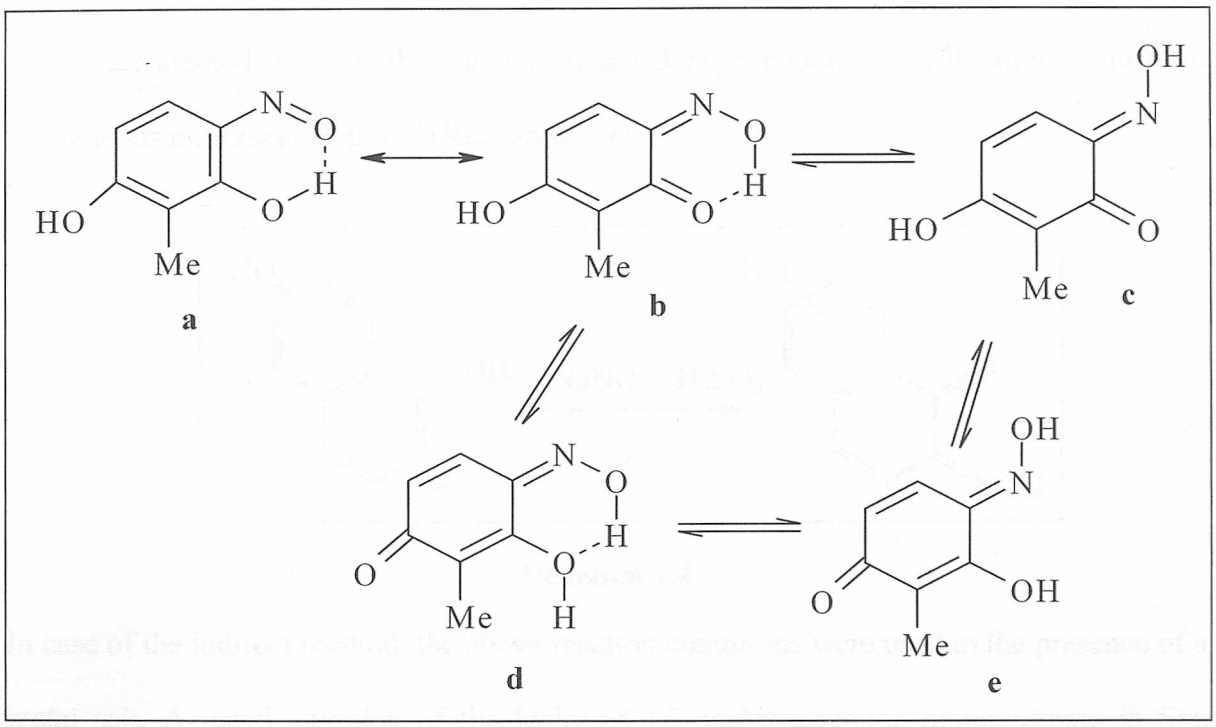
5-propoxy-2-nitrosophenol has also isolated into α- and β-forms, X-ray studies showed this compound has quinone oximic characteristics rather than nitrosophenolic.[11] This compound has the OH of the NOH group *syn* to the CO group (**1.4b**, R = Pr). On this basis and as in the case of the 4-nitrosated compounds, it is evident that these compounds have quinone oximic structures in the solid state. The existence of the oximic structure has also been demonstrated by the recent X-ray crystallographic studies of several other 2-nitrosophenols. In solution, IR, UV and NMR studies have indicated the presence of an equilibrium between quinone oximic and nitrosophenolic species for both 2- and 4-nitrosated compounds.[12, 13] In view of the above the 1,2-quinone monooxime/2-nitrosophenol system may be represented as shown in (Scheme 1.1).



Scheme 1.1

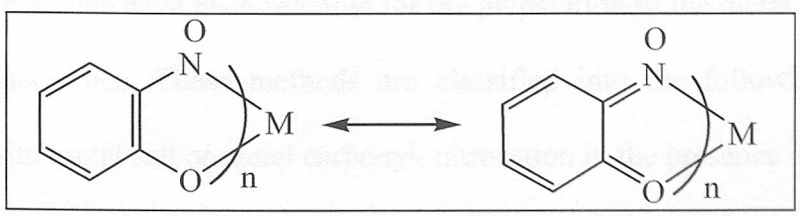
In the case of 5-hydroxy-2-benzoquinone 2-oximes additional contribution from the 1,4-quinone 4-oxime isomers is possible (Scheme 1.2).

Significantly, X-ray crystallographic studies have shown that the product arising from the nitrosation of 3-hydroxy-2-methyl-hydroxybenzene exists in the 1,4-quinone 4-oxime form structure (**e**) in (Scheme 1.2) rather than in the 1,2-quinone 2-oxime form (**c**).[14]



Scheme 1.2

The metal complexes, which are obtainable by replacing the acidic proton of a 1,2-quinone 2-oxime with a metal, can be described in valence bond terms as shown in **1.5**. Several X-ray crystallographic studies of such complexes have indicated that they are essentially quinone oximic.[15, 16]

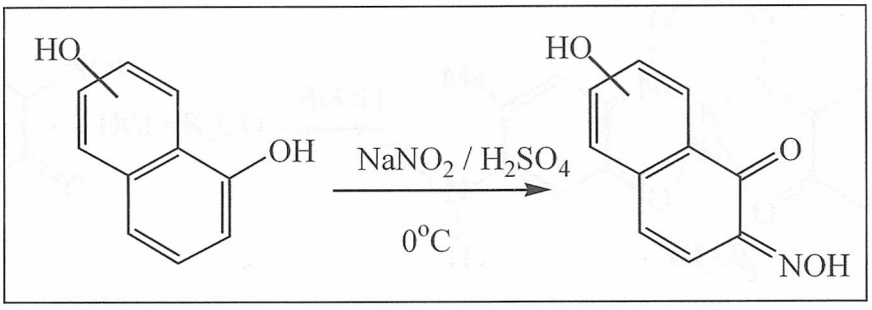


1.5

1.2 Preparation of 1,2-quinone monooximes

Varieties methods for the synthesis of 1,2-quinone monooximes have been reported but the most widely used are the so-called direct and indirect methods. In this study, these two methods have been used for preparation of hydroxyl-1,2-naphthoquinone monooximes.

The direct method involves the reaction of dihydroxynaphthalenes with sodium nitrite in the aqueous mineral acid at 0°C (Reactions 1.4).



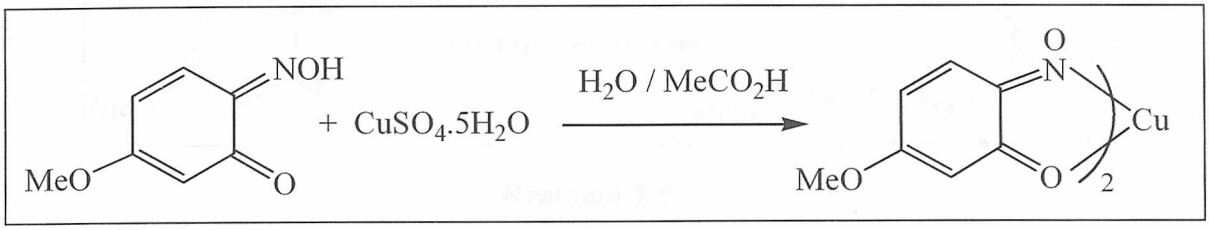
Reaction 1.4

In case of the indirect method, the above reaction conditions were used in the presence of a metal salt. A metal complex of the hydroxyl-1,2-naphthoquinone monooximato is first formed, from which the free oxime may be isolated. The isolation is achieved by acidification of the complex[17] or by passing a solution of the complex over an ion exchange resin.[18]

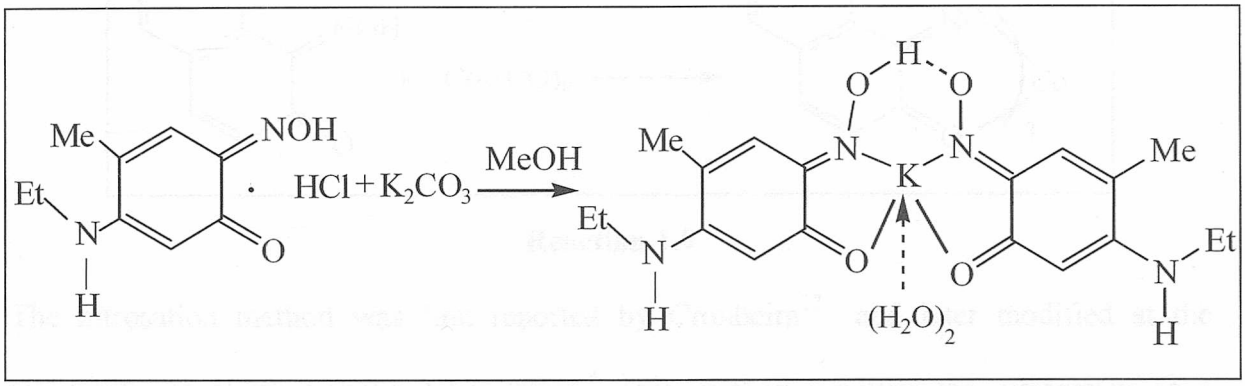
1.3 Preparation of complexes of 1,2-quinone monooximes

A variety of methods have been reported for the preparation of the metal complexes of 1,2-quinone monooximes. These methods are classified into the following groups: direct interaction with metal salt or metal carbonyl, nitrosation in the presence of transition metal, Baudisch reaction, nitro rearrangement, amyl nitrite and alkali metal cyanide reactions.

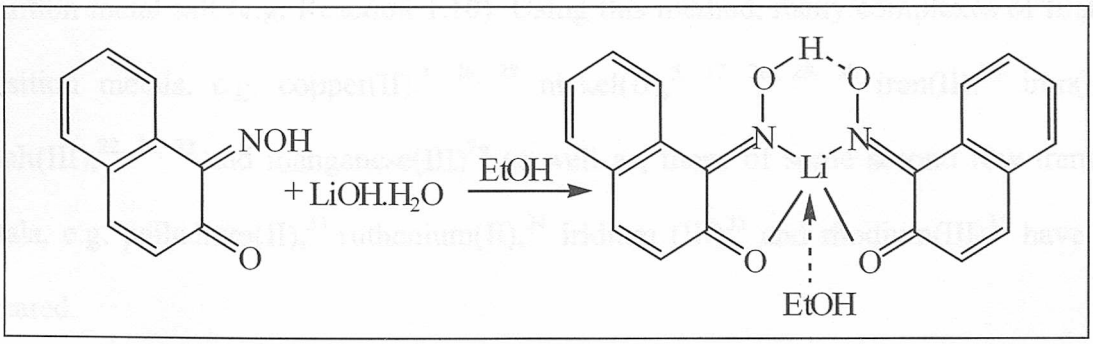
Interaction of a 1,2-quinone monooxime with a metal salt or hydroxide[4, 19-26] has been used for preparation of both main group and transition metal complexes (e.g. Reactions 1.5-1.7).



Reaction 1.5

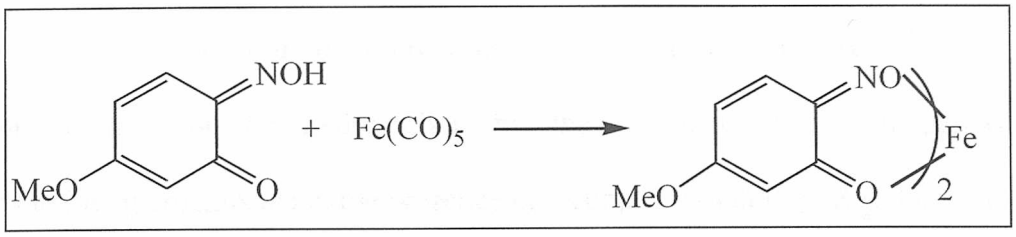


Reaction 1.6

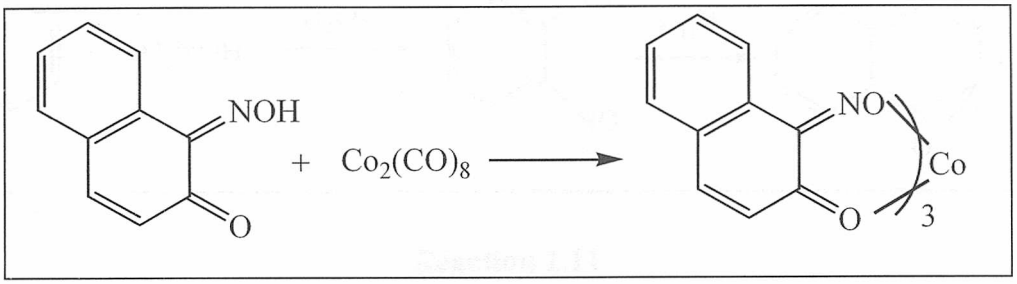


Reaction 1.7

The metal carbonyl method involves also the direct reaction of the free ligand with iron pentacarbonyl or dicobalt octacarbonyl (e.g. Reactions 1.8 and 1.9). Nevertheless, these methods have limited application as there are only a few 1,2-quinone monooximes available.

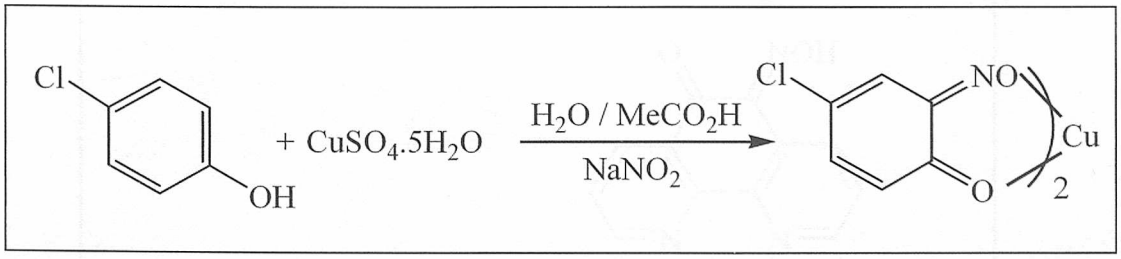


Reaction 1.8



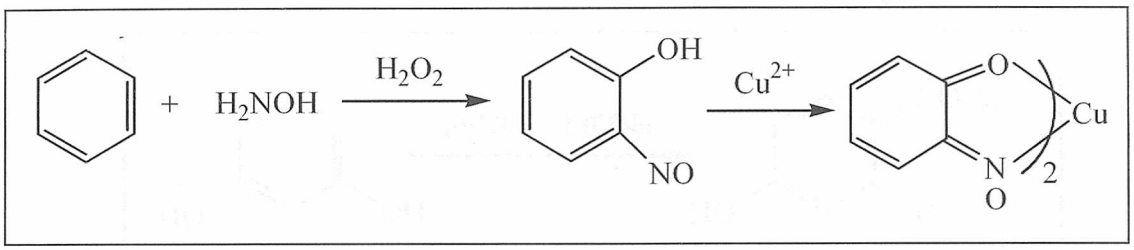
Reaction 1.9

The nitrosation method was first reported by Cronheim[27] and later modified at the University of North London laboratories.[4] This method involves the nitrosation of a hydroxybenzene, using sodium or potassium nitrite and acetic acid, in the presence of a transition metal salt (e.g. Reaction 1.10). Using this method, many complexes of first row transition metals, e.g. copper(II),[4, 26, 28] nickel(II),[5, 17, 26, 29, 30] iron(II),[26] iron(III),[31] cobalt(III),[22, 26, 32] and manganese(III)[26] as well as, those of some second row transition metals, e.g. palladium(II),[33] ruthenium(II),[34] iridium (III)[35] and rhodium(III)[35] have been prepared.



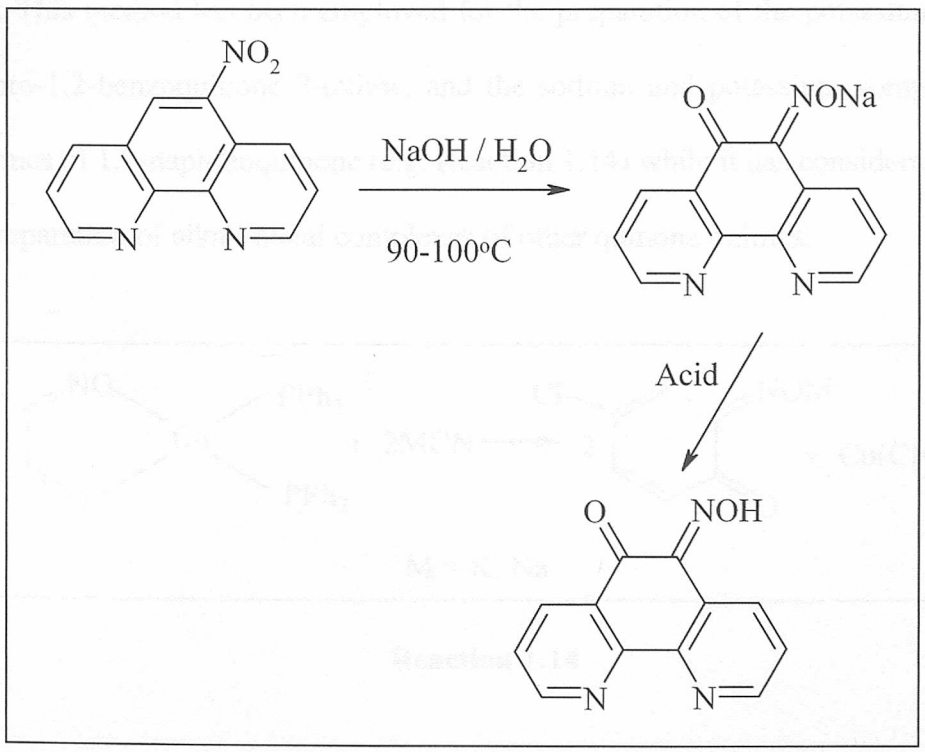
Reaction 1.10

Baudisch method has been used for preparing some copper(II) complexes.[36] This involves oxidation of an aromatic hydrocarbon by the action of hydrogen peroxide and hydroxylamine hydrochloride in the presence of a copper(II) salt (e.g. Reaction 1.11).



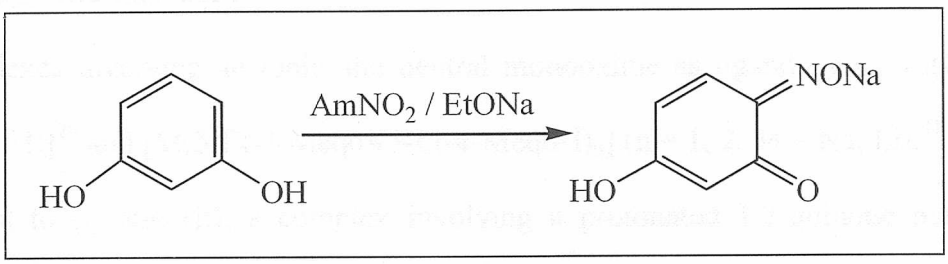
Reaction 1.11

Sodium complex of 1,10-phenanthroline-5,6-quinone 6-oxime has been obtained by the alkali induced rearrangement of 5-nitro-1,10-phenanthroline (e.g. Reaction 1.12).[37] This method was used for the preparation of other sodium quinone monooximates derived from heterocyclic nitro compounds.



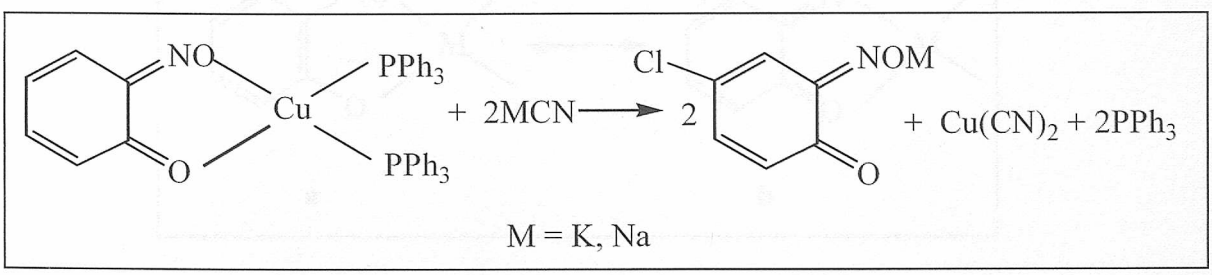
Reaction 1.12

The amyl nitrite involves treatment of 1,3-dihydroxybenzene or substituted-1,3-dihydroxybenzenes with amyl nitrite and an alkali metal hydroxide or alkoxide in ethanol (e.g. Reaction 1.13). This has been applied for the synthesis of main group metal complexes.[18, 38]



Reaction 1.13

Some studies have showed that the reaction of nickel(II) and copper(II)[39, 40] complexes of 1,2-quinone monooximes or their Lewis base adducts, e.g. $Cu(2\text{-nqo})_2(dipy)$ or $Cu(2\text{-nqo})(PPh_3)_2$ with an alkali metal cyanide gave the corresponding alkali metal complex. This method has been employed for the preparation of the potassium complexes of 4-chloro-1,2-benzoquinone 2-oxime, and the sodium and potassium complexes of the monooximes of 1,2-naphthoquinone (e.g. Reaction 1.14) while it has considerable potential for the preparation of alkali metal complexes of other quinone oximes.



Reaction 1.14

1.4 Types and structure of 1,2-quinone monooximes complexes

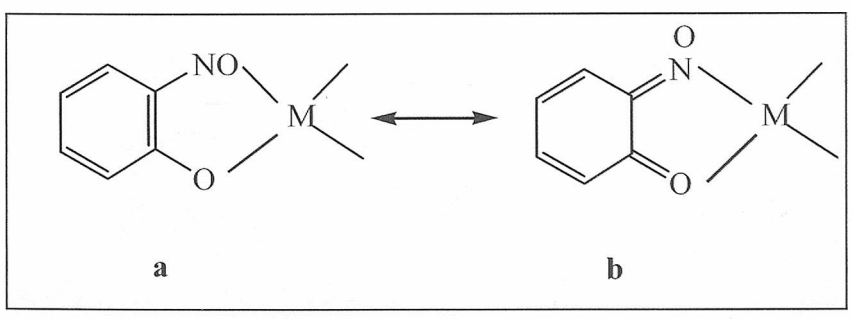
The complexes derived from 1,2-quinone monooximes are of two basic types:

(i) Complexes involving the anion of a 1,2-quinone monooxime (qo^-), e.g. $Cu(4\text{-}Clqo)_2$,[4] $Ni(4\text{-}Meqo)_2$,[5] and Li(1-nqo).[23]

(ii) Complexes involving an ionic and neutral monooxime as ligands, e.g. [Li(1-nqo)(1-nqoH)(EtOH)][29] and $[M(5\text{-}Et\text{-}4\text{-}Meqo)(5\text{-}Et\text{-}4\text{-}MeqoH)_n]$ (n = 1, 2; M = Na, Li).[41]

In addition to (i) and (ii), a complex involving a protonated 1,2-quinone monooxime species, $(qoH_2)_2CuCl_4$, has been reported to result from the reaction of bis(1,2-benzoquinone 2-oximato)copper(II) with hydrogen chloride gas in ethanol.[4]

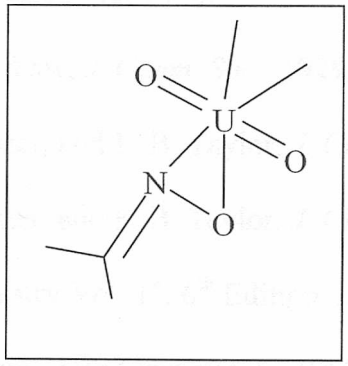
Several X-ray crystallographic studies of such complexes have showed that the structure is essentially quinone oximic **1.6b**.[15, 16, 22-24, 34, 35] This is evident because of the presence of four long and two short C-C bonds, as well as short C-O and C-N bonds.[4] In valence bond terms, the structures of the ligand in quinone oximato complexes has been described as involving resonance between the quinone oximic **1.6b** and nitrosophenolic forms **1.6a**.[4]



1.6

The X-ray studies have also showed that in the majority of complexes, the ligand chelates to the metal via the nitrogen atom of the NO group and the ring oxygen **1.6b**. The only

exception to this is shown by uranyl complexes in which the ligand bonds to the metal only through the NO group **1.7**.[42]



1.7

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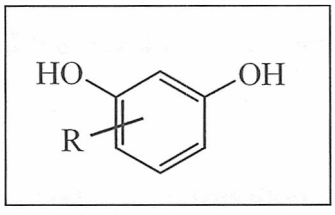
CHAPTER 2

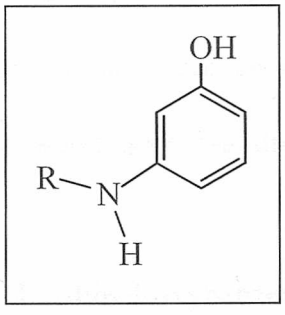
Literature survey for nitrosation of substituted-1,3-dihydroxybenzenes and 3-(substitutedamino)hydroxybenzenes

2.1 Introduction

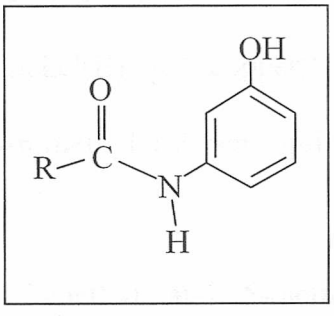
This chapter is concerned with studies of the nitrosation behaviour of 1,3-dihydroxybenzene **2.1** and of the related amino- or alkylamino- and acylamino-dihydroxybenzenes **2.2 and 2.3**. Before considering the findings of the present study an assessment of relevant previous results is presented as these have influenced the aims and interpretation of the results of this work.



2.1



2.2



2.3

2.1.1 Nitrosation of 1, 3-dihydroxybenzene

The study of the behaviour of 1,3-dihydroxybenzene has been both detailed and systematic. Investigations have involved studies of their behaviour towards sodium nitrite/acid and amyl nitrite/base (Tables 2.1-2.3). Nitrosation of 1,3-dihydroxybenzene and its derivatives could undergo mono- and/or di-nitrosation, depending on the position of the substituents, the molar ratio of the reactants and the method of the nitrosation employed. Nitrosation of 1,3-dihydroxybenzene and 5-methyl-1,3-dihydroxybenzene at room temperature, with an equimolar ratio using sodium nitrite/acid or amyl nitrite/base, gave the di-nitrosated products.[1] Whereas, mono-nitrosation of the above dihydroxybenzenes in both conditions have been achieved at -10 °C.[1]

In contrast, nitrosation of 1,3-dihydroxybenzene, 5-methyl- and 4-ethyl-1,3-dihydroxybenzenes with excess sodium nitrite in acid at room temperature gave the di-

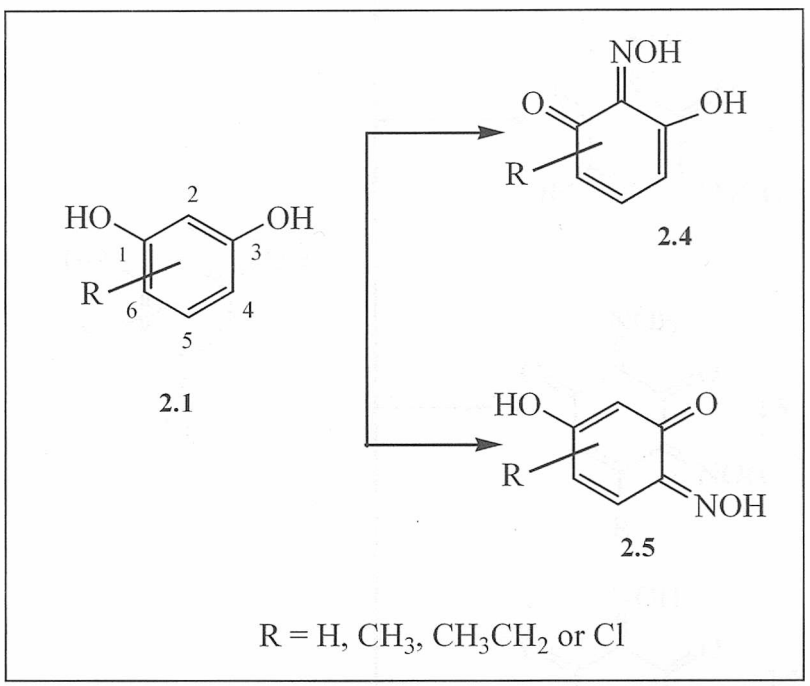
nitrosated compounds.[2] Similarly, the indirect nitrosation of these compounds with sodium nitrite/acid in the presence of transition metal like nickel(II) and copper(II), gave polymeric complexes of the type Ni(X-dnr) and Cu(X-dnr), where X-dnrH_2 is 1,2,3,4-benzoquinone 2,4-dioximato, 5-methyl-1,2,3,4-benzoquinone 2,4- dioximato, 6-chloro-1,2,3,4-benzoquinone 2,4- dioximato and 6-ethyl-1,2,3,4-benzoquinone 2,4- dioximato.[2, 3] In the case of 2-methyl-1,3-dihydroxybenzene, the mono-nitrosated product 5-hydroxy-6-methyl-1,2-benzoquinone 2-oxime was formed irrespective of the method of nitrosation used[1, 2] and its indirect nitrosation in the presence of nickel(II) and copper(II) ions, afforded the metal complex M(qo)$_2$, where qo is 5-hydroxy-6-methyl-1,2-benzoquinone 2-oximato.[2, 3]

In the case of nitrosation of 1,3-dihydroxybenzene, 2-methyl and 5-methyl-1,3-dihydroxybenzenes with amyl nitrite/base at -10 °C using a 1 : 1 mole ratio, mono-sodium derivative of the mono-nitrosated product was only obtained (Table 2.3). Whereas, when this nitrosation is carried out at room temperature involving a 1 : 1 mole ratio, 1,3-dihydroxybenzene and 5-methyl-1,3-dihydroxybenzene afforded the mono-sodium derivative of di-nitrosated products.[1] In contrast, analogous reaction of 2-methyl-1,3-dihydroxybenzene afforded mono-sodium derivative of the mono-nitrosated product.[1]

Nevertheless, nitrosation at -10 °C using 1 : 1.4 mole ratio of 1,3-dihydroxybenzene to amyl nitrite/base gave a mixture of the mono and di-sodium derivatives of the mono-nitrosated products, whereas di-sodium derivatives of the mono-nitrosated products was obtained at -10 °C using a 1 : 2 mole ratio.[1] Analogous behaviour is shown by 2-methyl and 5-methyl-1,3-dihydroxybenzenes.[1]

A plausible explanation of the report results could be given as follow:

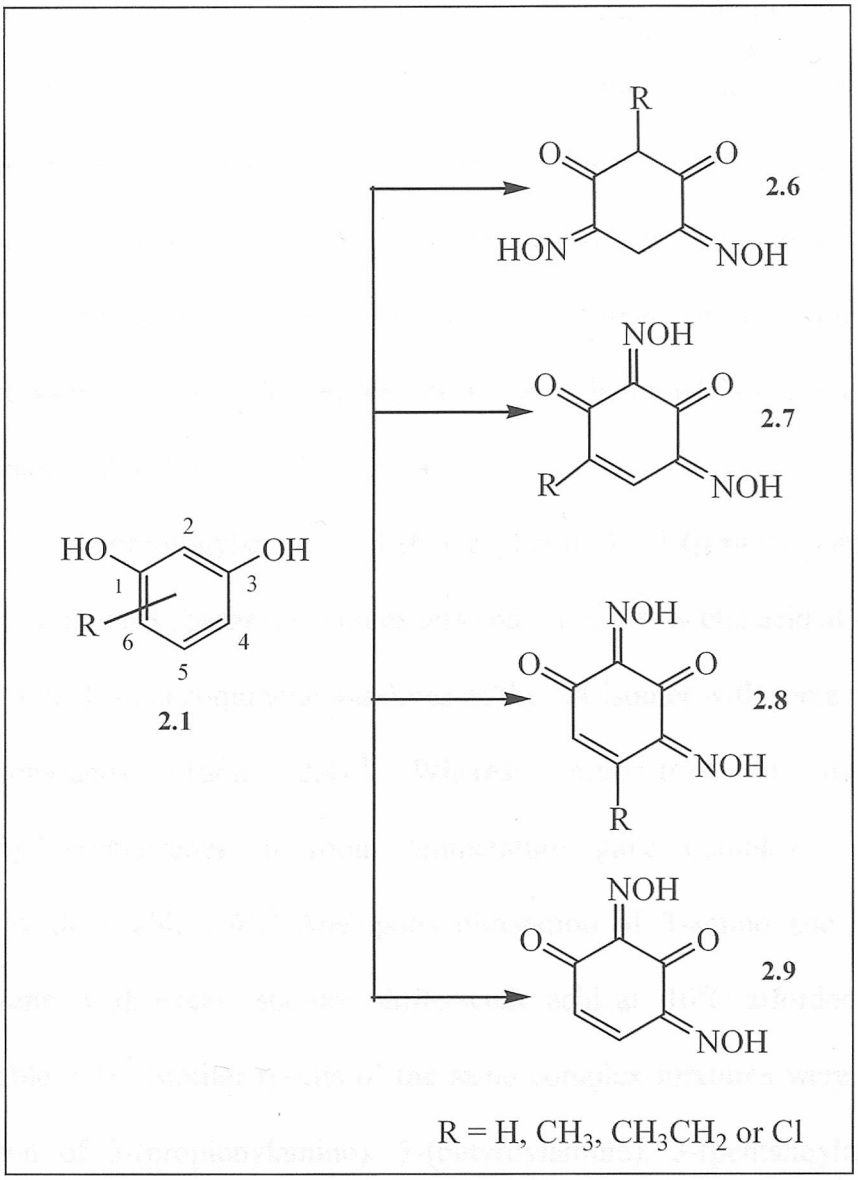
Mono-nitrosation of 1,3-dihydroxybenzene or the substituted-1,3-dihydroxybenzenes **2.1** can occur at positions 2, 4 or 6 to obtain the 1,2-isomer **2.4** and **2.5** respectively. Attack at positions 4 or 6 are more favourable and could give the most stable compound. Mono-nitrosation of 1,3-dihydroxybenzene or 5-substituted-1,3-dihydroxybenzene **2.1** at positions 4 or 6 will give the same result due to their symmetrical structure (Scheme 2.1).



Scheme 2.1

The possible di-nitrosation of 1,3-dihydroxybenzene or 5-substituted-1,3-dihydroxybenzene **2.1** at positions 2 and 4 or 2 and 6 will give the same result due to their symmetrical structure **2.9** and **2.8** respectively. Di-nitrosation of 6-substituted-1,3-dihydroxybenzene **2.1** can occur at positions 2 and 4 (**2.7**). Whereas, di-nitrosation of 2-substituted-1,3-dihydroxybenzene **2.1** is unfavorable because its formation will destroy the aromaticity of the ring **2.6** (Scheme 2.2). This might explain why the mono-nitrosated

product of 5-hydroxy-6-methyl-1,2-benzoquinone 2-oxime **2.5** is formed irrespective of the method of nitrosation used (Schemes 2.1 and 2.2).



Scheme 2.2

2.1.2 Nitrosation of 3-amino, 3-(alkylamino), 3-(acylamino) and 3-(phenylamino) hydroxybenzenes

It was reported that nitrosation of 3-amino, 3-(alkylamino), 3-(acylamino) and 3-(phenylamino)hydroxybenzenes under various experimental conditions afforded only the mono-nitrosated products (Tables 2.4-2.8).[4-6] No dinitrosation products were ever isolated. Thus, nitrosation of 3-(acetylamino)hyroxybenzene with excess sodium nitrite/acetic acid at room temperature, gave a mixture of 5-acetylamino-1,2-benzoquinone 2-oxime and 3-acetylamino-1,4-benzoquinone 4-oxime (Table 2.4).[4] While nitrosation with excess sodium nitrite in neat acetic acid at -10°C afforded only 5-acetylamino-1,2-benzoquinone 2-oxime as the1,2-isomer (Table 2.5).[4]

Nitrosation of 3-(propionylamino), 3-(butyroylamino), 3-(pentanoylamino) and 3-(heptanoylamino)hydroxybenzenes with excess sodium nitrite/acetic acid at -10°C afforded only 3-acylamino-1,4-benzoquinone 4-oximes as the 1,4-isomer with some recovery of the starting compounds (Table 2.4).[5] Whereas nitrosation of the above 3-(acylamino)hydroxybenzenes at room temperature gave complex mixtures, multi component by tlc (Table 2.4).[4] Analogous nitrosation of 3-amino and 3-(alkylamino) hydroxybenzenes with excess sodium nitrite/acetic acid at -10°C afforded also complex mixtures (Table 2.4).[5] Similar results of the same complex mixtures were obtained from the nitrosation of 3-(propionylamino), 3-(butyroylamino), 3-(pentanoylamino) and 3-(heptanoylamino)hydroxybenzenes with excess sodium nitrite in neat acetic acid at -10°C (Table 2.5).[4,5] While nitrosation of these compounds at -10°C using a 1:1 molar ratio of sodium nitrite/neat acetic acid afforded, the corresponding 5-acylamino-1,2-benzoquinone 2-oximes and 3-acylamino-1,4-benzoquinone 4-oximes with some recovery of the starting material (Table 2.5).[5]

In contrast, nitrosation of 3-amino, 3-(hexylamino), 3-(heptylamino), 3-(phenylamino) and 3-ethylamino-4-methylhydroxybenzenes which are carried out in concentrated hydrochloric acid at -10°C using a 1:1 molar ratio or with excess of sodium nitrite afforded only the corresponding 1,2-isomers (Table 2.7).[4-6]

In the case of nitrosation of 3-(acylamino)hydroxybenzenes with amyl nitrite/base at -10 °C using a 1 : 1 mole ratio gave only the recovery of the starting compounds (Table 2.6).[5] Whereas, when this nitrosation is carried out at room temperature involving a 1 : 2.5 mole of 3-(acetylamino), 3-(butyroylamino), 3-(pentanoylamino) and 3-(heptanoylamino)hydroxybenzenes to amyl nitrite/base gave complex mixtures, multi component by tlc (Table 2.6).[4] While nitrosation of 3-(alkylamino)hydroxybenzenes namely, 3-(hexylamino), 3-(heptylamino)hydroxybenzenes with amyl nitrite/base at -10 °C using a 1 : 1 mole ratio afforded the 3-alkylamino-1,4-benzoquinone 4-oxime as the 1,4-isomer (Table 2.6).[5] In contrast, analogous reaction of 3-ethylamino-4-methylhydroxybenzene gave 5-ethylamino-4-methyl-1,2-benzoquinone 2-oxime as the 1,2-isomer (Table 2.6).[5]

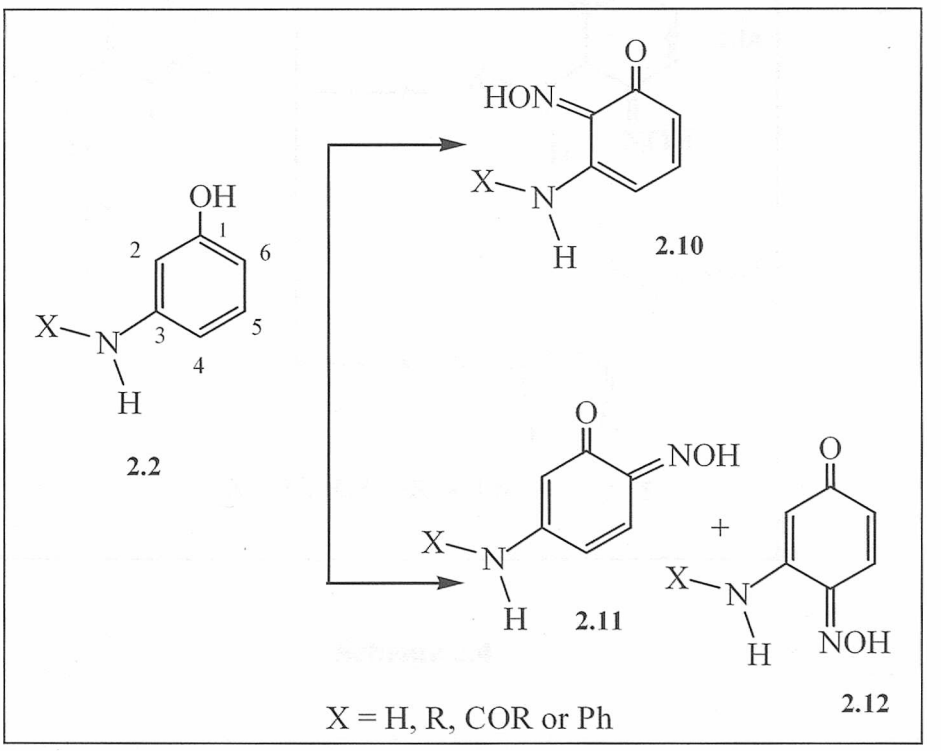
In the case of indirect nitrosation of 3-(acetylamino)hydroxybenzene at room temperature using excess of sodium nitrite/acetic acid in the presence of nickel(II) and copper(II), nickel and copper complexes is only obtained (Table 2.8).[4] Whereas analogous nitrosation reaction of 3-(propionylamino), 3-(butyroylamino), 3-(pentanoylamino), 3-(heptanoylamino) and 3-(phenylamino)hydroxybenzenes gave nickel and copper complexes together with their 1,4-isomers (Table 2.8).[4,5] Nevertheless, the indirect nitrosation of 3-(hexylamino), 3-(heptylamino), and 3-ethylamino-4-methylhydroxybenzenes at room temperature using excess of sodium nitrite/acetic acid in the presence of nickel(II) and copper(II) afforded metal complexes as well as unidentified mixtures, multi component by tlc (Table 2.8).[5] Others indirect nitrosation of 3-

(propionylamino), 3-(butyroylamino), 3-(pentanoylamino) and 3-(benzoylamino)hydroxybenzenes at room temperature using excess of sodium nitrite/acetic acid in the presence of either iron(II) or iron(III) salts gave, metal complexes of types $Fe(qo)_3$ as iron(III) and $Na[Fe(qo)_3]$ as iron(II) together with their 1,4-isomers (Table 2.8).[6] On the other hand, under similar reaction conditions, 3-(phenylamino) and 3-ethylamino-4-methylhydroxybenzenes afforded the iron(II) complex of the type $Na[Fe(qo)_3]$ only (Table 2.8).[6]

The resultant metal complexes of above compounds were $M(qo)_2$, $M(qo)_3$ and $Na[M(qo)_3]$ where qo are 5-acetylamino-, 5-propionylamino-, 5-butyrylamino-, 5-pentanoylamino-, 5-heptanoylamino-, 5-benzoylamino-, 5-phenylamino-, 5-hexylamino-, 5-heptylamino- and 5-ethylamino-4-methyl-1,2-benzoquinone 2-oximatoes.[4,5]

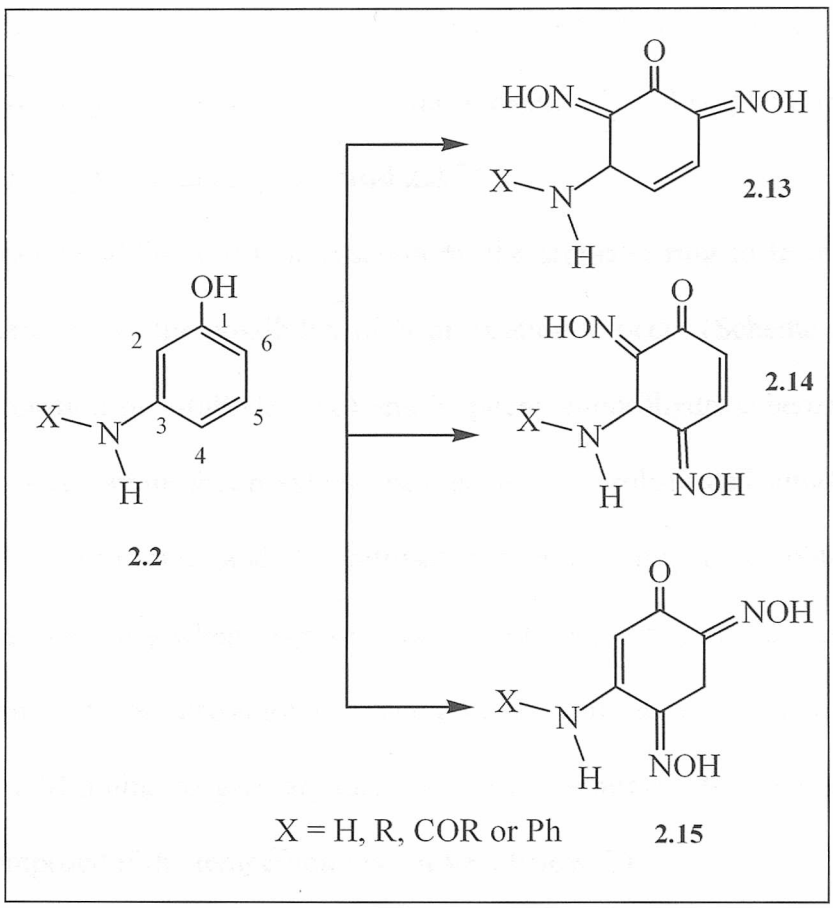
A plausible explanation of the report results could be given as follow:

In the case of 3-amino, 3-(alkylamino), 3-(acylamino) and 3-(phenylamino)hydroxybenzenes **2.2**, mono-nitrosation can occur either in positions 2 or 6 to give the 1,2-isomer **2.10** and **2.11** respectively. Whereas nitrosation at position 4 will afford the 1,4-isomer **2.12**. Attack at position 6 is more favourable and gives the most stable compound due to the following three reasons; the electron density on C_6 is more than that on C_2, the hydrogen bonding stabilization is more effective and this position is less sterically hindered. This explains why the 1,2-isomer is not formed at position 2 (Scheme 2.3).



Scheme 2.3

The possible di-nitrosation on the aromatic ring of 3-amino, 3-(alkylamino), 3-(acylamino) and 3-(phenylamino)hydroxybenzenes **2.2** can occur at positions 2 and 6 **(2.13)**; 2 and 4 **(2.14)** or 4 and 6 **(2.15)**. However, di-nitrosation in these positions are unfavorable because their formations will destroy the aromaticity of the ring (Scheme 2.4). This might explain why the di-nitrosated products were not formed.



Scheme 2.4

It is well documented that primary aromatic amines react with nitrous acid at low temperatures to give aromatic diazonium salts.[7] Whereas, when secondary amines are treated with nitrous acid, N-nitroso compounds are formed. This reaction may be accomplished with dialkyl; diaryl or alkylaryl amines and even with mono-N-substituted amides.[7]

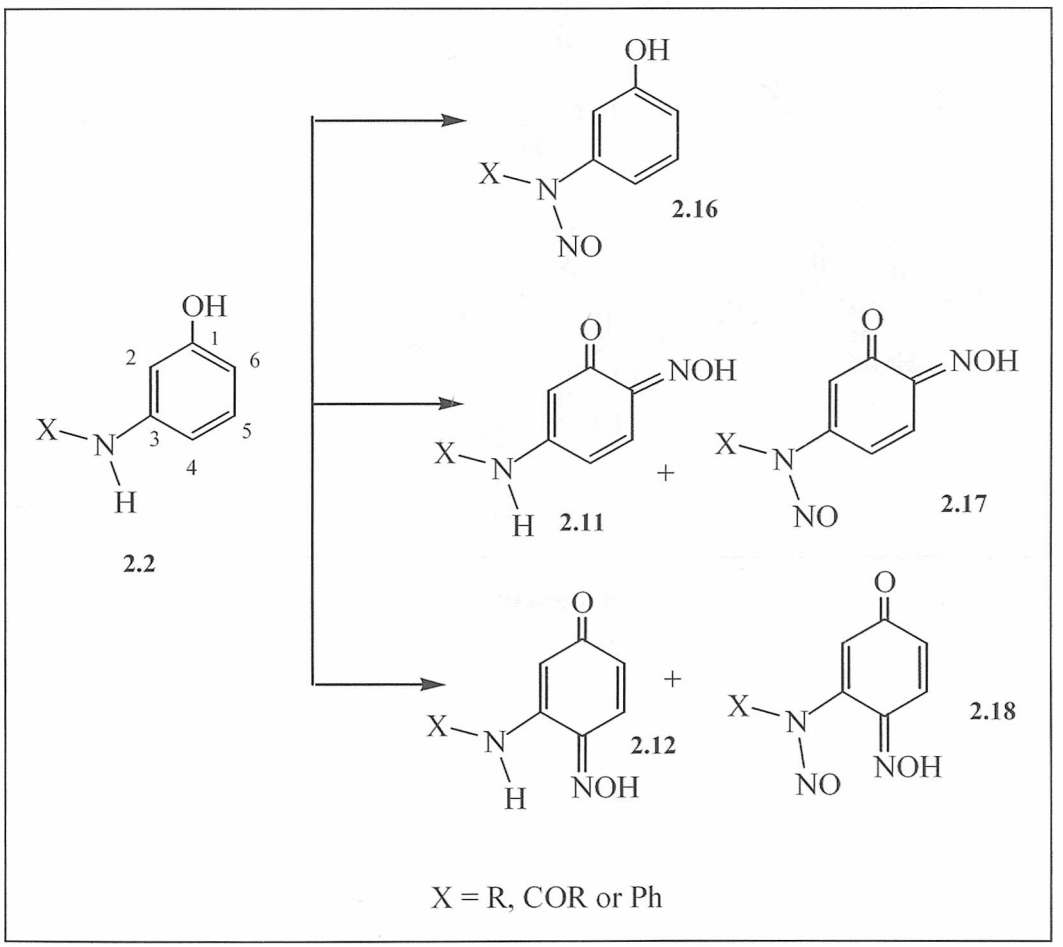
This tendency complicates the nitrosation behaviour of 3-(substitutedamino)hydroxybenzenes which were studied in the previous work described above namely, 3-amino, 3-(alkylamino), 3-(acylamino) and 3-(phenylamino)hydroxybenzenes **2.2 and 2.3**.[4-6]

In these cases in addition to C-nitrosation on the aromatic ring to form the 1,2- and 1,4-isomers, there is also the possibility of N-nitrosation to occur (Scheme 2.5). Hence in the case of nitrosation of 3-(alkylamino) and 3-(phenylamino)hydroxybenzenes as secondary amines or 3-(acylamino)hydroxybenzenes as mono-N-substituted amides, both types of structures, C- nitrosated and N- nitrosated products might be obtained as mixture components especially when excess of sodium nitrite or amyl nitrite were used. The other side reaction of the N-nitrosation can take place in nitrosation of 3-aminohydroxybenzene as primary aryl amine to give aryldiazonium salt (Scheme 2.6). This aryldiazonium salt might decomposed if the temperature is not kept below 5°C.[7]

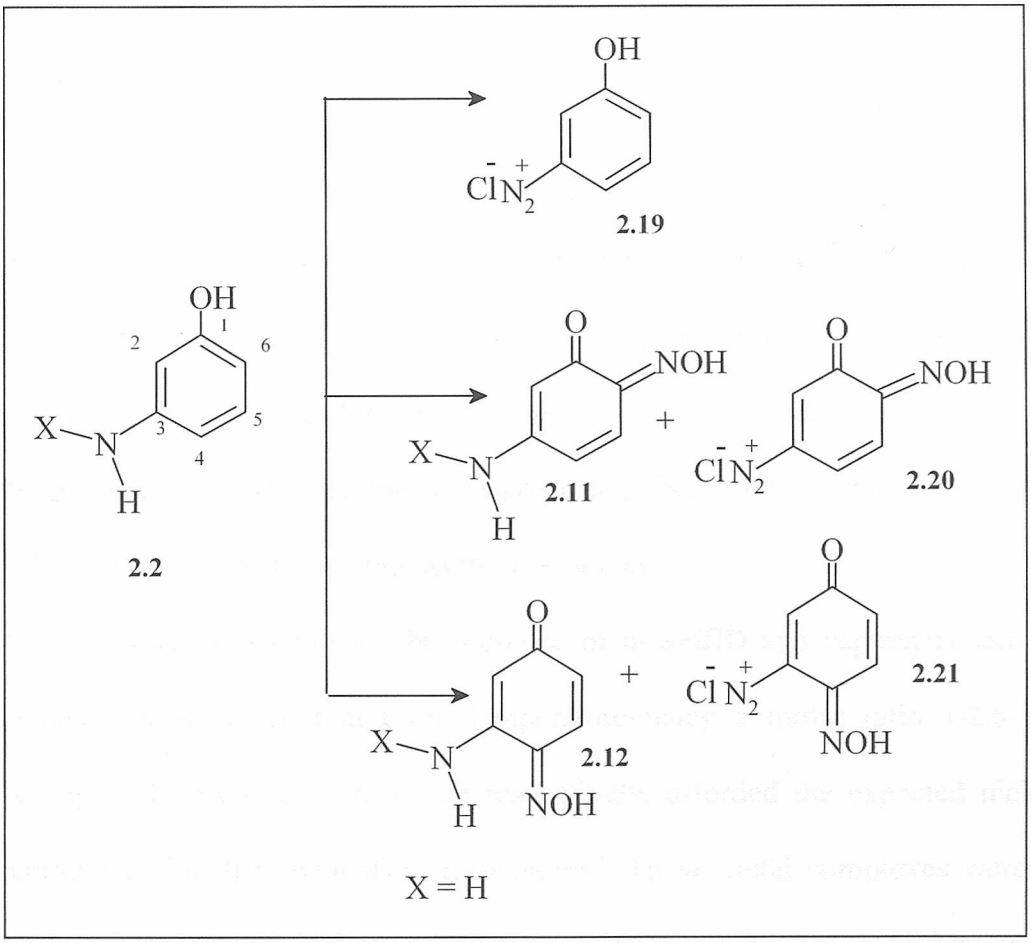
In the case of nitrosation with sodium nitrite in the presence of concentrated hydrochloric acid as strong acid, the nitrogen of the amines will be protonated and subside the N-nitrosation to occur. This might explain why the C-nitrosation on the aromatic benzene ring is only formed even when excess of sodium nitrite is used (Table 2.7).

The formation of the complex mixtures (multi component by tlc) obtained previously might be due to the possible formation of C-nitrosation and/or N-nitrosation products.

However, the previous workers did not mention in their studies that, such compounds can undergo N-nitrosation in addition to C-nitrosation. Whereas, intensive precautions and theoretical investigations should take place prior starting the research work on these compounds as the N-nitrosation products have carcinogenic properties.



Scheme 2.5


OH
$Cl^- N_2^+$
2.19
OH
2
1
6
X
N
3
5
4
H
2.2
O
NOH
X
N
H
2.11
+
O
NOH
$Cl^- N_2^+$
2.20
O
X
N
H
2.12
NOH
+
O
$Cl^- N_2^+$
2.21
NOH
X = H

Scheme 2.6

2.1.3 Nitrosation of 1,7-dihydroxynaphthalene.

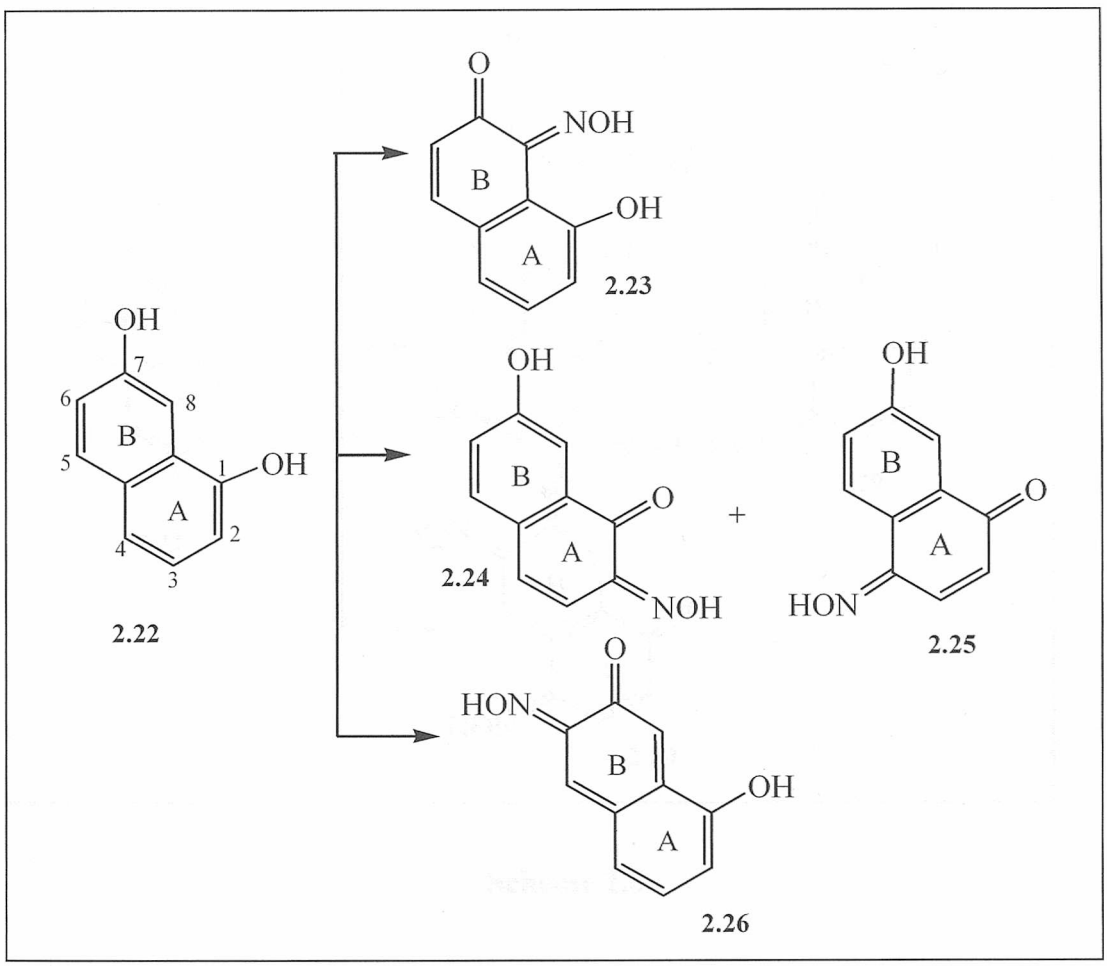
As far as we know, there was only one report coming from this laboratory describing the nitrosation of one of the possible isomers of dihydroxybenzenes, namely the 1,7-dihydroxybenzene.[4] The nitrosation of 1,7-dihydroxynaphthalene with sodium nitrite in the presence of acetic acid was carried out at $-10^{o}C$. This nitrosation which involved a 1:10 molar ratio of 1,7-dihydroxynaphthalene and sodium nitrite respectively, gave 7-hydroxy-1,2-naphthoquinone 2-oxime as the 1,2-isomer together with a small quantity of 7-hydroxy-1,4-naphthoquinone 4-oxime as the 1,4-isomer.

Similarly, the indirct-nitrosation in the presence of nickel(II) and copper(II) salts which was conducted in acetic acid at room temperature using a molar ratio 1:2.5 of 1,7-dihydroxynaphthalene and sodium nitrite respectively, afforded the expected nickel and copper complexes together with their 1,4-isomers.[4] These metal complexes were of the type $M(qo)_2$ where qo is 7-hydroxy-1,2-naphthoquinone 2-oximato. Acidification of the nickel metal complex gives the mono-nitrosated of 7-hydroxy-1,2-naphthouinone 2-oxime.[4]

A plausible explanation of the report results could be given as follow:

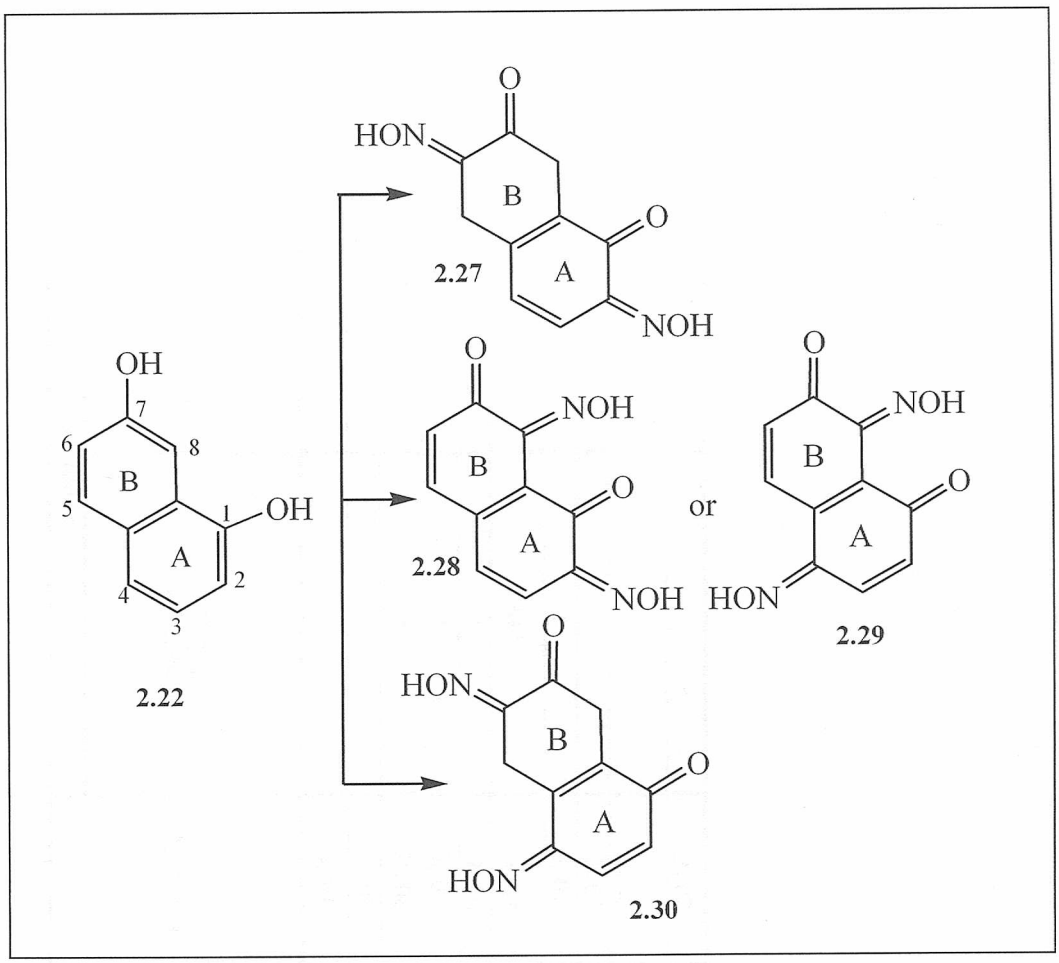
In principle, mono-nitrosation of 1,7-dihydroxynaphalene **2.22** can undergo in ring A or B. Nitrosation in ring B can occur either in positions 6 or 8. Attack at position 6 (**2.26**) is considered to be forbidden because its formation will destroy the aromaticity of ring A, while attack at position 8 (**2.23**) is not favourable due to the steric hindrance with the other ring as well as due to the weakness stability of the hydrogen bonding. The 1,4-isomer in the ring B will not occur because para position to the OH group is blocked. In contrast,

mono-nitrosation could be formed in ring A either at position 2 (**2.24**) to give the 1,2-isomer or at position 4 (**2.25**) to obtain the 1,4-isomer (Scheme 2.7).



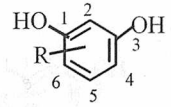
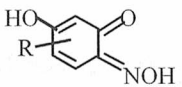
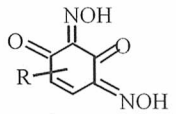
Scheme 2.7

The possible di-nitrosation of 1,7-dihydroxynaphthalene **2.22** in positions 2 of ring A and 8 of ring B **2.28** as well as in positions 4 of ring A and 8 of ring B **2.29** are not favourable due to the steric hindrance and the weakness stability of the hydrogen bonding. Whereas di-nitrosation in positions 2 of ring A and 6 of ring B **2.27** as well as in the positions 4 of ring A and 6 of ring B **2.30** are considered to be forbidden because their formations will destroy the aromaticity of the ring B (Scheme 2.8).


OH
7
6
8
B
5
1
OH
A
4
2
3
2.22
O
HON
B
O
2.27
A
NOH
O
NOH
B
O
2.28
A
NOH
or
O
NOH
B
O
A
HON
2.29
O
HON
B
O
A
HON
2.30

Scheme 2.8

Table 2.1 Products arising from nitrosation of substituted-1,3-dihydroxybenzenes (2.1) with sodium nitrite/acid

 2.1	**Molar ratio of $NaNO_2$/acid to 2.1**	**Temp., °C**	**Products** 		**Ref.**
R = H	1 : 1	-10 °C	√	-	1
	1 : 1	20 °C	-	√	
	2.66 : 1	20 °C	-	68%	2
R = 2-Me	1 : 1	-10 °C	√	-	1
	1 : 1	20 °C	√	-	
	2.66 : 1	20 °C	60%	-	2
R = 5-Me	1 : 1	-10 °C	√	-	1
	1 : 1	20 °C	-	√	
	2.66 : 1	20 °C	-	75%	2
R = 4-Et	2.66 : 1	20 °C	-	81%	

√ = the yield percentage is not mentioned

Table 2.2 Products arising from nitrosation of substituted-1,3-dihydroxybenzenes (2.1) with sodium nitrite/acid in the presence of metal salts

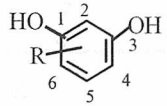
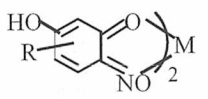
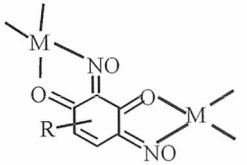
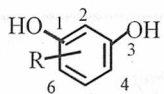
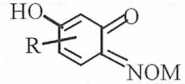
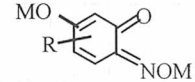
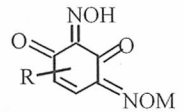
 2.1	**Molar ratio of $NaNO_2$/acid to 2.1**	**Temp., °C**	**Metal salt**	**Products** 		**Ref.**
R = H	2.66 : 1	20 °C	$NiCl_2.6H_2O$	-	85%	2
	2.9 : 1	20 °C	$CuCl_2.2H_2O$	-	87%	3
R = 2-Me	2.66 : 1	20 °C	$NiCl_2.6H_2O$	48%	-	2
	2.9 : 1	20 °C	$CuCl_2.2H_2O$	50%	-	3
R = 5-Me	2.66 : 1	20 °C	$NiCl_2.6H_2O$	-	95%	2
	2.9 : 1	20 °C	$CuCl_2.2H_2O$	-	62%	3
R = 4-Et	2.66 : 1	20 °C	$NiCl_2.6H_2O$	-	95%	2
	2.9 : 1	20 °C	$CuCl_2.2H_2O$	-	61%	3
R = 4-Cl	2.9 : 1	20 °C	$CuCl_2.2H_2O$	-	79%	

Table 2.3 Products arising from nitrosation of substituted-1,3-dihydroxybenzenes (2.1) with amyl nitrite/base

 2.1	**Molar ratio of amyl nitrite/base to 2.1**	**Base**	**Temp., °C**	**Products**			**Ref.**
							
R = H	1 : 1	Soudim hydroxide	-10 °C	55%	-	-	1
		Sodium ethoxide		89%	-	-	
		Soudim hydroxide	20 °C	-	-	48%	
		Sodium ethoxide		-	-	72%	
	1.4 : 1	Soudim hydroxide	-10 °C	√	√	-	
		Sodium ethoxide		√	√	-	
	2 : 1	Soudim hydroxide	-10 °C	-	44%	-	
		Sodium ethoxide		-	83%	-	
R = 2-Me	1 : 1	Soudim hydroxide	-10 °C	47%	-	-	
		Sodium ethoxide		85%	-	-	
		Soudim hydroxide	20 °C	50%	-	-	
		Sodium ethoxide		81%	-	-	
	2 : 1	Soudim hydroxide	-10 °C	-	57%	-	
		Sodium ethoxide		-	87%	-	
		Soudim hydroxide	20 °C	-	56%	-	
		Sodium ethoxide		-	84%	-	
R = 5-Me	1 : 1	Soudim hydroxide	-10 °C	61%	-	-	
		Sodium ethoxide		91%	-	-	
		Soudim hydroxide	20 °C	-	-	44%	
		Sodium ethoxide		-	-	77%	
	2 : 1	Soudim hydroxide	-10 °C	-	58%	-	
		Sodium ethoxide		-	95%	-	

√ = the yield percentage is not mentioned

Table 2.4 Products arising from nitrosation of 3-(substitutedamino)hydroxybenzenes (2.2) with sodium nitrite/acetic acid

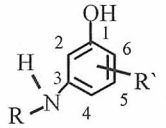
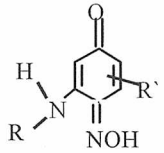
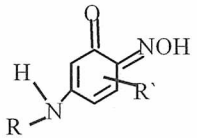
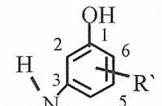
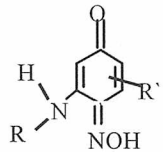
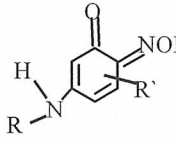
 2.2	**Molar ratio of $NaNO_2$/acid to 2.2**	**Temp., °C**	**Products**				**Ref.**
					**Recovery of starting compound**	**Others**	
R = CH_3CO, R` = H	2.4 : 1	20 °C	24%	17%	-	-	4
R = C_2H_5CO, R` = H	1.70 : 1	-10 °C	48%	-	40%	-	5
R = C_3H_7CO, R` = H	1.83 : 1	-10 °C	40%	-	44%	-	
	2.4 : 1	20 °C	-	-	-	multi component by tlc	4
R = C_4H_9CO, R` = H	2.2 : 1	-10 °C	30%	-	63%	-	5
	2.4 : 1	20 °C	-	-	-	multi component by tlc	4
R = $C_6H_{13}CO$, R` = H	2.4 : 1	-10 °C	41%	-	54%	-	5
	2.4 : 1	20 °C	-	-	-	multi component by tlc	4
R = H, R` = H	2.4 : 1	-10 °C	-	-	-	multi component by tlc	5
R = alkyl, R` = H	2.4 : 1	-10 °C	-	-	-	multi component by tlc	

Table 2.5 Products arising from nitrosation of 3-(substitutedamino)hydroxybenzenes (2.2) with sodium nitrite/neat acetic acid

 2.2	**Molar ratio of $NaNO_2$/acid to 2.2**	**Temp., °C**	**Products**				**Ref.**
					**Recovery of starting compound**	**Others**	
R = CH_3CO, R` = H	2.4 : 1	-10 °C	-	√	-	-	4
R = C_2H_5CO, R` = H	0.69 : 1	-10 °C	53%	17%	27%	-	5
	excess : 1	-10 °C	-	-	-	multi component by tlc	
R = C_3H_7CO, R` = H	0.75 : 1	-10 °C	43%	20%	34%	-	
	excess : 1	-10 °C	-	-	-	multi component by tlc	
	2.4 : 1	-10 °C	-	-	-	multi component by tlc	4
R = C_4H_9CO, R` = H	0.90 : 1	-10 °C	50%	15%	36%	-	5
	excess : 1	-10 °C	-	-	-	multi component by tlc	
	2.4 : 1	-10 °C	-	-	-	multi component by tlc	4
R = $C_6H_{13}CO$, R` = H	1 : 1	-10 °C	46%	12%	38%	-	5
	excess : 1	-10 °C	-	-	-	multi component by tlc	
	2.4 : 1	-10 °C	-	-	-	multi component by tlc	4

√ = the yield percentage is not mentioned

Table 2.6 Products arising from nitrosation of 3-(substitutedamino)hydroxybenzenes (2.2) with amyl nitrite/base

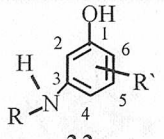
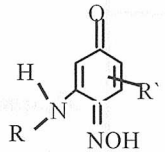
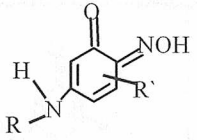
 2.2	**Molar ratio of amyl nitrite/base to 2.2**	**Temp., °C**	**Products** 		**Recovery of starting compound**	**Others**	**Ref.**
R = acyl, R` = H	1 : 1	-10 °C	-	-	89-95%	-	5
R = CH_3CO, R` = H	2.5 : 1	20 °C	-	-	-	multi component by tlc	4
R = C_3H_7CO, R` = H	2.5 : 1	20 °C	-	-	-	multi component by tlc	
R = C_4H_9CO, R` = H	2.5 : 1	20 °C	-	-	-	multi component by tlc	
R = $C_6H_{13}CO$, R` = H	2.5 : 1	20 °C	-	-	-	multi component by tlc	
R = C_6H_{13}, R` = H	1 : 1	-10 °C	45%	-	-	-	5
R = C_7H_{15}, R` = H	1 : 1	-10 °C	73%	-	-	-	
R = C_2H_5, R` = CH_3	1 : 1	-10 °C	-	88%	-	-	

Table 2.7 Products arising from nitrosation of 3-(substitutedamino)hydroxybenzenes (2.2) with sodium nitrite/conc. hydrochloric acid

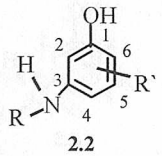
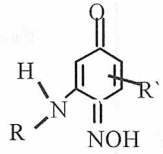
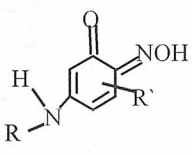
 2.2	**Molar ratio of $NaNO_2$/acid to 2.2**	**Temp., °C**	**Products** 		**Ref.**
R = H, R` = H	1 : 1	-10 °C	-	63%	5
R = C_6H_{13}, R` = H	1.14 : 1	-10 °C	-	78%	
R = C_7H_{15}, R` = H	1.45 : 1	-10 °C	-	69%	
R = C_2H_5, R` = CH_3	1.47 : 1	-10 °C	-	93%	
	1 : 1	-10 °C	-	91%	6
R = C_6H_5, R` = H	1 : 1	-10 °C	-	83%	
	1.72 : 1	-10 °C	-	73%	4

Table 2.8 Products arising from nitrosation of 3-(substitutedamino)hydroxybenzenes (2.2) with sodium nitrite/acetic acid in the presence of metal salts

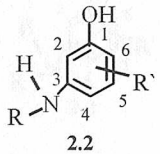
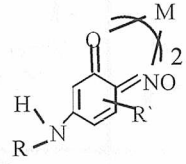
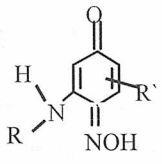
 2.2	**Molar ratio of $NaNO_2$/acid to 2.2**	**Temp., °C**	**Metal salt**	**Products** 		**Recovery of starting compound**	**Ref.**
R = CH_3CO, R` = H	2.67 : 1	20 °C	$NiCl_2.6H_2O$	72%	-	-	4
	2.67 : 1	20 °C	$CuCl_2.2H_2O$	90%	-	-	
R = C_2H_5CO, R` = H	2.67 : 1	20 °C	$NiCl_2.6H_2O$	69%	22%	-	5
R = C_3H_7CO, R` = H	2.64 : 1	20 °C	$NiCl_2.6H_2O$	72%	17%	-	
	2.60 : 1	20 °C	$CuCl_2.2H_2O$	65%	12%	11%	
	2.67 : 1	20 °C	$NiCl_2.6H_2O$	72%	17%	-	4
	2.67 : 1	20 °C	$CuCl_2.2H_2O$	89%	10%	-	
R = C_4H_9CO, R` = H	2.60 : 1	20 °C	$NiCl_2.6H_2O$	68%	19%	-	5
	2.67 : 1	20 °C	$NiCl_2.6H_2O$	70%	19%	-	4
	2.67 : 1	20 °C	$CuCl_2.2H_2O$	42%	30%	-	
R = $C_6H_{13}CO$, R` = H	2.67 : 1	20 °C	$NiCl_2.6H_2O$	67%	16%	-	5
	2.60 : 1	20 °C	$CuCl_2.2H_2O$	50%	6%	-	
	2.67 : 1	20 °C	$CuCl_2.2H_2O$	35%	20%	-	4
R = C_6H_5, R` = H	2.65 : 1	20 °C	$Ni(CH_3COO)_2.4H_2O$	33%	62%	-	
	2.68 : 1	20 °C	$CuSO_4.5H_2O$	26%	61%	-	

Table 2.8 cont.

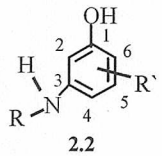
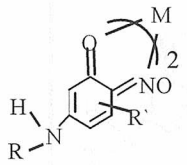
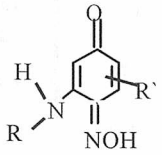
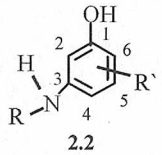
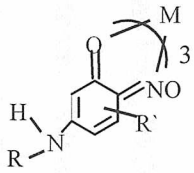
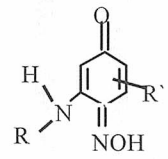
 2.2	**Molar ratio of $NaNO_2$/acid to 2.2**	**Temp., °C**	**Metal salt**	**Products**			**Ref.**
						**Others**	
$R = C_2H_5$, $R` = CH_3$	2.24 : 1	20 °C	$NiCl_2.6H_2O$	23%	-	multi component by tlc	5
$R = C_6H_{13}$, $R` = H$	2.85 : 1	20 °C	$NiCl_2.6H_2O$	11%	-	multi component by tlc	
$R = C_7H_{15}$, $R` = H$	2.96 : 1	20 °C	$NiCl_2.6H_2O$	13%	-	multi component by tlc	

Table 2.8 cont.

 2.2	**Molar ratio of $NaNO_2$/acid to 2.2**	**Temp., °C**	**Metal salt**	**Products**			**Ref.**
						**$Na[Fe(qo)_3]$**	
$R = C_2H_5CO$, $R` = H$	1.71 : 1	20 °C	$(NH_4)_2Fe(SO_4)_2.6H_2O$	√	√	65%	6
	1.71 : 1	20 °C	$FeCl_3$	√	√	46%	
$R = C_3H_7CO$, $R` = H$	1.71 : 1	20 °C	$(NH_4)_2Fe(SO_4)_2.6H_2O$	√	√	63%	
	1.71 : 1	20 °C	$FeCl_3$	√	√	39%	
$R = C_4H_9CO$, $R` = H$	1.71 : 1	20 °C	$(NH_4)_2Fe(SO_4)_2.6H_2O$	√	√	58%	
	1.71 : 1	20 °C	$FeCl_3$	√	√	32%	
$R = C_6H_5CO$ $R` = H$	1.71 : 1	20 °C	$(NH_4)_2Fe(SO_4)_2.6H_2O$	√	√	67%	
	1.71 : 1	20 °C	$FeCl_3$	√	√	41%	
$R = C_2H_5$, $R` = CH_3$	1.90 : 1	20 °C	$(NH_4)_2Fe(SO_4)_2.6H_2O$	-	-	49%	
	1.90 : 1	20 °C	$FeCl_3$	-	-	24%	
$R = C_6H_5$, $R` = H$	1.90 : 1	20 °C	$(NH_4)_2Fe(SO_4)_2.6H_2O$	-	-	33%	
	1.90 : 1	20 °C	$FeCl_3$	-	-	19%	

√ = the yield percentage is not mentioned

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3. J. Charalambous, Colin. W. Newnham, F. B. Taylor, Martin. J. Whelehan, Keith W. P. White and Ivan G. H. Wilson, *Polyhedron,* 1987, **6**, 1033.
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CHAPTER 3

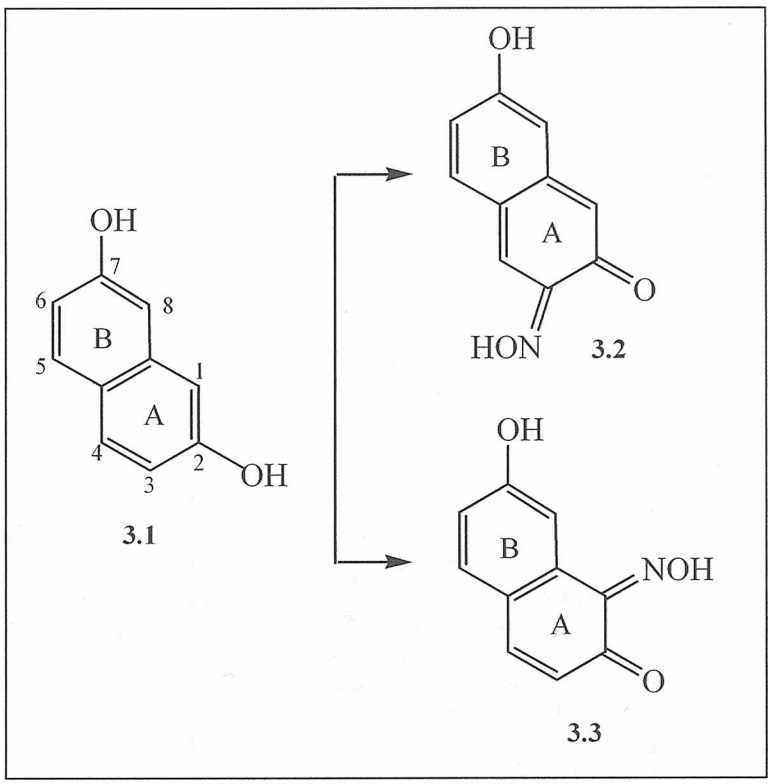
Studies of 5-hydroxy, 6-hydroxy-1,2-naphthoquinone 2-oximes; 6-hydroxy-1,4-naphthoquinone 4-oxime and 7-hydroxy-1,2-naphthoquinone 1-oxime and their acylated derivatives; nickel(II), copper(II) and dioxouranium(VI) complexes

3.1 Aim of the present work

The aim of this study is to investigate the nitrosation behavior of three dihydroxynaphthalenes, namely, 1,5-, 1,6- and 2,7-dihydroxynaphthalenes. The direct and indirect methods of nitrosations will be tried. Attempts will be made to prepare mono- and di-nitrosated products. The *syn* and *anti* configuration of the resultant oximes will be examined by IR spectroscopy of the acylated products and uranyl complexes. The complex formation of the oximes with nickel(II), copper(II) and uranium(VI) will be investigated.

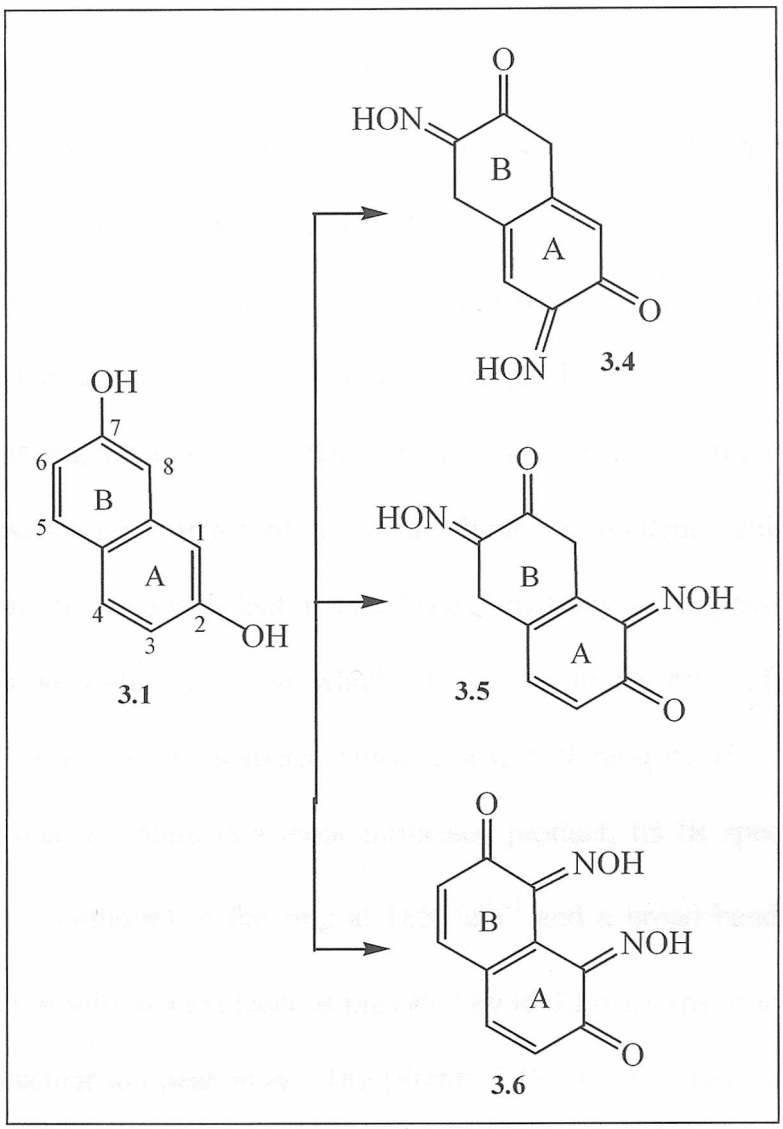
3.1.1 Nitrosation of 2,7-dihydroxynaphthalene.

Mono-nitrosation at either ring A or ring B will give the same results due to the symmetrical structure of 2,7-dihydroxynaphthalene **3.1**. This mono-nitrosation can occur either in positions 1 or 3 of ring A or positions 6 or 8 of ring B. Attack at position 3 of ring A or at 6 of ring B, is not preferred because its formation destroys the aromaticity of the ring **3.2**. In contrast, mono-nitrosation at position 1 of ring A or at 8 of ring B is more preferred and could give the most stable compound as the 1,2-isomer **3.3**. The 1,4-isomer will not form from this compound because para positions to the OH group are blocked (Scheme 3.1).



Scheme 3.1

Similarly, di-nitrosation of 2,7-dihydroxynaphthalene **3.1** at positions 1 of ring A and 6 of ring B **3.5** as well as at positions 3 of ring A and 6 of ring B **3.4** are considered to be unfavorable because their formations will destroy the aromaticity of the ring B. Di-nitrosation in positions 1 of ring A and 8 of ring B **3.6** is unfavorable due to the steric hindrance and the weakness stability of the hydrogen bonding (Scheme 3.2).



Scheme 3.2

In this study, the direct nitrosation of a solution of sodium hydroxide and 2,7-dihydroxynaphthalene **3.1** with sodium nitrite/sulphuric acid is carried out at 0°C. This nitrosation which involves a 1:1 molar ratio of 2,7-dihydroxynaphthalene and sodium nitrite gives a brown solid in a high yield (92%). This brown solid has been characterised by elemental analysis, IR spectroscopy and mass spectrometry. The elemental analysis of this solid indicates a C : N ratio of 10 : 1 suggesting formation of mono-nitrosated product. The IR spectrum of this solid exhibits a band at 1650 cm^{-1} assignable to ν_{CO} (quinone) of

the ring and a broad band of ν_{OH} at 3145 cm^{-1} (Figure 3.1). The EI mass spectrum shows an intense molecular ion peak at *m/z* 189 (100%) (Figure 3.18). These findings suggesting that, nitrosation reaction affords the mono-nitrosated product which was assigned as 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3**.

Thus, di-nitrosation reaction which involves a 1:2.5 molar ratio of 2,7-dihydroxynaphthalene **3.1** and sodium nitrite respectively, was carried out. In this reaction, 2,7-dihydroxynaphthalene is treated also with sodium nitrite/sulphuric acid at 0°C. This direct-nitrosation reaction affords a brown solid in an excellent yield (93%). Comparing tlc behaviour of this solid with that obtained (i.e. 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3**) from mono-nitrosation reaction which involves a molar ratio of 1:1, shows they are identical. The elemental analysis indicates a C : N ratio of 10 : 1 rather than 10 : 2, suggesting that this solid is a mono-nitrosated product. Its IR spectrum shows only one band of ν_{CO} (quinone) of the ring at 1650 cm^{-1} and a broad band of ν_{OH} at 3145 cm^{-1} (Figure 3.2). Additional evidence is provided by its EI mass spectrum which shows also an intense molecular ion peak at *m/z* 189 (Figure 3.19). On the basis of the results of similar tlc behaviour, elemental analysis, IR spectroscopy, and mass spectrometry, it is clear that di-nitrosation product is not formed and only mono-nitrosated product namely, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** is obtained under these conditions.

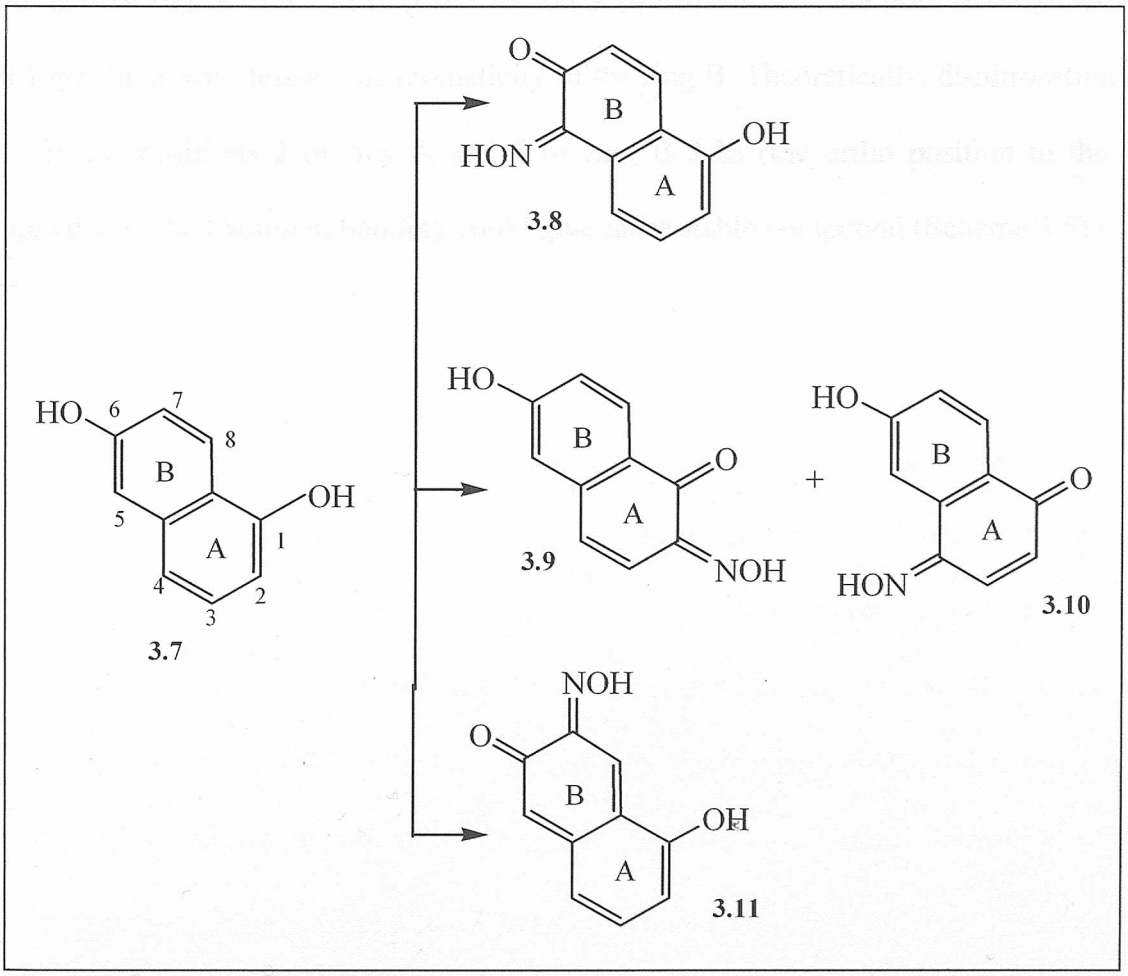
Furthermore, indirect nitrosation of 2,7-dihydroxynaphthalene **3.1** with sodium nitrite using a 1:2.5 molar ratio in the presence of nickel sulphate affords the nickel complex $M(qo)_2$. The acidification of this metal complex liberates the organic ligand as a brown solid. Again this brown solid was found to be the 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3**.

This was evident from comparing the tlc of this organic compound with those of both solids obtained from the direct-nitrosation mentioned above, which clearly shows they have similar spots. The IR spectrum of this organic compound exhibits absorption band at 1650 cm^{-1} assignable to ν_{CO} (quinone) of the ring and a broad band of ν_{OH} at 3144 cm^{-1} (Figure 3.3), suggesting this organic compound is the 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3**. This indicates that, in spite of the presence of excess sodium nitrite, the mono-nitrosated product is again arising from nitrosation of 2,7-dihydroxynaphthalene **3.1** in the presence of nickel sulphate.

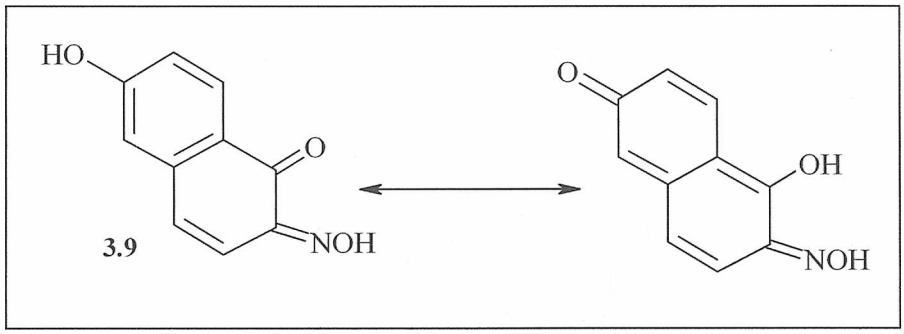
As additional investigation, pure compound of 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** was also treated with sodium nitrite using a 1:1.5 molar ratio respectively. Comparing tlc of the resulting solid with same starting material of 7-hydroxy-1,2-naphthoquinone 1-oxime shows they are identical. The elemental analysis indicates a C : N ratio of 10 : 1 suggesting no reaction occurred. It might be possible that mono-nitrosation at one of the two rings deactivate the other ring towards the dinitrosation.

3.1.2 Nitrosation of 1,6-dihydroxynaphthalene

1,6-Dihydroxynaphthalene **3.7** could undergo mono-nitrosation in ring A or B. Mono-nitrosation in ring B can occur either in positions 5 or 7. Attack at position 7 is not preferred because its formation will destroy the aromaticity of ring A **3.11**, whereas the attack at position 5 could occur without changing the aromaticity of the ring A **3.8**. However, attack at position 2 of the ring A to give the 1,2-isomer is more favorable **3.9**. This will increase stability of the 1,2-isomer which could be occurred through resonance system as illustrated in (Scheme 3.4). Similarly, attack at position 4 in the ring A will form the 1,4-isomer **3.10** (Scheme 3.3).

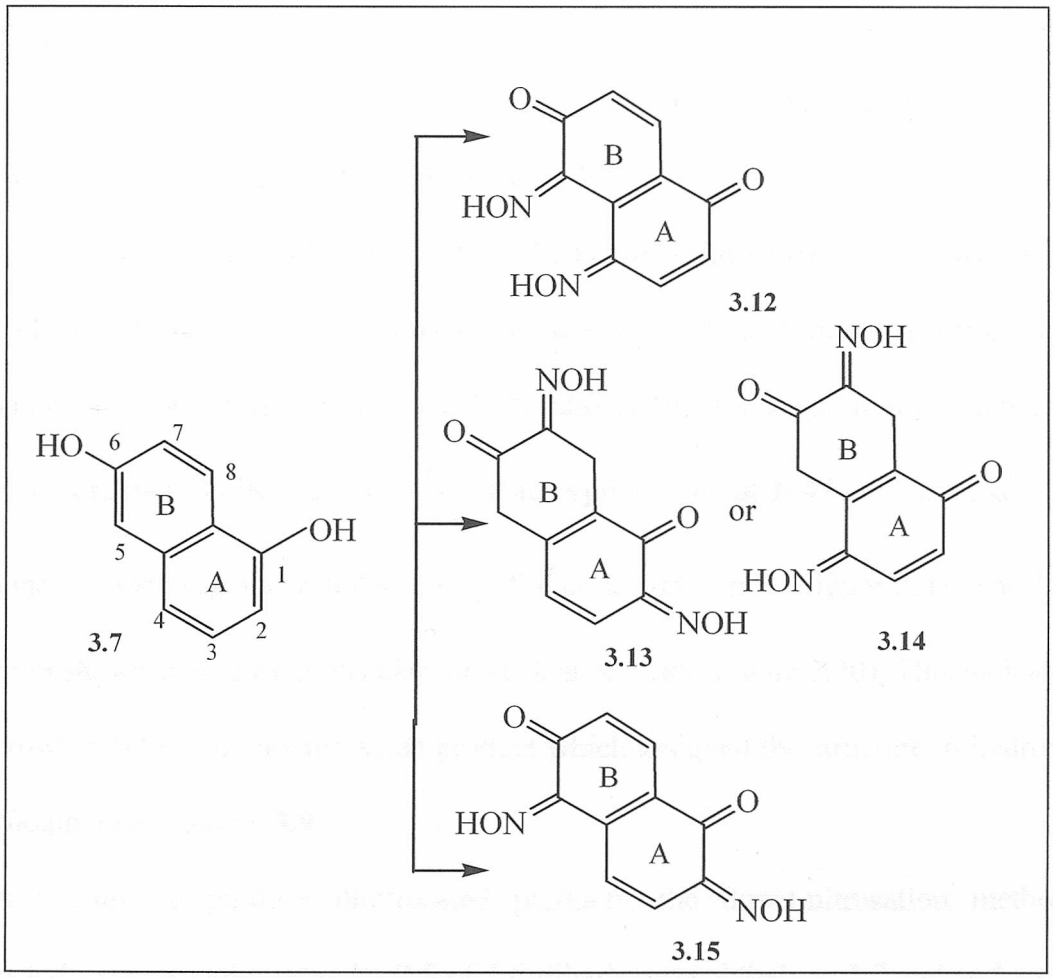


Scheme 3.3



Scheme 3.4

The possible di-nitrosation of 1,6-dihydroxynaphthalene **3.7** in positions 4 of ring A and 5 of ring B is not favorable due to the steric hindrance and the weakness stability of the hydrogen bonding **3.12**. Di-nitrosation in positions 2 of ring A and 7 of ring B as well as in positions 4 of ring A and 7 of ring B **3.13** and **3.14** respectively, are not preferred because their formations will destroy the aromaticity of the ring B. Theoretically, di-nitrosation can occur in the positions 2 of ring A and 5 of ring B **3.15** (the ortho position to the OH groups) due to the hydrogen bonding could give more stable compound (Scheme 3.5).



Scheme 3.5

The direct nitrosation of 1,6-dihydroxynaphthalene **3.7** with sodium nitrite involves a molar ratio of 1:1. In this reaction, a solution of sodium hydroxide of 1,6-dihydroxynaphthalene **3.7** has been treated with sodium nitrite/sulphuric acid at 0°C. This nitrosation gives a yellow-brown solid (two components by tlc). Mixing this solid with nickel sulphate gives a nickel complex and an organic compound, which has been separated by soxhlet extraction using diethyl ether to obtain a yellow compound (21%). The IR spectrum of this yellow solid exhibits a band at 1638 cm^{-1} assignable to ν_{CO} (quinone) of the ring and a broad band of ν_{OH} at 3086 cm^{-1} (Figure 3.7).

Its EI mass spectrum shows an intense molecular ion peak at *m/z* 189 (Figure 3.22). The elemental analysis of this solid indicates a C : N ratio of 10 : 1 suggesting formation of mono-nitrosated product as 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** which has been confirmed by the X-ray crystallography (Figure 3.41).

Acidification of the nickel complex affords a brown solid (70%). This brown solid has been identified by elemental analysis, IR spectroscopy and mass spectrometry. The elemental analysis of this solid gives a C : N ratio of 10 : 1 suggesting formation of mono-nitrosated product. Its IR spectrum show a absorption band at 1647 cm^{-1} assignable to ν_{CO} (quinone) of the ring and a broad band of ν_{OH} at 3057 cm^{-1} (Figure 3.4). The EI mass spectrum shows an intense molecular ion peak at *m/z* 189 (Figure 3.20). This indicates that, this brown solid is a mono-nitrosated product which assigned the structure, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9**.

In an attempt to produce dinitrosated products, the direct-nitrosation method was conducted using a molar ratio 1 : 2.5 of 1,6-dihydroxynaphthalene **3.7** and sodium nitrite respectively. This nitrosation reaction gives also a yellow-brown solid (two components by tlc). When this solid mixture reacts with nickel sulphate, affords a nickel complex and an organic compound which is separated by soxhlet extraction using diethyl ether to afford a yellow compound (22%). Comparing the tlc of this yellow solid with that obtained (i.e. 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10**) from mono-nitrosation reaction, shows they are identical. The elemental analysis indicates a C : N ratio of 10 : 1 suggesting this solid is a mono-nitrosated product. Its IR spectrum shows one band of ν_{CO} (quinone) of the ring at 1638 cm^{-1} and a broad band of ν_{OH} at 3087 cm^{-1} (Figure 3.8). The EI mass spectrum shows also an intense molecular ion peak at *m/z* 189 (Figure 3.23). Based on the above, this

yellow compound is assigned the structure 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** as the 1,4-isomer.

Acidification of the nickel complex gives a brown solid (70%). The elemental analysis gives a C : N ratio of 10 : 1 rather than 10 : 2, suggesting this solid is a mono-nitrosated product. Its IR spectrum shows only one band of ν_{CO} (quinone) of the ring at 1647 cm^{-1} and a broad band of ν_{OH} at 3058 cm^{-1} (Figure 3.5). Another evidence is provided by EI mass spectrum, which shows also an intense molecular ion peak at *m/z* 189 (Figure 3.21). Suggesting this brown solid is 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** as 1,2-isomer.

On the basis of the above results, it seems that these nitrosation reactions afford the mono-nitrosated products, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** as the major product and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** as the minor product.

The indirect-nitrosation which involves reaction of 1,6-dihydroxynaphthalene **3.7** with sodium nitrite using 1:2.5 molar ratio in the presence of nickel sulphate affords the nickel complex $Ni(qo)_2$ as a major product together with a yellow solid as an organic compound. The yellow compound has been separated by soxhlet extraction technique using diethyl ether as solvent.

Comparison of the tlc of this yellow solid with the obtained 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** from mono-nitrosation reaction, shows they have similar spots. Hence this organic compound is 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10**.

Acidification of the nickel complex gives brown solid as an organic ligand. Comparing the tlc of this organic compound with the tlc of both solids which were obtained from the direct-nitrosation above, shows they are identical. The IR spectrum of this brown solid shows absorption band at 1647 cm^{-1} assignable to ν_{CO} (quinone) of the ring and a broad band of ν_{OH} at 3057 cm^{-1} (Figure 3.6), suggesting this brown compound is 6-hydroxy-1,2-

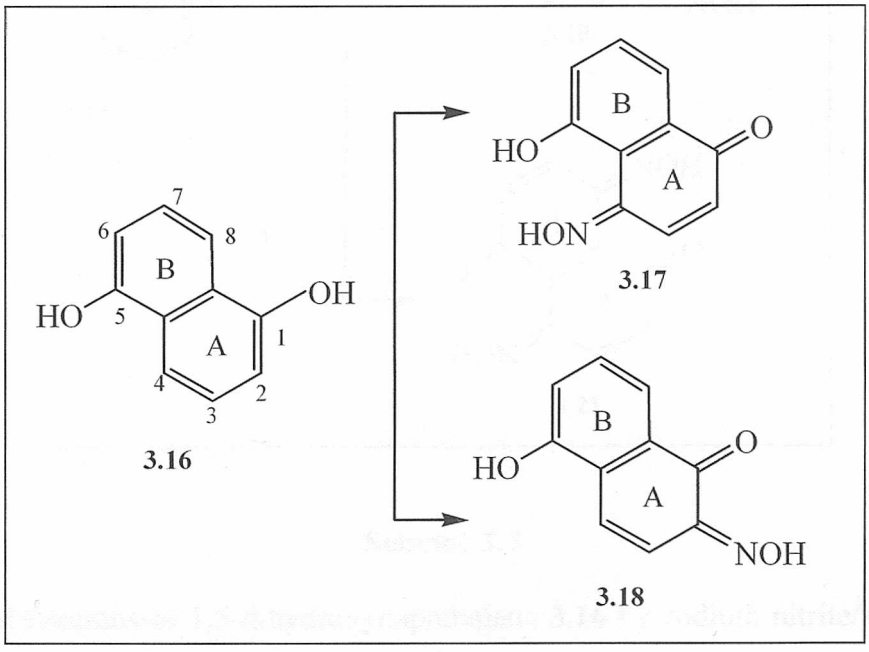
naphthoquinone 2-oxime **3.9**. These findings show that similar behaviours are observed from nitrosation of 1,6-dihydroxynaphthalene **3.7** under different conditions.

Moreover, treating pure 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** with sodium nitrite using 1:1.5 molar ratio respectively, recovered the mono-oxime unreacted This means that di-nitrosation product is not formed. This was evident from comparing the tlc behaviour of the starting material of 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** and the resulting solid which reveals they are similar. The elemental analysis indicates a C : N ratio of 10 : 1 suggesting no reaction was occurred. It might be possible that mono-nitrosation at one of the two rings deactivate the other ring towards the dinitrosation.

In conclusion, all attempts to obtain a di-nitrosated product were unsuccessful. Using the direct and indirect methods of nitrosation with excess sodium nitrite always give the mono-nitrosated oximes, namely, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** as the major 1,2-isomer and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** as the minor 1,4-isomer.

3.1.3 Nitrosation of 1,5-dihydroxynaphthalene

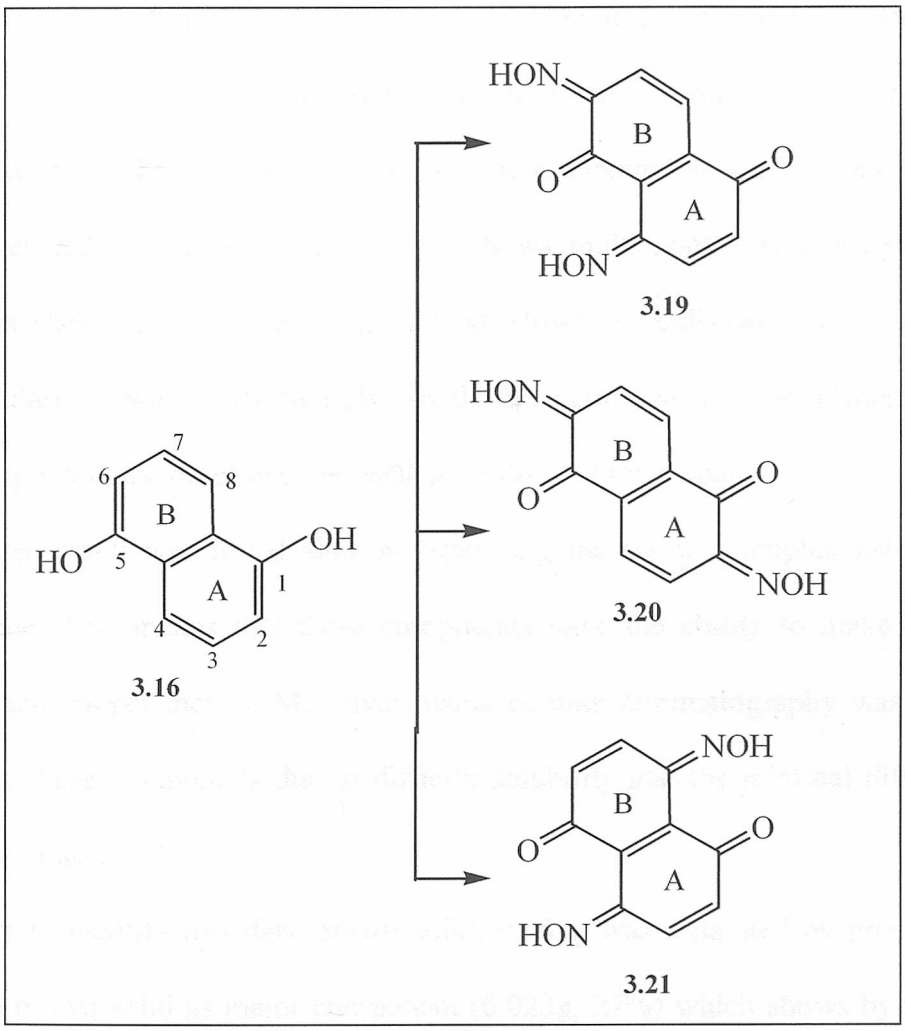
As 1,5-Dihydroxynaphthalene **3.16** has a symmetrical structure, therefore, mono-nitrosation either in ring A or ring B will give the same results. Mono-nitrosation can occur either in positions 2 or 4 of ring A or positions 6 or 8 of ring B. The 1,2-isomer could be formed through attack at position 2 or 6 (the ortho to the OH group) which could give the most stable compound **3.18**. Attack at position 4 or 8 are not favourable due to the steric hindrance with the other ring as well as due to the weakness stability of the hydrogen bonding **3.17**. This explains why the 1,4-isomer is not formed (Scheme 3.6).



Scheme 3.6

The possibility of di-nitrosation of 1,5-dihydroxynaphthalene **3.16** in positions 4 of ring A and 6 of ring B as well as in positions 4 of ring A and 8 in ring B **3.19** and **3.21** respectively, is not favourable due to the steric hindrance and the weakness stability of the hydrogen bonding. Theoretically, di-nitrosation could occur in the positions 2 of ring A

and 6 of ring B **3.20** (the ortho position to the OH groups) due to the hydrogen bonding could give more stable compound (Scheme 3.7).



Scheme 3.7

The direct nitrosations of 1,5-dihydroxynaphthalene **3.16** by sodium nitrite/sulphuric acid is carried out at 0°C. The behaviour of these nitrosations which involve a molar ratio of 1:1 (as mono-nitrosation) or 1:2.5 (as di-nitrosation) of 1,5-dihydroxynaphthalene **3.16** and sodium nitrite respectively, gives similar results. The tlc of these nitrosations show multi components. In this study, two different suppliers of starting material of 1,5-dihydroxynaphthalene **3.16** are used namely, Aldrich with assay 97% and Acros with assay

99%. The tlc of both starting materials show several compounds. Variety of techniques are carried out to purify 1,5-dihydroxynaphthalene **3.16** before using it in the nitrosation reactions. These attempts were unsuccessful due to difficult solubility of these compounds. One of these techniques was used to mix the resulting nitrosated component with nickel sulphate to form a nickel complex and an organic compound, which could then be separated by soxhlet extraction. This organic compound was a little bit gummy and was not investigated further because its tlc shows multi spots. Acidification of the nickel complex should give a pure organic ligand. However acidification of this nickel complex affords dark brown solid which give by tlc three components, one of them shows a strong brown spot and the other two are weak as yellow – brown spots.

The same result was found also by separating the copper complex using ion exchange technique. This means that these compounds have the ability to make complexes with nickel and copper metals. Moreover, using column chromatography was unsuccessful to separate these compounds due to difficult solubility and the minimal difference between their R_f values.

In order to identify this dark brown solid, 0.085g was separated by preparative tlc. This gives a brown solid as major component (0.023g, 27%) which shows by tlc one spot and yellow-brown solid (0.006g, 7%) which shows two spots. The IR of this yellow-brown solid shows two absorption bands at 1630 and 1731 cm^{-1} and no a broad band of ν_{OH} is found. The elemental analysis gives a C : N ratio of 82 : 1 suggesting this solid is unidentifiable. The comparative tlc with starting material of 1,5-dihydroxynaphthalene **3.16** shows, these two spots (yellow – brown) are appeared also as impurities.

In contrast, The IR spectrum of the brown solid exhibits a band at 1660 cm^{-1} assignable to ν_{CO} (quinone) of the ring and a broad band of ν_{OH} at 3199 cm^{-1} (Figure 3.9).

The elemental analysis of this solid indicate a C : N ratio of 10 : 1 suggesting formation of mono-nitrosated product. This indicates that this mono-nitrosation product is 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18** as the 1,2-isomer.

Similar results were found when the nitrostion reaction was carried out with excess sodium nitrite. Thus, nitrosation of 1,5-dihydroxynaphthalene **3.16** with sodium nitrite using a 1 : 2.5 molar ratio respectively, results in a dark brown solid. Part of this solid (0.100 g) was separated by preparative tlc. Two components were isolated, a major brown solid (0.025 g, 25%) and minor yellow-brown solid (0.009 g, 9%) which appears as two spots. The IR spectrum of the yellow-brown solid gives two absorption bands at 1630 and 1731 cm^{-1} and no broad band of ν_{OH} is found. The elemental analysis of this yellow-brown solid gives a C : N ratio of 82 : 1 suggesting this solid is unidentifiable. Comparing the tlc of this solid with that of the starting material 1,5-dihydroxynaphthalene **3.16** shows these two spots (yellow – brown) are appeared also as impurities.

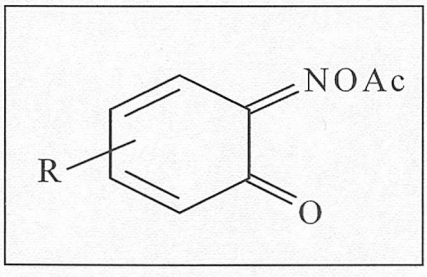
The elemental analysis of the brown solid indicates a C : N ratio of 10 : 1 rather than 10 : 2, suggesting this solid is a mono-nitrosated product. Its IR spectrum show only one band of ν_{CO} (quinone) of the ring at 1659 cm^{-1} and a broad band of ν_{OH} at 3202 cm^{-1} (Figure 3.10). The EI mass spectrum shows a molecular ion peak at *m/z* 189 (Figure 3.24). This reveals that under this condition, di-nitrosated product is not formed and only mono-nitrosated product 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18** is obtained as the 1,2-isomer.

Moreover, treating pure compound of 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18** with sodium nitrite using 1:1.5 a molar ratio respectively, recovered the mono-oxime unreacted. This was clear from comparing the tlc of the resulting solid with that of the starting material of 5-hydroxy-1,2-naphthoquinone 2-oxime which shows they are identical.

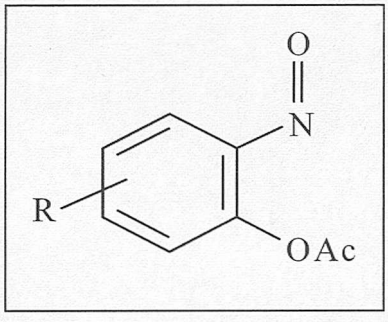
The elemental analysis indicates a C : N ratio of 10 : 1 suggesting no further nitrosation reaction was obtained. This means that di-nitrosation reaction is not occurred. It might be possible that mono-nitrosation at one of the two rings deactivate the other ring towards the dinitrosation.

3.2 Acylation of hydroxy-1,2-naphthoquinone monooximes

The aim of preparing the acylated compounds of these oximes is to establish the configuration of the 1,2-quinone oximes using infrared spectroscopy. During the present work, the quinone oximes of 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** and 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** are successfully acylated at 20°C using acetic anhydride in acetone as a solvent. This acylation could involve either the quinone oxime form such as **3.22** or nitrosophenolic form such as **3.23**. The structural studies using elemental analysis, infrared, nuclear magnetic resonance spectroscopy and mass spectrometry indicate that these acylated derivatives of 1,2-oxime products are presented in the quinone oxime form such as **3.22**.



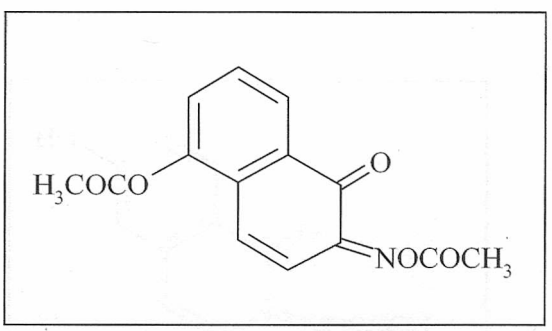
3.22



3.23

3.2.1 Characterisation of acylated compound derived from 5-hydroxy-1,2-naphthoquinone 2-oxime

Reaction of 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18** with acetic anhydride affords a green solid. The structure of this acylated product was inferred from elemental analysis, ^{1}H NMR, IR spectroscopy and mass spectrometry. The IR spectrum shows two bands of ν_{CO} at 1684 and 1779 cm^{-1} and no broad band of ν_{OH} is found. The absorption band at 1684 cm^{-1} is assignable to ν_{CO} (quinone) of the ring, whereas the band of ν_{CO} (acyl) appears higher at 1779 cm^{-1} (Figure 3.11). The ^{1}H NMR spectrum exhibits 5 aromatic protons and 6 aliphatic protons corresponding to methyl groups in $OCOCH_3$ and $NOCOCH_3$ (Table 3.4). The elemental analysis of the product indicates a C : H : N ratio of 14 : 11 : 1. The presence of a molecular ion peak at *m/z* 273 in its mass spectrum (Figure 3.25) indicates that, di-acetoxy compound is formed. From these data, the structure 2-acetoxyimino-5-acetoxy-1,2-naphthoquinone **3.24** is assigned to this product.

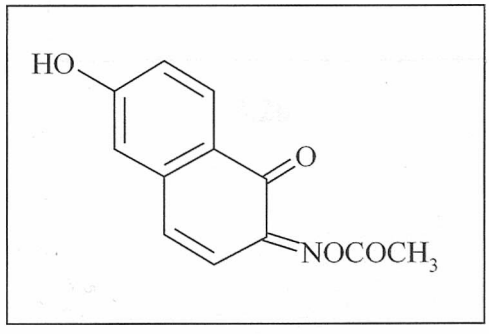


3.24

3.2.2 Characterisation of acylated compound derived from 6-hydroxy-1,2-naphthoquinone 2-oxime

The acylated product obtained from reaction of 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** with acetic anhydride is a yellow solid. The IR spectrum of this solid show two strong bands at 1660 and 1770 cm^{-1} and a broad band of ν_{OH} at 3453 cm^{-1} (Figure 3.12) The absorption band of ν_{CO} (quinone) appears at 1660 cm^{-1}, whereas, the higher band at 1770 cm^{-1} was assigned to ν_{CO} (acyl). The ^1H NMR spectrum exhibits 5 aromatic protons, 1 proton assignable to OH group and 3 aliphatic protons due to methyl group of $NOCOCH_3$ (Table 3.4).

The elemental analysis of the product gives a C : H : N ratio of 12 : 9 : 1 suggesting that, this product is a mono-acetoxy compound. The mass spectrum, which exhibits a molecular ion at peak *m/z* 231 (Figure 3.26) confirmed this compound to be 2-acetoxyimino-6-hydroxy-1,2-naphthoquinone **3.25**. It might be possible that, the resonance structure as illustrated in (Scheme 3.4) prevents the hydroxy group in ring B from reacting with acetic anhydride to produce the di-acetoxy compound.

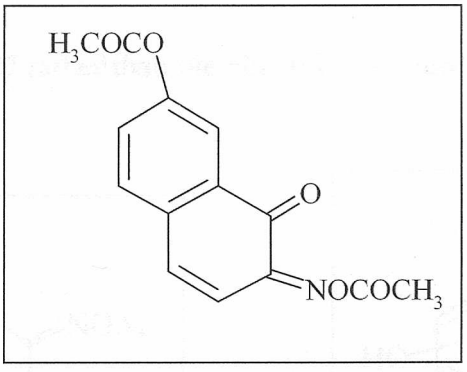


3.25

3.2.3 Characterisation of acylated compound derived from 7-hydroxy-1,2-naphthoquinone 1-oxime

When 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** react with acetic anhydride a brown solid is formed. Its IR spectrum shows two bands of ν_{CO} at 1666 and 1768 cm^{-1} and no broad band of ν_{OH} is observed (Figure 3.13). The band of ν_{CO} (quinone) appears at 1666 cm^{-1} while, the higher absorption band at 1768 cm^{-1} is assignable to ν_{CO} (acyl). The ^1H NMR spectrum exhibits 5 aromatic protons and 6 aliphatic protons due to methyl group in $OCOCH_3$ and $NOCOCH_3$ (Table 3.4).

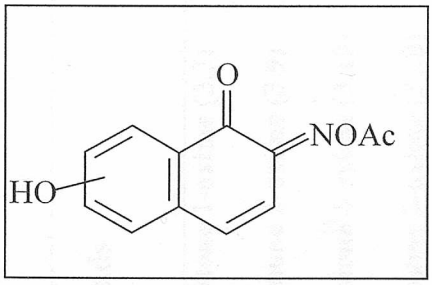
The elemental analysis of the product indicates a C : H : N ratio of 14 : 11 : 1. The mass spectrum shows a molecular ion peak at *m/z* 273 (Figure 3.27). From these data, the 1-acetoxyimino-7-acetoxy-1,2-naphthoquinone **3.26** is assigned to this di-acetoxy compound.



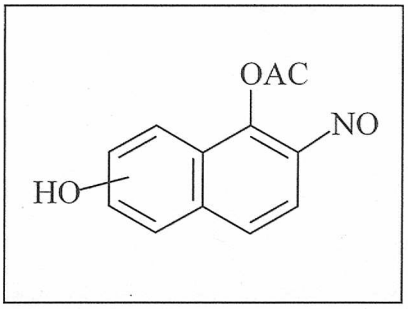
3.26

3.3 Infrared studies

During this study the IR spectra of 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9**, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** have been recorded (Figures 3.1-3.10). The IR spectra of nickel and copper complexes (Figures 3.29-3.34) of the above oximes and their acylated derivatives (Figures 3.11-3.13) are also recorded. They exhibit a strong absorption band in the range of 1600–1800 cm^{-1} due to the ν_{CO} (ring) and a broad band due to ν_{OH} in the range of 3450–3050 cm^{-1}. These observations indicate that the parent compounds and their derivates have quinone oximic rather than nitrosophenolic structure. In the case of the acylated derivatives additional absorption appears due to ν_{CO} (acyl), which in all cases appears higher than that of the ν_{CO} (ring) as shown in (Table 3.1). The presence of two ν_{CO} absorptions in the acylated derivatives suggests that these compounds have oximic structure **3.27** rather than the phenolic structure **3.28**.



3.27

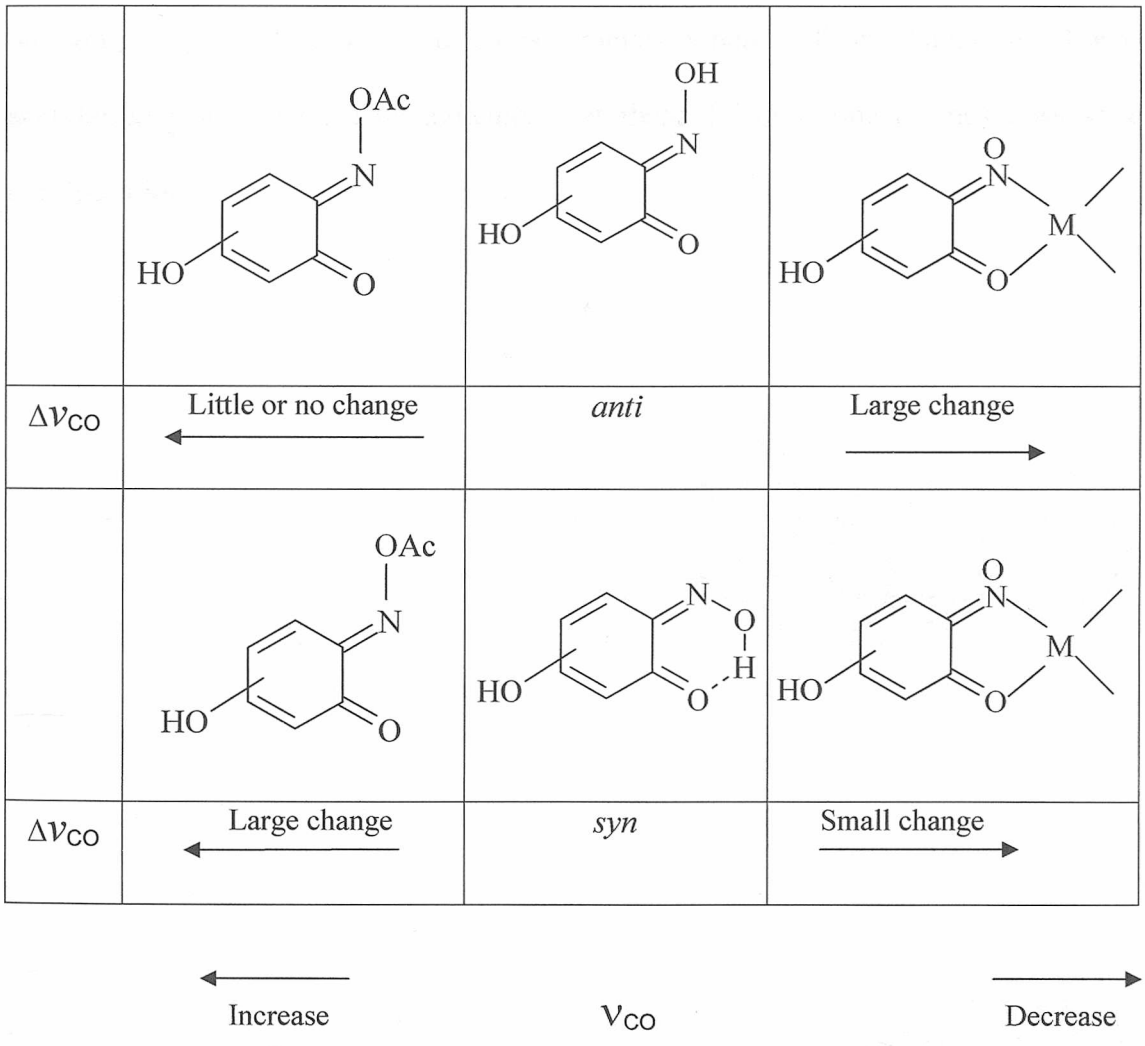


3.28

Table 3.1 ν_{CO} absorption in 1,2-, 1,4-oximes, copper(II) and nickel(II) complexes and acylated derivatives

Compounds	1,2-Oxime	1,4-Oxime	Acylatd 1,2-oxime		Copper complex	Nickel complex	Configuration
	ν_{CO} (ring)	ν_{CO} (ring)	ν_{CO} (ring)	ν_{CO} (acyl)	ν_{CO} (ring)	ν_{CO} (ring)	of qoH
7-Hydroxy-1,2-naphthoquinone 1-oxime (3.3)	1650	-	1666	1768	1600	1602	*anti*
6-Hydroxy-1,2-naphthoquinone 2-oxime (3.9)	1647	-	1660	1770	1605	1607	*anti*
6-Hydroxy-1,4-naphthoquinone 4-oxime (3.10)	-	1638	-	-	-	-	*anti*
5-Hydroxy-1,2-naphthoquinone 2-oxime (3.18)	1659	-	1684	1779	1603	1606	*anti*

The IR spectroscopy has been used as a convenient method for establishing the *syn/anti* configuration of 1,2-quionone oximes by consideration of their ν_{CO} and the $\Delta\nu_{CO}$ observed on complexation to the transition metals and their acylated derivatives (Scheme 3.8).



Scheme 3.8

For quinone oxime with *syn* configuration, the ν_{CO} appears lower than in their *anti* analogues due to intramolecular hydrogen-bonding. Therefore, the lowering of ν_{CO} on complexation is expected to be relatively small whereas a considerable increase in ν_{CO} is expected on acetylation. In contrast, in the case of quinone oxime having *anti*

configuration a large shift of ν_{CO} is expected on complexation to the metal whereas little or no change is expected on acetylation. Similar trends are showed by 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** and 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3**. These compounds show a considerable lowering of ν_{CO} on complexation to nickel and copper metals whereas little change is observed on acetylation (Table 3.1). This indicates that these 1,2-quionone oximes possess an *anti* configuration.

Fig 3.1 IR spectrum of 7-hydroxy-1,2-naphthoquinone 1-oxime (1:1)

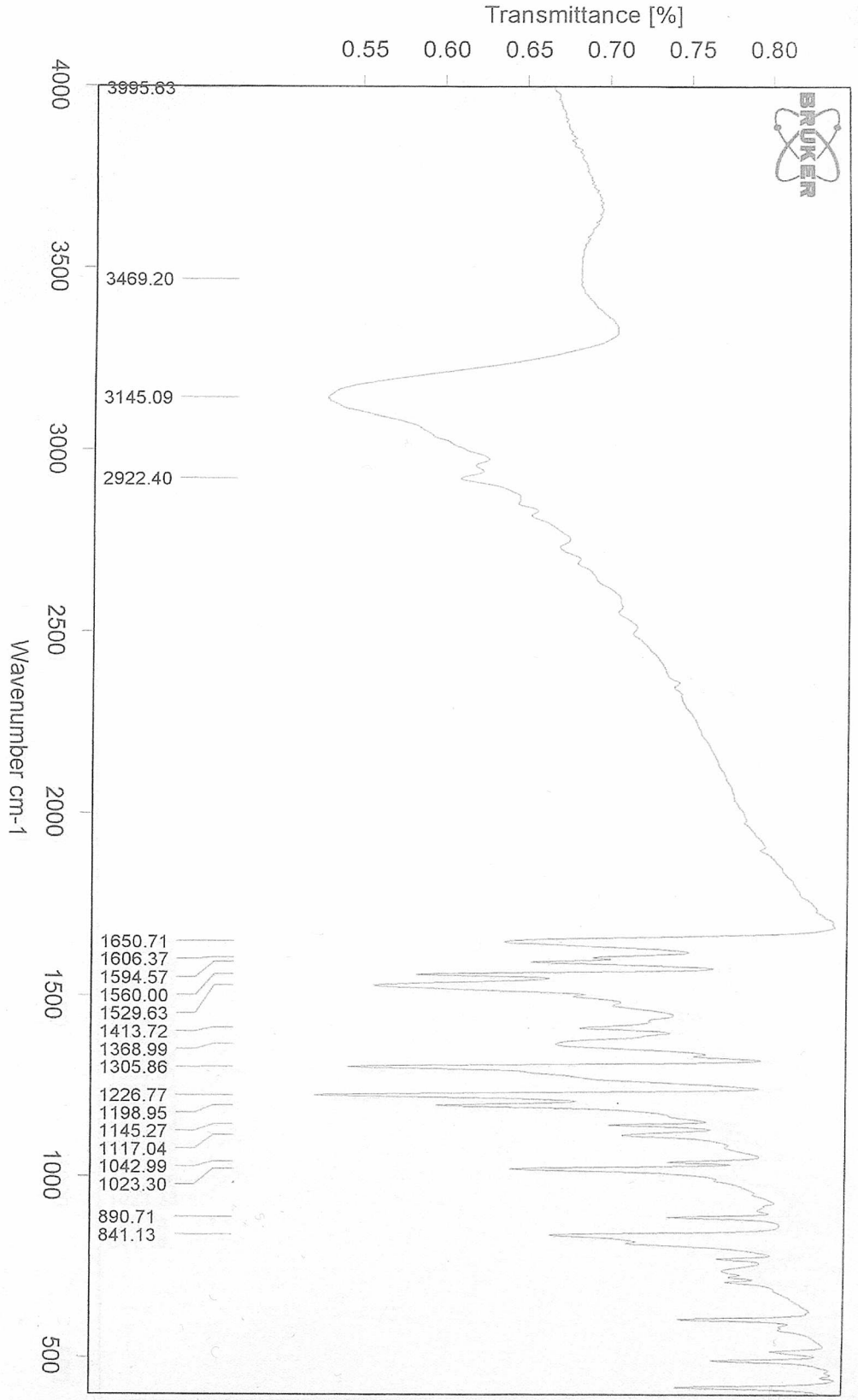


Fig 3.2 IR spectrum of 7-hydroxy-1,2-naphthoquinone 1-oxime (1:2.50)

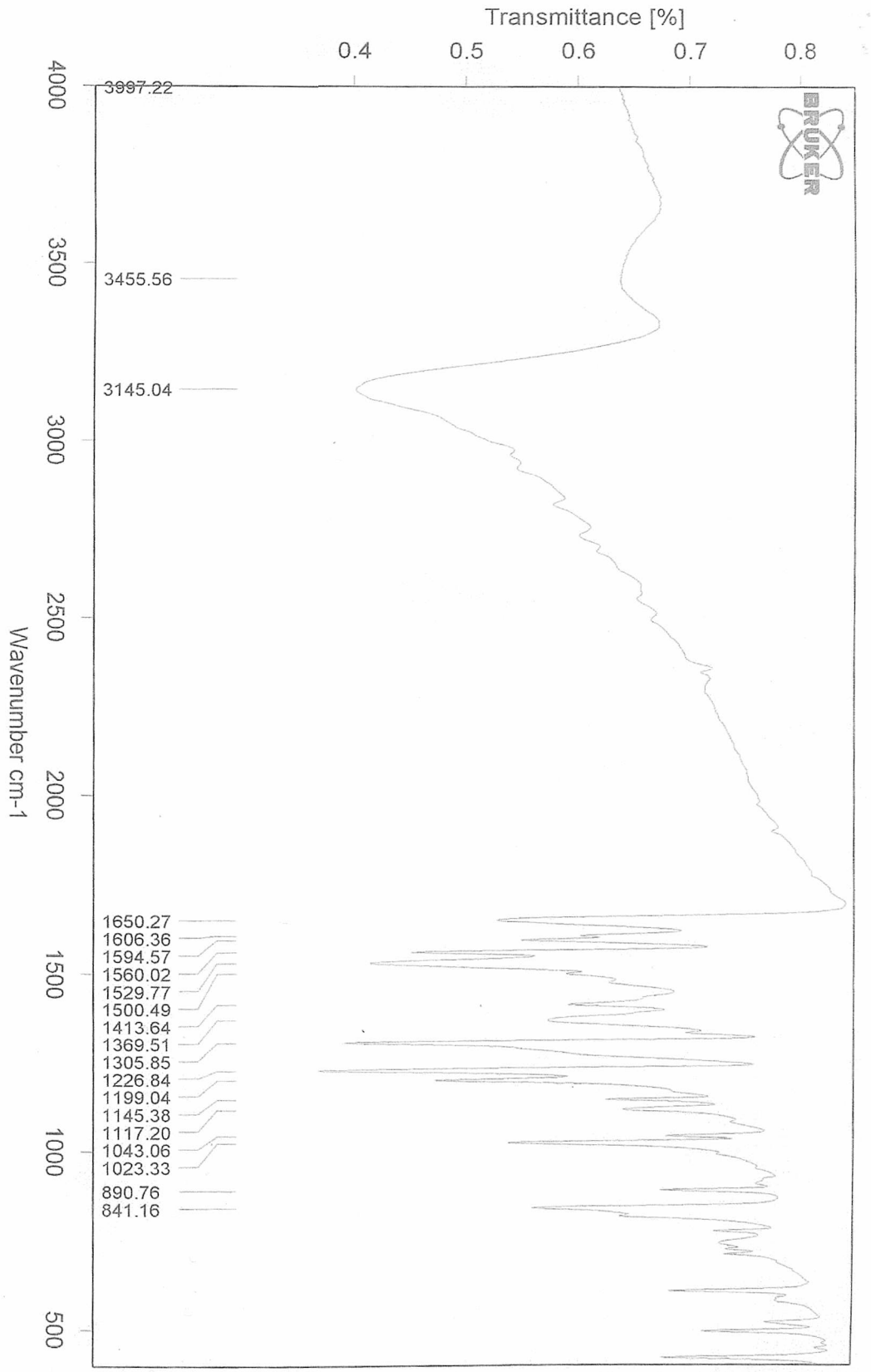


Fig 3.3 IR spectrum of 7-hydroxy-1,2-naphthoquinone 2-oxime from nickel(II) complex acidification

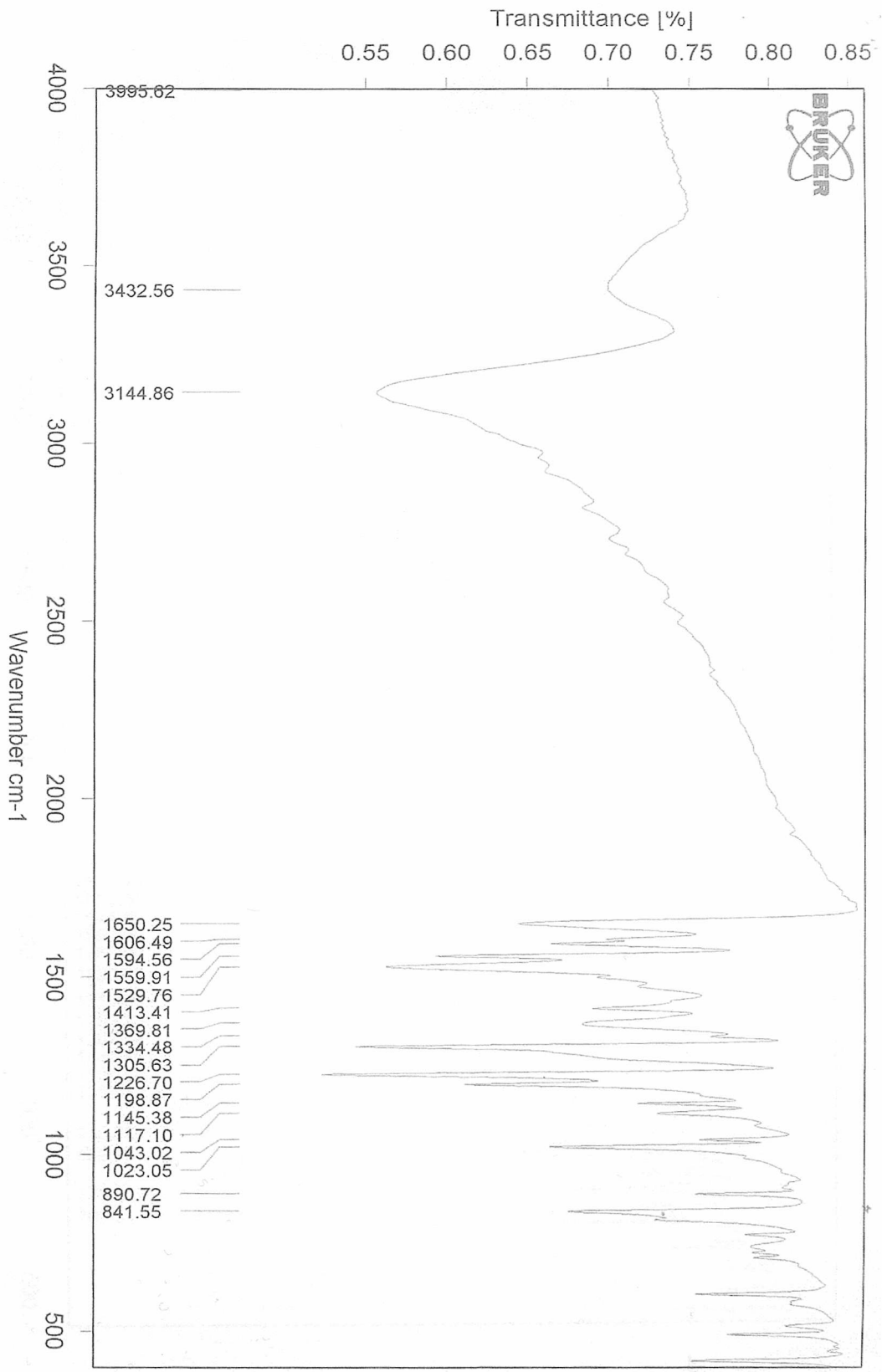


Fig 3.4 IR spectrum of 6-hydroxy-1,2-naphthoquinone 2-oxime (1:1)

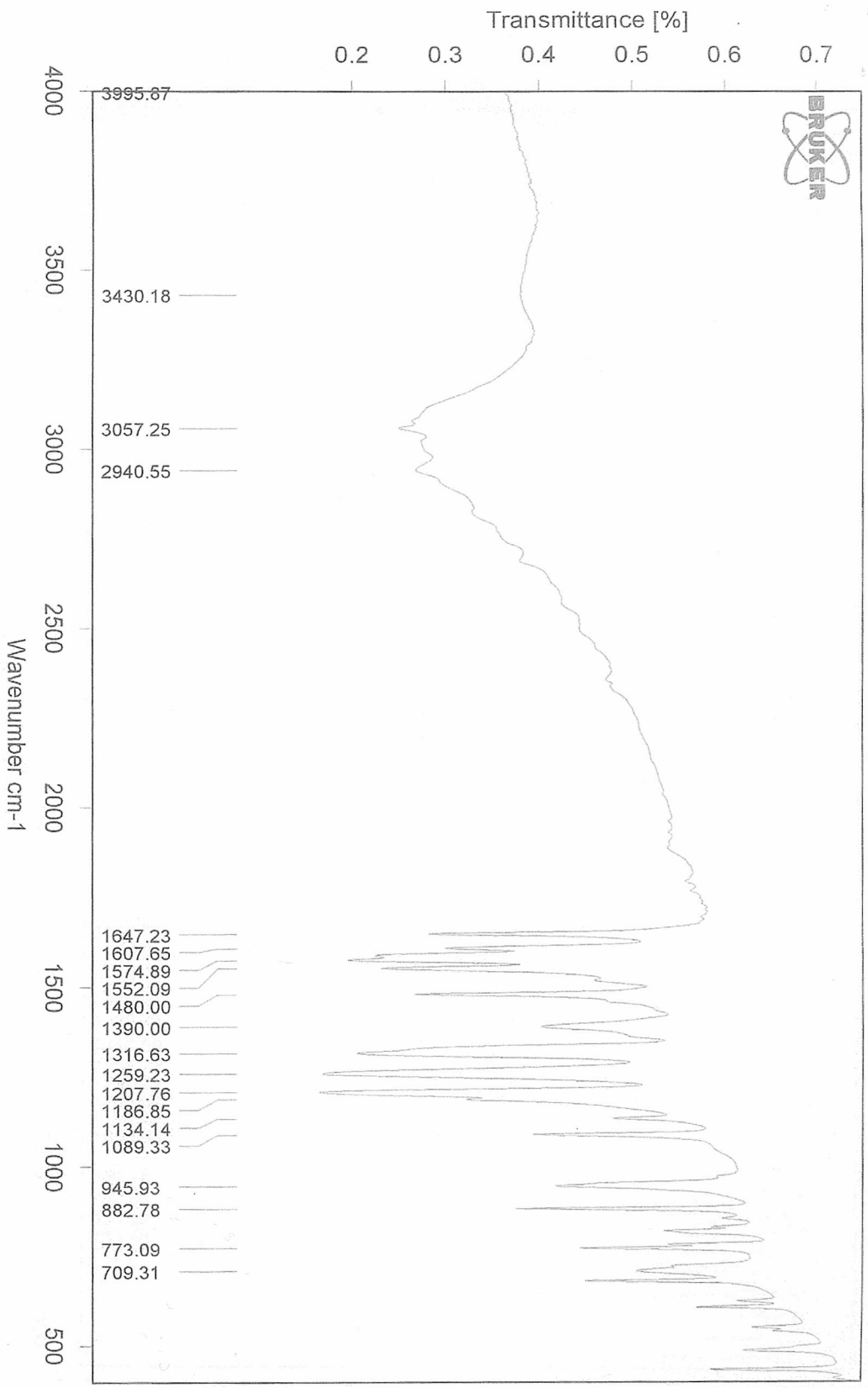


Fig 3.5 IR spectrum of 6-hydroxy-1,2-naphthoquinone 2-oxime (1:2.5)

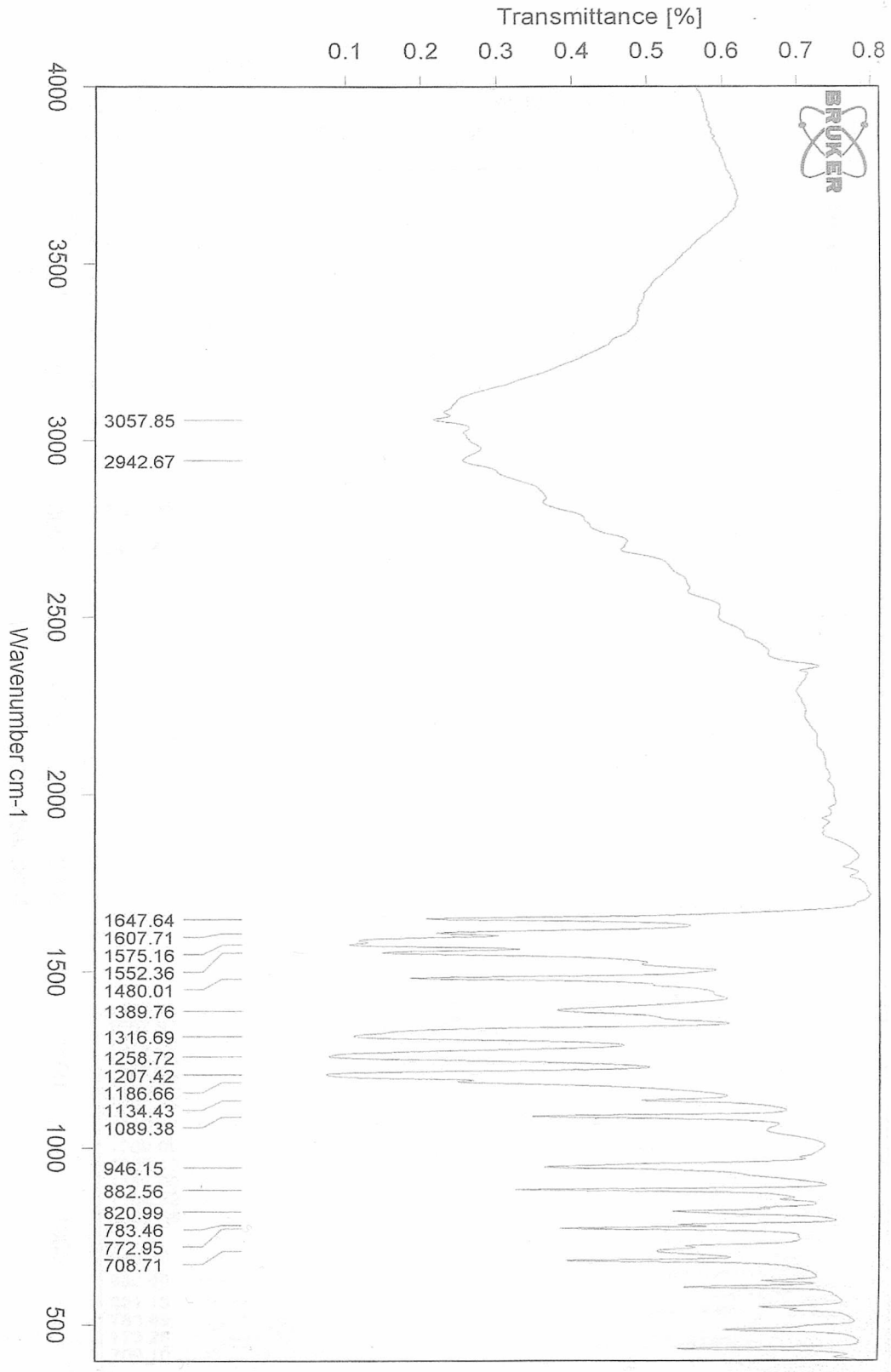


Fig 3.6 IR spectrum of 6-hydroxy-1,2-naphthoquinone 2-oxime from nickel(II) complex acidification

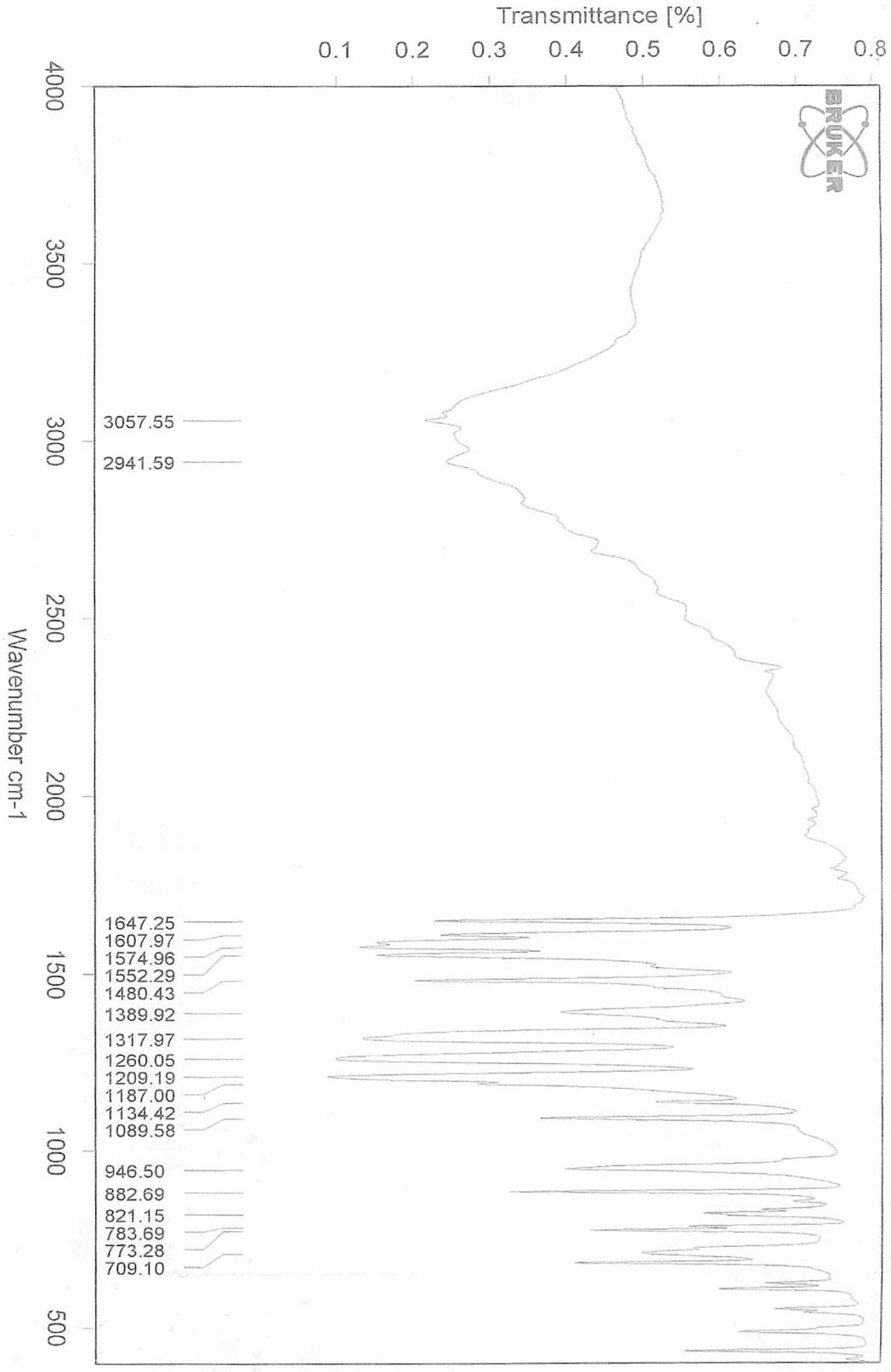


Fig 3.7 IR spectrum of 6-hydroxy-1,4-naphthoquinone 4-oxime (1:1)

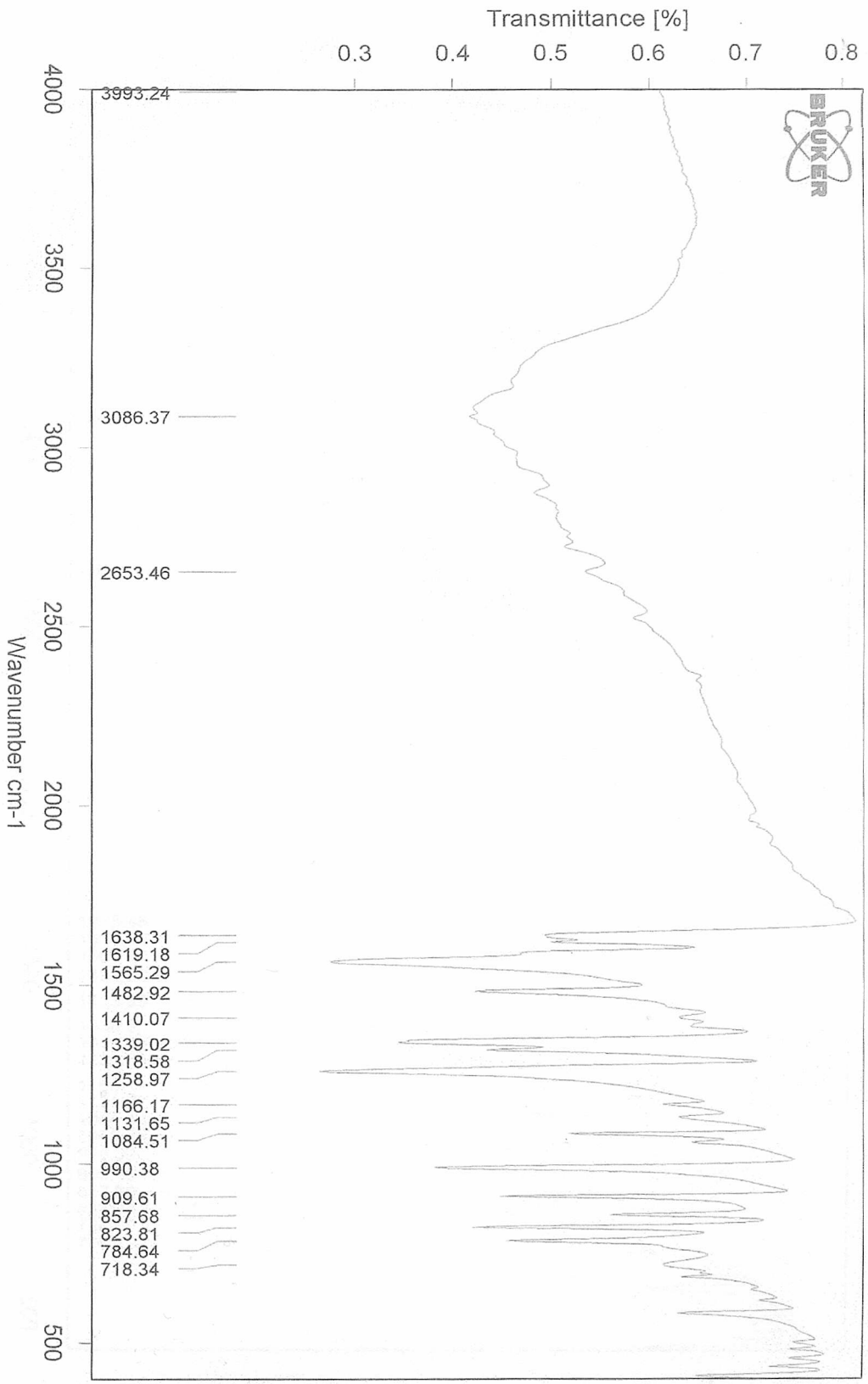


Fig 3.8 IR spectrum of 6-hydroxy-1,4-naphthoquinone 4-oxime (1:2.5)

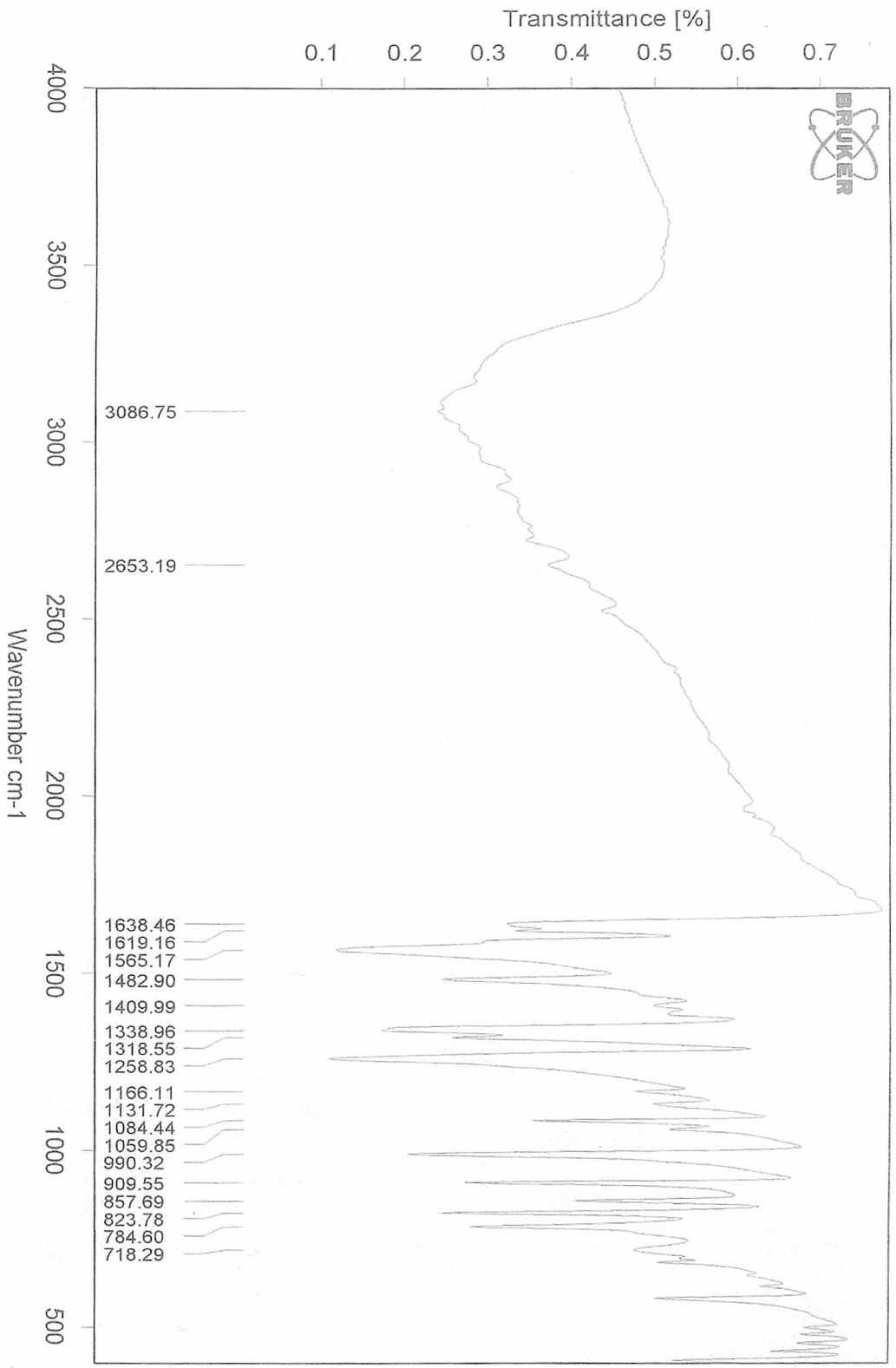


Fig 3.9 IR spectrum of 5-hydroxy-1,2-naphthoquinone 2-oxime (1:1)

Fig 3.10 IR spectrum of 5-hydroxy-1,2-naphthoquinone 2-oxime (1:2.5)

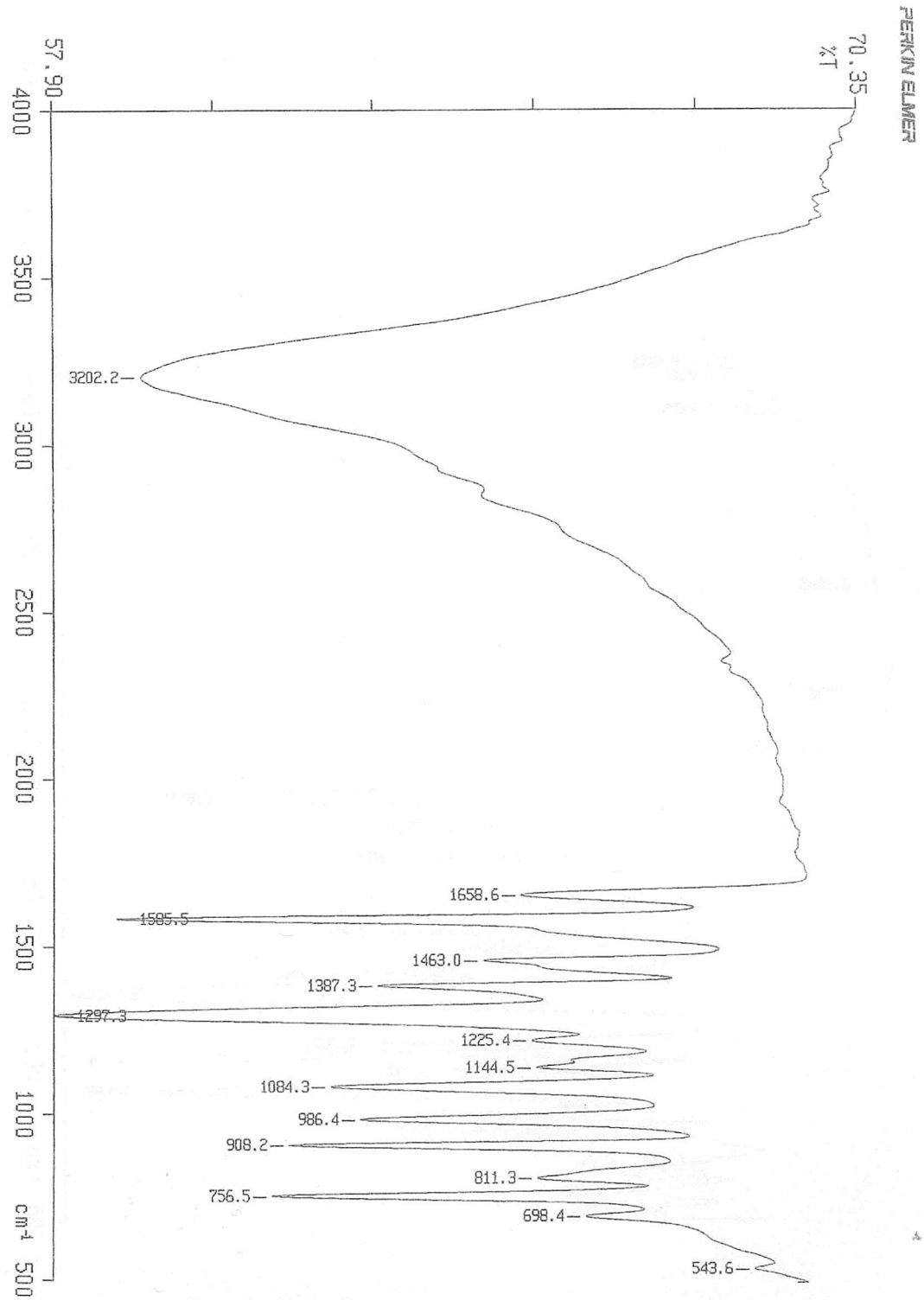


Fig 3.11 IR spectrum of 2-acetoxyimino-5-acetoxy-1,2-naphthoquinone

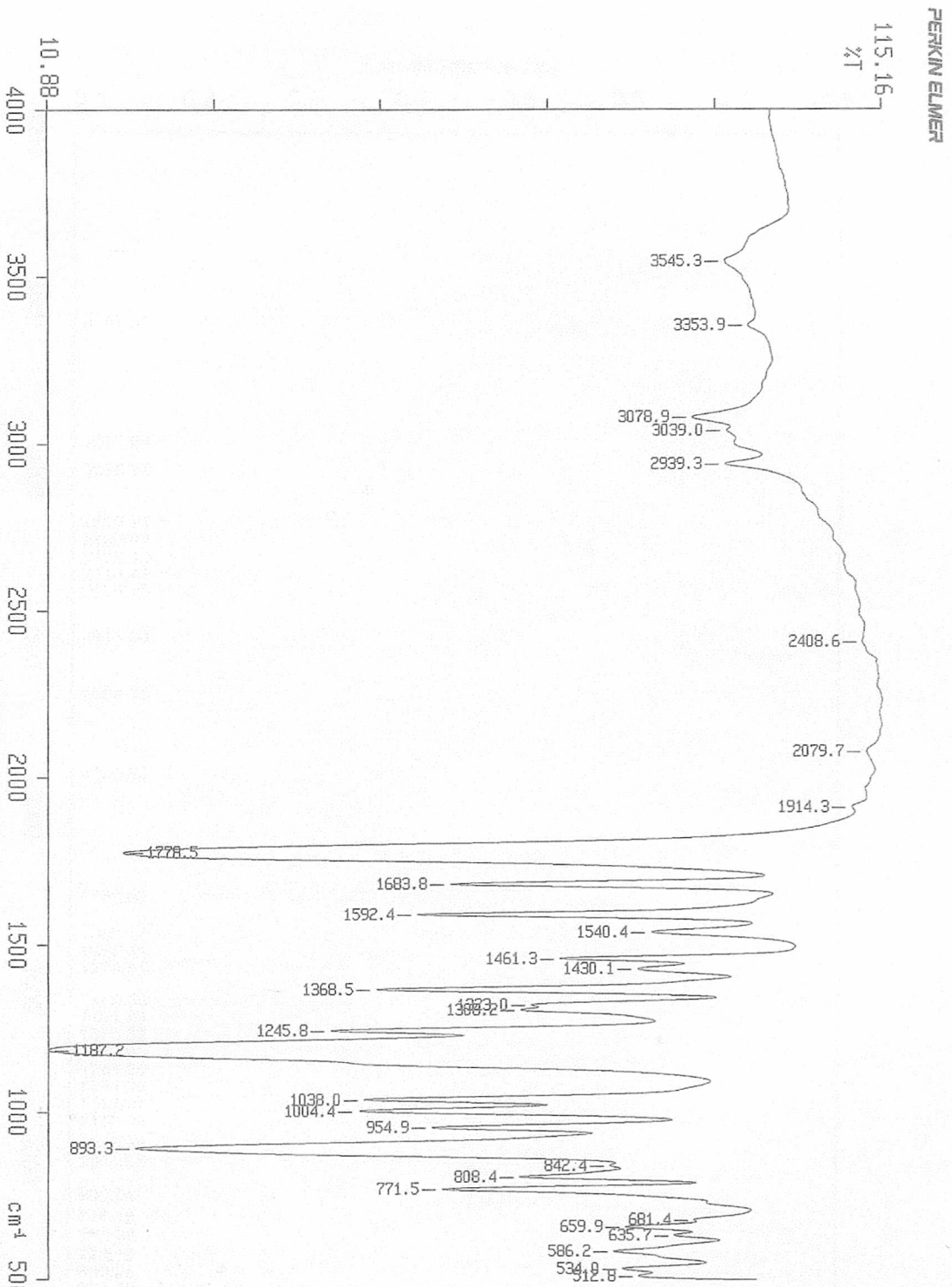


Fig 3.12 IR spectrum of 2-acetoxyimino-6-hydroxy-1,2-naphthoquinone

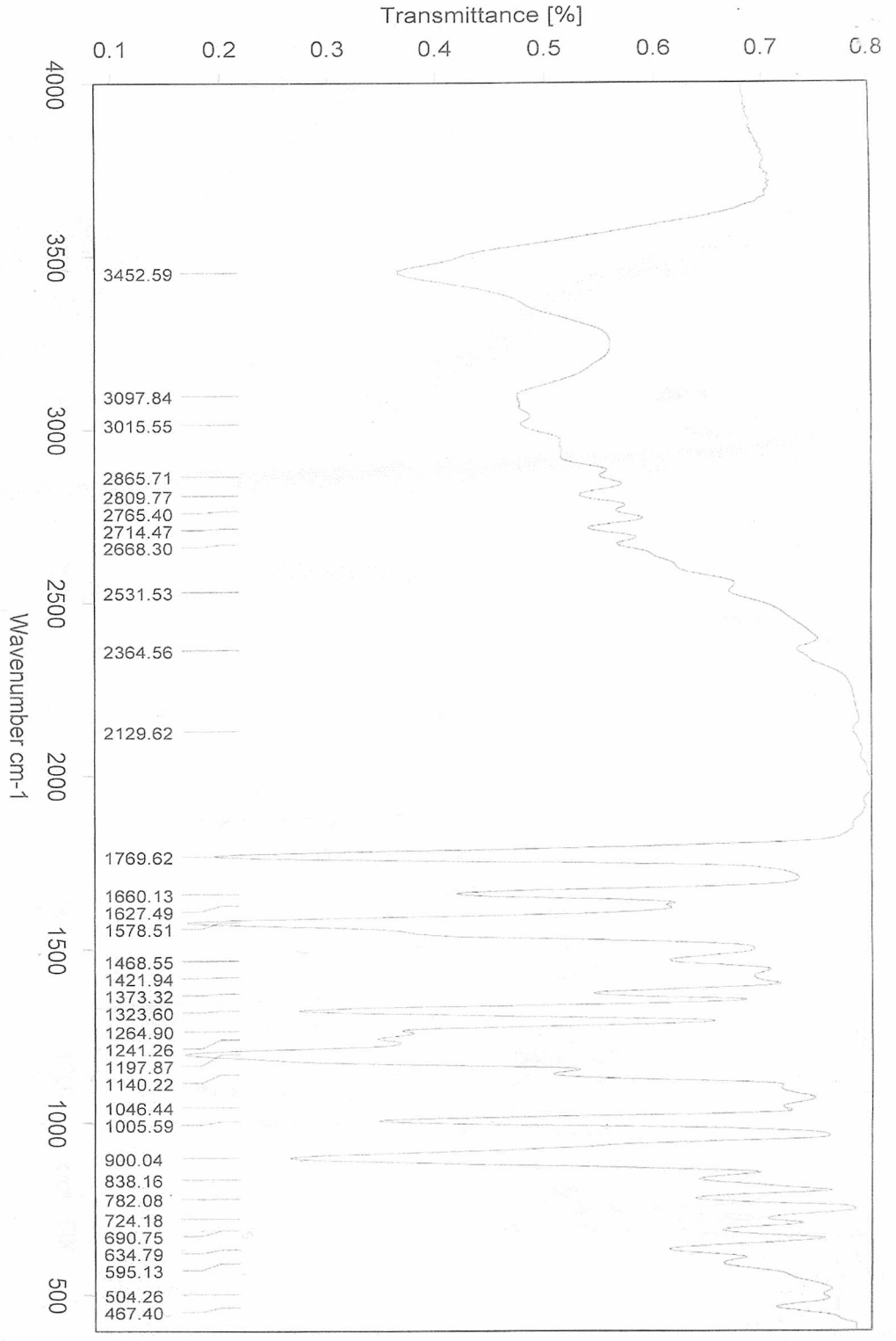
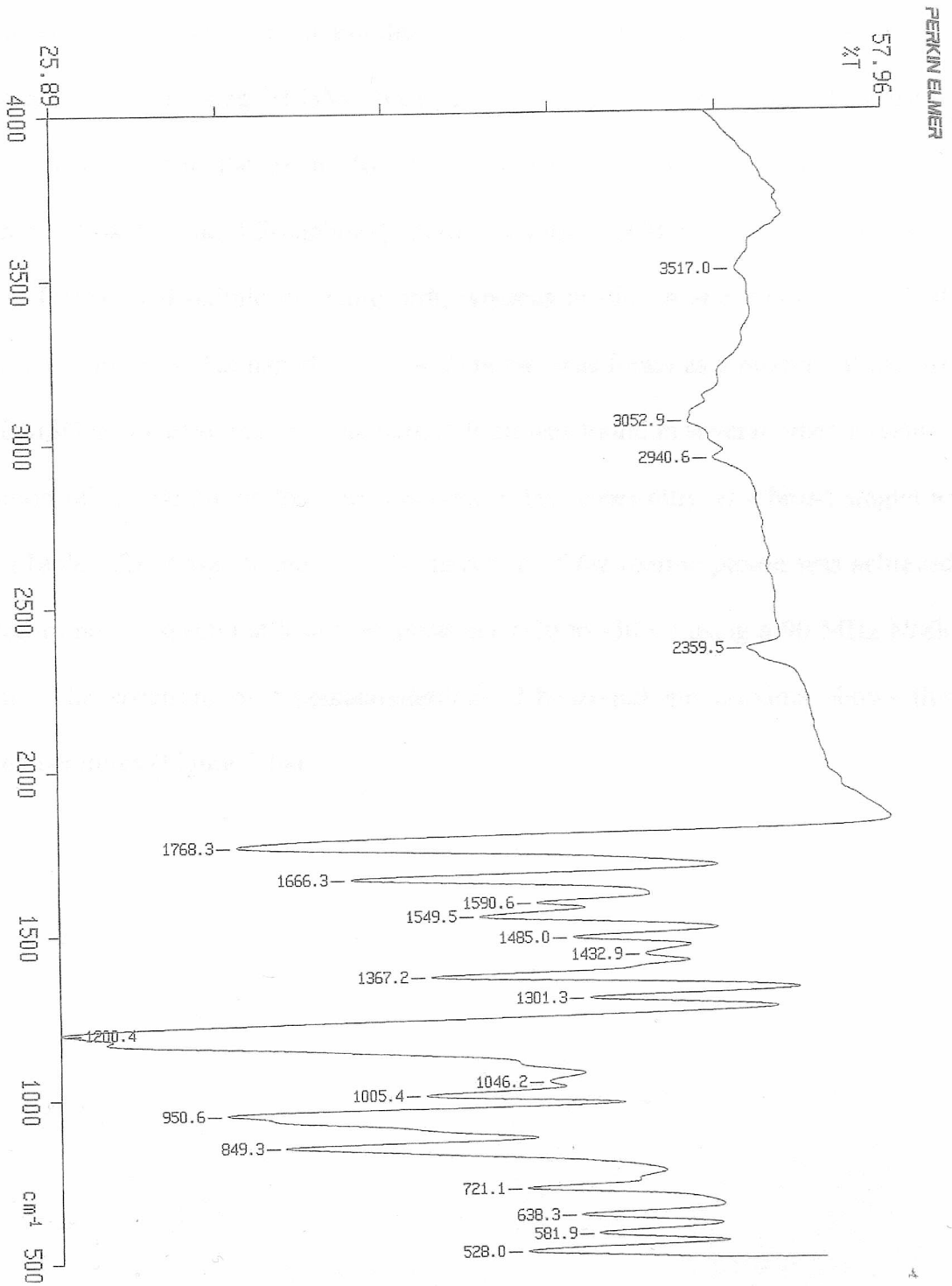


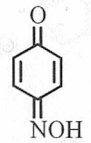
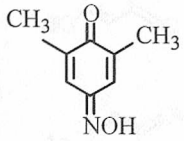
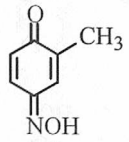
Fig 3.13 IR spectrum of 1-acetoxyimino-7-acetoxy-1,2-naphthoquinone



3.4 Nuclear magnetic resonance studies

Several workers have studied the possibility of phenolic-oximic tautomerism in quinone monooximes in solution using ^{1}H NMR techniques.[1, 3-6] as shown in (Table 3.2). Most of these compounds exist in the oxime form irrespective of the solvent used except 1,4-benzoquinone 4-oxime and 1,2-naphthoquinone 2-oxime. 1,4-Benzoquinone 4-oxime is phenolic in DMSO and oximic in chloroform, whereas in dioxan and diethyl ether both forms coexist.[5] Similarly, 1,2-naphthoquinone 2-oxime, was found as a mixture of the two forms in DMSO/acetic acid, but only the oximic form was found in several other solvents.[4] The detection of the oximic proton was observed in few cases only as a broad singlet as shown in (Table 3.2). It was found that, the detection of the oximic proton was achieved only by recording the spectra at lower temperatures (-20 to -50°C) using a 90 MHz NMR instrument.[2] The spectrum of 5-pentanoylamino-1,2-benzoquinone 2-oxime shows this variable temperatures (Figure 3.14).

Table 3.2 ^{1}H NMR studies of quinone monooximes

Compound	Solvent	Tautomer	Oximic proton δ (ppm)	Ref.
	DMSO	Phenol	-	5
	Chloroform	Oxime	-	5
	Dioxan	Oxime (83%) Phenol (17%)	-	6
	Diethyl ether	Oxime (83%) Phenol (17%)	-	6
	DMSO	Oxime	-	5, 6
	Chloroform	Oxime	-	6
	Dioxan	Oxime	-	6

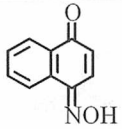
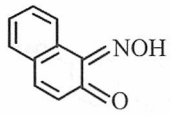
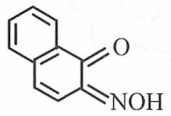
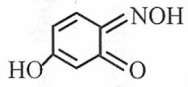
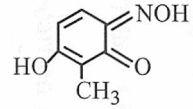
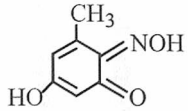
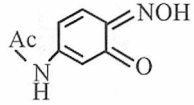
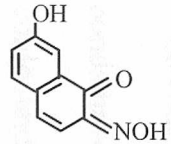
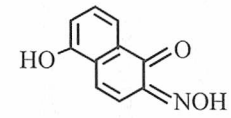
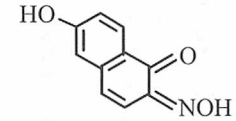
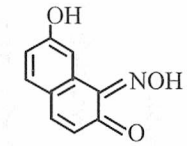
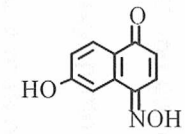
Compound	Solvent	Tautomer	Oximic proton δ (ppm)	Ref.
	Dioxan	Oxime	-	6
	DMSO	Oxime	-	4
	HMPA	Oxime	17.00	
	Chloroform	Oxime	17.33	
	Dioxan	Oxime	-	
	DMSO/Acetic acid (5%)	Oxime	-	
	DMSO	Oxime	-	4
	DMSO/Dioxane	Oxime (80%) Phenol (20%)	-	
	DMSO/Acetic acid (5%)	Oxime (80%) Phenol (20%)	-	

Table 3.2 cont.

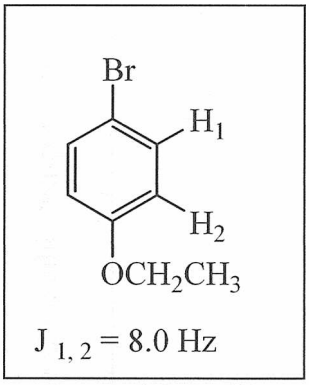
Compound	Solvent	Tautomer	Oximic proton δ (ppm)	Reference
	DMSO	Oxime	13.55	1
	DMSO	Oxime	13.43	1
	DMSO	Oxime	9.14	1
	DMSO	Oxime	13.10	3
	DMSO	Oxime	13.50	2

Compound	Solvent	Tautomer	Oximic proton δ (ppm)	Ref.
	DMSO	Oxime	13.54	This study
	DMSO	Oxime	13.97	This study
	Chloroform	Oxime	17.73	This study
	DMSO	Oxime	12.99	This study

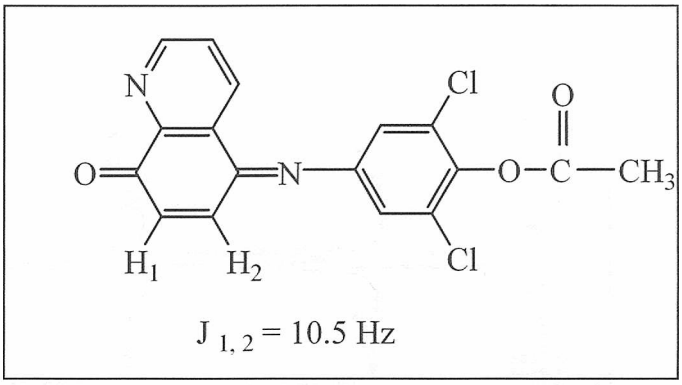
In this study 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9**, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** are investigated by ^{1}H NMR spectroscopy. All ^{1}H NMR measurements are recorded at room temperature using 250 MHz and 400 MHz instruments (Figures 3.15-3.17). The deuterated solvents which have been used are dimethylsulphoxide (d_6-DMSO) and chloroform (d_1-$CDCl_3$). The ^{1}H NMR spectra obtained for 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9**, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** are agreed with those reported previously (Table 3.3). Evidence that the compounds exist as naphthoquinone monooximes comes from the fact that two hydroxyl protons are observed. If the compounds have a nitroso naphthol structure then both acidic protons would be very similar and hence have similar chemical shifts. However, for these compounds two acidic protons are observed at *ca.* 10.50 ppm and 13.50 ppm (Table 3.3), suggesting the presence of two different OH groups and hence of an oximic structure. In case of 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9** and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** the detection of oximic (NOH) and phenolic (OH) protons using 250 MHz instrument showed a broad single peak (Figures 3.16 and 3.17). When, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** is recorded by 400 MHz instrument, the oximic proton appears clearly as a single peak whereas, the phenolic proton observed as a single broad peak (Figure 3.15).

Further evidence for the quinone oximic structure is provided by consideration of the values of ortho coupling constant (J_{ortho}). Aromatic carbon-carbon bonds have less double bond character than carbon-carbon double bonds in quinone type compounds and hence, are longer. As a result, the ortho coupling constant is less for a benzenoid system, e.g. **3.29**,

than for a quinoid system, e.g. **3.30**. [7, 8] Typically, the value for J_{ortho} for a benzenoid system is *ca.* 8 Hz whereas for a quinoid system is *ca.* 10.5 Hz.



3.29



3.30

The ortho coupling constants observed for 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18**, 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9**, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** are *ca.* (9.6–10.6 Hz), suggesting that in these compounds the bonds are quinonoidal in character (Table 3.3). In addition the chemical shifts of the aromatic proton in the α-position for 5-hydroxy-1,2-benzoquinone 2-oxime **3.18** and 6-hydroxy-1,2-benzoquinone 2-oxime **3.9** or in the β-position for 7-hydroxy-1,2-benzoquinone 1-oxime **3.3** and 6-hydroxy-1,4-benzoquinone 4-oxime **3.10** appear at low field indicating that these protons are highly deshielded as a consequence of the electron withdrawing effect of the neighbouring carbonyl and oximic groups as shown in (Table 3.3).

Fig 3.14 ^{1}H NMR spectra of 5-pentanoylamino-1,2-quinone 2-oxime at variable temperature[2]

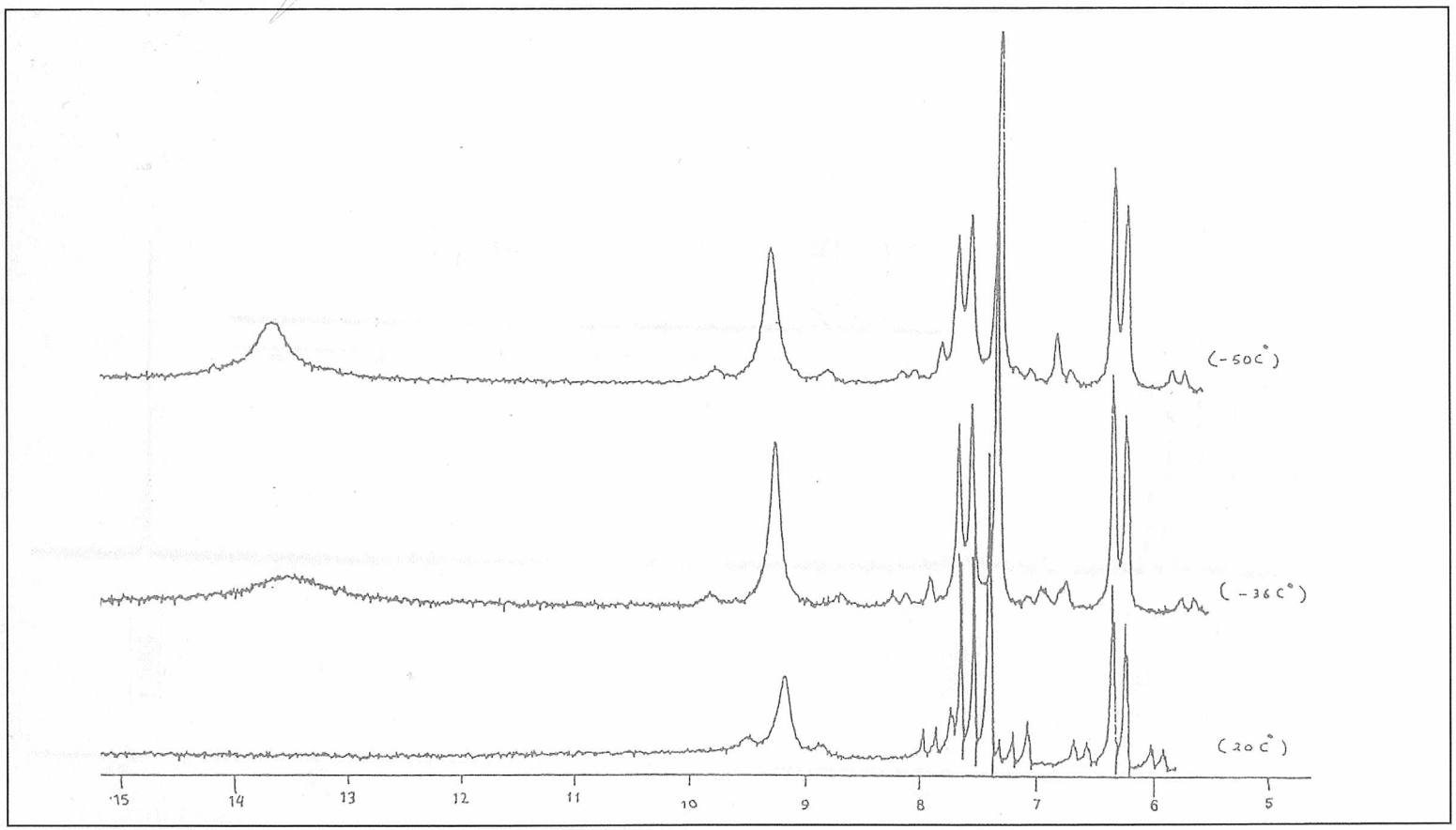


Fig 3.15 ^{1}H NMR spectra of 7-hydroxy-1,2-naphthoquinone 1-oxime in d_1-$CDCl_3$

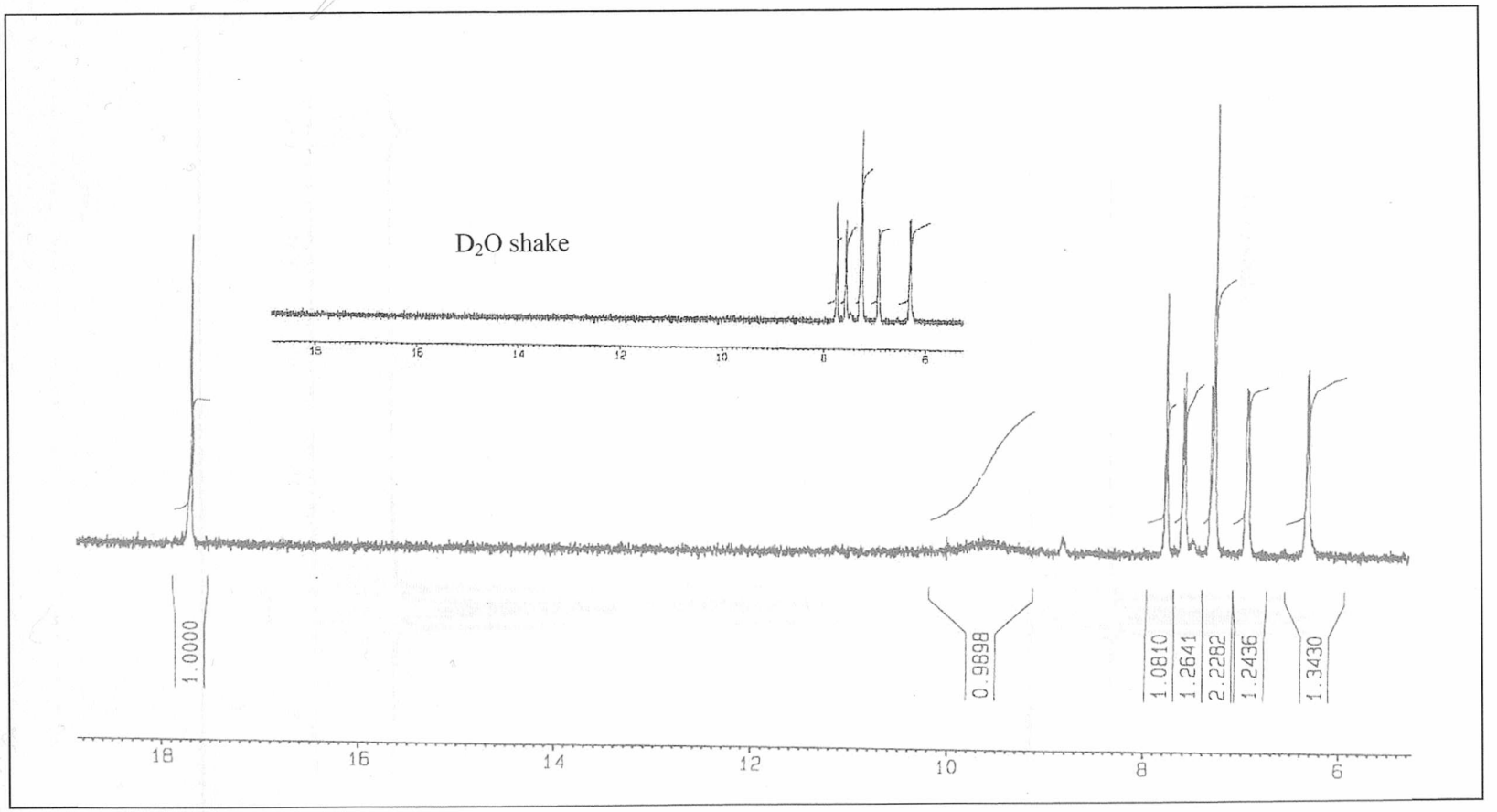


Fig 3.16 ^{1}H NMR spectra of 5-hydroxy-1,2-naphthoquinone 2-oxime in d_6-DMSO

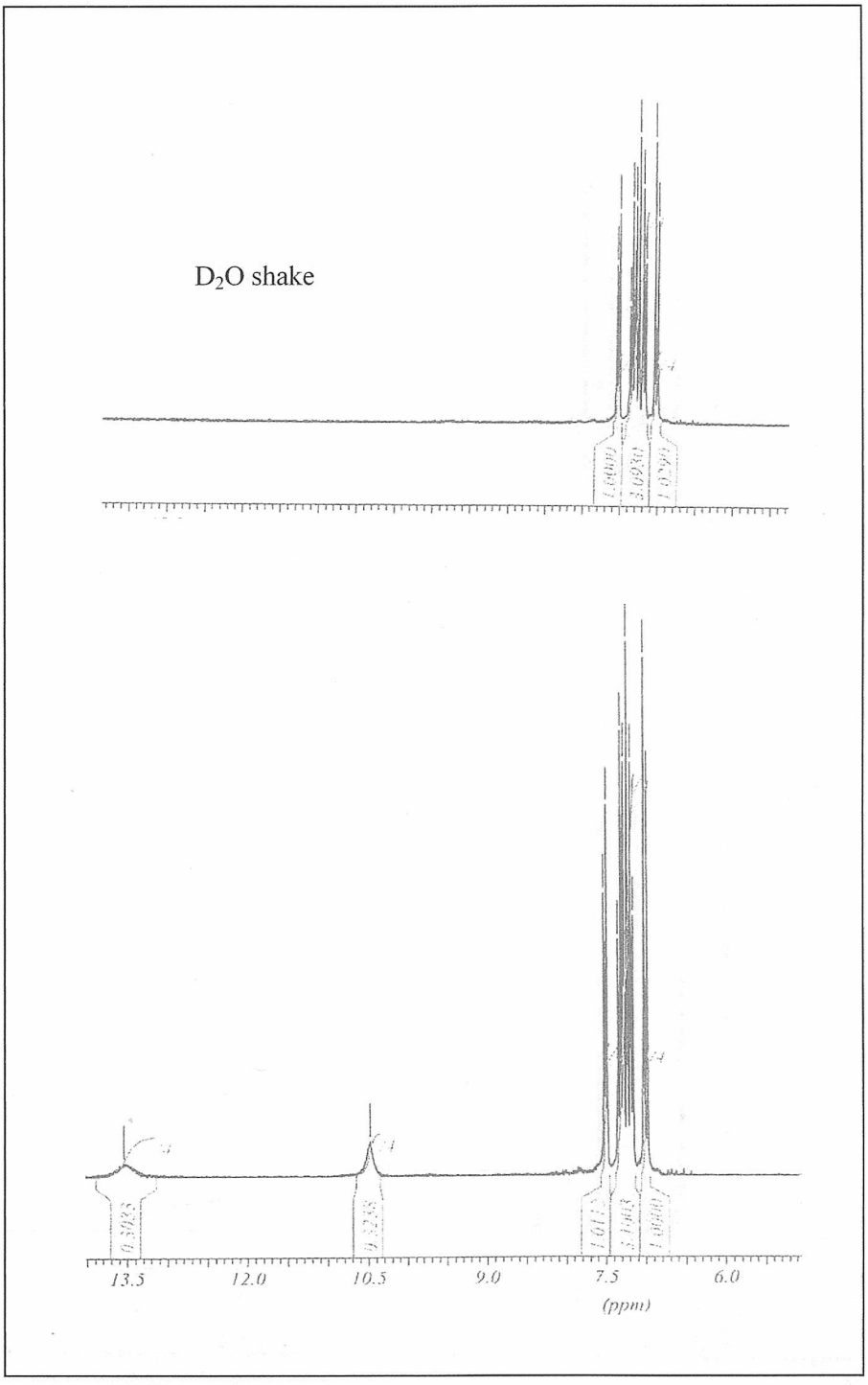


Fig 3.17 ^{1}H NMR spectra of 6-hydroxy-1,4-naphthoquinone 4-oxime in d_6-DMSO

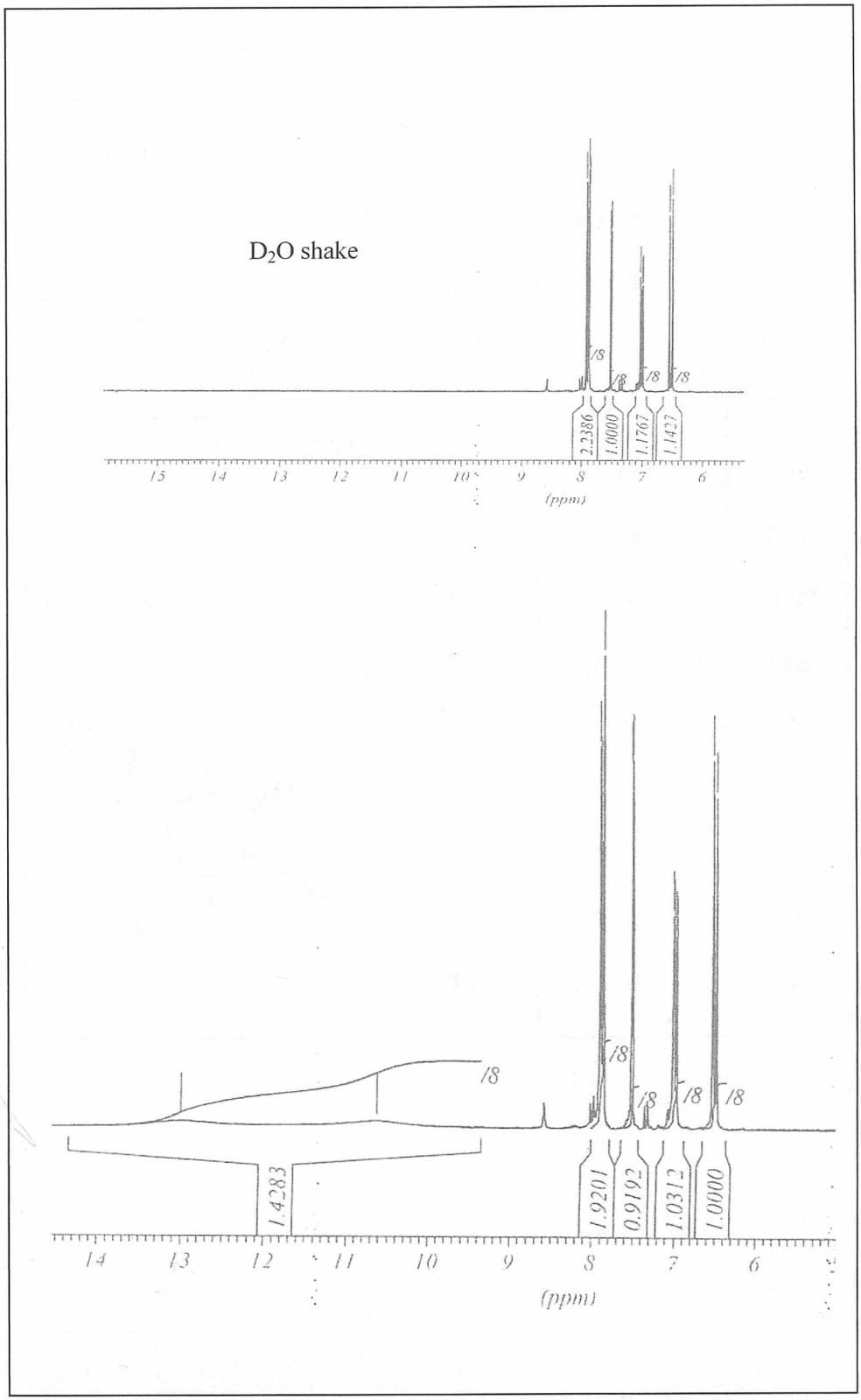


Table 3.3 ^{1}H NMR of hydroxynaphthoquinone monooximes

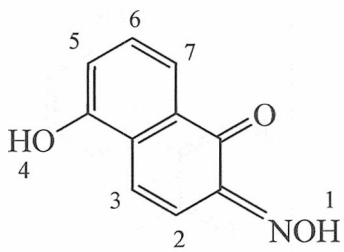
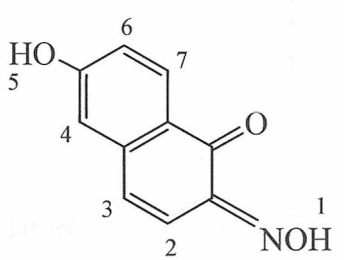
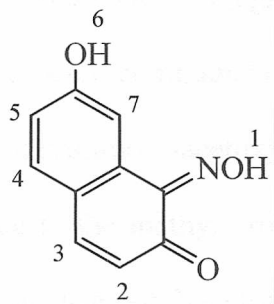
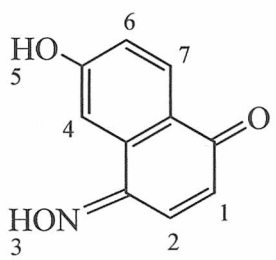
Compound	At 20°C		
	Assignment	Multiplicity	δ ppm
This study  **3.18**	1	s	13.54
	2	d ($J_{2,3}$ = 10.5)	7.26
	3	d	7.01
	4	s	10.48
	5	d	7.18
	6	dd	7.32
	7	d	7.51
This study  **3.9**	1	s	13.97
	2	d ($J_{2,3}$ = 9.6)	7.66
	3	d	6.24
	4	s	8.38
	5	s	10.22
	6	dd	6.96
	7	d	7.46

Table 3.3 cont.

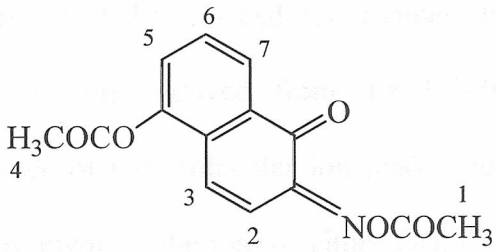
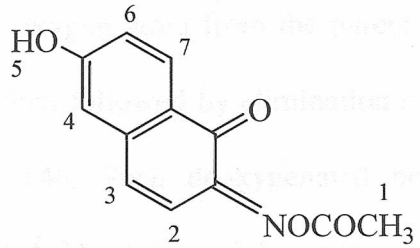
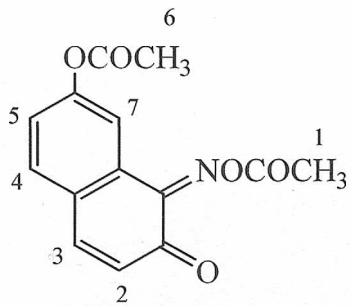
Compound	At 20°C		
	Assignment	Multiplicity	δ ppm
This study  **3.3**	1	s	17.73
	2	d ($J_{2,3}$ = 9.5)	6.35
	3	d	7.60
	4	d	7.32
	5	dd	6.97
	6	s	10.01
	7	s	7.78
This study  **3.10**	1	d ($J_{1,2}$ = 10.65)	6.51
	2	d	7.89
	3	s	12.99
	4	d	7.52
	5	s	10.62
	6	dd	6.99
	7	d	7.88

s = singlet d = doublet dd = double doublet

In this study the compounds obtained by acylation of the 1,2-oximes have provided the conclusion that the 1,2-oximes have oximic structure rather than nitrosophenolic. In their ^{1}H NMR spectra (Table 3.4) the chemical shift of the proton in the α-position for 1-isomer form and in the β-position for 2-isomer form appears at low field due to the deshielding effect of the CO and $NOCOCH_3$ groups.

In case of di-acetoxy compounds such as 2-acetoxyimino-5-acetoxy-1,2-naphthoquinone **3.24** and 1-acetoxyimino-7-acetoxy-1,2-naphthoquinone **3.26**, two single peaks appeared at the up field due to the methyl groups in $OCOCH_3$ and $NOCOCH_3$ (Table 3.4). Whereas, The ^{1}H NMR spectrum of 2-acetoxyimino-6-hydroxy-1,2-naphthoquinone **3.25** as a mono-acetoxy compound, shows one single peak at the up field due to the methyl group in $NOCOCH_3$ and one single peak at low-field assignable to OH group (Table 3.4).

Table 3.4 ^{1}H NMR for acylated 1,2-oximes

Compound	Assignment	Multiplicity	δ ppm
This study  **3.24**	1	s	2.42
	2	d	7.11
	3	d	6.89
	4	s	2.40
	5	d	7.10
	6	d.d	7.30
	7	d	7.49
This study  **3.25**	1	s	2.39
	2	d	7.54
	3	d	6.19
	4	s	8.30
	5	s	10.20
	6	d.d	6.95
	7	d	7.40
This study  **3.26**	1	s	2.44
	2	d	6.29
	3	d	7.56
	4	d	7.31
	5	d.d	6.92
	6	s	2.36
	7	s	7.71

s = singlet d = doublet dd = double doublet

3.5 Mass spectrometric studies

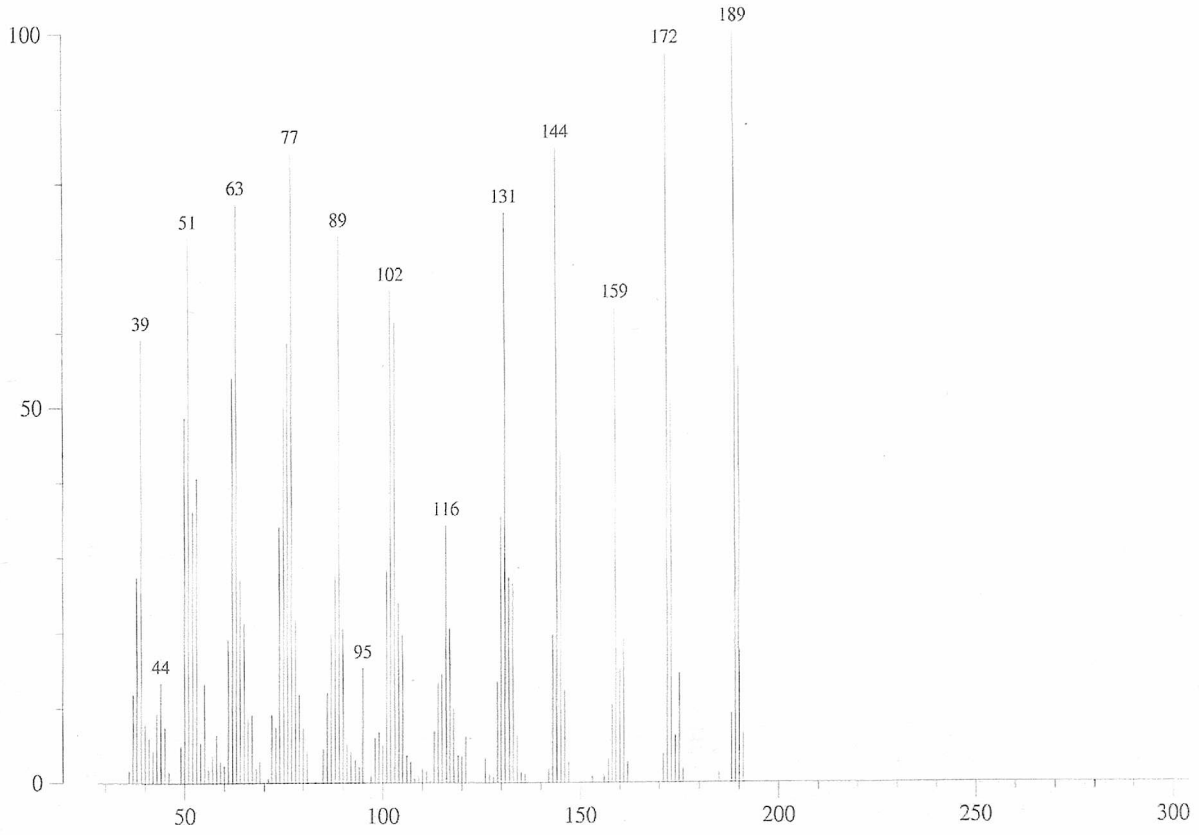
The EI mass spectra of all the 1,2- and 1,4- oximes and the acylated 1,2-oximes prepared during this study are presented in (Tables 3.5 and 3.7), respectively, and illustrated in (Figures 3.18 – 3.27)

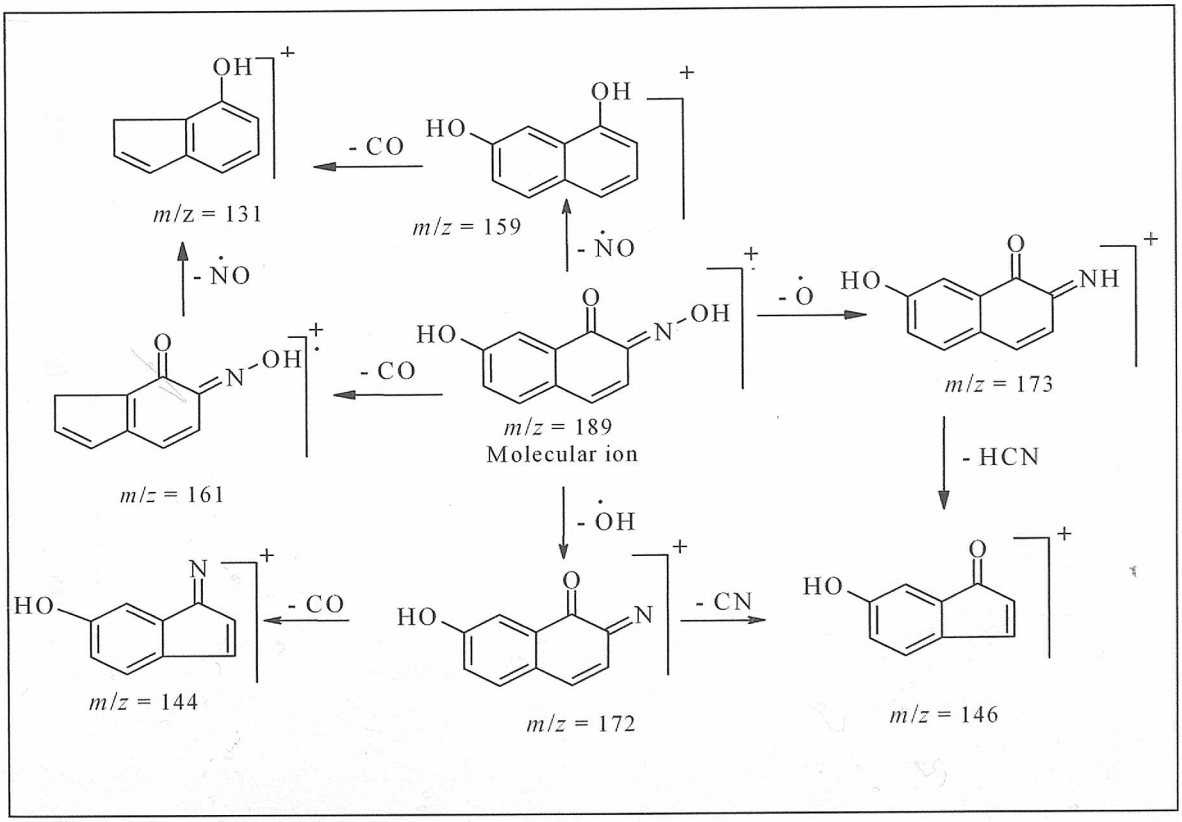
The spectra of the 1,2- and 1,4- oximes show the molecular ion peaks as the base peaks except the one derived from the 1,5-dihydroxyphthalene which shows a moderate abundance of the molecular ion peak (Figures 3.18 – 3.24). The primary fragmentation pathway involves the loss of either OH, CO or NO groups from the molecular ion to give the corresponding ion peaks at m/z = 172, 161, 159 respectively. From the relative intensities of these peaks, it seems that the ease of loss of these groups follows the sequence OH, NO then CO. The other less preferred fragmentation pathway involves the loss of an oxygen atom from the parent molecular ion to give an ion peak at m/z = 173. This was then followed by elimination of hydrogen cyanide molecule to give an ion peak at m/z = 146. Such deoxygenated behaviour is well documented for this type of compounds.[2] The principal fragmentation pathways are summarized in (Schemes 3.9 – 3.12).

Table 3.5 Ion abundance of principal ions in the EI mass spectra of 1,2- and 1,4-oximes

	5-OH-2-nqoH		6-OH-2-nqoH		7-OH-1-nqoH		6-OH-4-nqoH	
	m/z	(%)	*m/z*	(%)	*m/z*	(%)	*m/z*	(%)
M^+	189	(72)	189	(100)	189	(100)	189	(100)
$[M-O]^+$	173	(24)	173	(11)	173	(41)	173	(13)
$[M-OH]^+$	172	(66)	172	(96)	172	(97)	172	(71)
$[M-CO]^+$	161	(2)	161	(7)	161	(15)	161	(13)
$[M-NO]^+$	159	(44)	159	(29)	159	(64)	159	(12)
$[M-(O+HCN)]^+$	146	(21)	146	(5)	146	(12)	146	(19)
$[M-(OH+CN)]^+$	146	(21)	146	(5)	146	(12)	146	(19)
$[M-(OH+CO)]^+$	144	(6)	144	(69)	144	(84)	144	(33)
$[M-(NO+CO)]^+$	131	(63)	131	(47)	131	(76)	131	(48)

Fig 3.18 EI mass spectrum of 7-hydroxy-1,2-naphthoquinone 1-oxime (1:1)





Scheme 3.9

Fig 3.19 EI mass spectrum of 7-hydroxy-1,2-naphthoquinone 1-oxime (1:2.5)

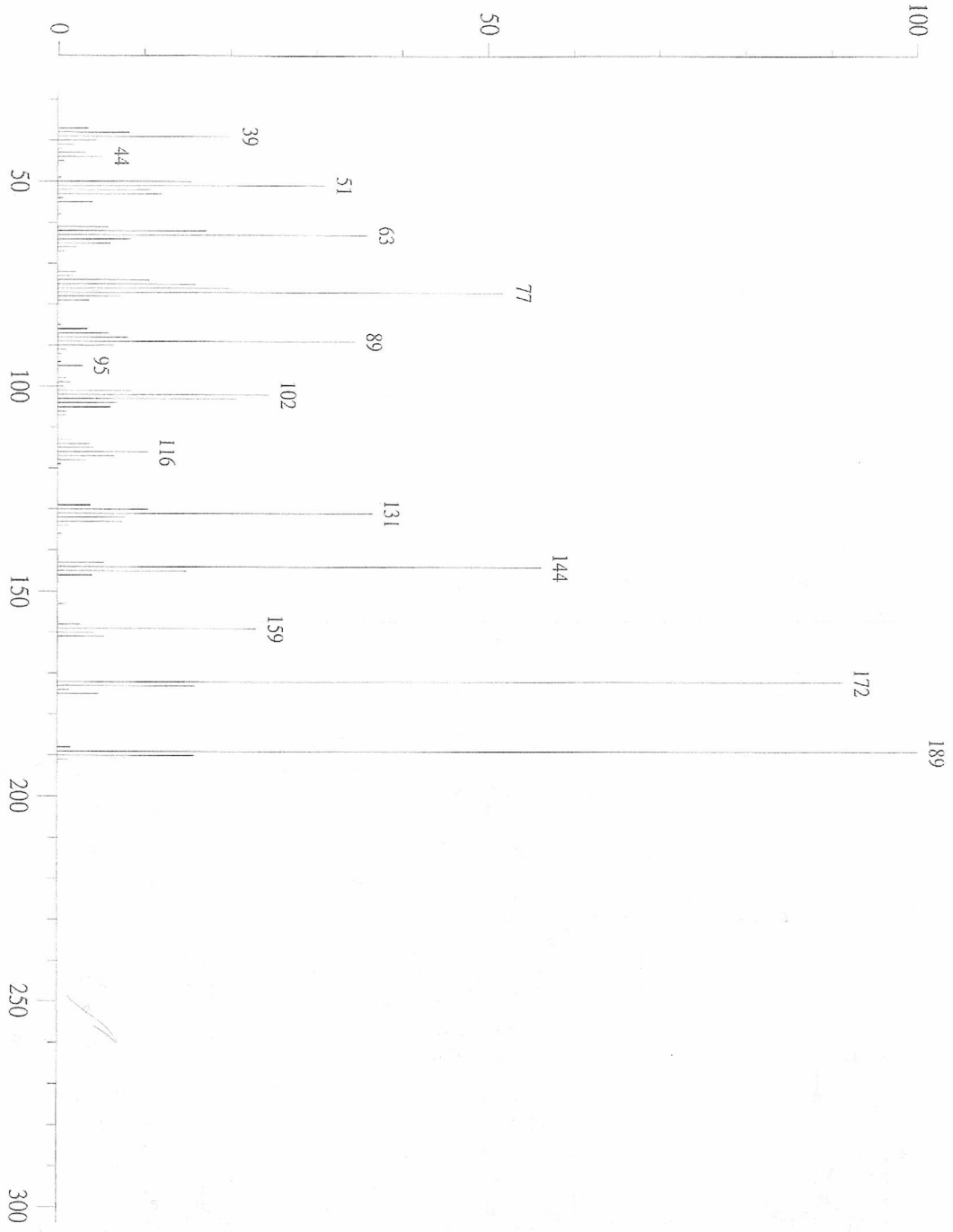
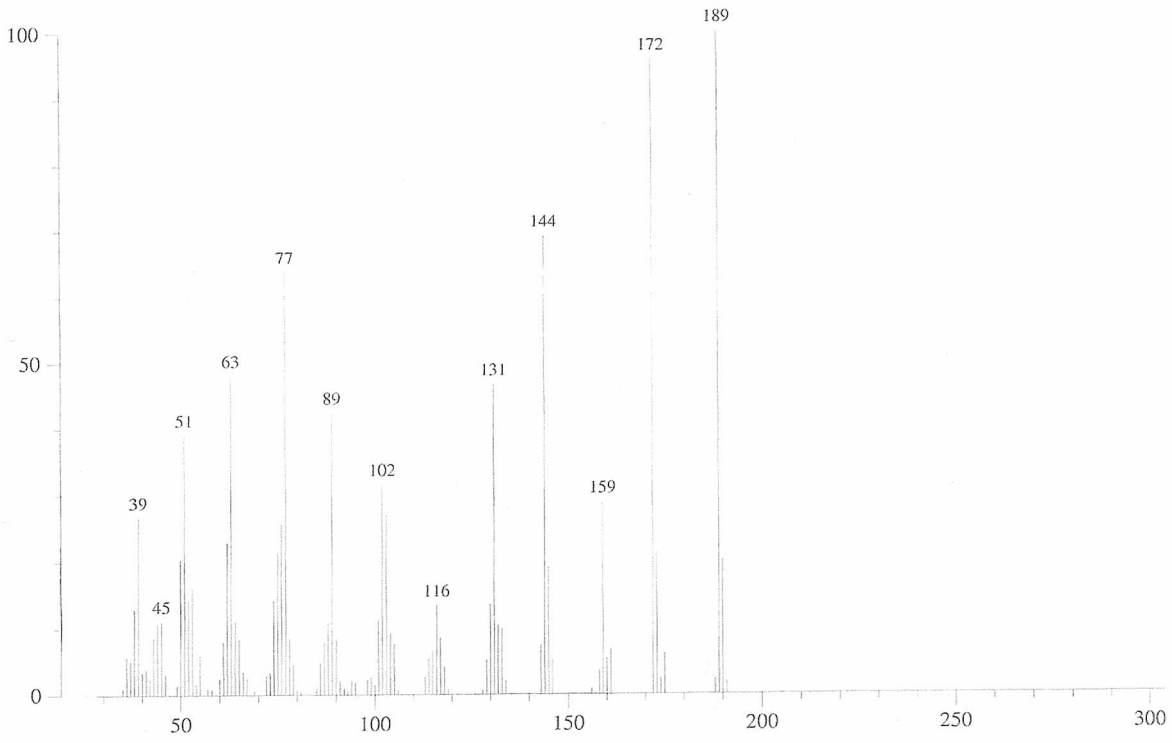
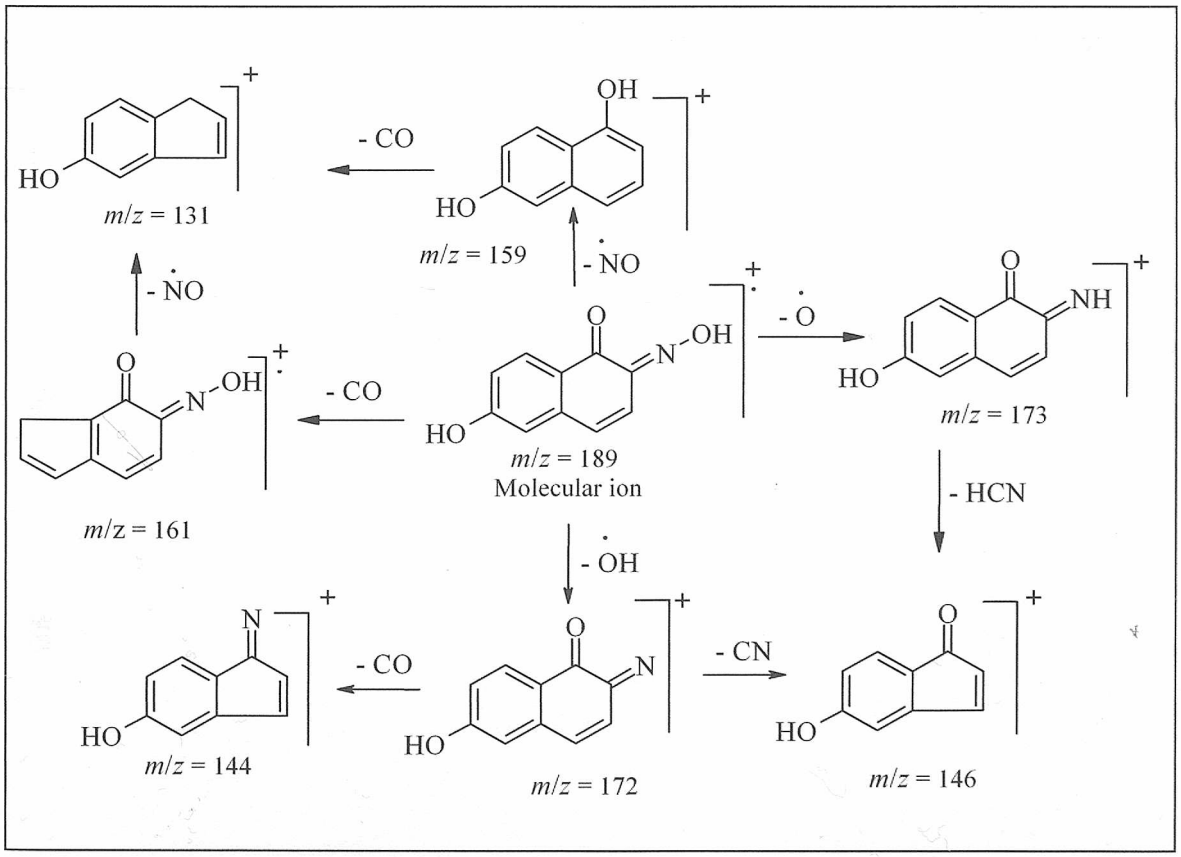


Fig 3.20 EI mass spectrum of 6-hydroxy-1,2-naphthoquinone 2-oxime (1:1)





Scheme 3.10

Fig 3.21 EI mass spectrum of 6-hydroxy-1,2-naphthoquinone 2-oxime (1:2.50)

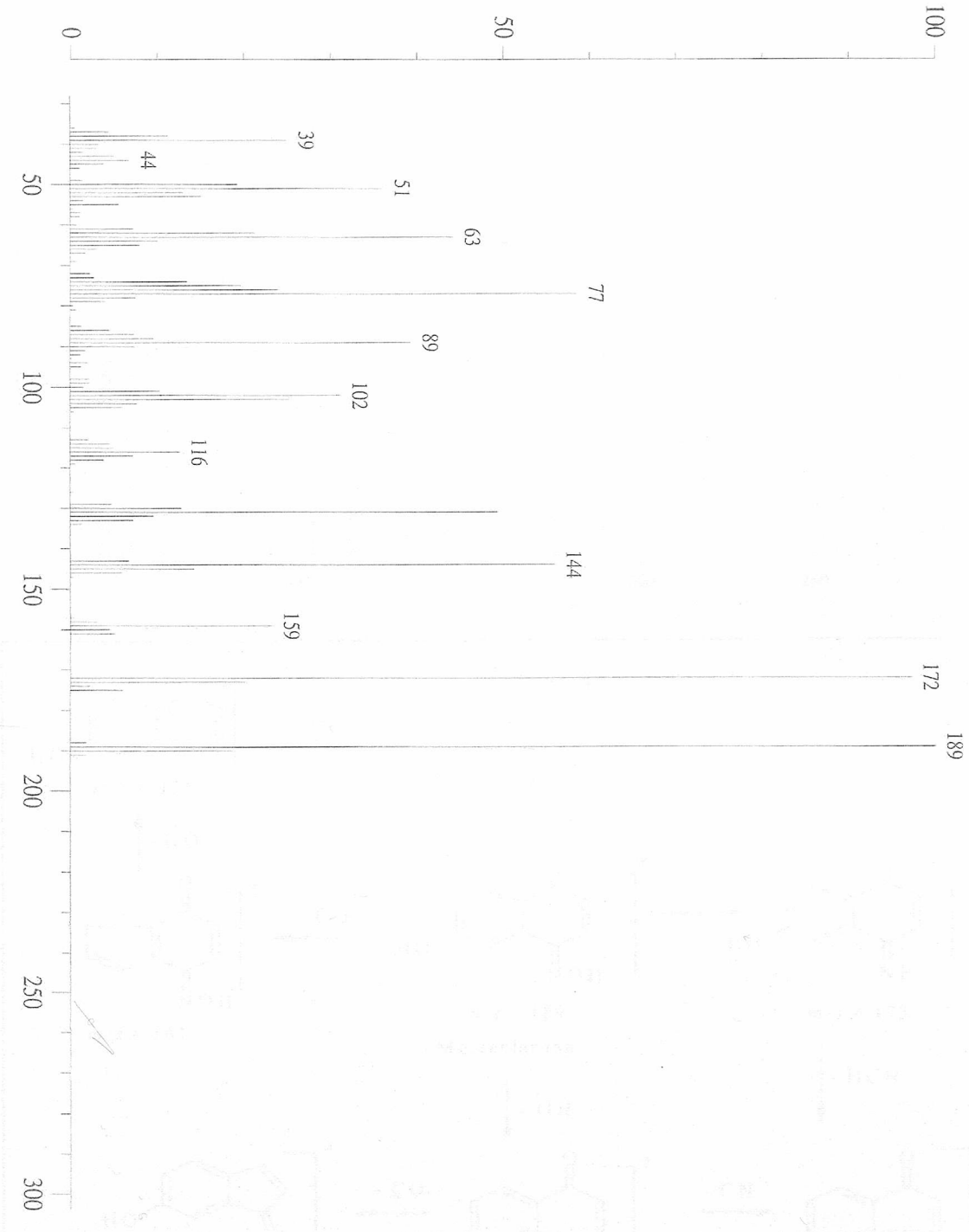
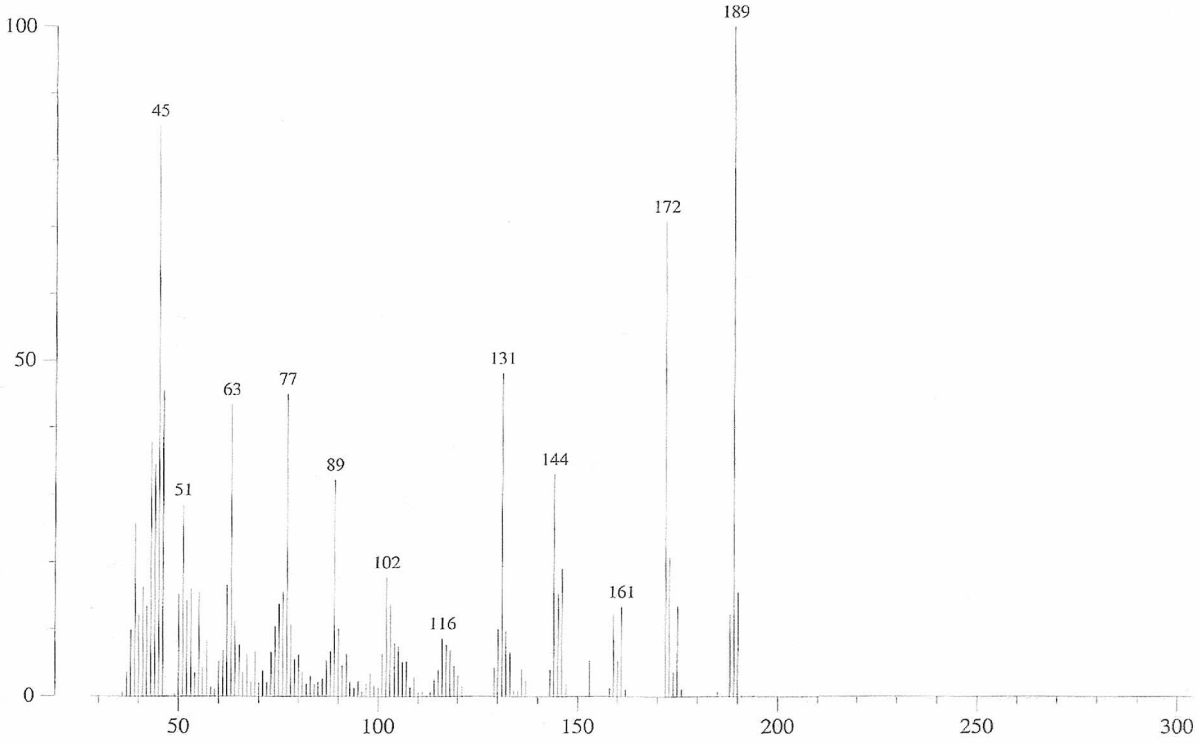
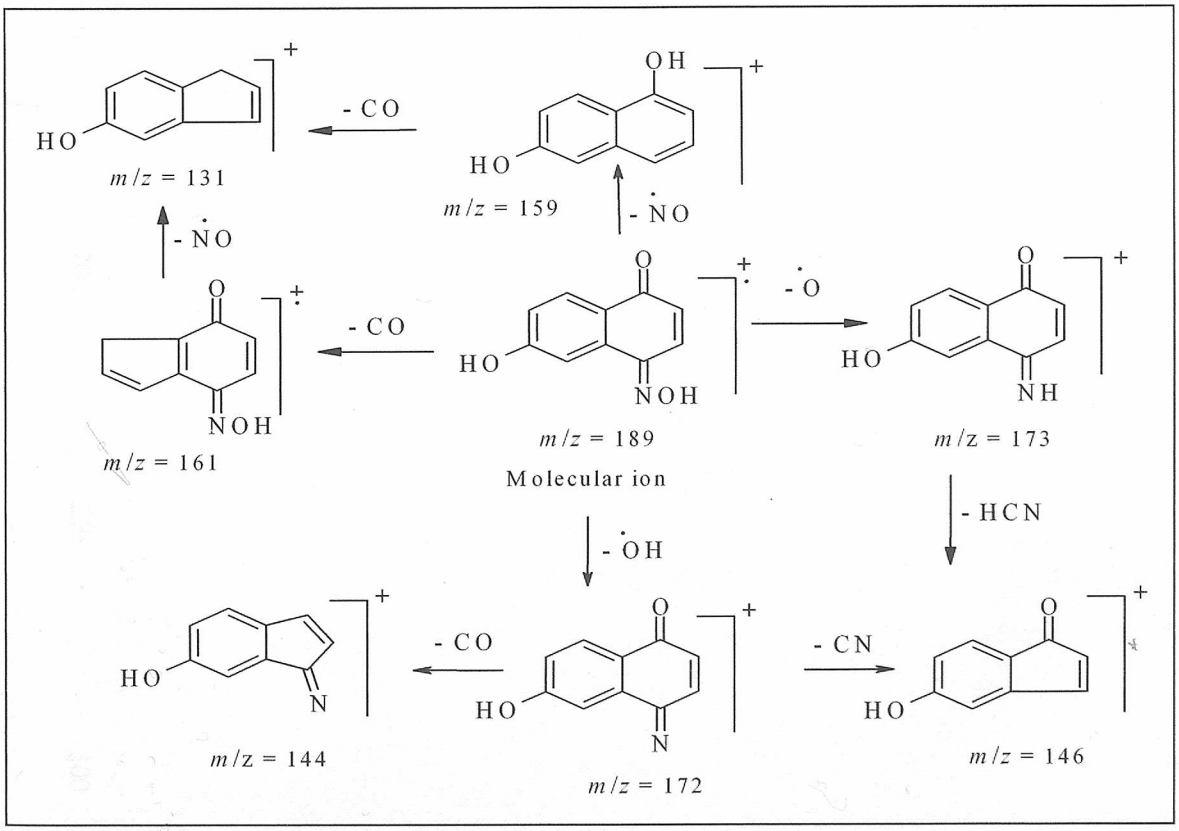


Fig 3.22 EI mass spectrum of 6-hydroxy-1,4-naphthoquinone 4-oxime (1:1)





Scheme 3.11

Fig 3.23 EI mass spectrum of 6-hydroxy-1,4-naphthoquinone 4-oxime (1:2.50)

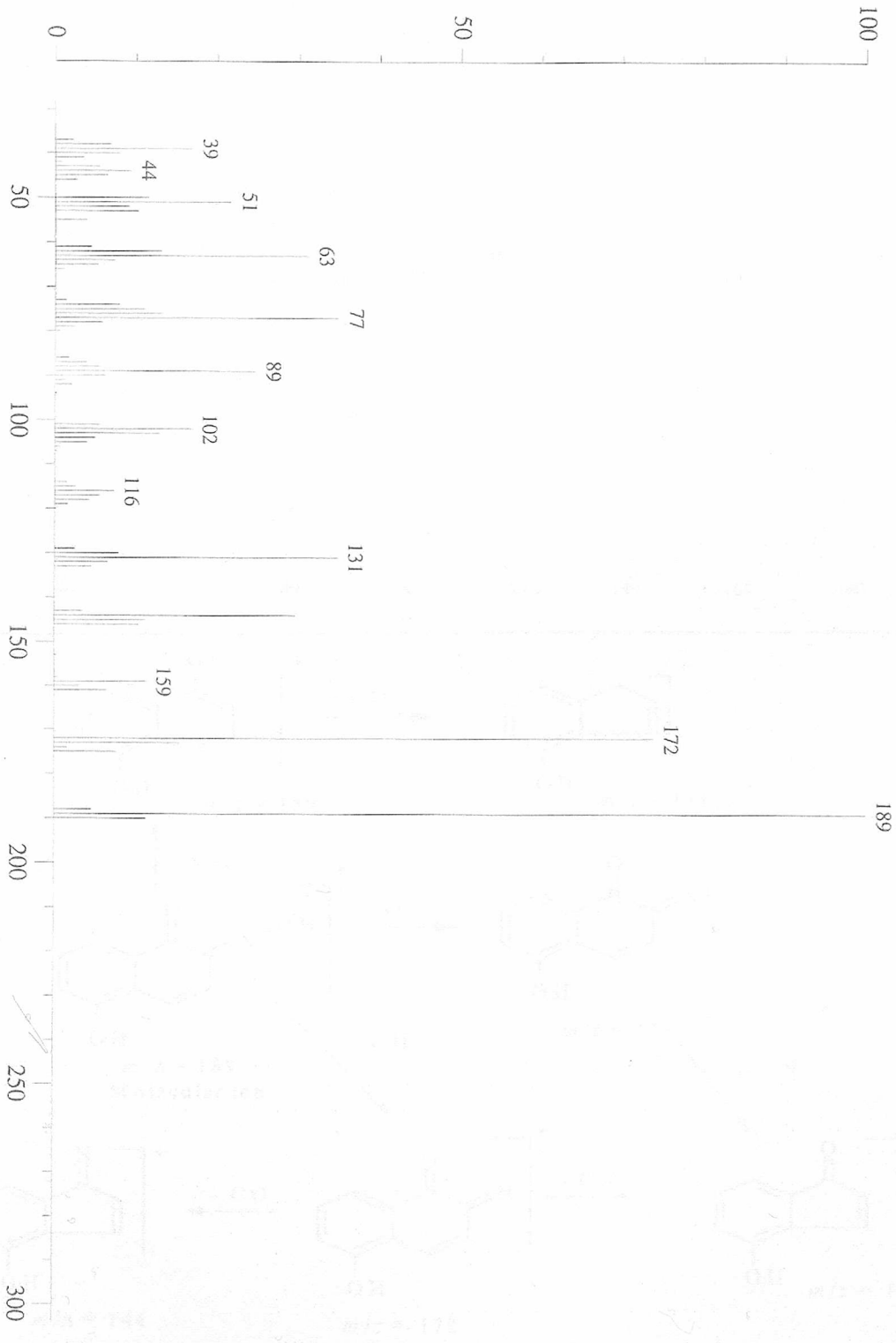
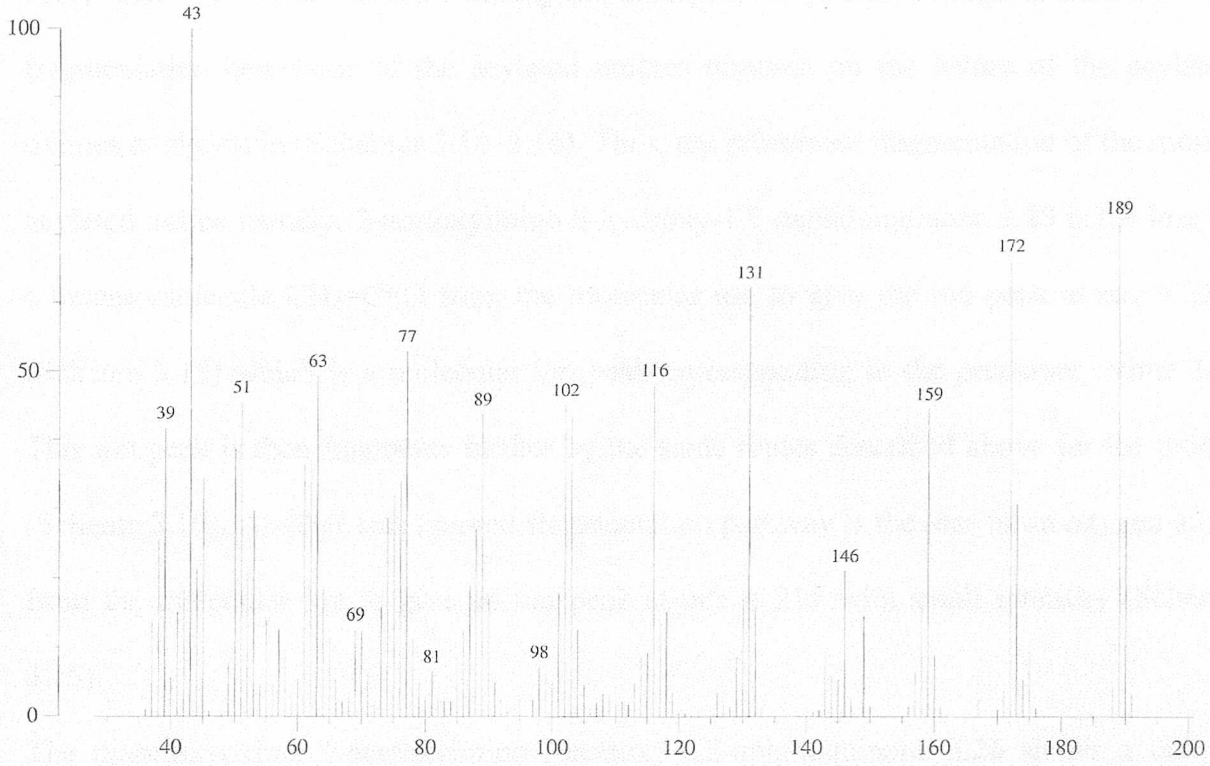
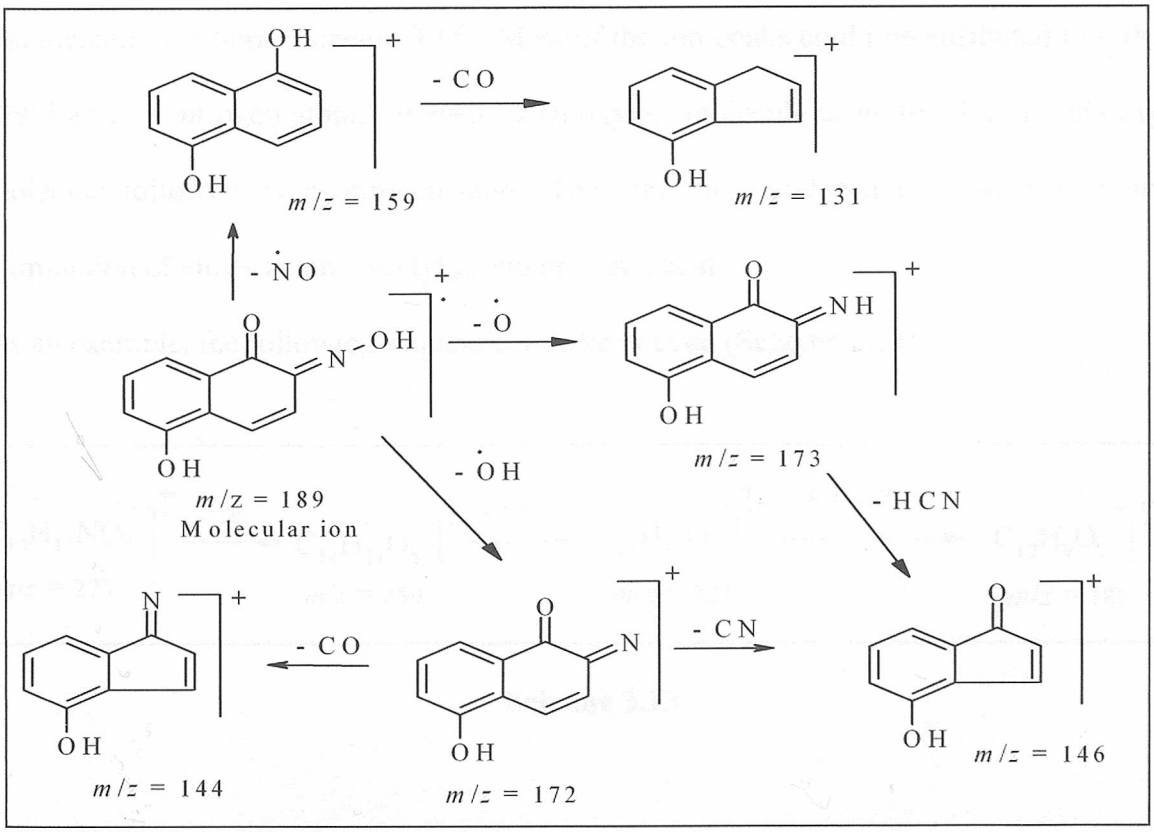


Fig 3.24 EI mass spectrum of 5-hydroxy-1,2-naphthoquinone 2-oxime (1:2.50)



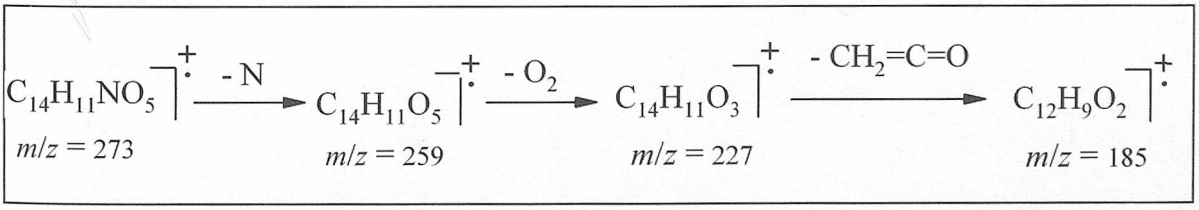


Scheme 3.12

The mono- and di- acetyloximes show a relatively small molecular ion peak (Figures 3.25–3.27). The acylium ion CH_3CO^+ being the base peak or present in high abundance. The fragmentation behaviour of the acylated omixes depends on the nature of the acylated oximes as shown in (Schemes 3.14–3.16). Thus, the prominent fragmentation of the mono-acylated oxime namely, 2-acetoxyimino-6-hydroxy-1,2-naphthoquinone **3.25** is the loss of a ketene molecule CH_2=C=O from the molecular ion to give the ion peak at *m/z* = 189 (Scheme 3.15) which is a molecular ion peak corresponding to the precursor oxime **3.9**. This ion peak is then fragments further by the same routes described above for the oxime (Scheme 3.10). Another less favored fragmentation pathway is the loss of an oxygen atom from the molecular ion to give an ion peak at *m/z* = 215 with small intensity (Scheme 3.15).

The diacetoxyoxime 1-acetoxyimino-7-acetoxy-1,2-nphthoquinone **3.26** shows a unique fragmentation pattern (Scheme 3.16). Most of the ion peaks could be attributed to either a first loss of a nitrogen atom followed by an oxygen molecule or by first loss of an oxygen molecule followed by a nitrogen atom. The ions thus produced underwent subsequent elimination of either ketene, acetyl group or acetic acid.

As an example, the following sequence may be noticed (Scheme 3.13).



Scheme 3.13

An accurate mass determination for the ion peaks at *m/z* = 273, 259, and 227 (Figure 3.28) supports the assigned molecular formula as shown in (Table 3.6).

Table 3.6 Accurate mass determination for the ion peaks at *m/z* = 273, 259, and 227

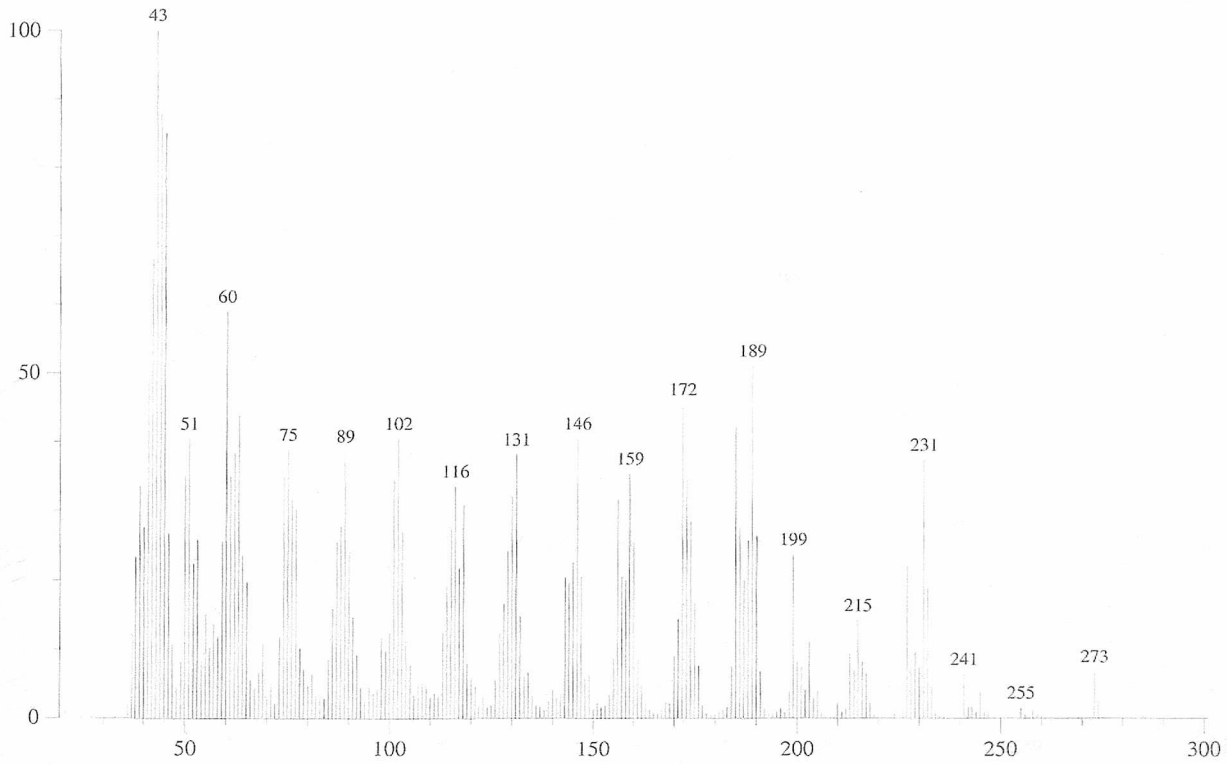
	$C_{14}H_{11}NO_5$	$C_{14}H_{11}O_5$	$C_{14}H_{11}O_3$
Calculated	273.06375	259.06068	227.07086
found	273.06380	259.06096	227.07057

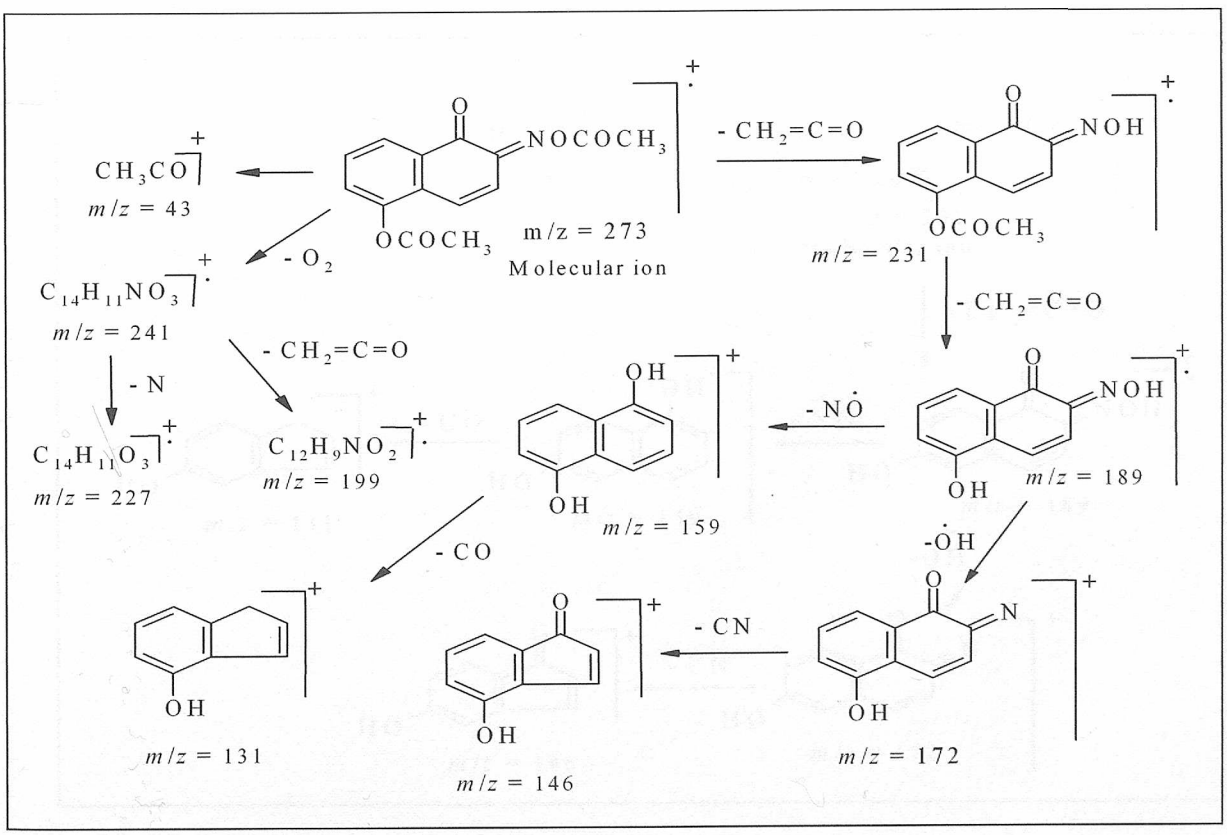
In contrast, the main fragmentation pathway of the diacetoxyoxime 2-acetoxyimino-5-acetoxy-1,2-naphthoquinone **3.24** is the successive loss of ketene molecule CH_2=C=O to give mono-acetoxyoxime ion peak at *m/z* = 231 and the oxime ion peak at *m/z* = 189, respectively (Scheme 3.14). This then fragment by the same routes observed for the oxime **3.18** (Scheme 3.12). A less favored fragmentation pathway is the loss of an oxygen molecule followed by a loss of nitrogen atom to give ion peaks at *m/z* = 241 and 227, respectively. Loss of an oxygen atom from the mono-acetoxyoxime ion peak at *m/z* = 231 was also observed to give an ion peak at *m/z* = 215. The principal ion abundances in the EI mass spectra of the aceylated oximes are showed in. (Table 3.7)

Table 3.7 Ion abundances of principal ion observed in the EI mass spectra of acylated derivatives

6-OH-2-nqo-2-NOCOCH$_3$	**M^+**	**$[M-CH_2CO]^+$= L**	**$[L-OH]^+$**	**$[L-NO]^+$**	**$[L-(OH+CN)]^+$**	**$[L-(NO+CO)]^+$**
***m/z* (%)**	231 (26)	189 (64)	172 (81)	159 (2)	146 (24)	131 (23)
5-OCOCH$_3$-2-nqo-2-NOCOCH$_3$	**M^+**	**$[M-CH_2CO]^+$= L1**	**$[L1-CH_2CO]^+$= L2**	**$[L2-OH]^+$**	**$[L2-NO]^+$**	**$[L2-(OH+CN)]^+$**
***m/z* %**	273 (7)	231 (37)	189 (51)	172 (45)	159 (35)	146 (41)
7-OCOCH$_3$-2-nqo-1-NOCOCH$_3$	**M^+**	**$[M-N]^+$= L1**	**$[L1-CH_3COOH]^+$= L2**	**$[L2-CH_3CO]^+$**	**$[L1-O_2]^+$= L3**	**$[L3-CH_2CO]^+$**
***m/z* %**	273 (0.40)	259 (3)	199 (52)	156 (24)	227 (29)	185 (100)

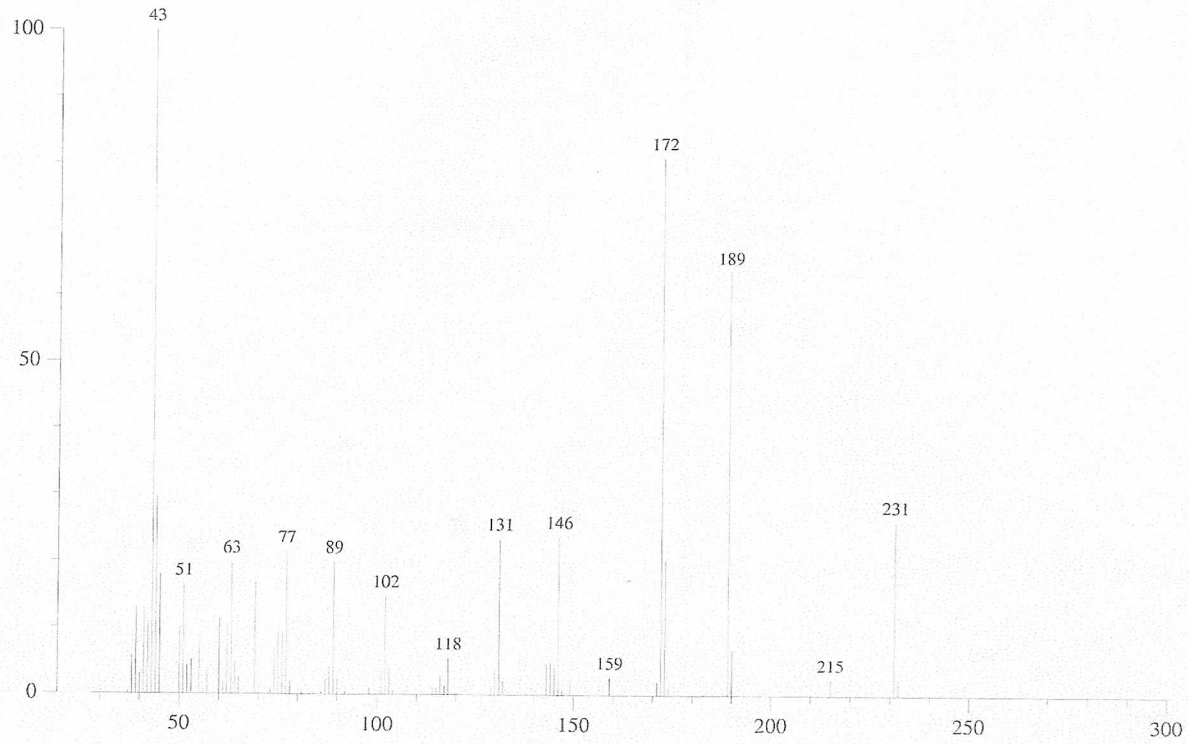
Fig 3.25 EI mass spectrum of 2-acetoxyimino-5-acetoxy-1,2-naphthoquinone

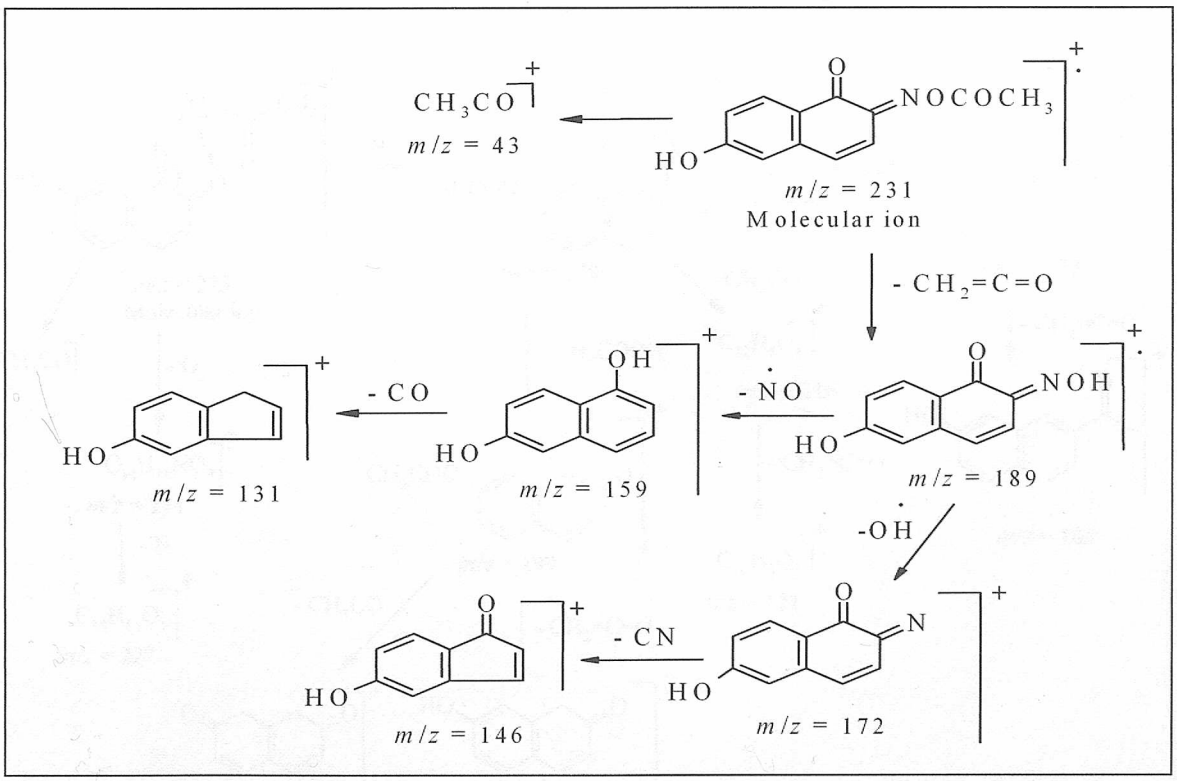




Scheme 3.14

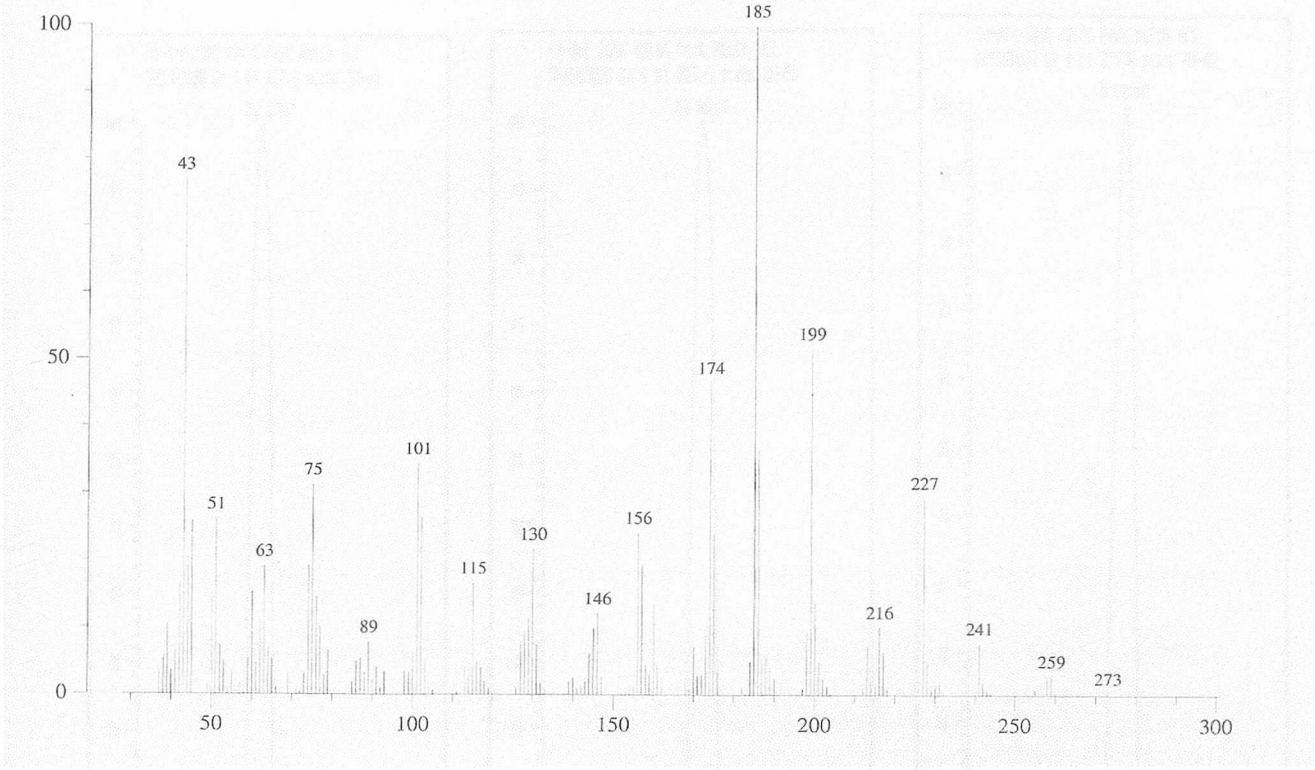
Fig 3.26 EI mass spectrum of 2-acetoxyimino-6-hydroxy-1,2-naphthoquinone

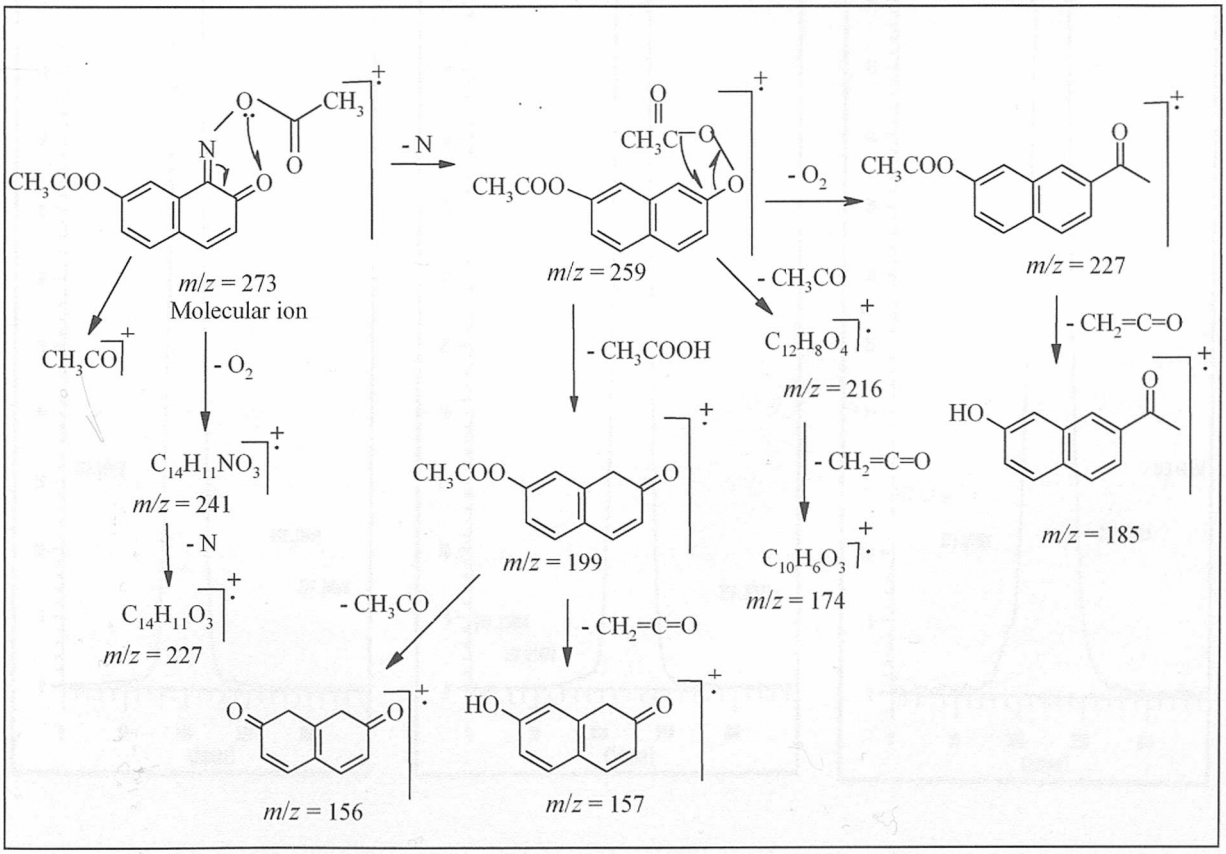




Scheme 3.15

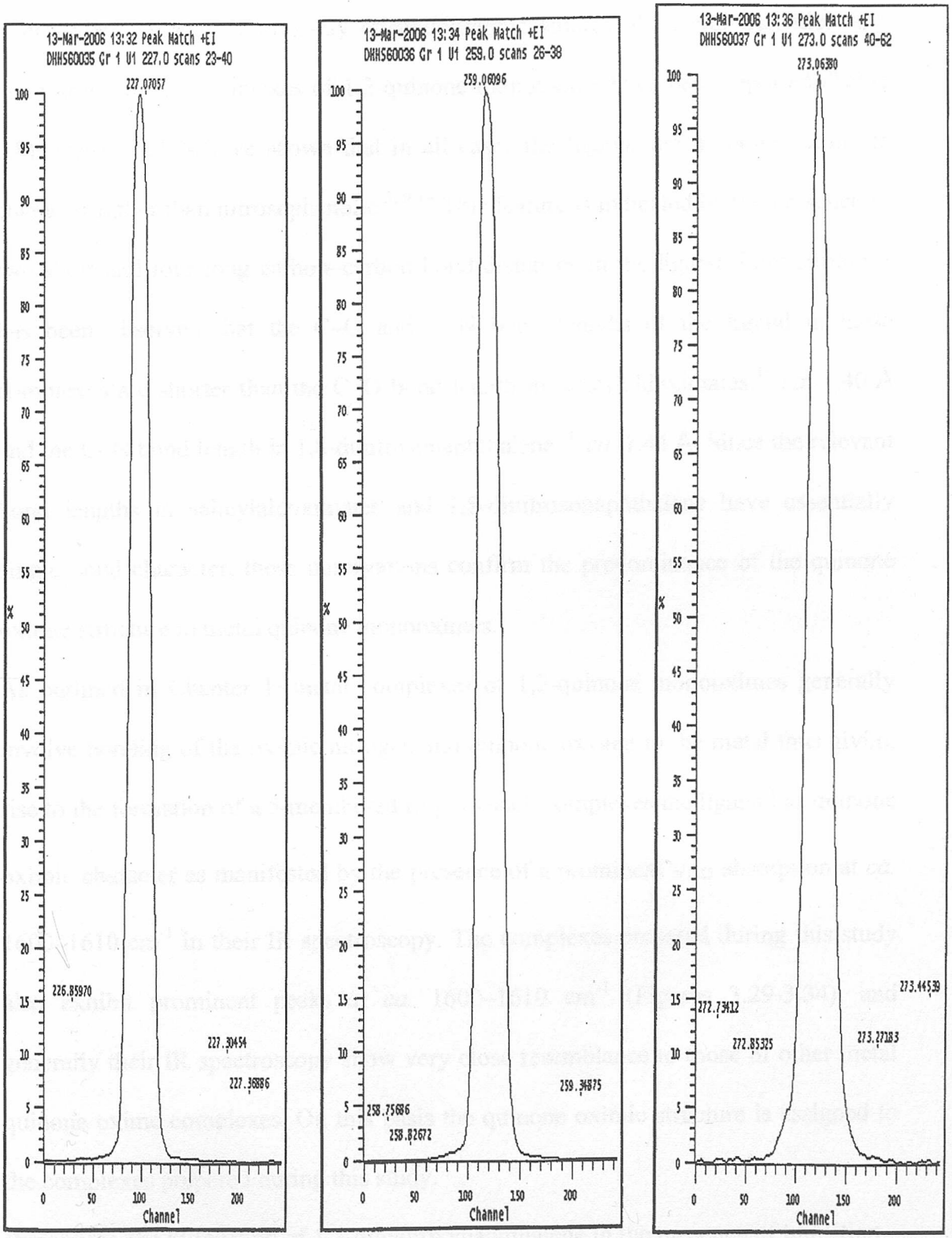
Fig 3.27 EI mass spectrum of 1-acetoxyimino-7-acetoxy-1,2-naphthoquinone





Scheme 3.16

Fig 3.28 Accurate mass of 1-acetoxyimino-7-acetoxy-1,2-naphthoquinone



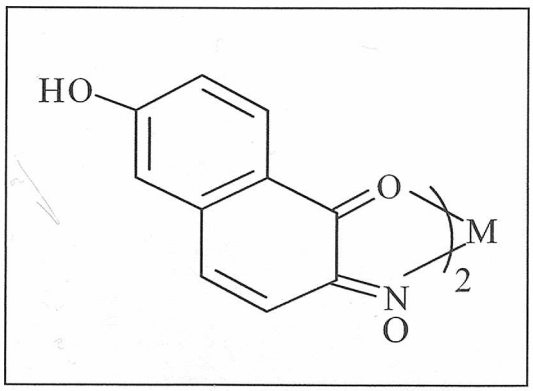
3.6 Synthesis of copper(II) and nickel(II) complexes of hydroxy-1,2-naphthoquinone monooximes

A considerable number of x–ray crystallographic studies of several transition and main group metal complexes of 1,2-quinone monooxime have been reported (Table 3.8). These studies have shown that in all cases the ligands are quinone oximic in character rather than nitrosophenolic.[3, 9-14] This feature is indicated by the presence of two short and four long carbon–carbon bond distances in the ligand. Furthermore it has been observed that the C–O and C–N bond lengths of the ligand in these complexes are shorter than the C–O bond length in salicylaldoximates,[15] *ca.* 1.40 Å and the C–N bond length in 1,8-dinitrosonaphthalene,[16] *ca.* 1.44 Å. Since the relevant bond lengths in salicylaldoximates and 1,8-dinitrosonaphthalene have essentially single bond character, these observations confirm the predominance of the quinone oximic structure in metal quinone monooximes.

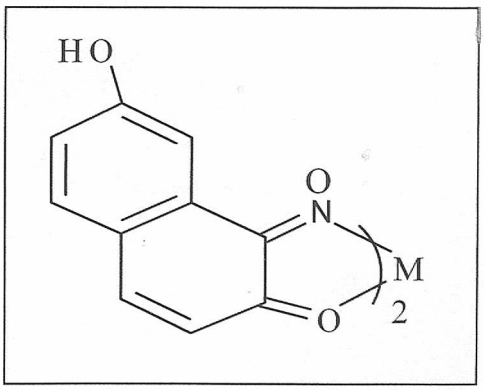
As outlined in Chapter 1, metal complexes of 1,2-quinone monooximes generally involve bonding of the oximic nitrogen and quinone oxygen to the metal thus giving rise to the formation of a 5-membered ring. In such complexes the ligand has quinone oximic character as manifested by the presence of a prominent ν_{CO} absorption at *ca.* 1600–1610 cm^{-1} in their IR spectroscopy. The complexes prepared during this study also exhibit prominent peaks at *ca.* 1600–1610 cm^{-1} (Figures 3.29-3.34), and generally their IR spectroscopy show very close resemblance to those of other metal quinone oxime complexes. On this basis the quinone oximic structure is assigned to the complexes prepared during this study.

Previously, the nitrosation of 1,7-dihydroxynaphthalene in the presence of transition

metal salts affords the metal complex of the respective 7-hydroxy-1,2-naphthoquinone 2-oxime together with the corresponding 4-isomer as 7-hydroxy-1,4-naphthoquinone 4-oxime.[2] This nitrosation is carried out at room temperature and usually the mixture stirred for a long time (48 h). In this study the nitrosation with sodium nitrite in the presence of transition metal salts is carried out at 0°C and the mixture is stirred for a shorter time (2 h). The nitrosation of 1,6-dihydroxynaphthalene **3.7** and 2,7-dihydroxynaphthalene **3.1** in the presence of copper(II) and nickel(II) salts afford in each case, the metal complex $M(qo)_2$ as a major product, (M = Cu or Ni; qo = 6-hydroxy-1,2-naphthoquinone 2-oximato **3.31** and 7-hydroxy-1,2-naphthoquinone 1-oximato **3.32**. The 4-isomer product **3.10** is obtained only from the nitrosation of 1,6-dihydroxynaphthalene **3.7** in the presence of both copper and nickel salts. In the case of 1,5-dihydroxynaphthalene **3.16**, nitrosation with sodium nitrite in the presence of either copper or nickel salts afforded a mixture of compounds.



3.31



3.32

Table 3.8 Selected bond lengths of metal complexes of 1,2-quinone monooximes

Complex (qoH)	Bond Length (Å)					
	C–O	C–N	N–O	C–C^{+}	C–C^{++}	Ref.
Cu (2-nqo)$_2$ (H_2O)	1.28	1.35	1.26	1.39	1.44	17
Cu (1-nqo)$_2$ (Me_2CO)$_2$	1.29	1.35	1.26	1.38	1.44	18
Cu (1-nqo)$_2$ (Ph_3P)$_2$	1.26	1.37	1.29	1.4	1.44	19
Cu (4-methyl-2-nqo)$_2$ (py)	1.27	1.35	1.25	1.35	1.43	20
K[Ni(4-chloro-2-nqo)$_3$] (Me_2CO)	1.25	1.33	1.27	1.35	1.45	21
Ru(1-nqo)$_2$ (py)$_2$	1.28	1.38	1.27	-	-	13
UO_2(2-nqo)$_2$ (H_2O)$_2$ .1/2CH_3Cl	1.23	1.30	1.34	1.32	1.45	22
UO_2(1-nqo)$_2$ (Ph_3PO) (H_2O)	1.25	1.33	1.35	1.37	1.46	22
Li(1-nqo)(1-nqoH) (EtOH)	1.25	1.31	1.36	1.33	1.48	23

+ = Average bond length of 2 short C–C bonds ++ = Average bond length of 4 long C–C bonds
1-nqo = 1,2-naphthoquinone 1-oxime 2-nqo = 1,2-naphthoquinone 2-oxime py = Pyridine

Fig 3.29 IR spectrum of bis(7-hydroxy-1,2-naphthoquinone 1-oximato)nickel(II) complex

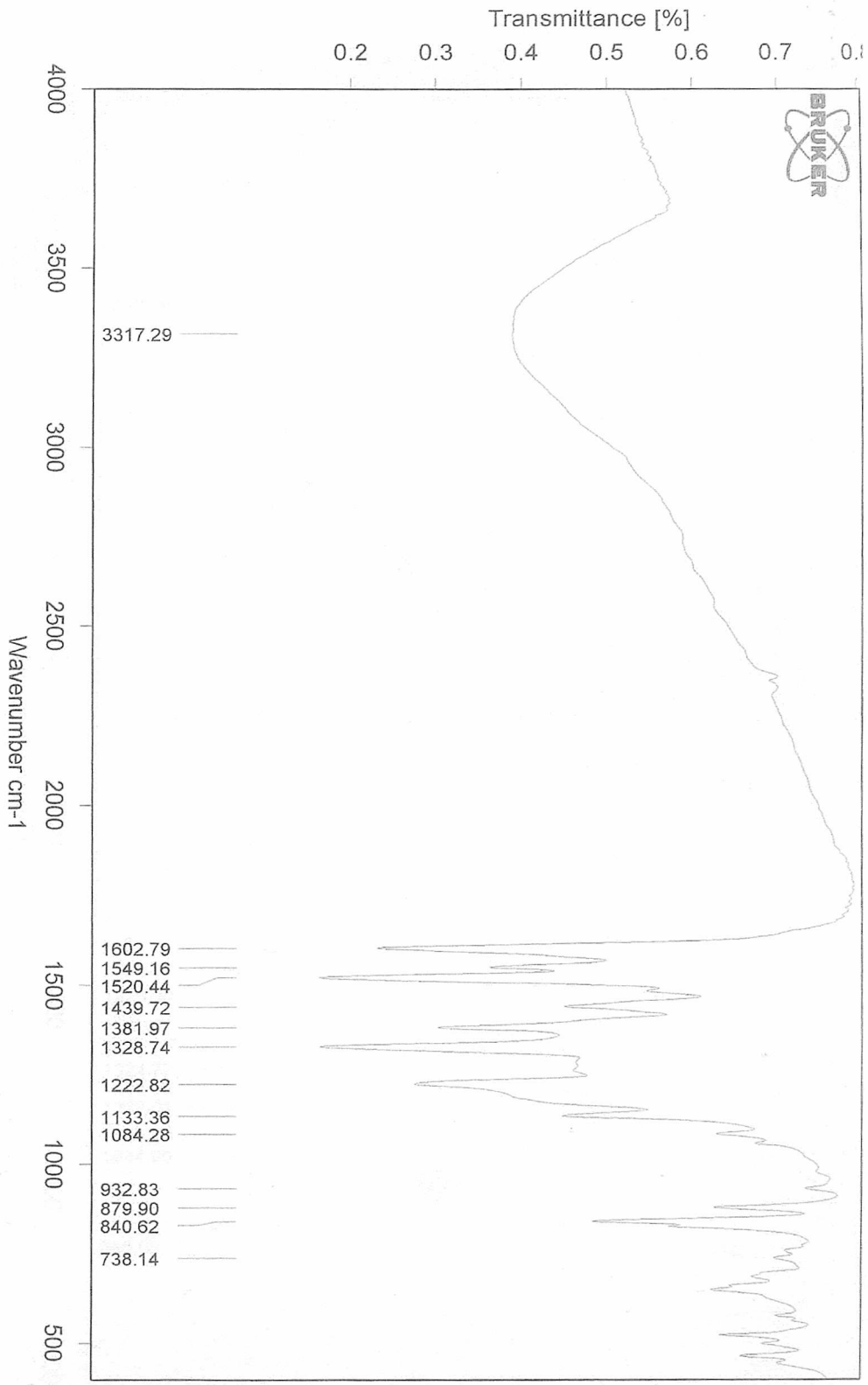


Fig 3.30 IR spectrum of bis(7-hydroxy-1,2-naphthoquinone 1-oximato)copper(II) complex

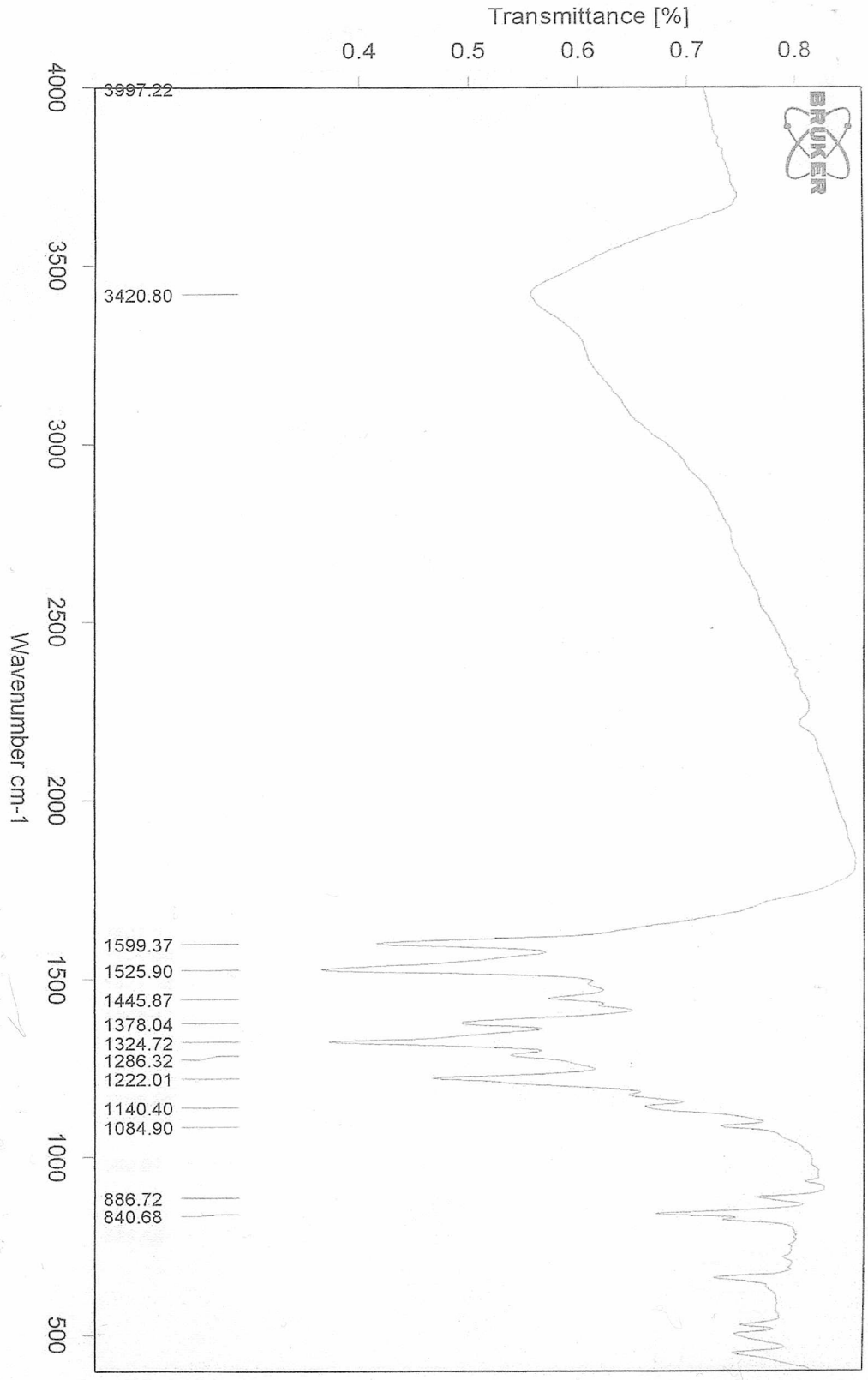


Fig 3.31 IR spectrum of bis(6-hydroxy-1,2-naphthoquinone 2-oximato)nickel(II) complex

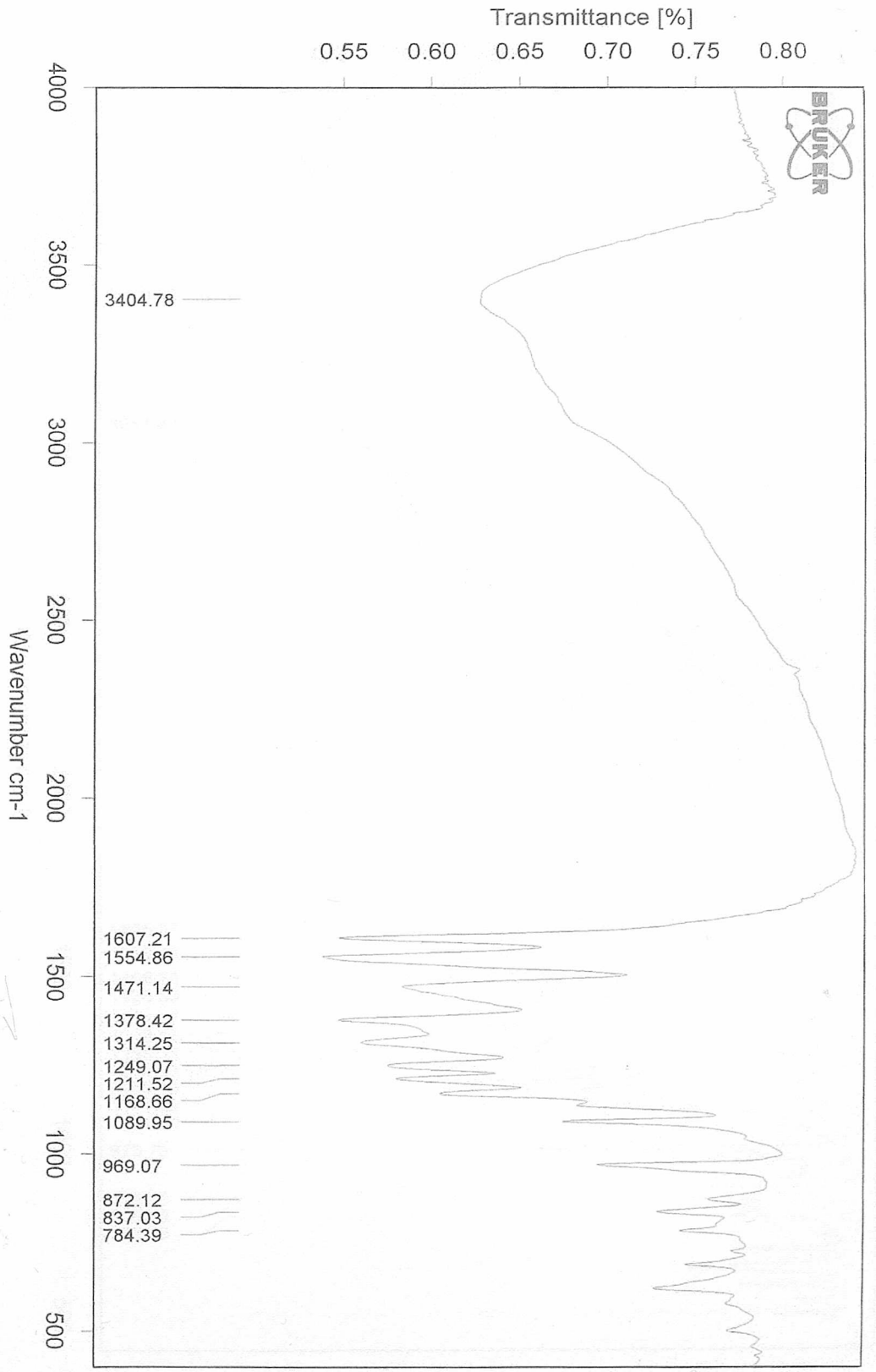


Fig 3.32 IR spectrum of bis(6-hydroxy-1,2-naphthoquinone 2-oximato)copper(II) complex

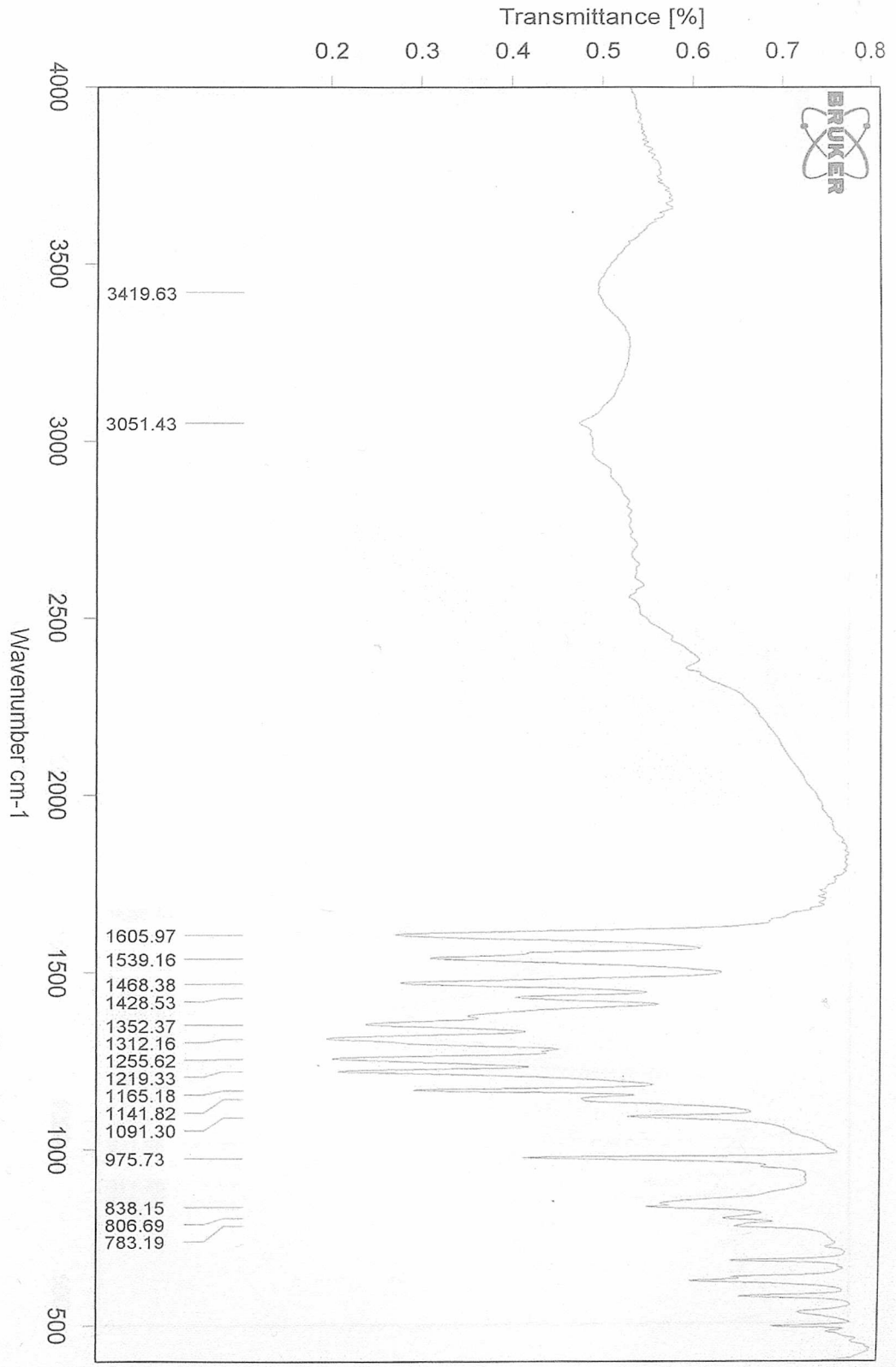


Fig 3.33 IR spectrum of nickel complex derived from 1,5-dihydroxynaphthalene

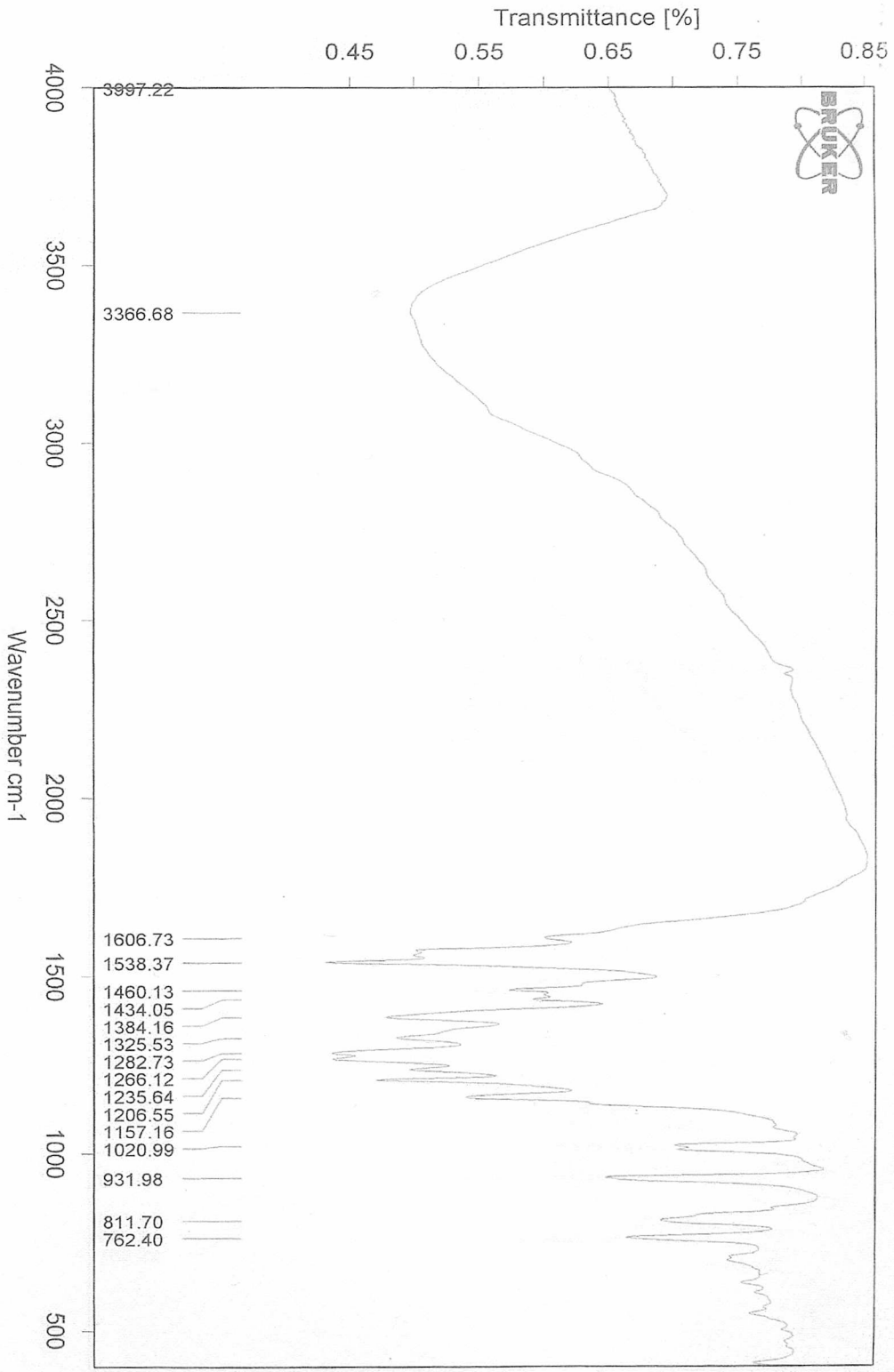
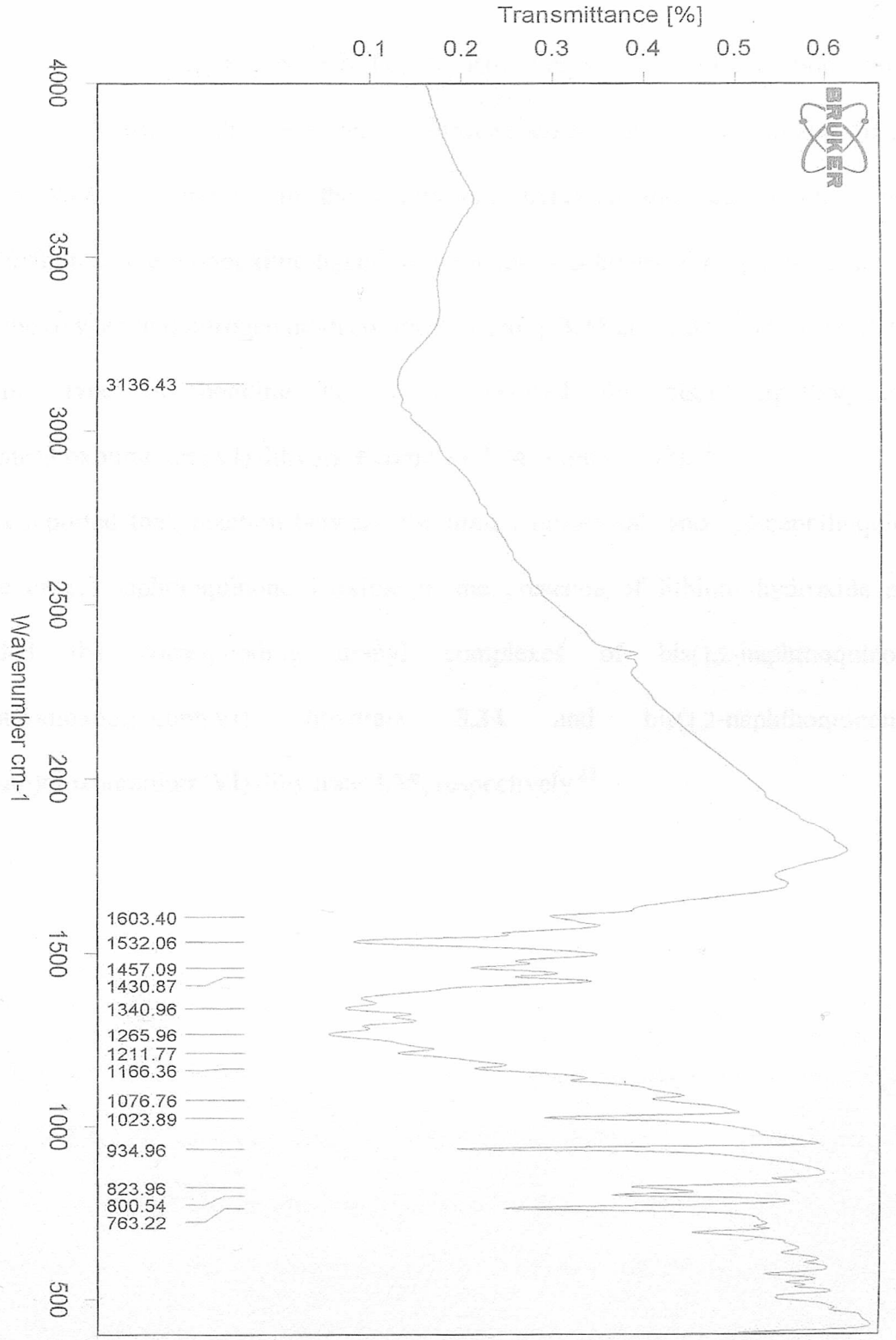


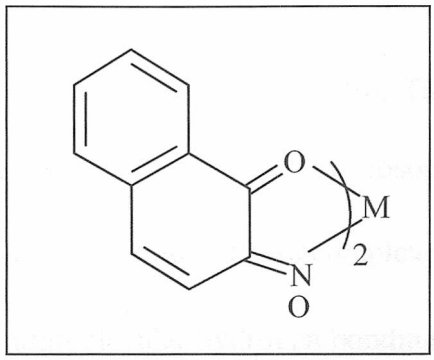
Fig 3.34 IR spectrum of copper complex derived from 1,5-dihydroxynaphthalene



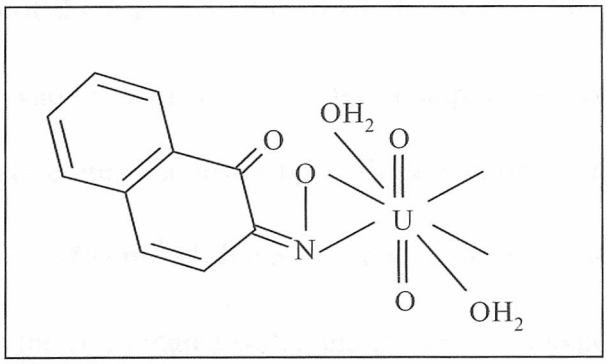
3.7 Synthesis of dioxouranium(VI) complexes of 1,2- and 1,4-naphthoquinone monooximes

In transition metal (e.g. Cu, Ni, Co, Fe, Ru, Rh) complexes of quinone monooximes, the ligands are chelated to the metal via the nitrogen atom of the NO group and the quinone oxygen **3.33**. In contrast, in the complexes involving the heavier metal uranium, coordination of the monooxime ligand to the metal is achieved through bidentate bonding from the oxygen and nitrogen atoms of the NO group **3.34** and **3.35**.[22] The crystal structure of this type of bonding has been reported for bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate complex **3.34** (Figure 3.42).[22]

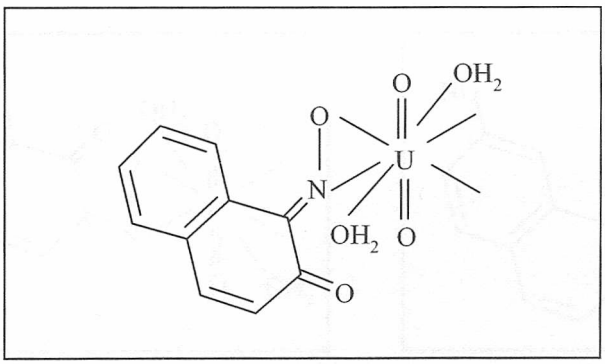
It was reported that, reaction between the uranyl nitrate salt and 1,2-naphthoquinone 2-oxime or 1,2-naphthoquinone 1-oxime in the presence of lithium hydroxide as base, afforded the corresponding uranyl complexes of bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate **3.34** and bis(1,2-naphthoquinone 1-oximato)dioxouranium(VI) dihydrate **3.35,** respectively.[22]



3.33



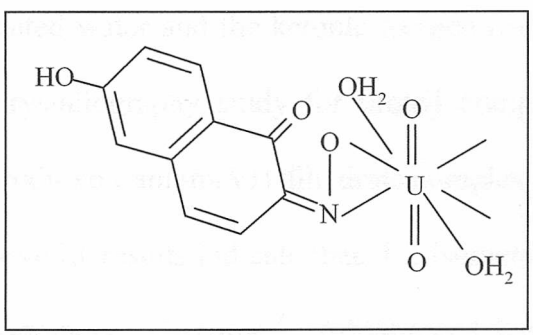
3.34



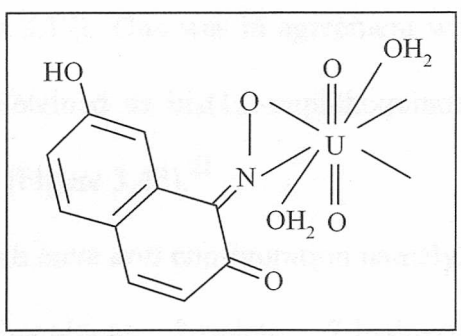
3.35

During this study, the uranium complexes are prepared by reaction of 6-hydroxy-1,2-naphthoquinone 2-oxime **3.9**, 7-hydroxy-1,2-naphthoquinone 1-oxime **3.3** and 6-hydroxy-1,4-naphthoquinone 4-oxime **3.10** with uranyl nitrate hexahydrate in the presence of triethyl amine as base using absolute methanol as solvent. The reason of using triethyl amine instead of lithium hydroxide is to avoid obtaining lithium complexes, especially with substituted hydroxy-1,2-naphthoquinone 2-oximes, which are being used in this study. These reactions give solids which are filtered and washed with methanol. These solids are insoluble in most solvents even in hot methanol.

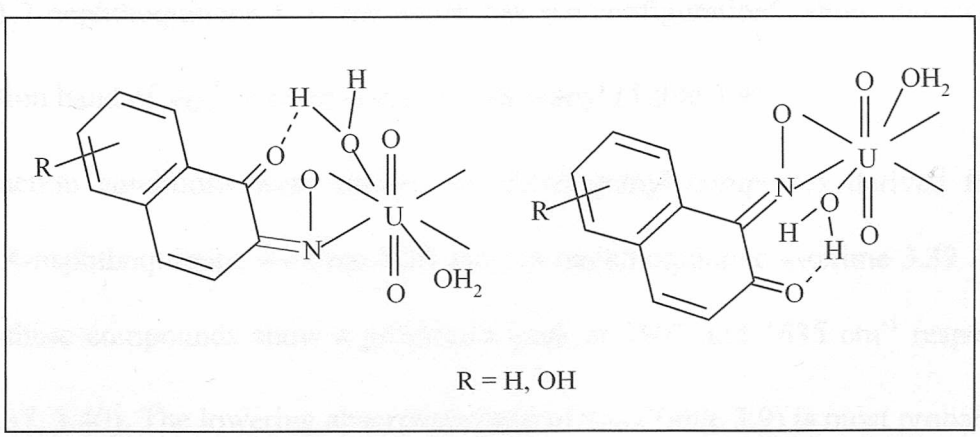
The uranyl complexes prepared during this study **3.36** and **3.37** exhibit prominent peaks at *ca.* ~1608 cm^{-1} assignable to ν_{CO} (quinone) of the ring and a broad band of ν_{OH} at 3430-3400 cm^{-1} (Figures 3.35, 3.36). These observations indicate that, these compounds have quinone oximic rather than nitrosophenolic structure. The lowering of the absorption band of ν_{CO} compared to the uncomplexed oxime ~ 1649 cm^{-1} (Table 3.9) is due to the existence of intramolecular hydrogen bonding between the coordinated water and the ketonic oxygen (Scheme 3.17).



3.36



3.37



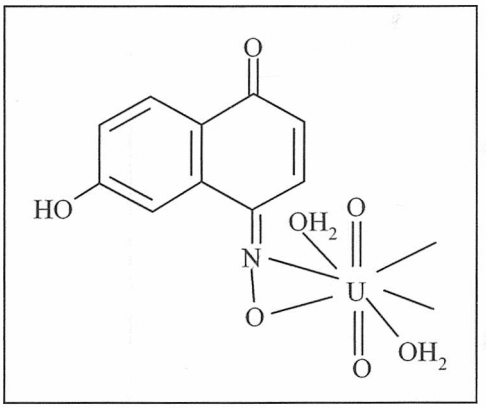
Scheme 3.17

As additional investigation, similar reactions to prepare uranyl complexes were carried out using 1,2-naphthoquinone 2-oxime or 1,2-naphthoquinone 1-oxime with uranyl nitrate hexahydrate in the presence of triethyl amine as base in absolute methanol. The IR spectra of the uranyl complexes obtained from 1,2-naphthoquinone 2-oxime **3.34** and 1,2-naphthoquinone 1-oxime **3.35** exhibited prominent peaks at *ca.* 1631 and 1623 cm^{-1} respectively, assignable to ν_{CO} (quinone) of the ring (Figures 3.38, 3.39). These results also indicate that, these compounds exist as quinone oximic rather than nitrosophenolic structure. The lowering of the absorption band of ν_{CO} compared to the uncomplexed oxime (Table 3.9) is due to the existence of intramolecular hydrogen bonding between the coordinated water and the ketonic oxygen (Scheme 3.17). This was in agreement with an x-ray crystallography study for uranyl complex obtained as bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate complex **3.34** (Figure 3.42).[22]

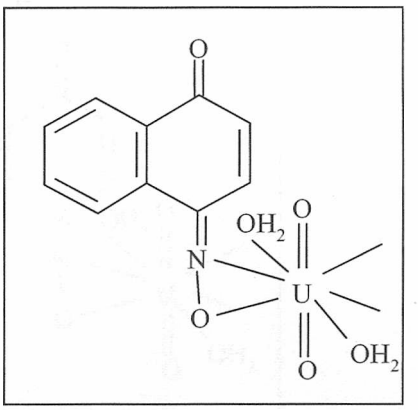
The above IR results indicate that, 1,2-isomers which have *anti* configuration namely, 1,2-naphthoquinone 2-oxime,[2] 6-hydroxy-1,2-naphthoquinone 2-oxime, 7-hydroxy-1,2-naphthoquinone 1-oxime show considerable lowering of ν_{CO} on complexation with uranyl. Whereas, 1,2-naphthoquinone 1-oxime which has *syn* configuration[24] shows no change in the absorption band of ν_{CO} on complexation with uranyl (Table 3.9).

Similar reaction conditions were applied to afford uranyl complexes derived from 6-hydroxy-1,4-naphthoquinone 4-oxime **3.38** and 1,4-naphthoquinone 4-oxime **3.39**. The IR spectra of these compounds show a prominent peak at 1607 and 1635 cm^{-1} respectively (Figures 3.37, 3.40). The lowering absorption band of ν_{CO} (Table 3.9) is most probably due to the existence of intermolecular hydrogen bonding between the coordinated water and the ketonic oxygen (Scheme 3.18). The IR spectrum of uranyl complex obtained from 6-hydroxy-1,4-naphthoquinone 4-oxime shows a strong broad band centered at 3422 cm^{-1}

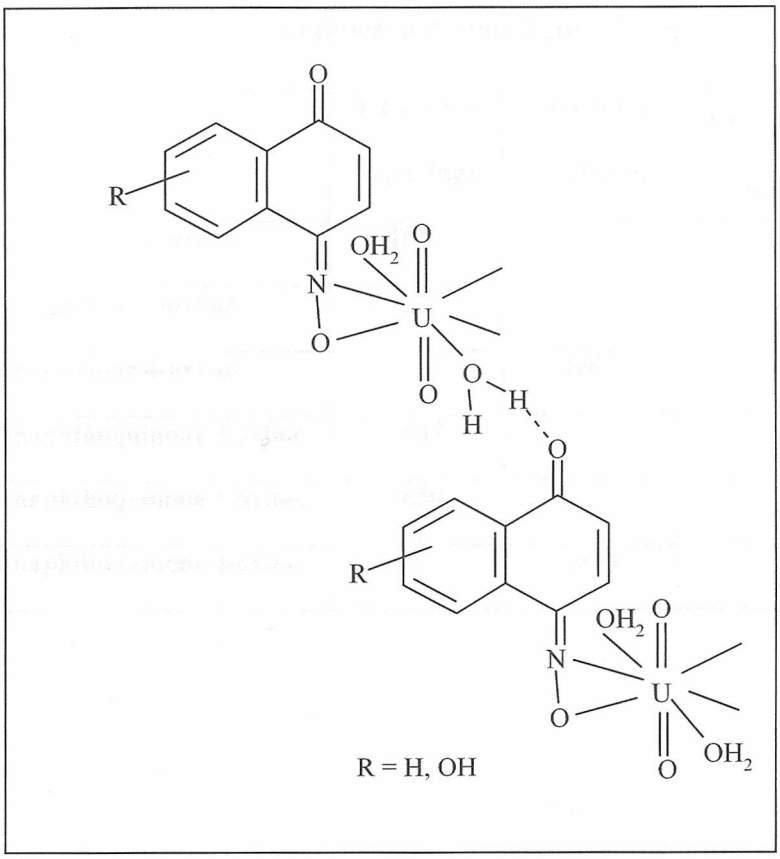
assigned to ν_{OH} (Figure 3.37). In fact, reaction of 6-hydroxy-1,4-naphthoquinone 4-oxime and 1,4-naphthoquinone 4-oxime as 1,4-isomers with uranyl nitrate hexahydrate to form uranyl complexes are further evidences for the chelating of these quinone monooximes as ligands through bidentate bonding from the oxygen and nitrogen atoms of the NO group.



3.38



3.39



Scheme 3.18

Moreover, the elemental analysis of these compounds indicates a C : N ratio of 20 : 2 suggesting, the obtained uranyl complexes are bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate **3.34,** bis(1,2-naphthoquinone 1-oximato)dioxouranium(VI) dihydrate **3.35,** bis(1,4-naphthoquinone 4-oximato)dioxouranium(VI) dihydrate **3.39,** bis(6-hydroxy-1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate **3.36**, bis(7-hydroxy-1,2-naphthoquinone 1-oximato)dioxouranium(VI) dihydrate **3.37** and bis(6-hydroxy-1,4-naphthoquinone 4-oximato)dioxouranium(VI) dihydrate **3.38**.

Due to problems associated with the purification and preparation of 5-hydroxy-1,2-naphthoquinone 2-oxime **3.18,** the reaction with uranyl nitrate hexahydrate was not conducted (see pages 57-60).

Table 3.9 ν_{CO} absorption in 1,2-, 1,4-oximes and uranyl complexes

Compounds	1,2-Oxime ν_{CO} (ring)	1,4-Oxime ν_{CO} (ring)	Uranyl complex ν_{CO} (ring)
1,2-naphthoquinone 2-oxime	1673	-	1631
1,2-naphthoquinone 1-oxime	1622	-	1623
1,4-naphthoquinone 4-oxime	-	1665	1635
6-Hydroxy-1,2-naphthoquinone 2-oxime	1647	-	1606
7-Hydroxy-1,2-naphthoquinone 1-oxime	1650	-	1608
6-Hydroxy-1,4-naphthoquinone 4-oxime	-	1638	1607

Fig 3.35 IR spectrum of bis(6-hydroxy-1,2-naphthoquinone 2-oximato)dioxouranium(VI) complex

Fig 3.36 IR spectrum of bis(7-hydroxy-1,2-naphthoquinone 1-oximato)dioxouranium(VI) complex

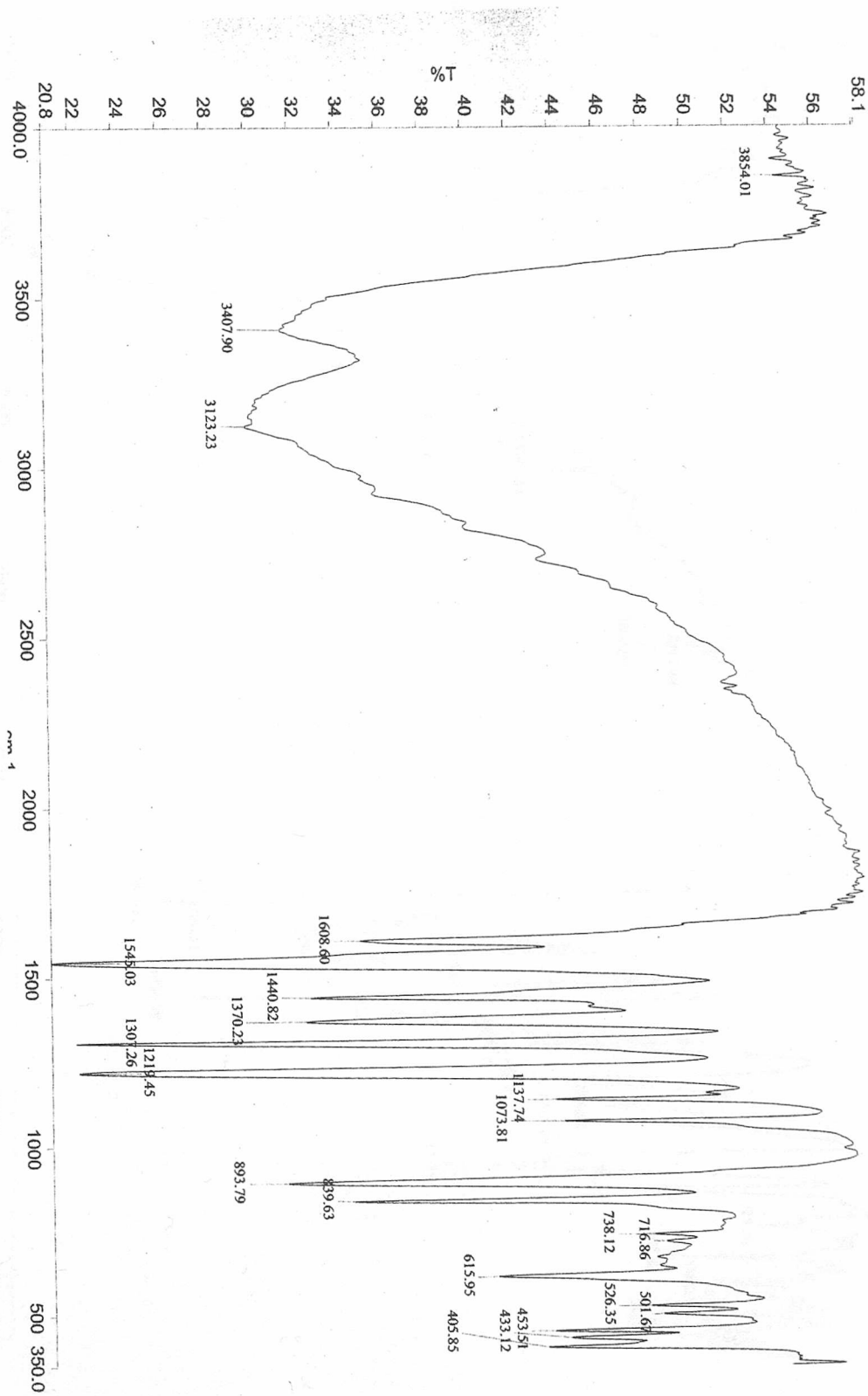


Fig 3.37 IR spectrum of bis(6-hydroxy-1,4-naphthoquinone 4-oximato)dioxouranium(VI) complex

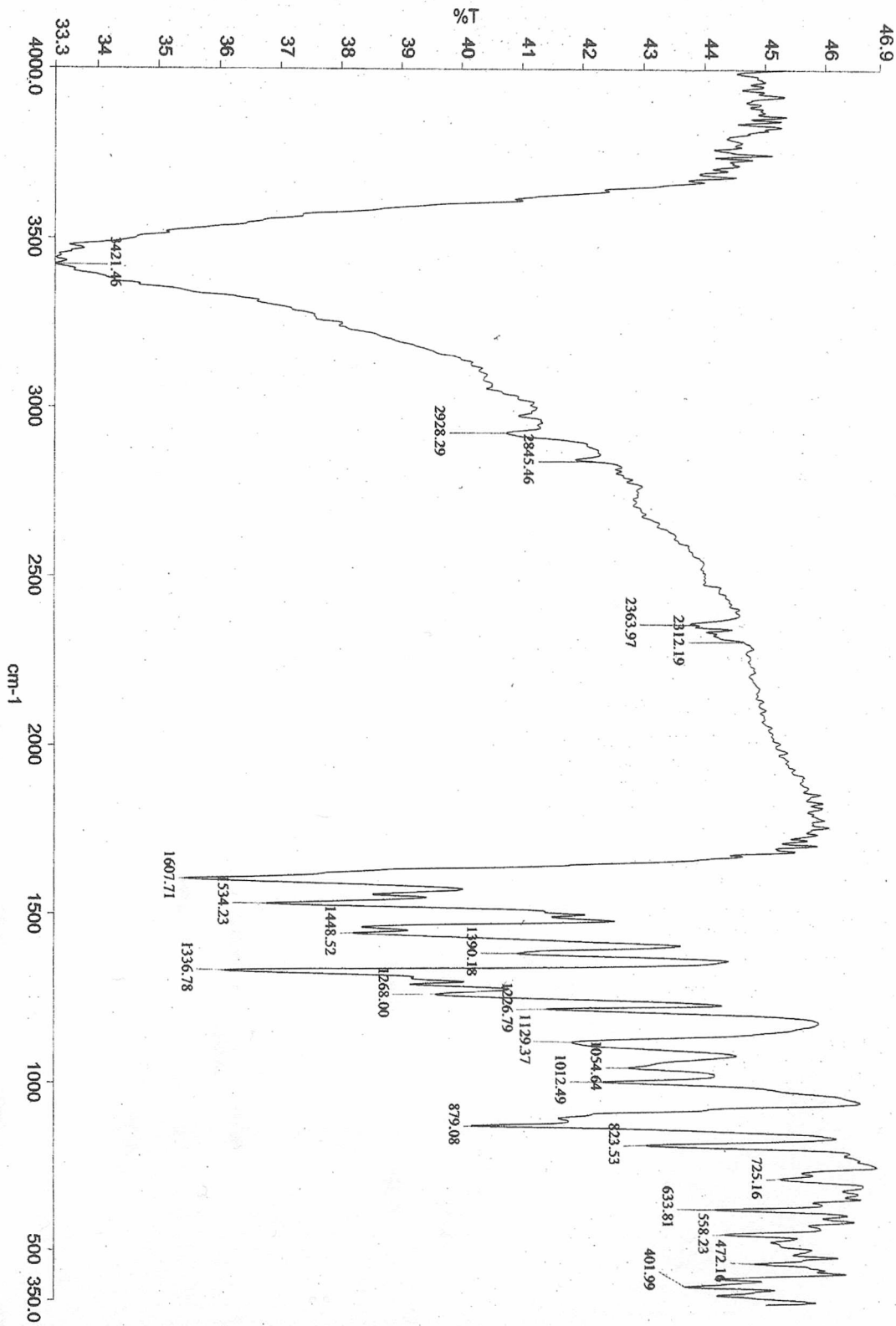


Fig 3.38 IR spectrum of bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) complex

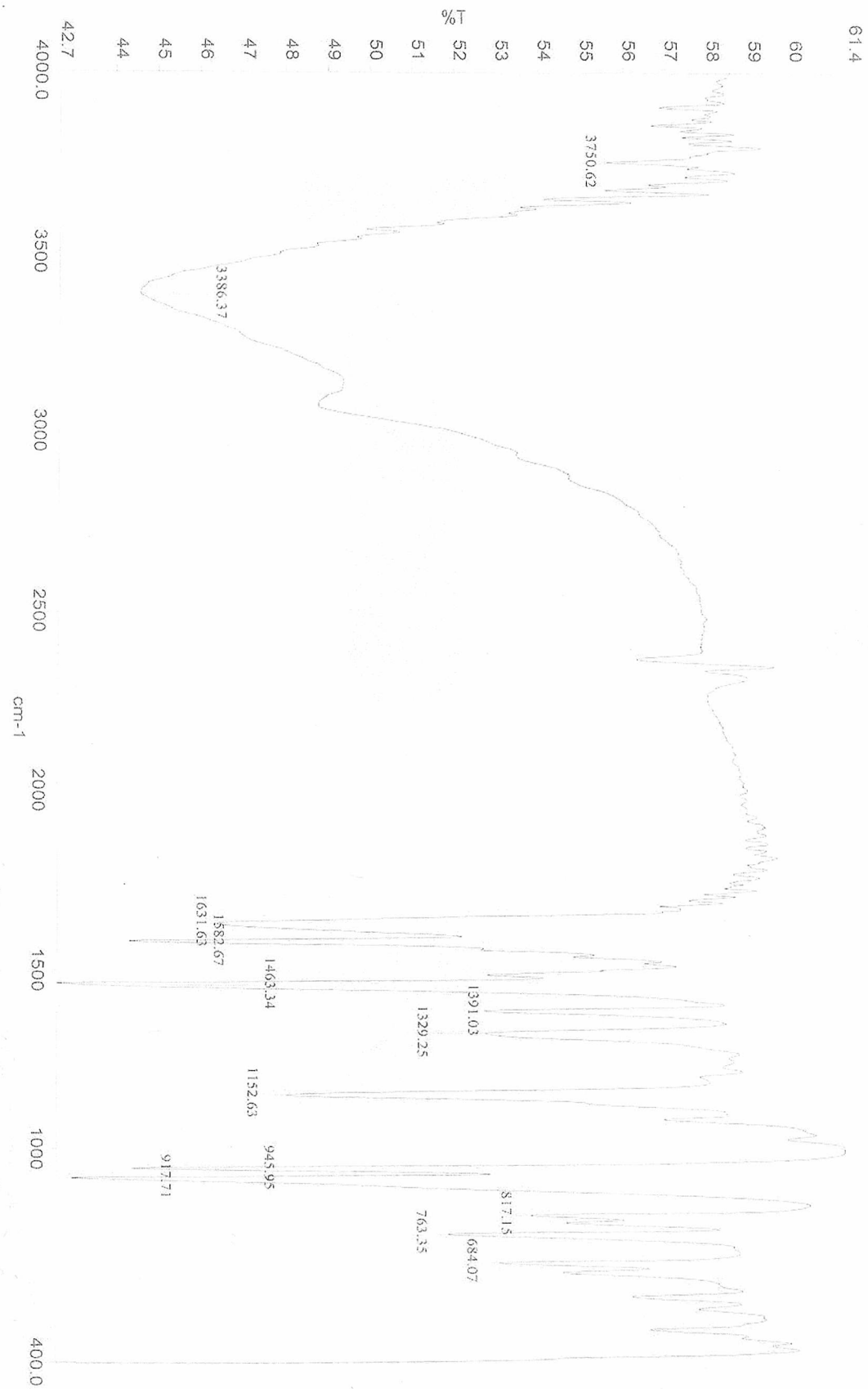


Fig 3.39 IR spectrum of bis(1,2-naphthoquinone 1-oximato)dioxouranium(VI) complex

Fig 3.40 IR spectrum of bis(1,4-naphthoquinone 4-oximato)dioxouranium(VI) complex

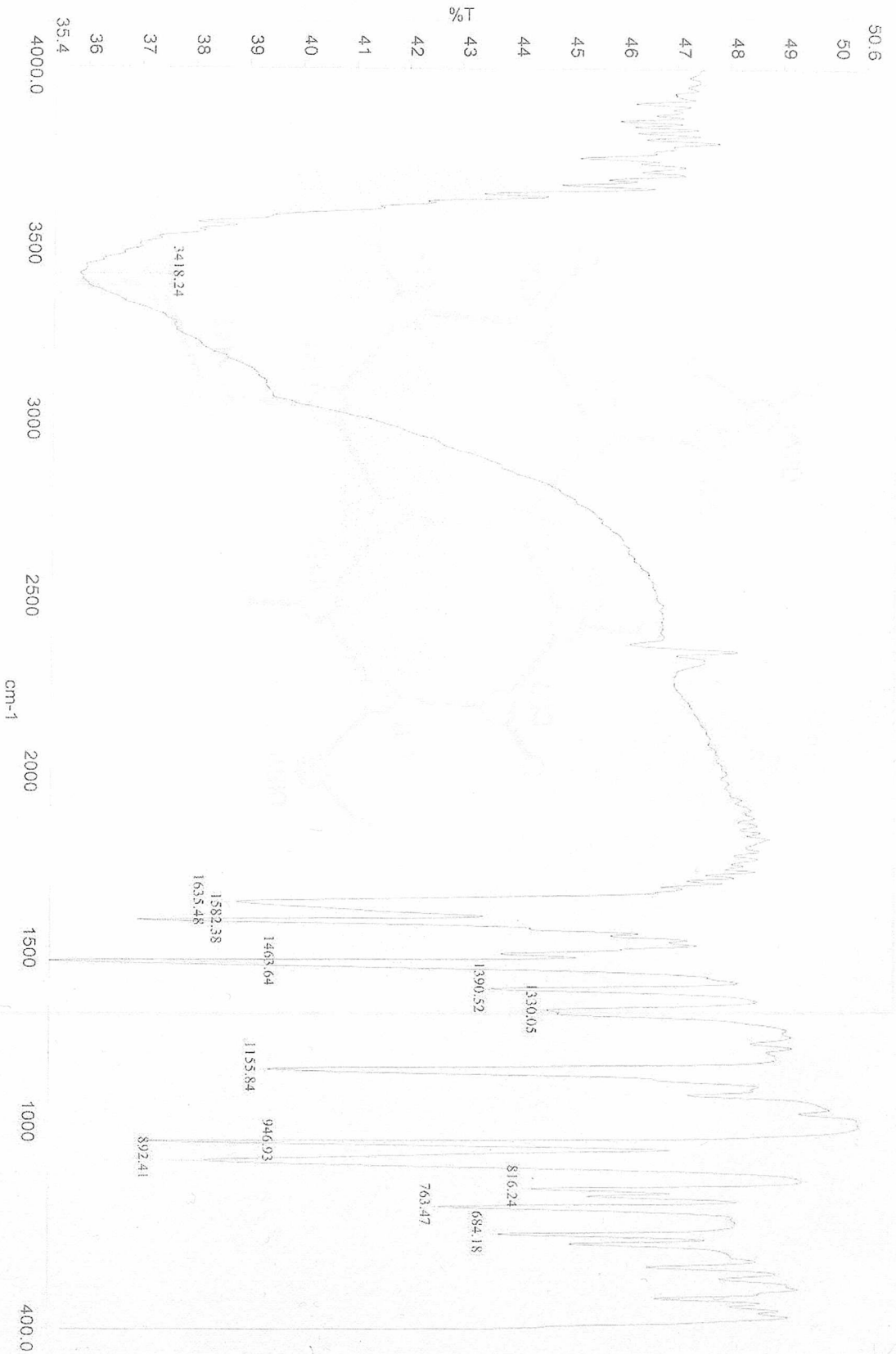


Fig 3.41 X–Ray of 6-hydroxy-1,4-naphthoquinone 4-oxime

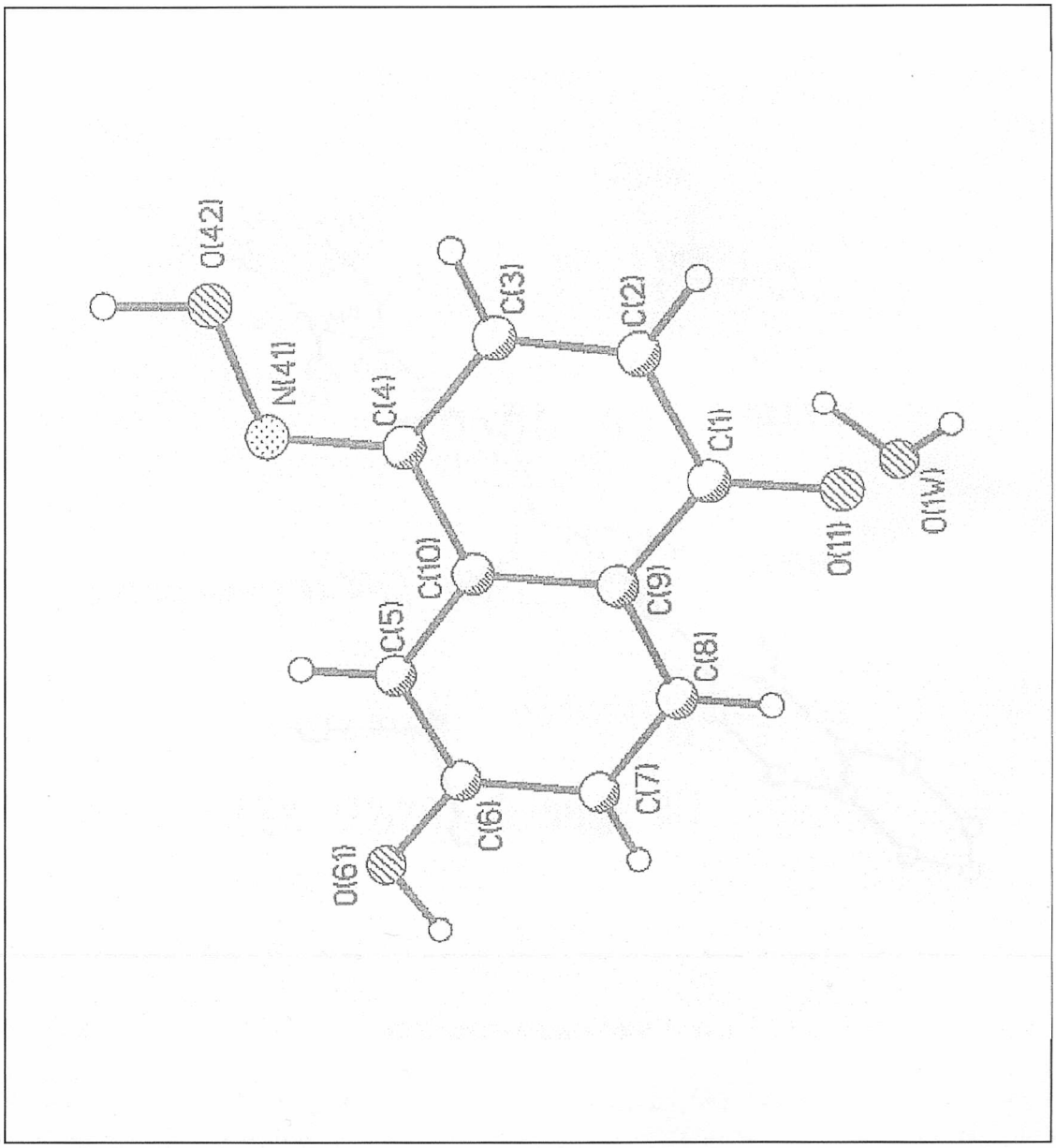
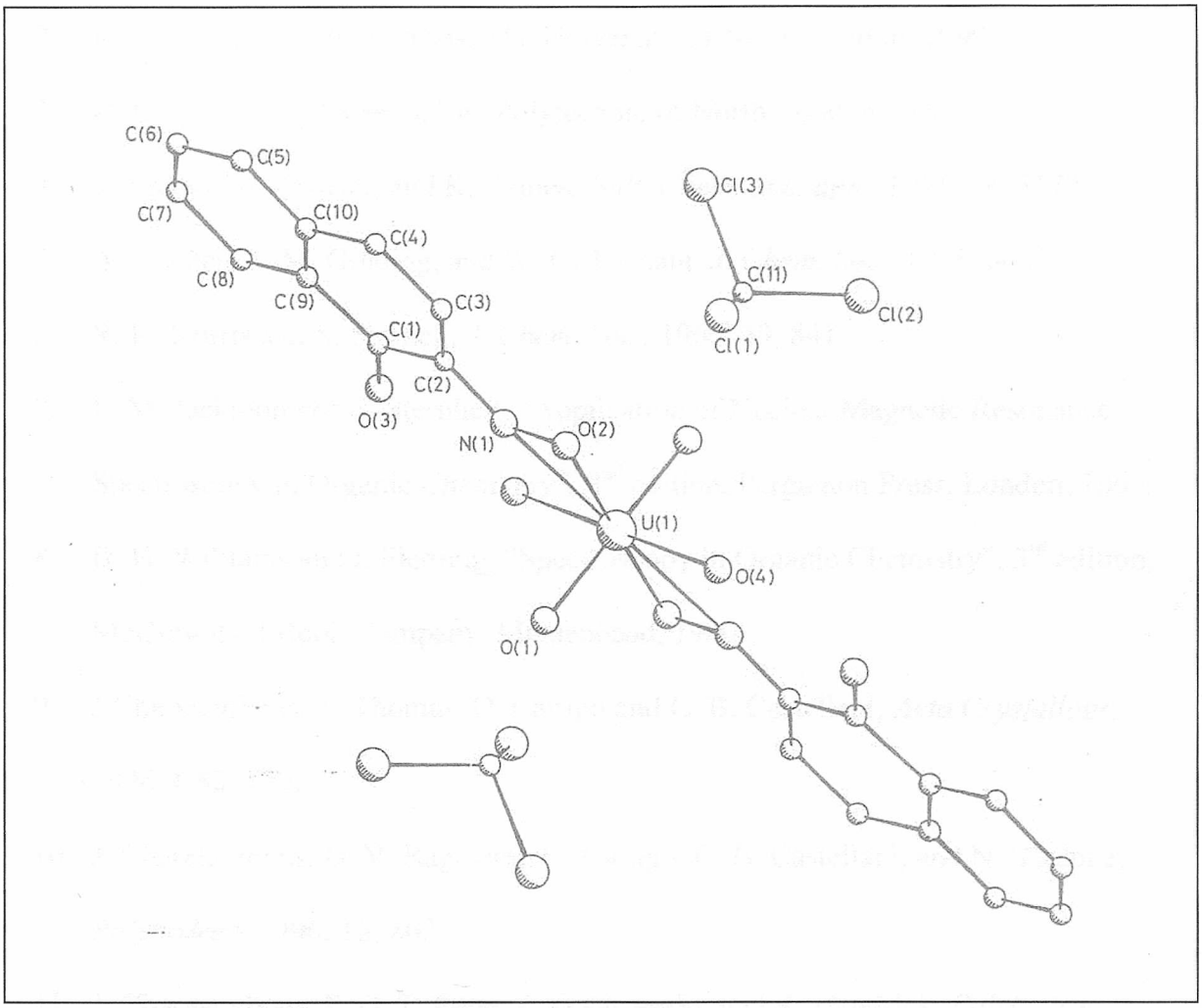


Fig 3.42 X–Ray of Diaquabis(1,2-naphthoquinone 2-oximato)dioxouranium(VI)[22]



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CHAPTER 4

Experimental

4.1 Reagent and General Techniques

The reagents and solvents used in this study were obtained commercially and used without further purification. 1,6-Dihydroxynaphthalene and 2,7-dihydroxynaphthalene supplied by Aldrich and 1,5-dihydroxynaphthalene supplied by Aldrich and Acros companies. Copper(II) sulphate pentahydrate and nickel(II) nitrate hexahydrate supplied by BDH. Sodium nitrite supplied by Acros and uranyl nitrate hexahydrate supplied by Fluka. The silica gel adsorbent used in the preparative tlc was Merck Silica gel GF254 and the ion exchange resin used was Dowex 50WX2 supplied by Fluka. Thin layer chromatography was carried out using commercially supplied silica coated alumina plates.

4.2 Analytical Techniques

Nickel and copper in the samples of metal complexes were determined quantitatively by atomic absorption spectrometry (AAS) using a Perkin Elmer AAnalyst-800. The uranium in the metal complexes was determined quantitatively by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer Elan–DRCII. A known mass (0.050 g) of the metal complex under investigation was warmed with concentrated nitric acid (8 cm^3) and hydrogen peroxide (2 cm^3). After allowing the mixture to digest, the inorganic residue was diluted to a known volume with deionised water. Elemental analyses of carbon, hydrogen and nitrogen were obtained using a Perkin Elmer II CNHS/O analyzer 2400.

4.3 Physical Techniques

All melting points were recorded in open-ended glass capillary tubes with a Stuart Scientific melting point apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Vector 22 FT-IR or Perkin Elmer Spectrum RX1 FT-IR spectrophotometer with samples prepared as pressed potassium bromide discs. Nuclear Magnetic Resonance Spectroscopy – Fourier transform ^{1}H spectra were recorded on a Bruker AM250 or Bruker 400 MHz spectrometer. Tetramethylsilane (TMS) was used as internal reference standard for spectra recorded in d_6-dimethylsulphoxide and deuterated chloroform. Electron Impact (EI) as low or high resolution mass was recorded on Kratos Analytical Profile HV3 high resolution mass spectrometer.

4.4 Reactions

4.4.1 Nitrosation of 1,6-dihydroxynaphthalene with sodium nitrite at 0°C

1,6-Dihydroxynaphthalene (2 g, 12.50 mmol) was dissolved in a warm solution of sodium hydroxide (0.50 g, 12.50 mmol) in water (40 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (0.86 g, 12.50 mmol) was added followed by dropwise addition of conc. sulphuric acid (1.1 cm^3) over a period of 30 mins. The reaction mixture was allowed to reach 20°C over a period of 1 h. Filtration afforded a brown solid, which was reacted with nickel nitrate hexahydrate then followed by Soxhlet extraction for the resultant solid with diethyl ether to give nickel complex which was acidified by diluted hydrochloric acid (6 M) to afford a brown solid which was dried at 0.1 mm/20°C to obtain *6-hydroxy-1,2-naphthoquinone 2-oxime* (1.64g, 70%), m.p. 249-250°C, [Found C, 62.95; H, 3.68; N, 7.29%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189]. Removal of the solvent from diethyl ether extract afforded yellow *6-hydroxy-1,4-naphthoquinone 4-oxime*

(0.50g, 21%), m.p. 254-255°C [Found C, 63.01; H, 3.71; N, 7.38%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189]. To obtain a suitable crystal for X-ray determination, a small portion of this solid is recrystallised from ethanol-water.

4.4.2 Nitrosation of 1,6-dihydroxynaphthalene with an excess of sodium nitrite at 0°C

1,6-Dihydroxynaphthalene (2 g, 12.50 mmol) was dissolved in a warm solution of sodium hydroxide (0.50 g, 12.50 mmol) in water (40 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (2.16 g, 31.30 mmol) was added followed by dropwise addition of conc. sulphuric acid (1.1 cm^3) over a period of 30 mins. The reaction mixture was allowed to reach 20°C over a period of 1 h. Filtration afforded a brown solid, which was reacted with nickel nitrate hexahydrate then followed by Soxhlet extraction for the resultant solid with diethyl ether to give nickel complex which was acidified by diluted hydrochloric acid (6 M) to afford a brown solid which was dried at 0.1 mm/20°C to obtain *6-hydroxy-1,2-naphthoquinone 2-oxime* (1.65 g, 70%), m.p. 249-250°C, [Found C, 63.00; H, 3.64; N, 7.31%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189]. Removal of the solvent from diethyl ether extract afforded yellow *6-hydroxy-1,4-naphthoquinone 4-oxime* (0.51 g, 22%), m.p. 254-255°C [Found C, 62.89; H, 3.64; N, 7.32%;M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.3 Nitrosation of 2,7-dihydroxynaphthalene with sodium nitrite at 0°C

2,7-Dihydroxynaphthalene (2 g, 12.50 mmol) was dissolved in a warm solution of sodium hydroxide (0.50 g, 12.50 mmol) in water (40 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (0.86 g, 12.50 mmol) was added followed by dropwise addition of conc. sulphuric acid (1.1 cm^3) over a period of 30 mins. The reaction mixture was allowed

to reach 20°C over a period of 1 h. Filtration afforded a brown solid which was washed with water and then dried at 0.1 mm/20°C to obtain *7-hydroxy-1,2-naphthoquinone 1-oxime* (2.17 g, 92%), m.p. 237-238°C, [Found C, 63.24; H, 3.71; N, 7.34%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.4 Nitrosation of 2,7-dihydroxynaphthalene with an excess of sodium nitrite at 0°C

2,7-Dihydroxynaphthalene (2 g, 12.50 mmol) was dissolved in a warm solution of sodium hydroxide (0.50 g, 12.50 mmol) in water (40 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (2.16 g, 31.30 mmol) was added followed by dropwise addition of conc. sulphuric acid (1.1 cm^3) over a period of 30 mins. The reaction mixture was allowed to reach 20°C over a period of 1 h. Filtration afforded a brown solid which was washed with water and then dried at 0.1 mm/20°C to obtain *7-hydroxy-1,2-naphthoquinone 1-oxime* (2.19 g, 93%), m.p. 237-238°C, [Found C, 63.36; H, 3.66; N, 7.38%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.5 Nitrosation of 1,5-dihydroxynaphthalene with sodium nitrite at 0°C

1,5-Dihydroxynaphthalene (2 g, 12.50 mmol) was dissolved in a warm solution of sodium hydroxide (0.50 g, 12.50 mmol) in water (40 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (0.86 g, 12.50 mmol) was added followed by dropwise addition of conc. sulphuric acid (1.1 cm^3) over a period of 30 mins. The reaction mixture was allowed to reach 20°C over a period of 1 h. Filtration afforded a dark brown solid, multicomponents by tlc (1.91 g), which was reacted with nickel nitrate hexahydrate then followed by Soxhlet extraction of the resultant solid with ethyl acetate to give nickel complex which was acidified by diluted hydrochloric acid (6 M) to afford a dark brown solid, three

components by tlc (0.94 g). Removal of the solvent from ethyl acetate extract gave a gummy residue, a multicomponents by tlc (0.49g).

In order to identify the dark brown solid, 0.085g was separated by preparative tlc which resulted unidentifiable mixture solid, yellow-brown solid (0.006g 7%). The brown strip was then scratched and dissolved in methanol and filtered. The filtrate was rotary evaporated and dried at 0.1 mm/20°C to afford a brown solid *5-hydroxy-1,2-naphthoquinone 2-oxime* (0.023 g, 27%), m.p. 201-202°C, [Found C, 63.25; H, 3.68; N, 7.36%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.6 Nitrosation of 1,5-dihydroxynaphthalene with an excess of sodium nitrite at 0°C

1,5-Dihydroxynaphthalene (2 g, 12.50 mmol) was dissolved in a warm solution of sodium hydroxide (0.50 g, 12.50 mmol) in water (40 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (2.16 g, 31.30 mmol) was added followed by dropwise addition of conc. sulphuric acid (1.1 cm^3) over a period of 30 mins. The reaction mixture was allowed to reach 20°C over a period of 1 h. Filtration afforded a dark brown solid, multicomponents by tlc (1.93 g), which was reacted with nickel nitrate hexahydrate then followed by Soxhlet extraction for the resultant solid with ethyl acetate to give nickel complex which was acidified by diluted hydrochloric acid (6 M) to afford a dark brown solid, three components by tlc (0.95 g). Removal of the solvent from ethyl acetate extract gave a gummy residue, a multicomponents by tlc (0.50g).

In order to identify the dark brown solid, 0.10 g was separated by preparative tlc which resulted unidentifiable mixture solid, yellow-brown solid (0.009g 9%). The brown strip was then scratched and dissolved in methanol and filtered. The filtrate was rotary evaporated and dried at 0.1 mm/20°C to afford a brown solid *5-hydroxy-1,2-*

naphthoquinone 2-oxime (0.025 g, 25%), m.p. 201-202°C, [Found C, 63.12; H, 3.69; N, 7.31%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.7 Reaction of 6-hydroxy-1,2-naphthoquinone 2-oxime with an excess of sodium nitrite at 0°C

6-hydroxy-1,2-naphthoquinone 2-oxime (0.112 g, 0.592 mmol) was dissolved in methanol (30 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (0.061 g, 0.884 mmol) was added followed by dropwise addition of conc. sulphuric acid (0.20 cm^3) over a period of 30 mins. The reaction mixture was stirred for 24 h at 20°C and concentrated to low volume then water was added. The mixture was allowed to stand and filtration afforded a brown solid which was washed with water and then dried at 0.1 mm/20°C to recover 6-hydroxy-1,2-naphthoquinone 2-oxime. The results of elemental analyses, melting point and comparative tlc with starting compound show the two compounds are identical and suggesting that no di-nitrosation reaction took place.

4.4.8 Reaction of 7-hydroxy-1,2-naphthoquinone 1-oxime with an excess of sodium nitrite at 0°C

7-hydroxy-1,2-naphthoquinone 1-oxime (0.114 g, 0.603 mmol) was dissolved in methanol (30 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (0.062 g, 0.898 mmol) was added followed by dropwise addition of conc. sulphuric acid (0.20 cm^3) over a period of 30 mins. The reaction mixture was stirred for 24 h at 20°C and concentrated to low volume then water was added. The mixture was allowed to stand and filtration afforded a brown solid which was washed with water and then dried at 0.1 mm/20°C to recover 7-hydroxy-1,2-naphthoquinone 1-oxime. The results of elemental analyses,

melting point and comparative tlc with starting compound show the two compounds are identical and suggesting that no di-nitrosation reaction took place.

4.4.9 Reaction of 5-hydroxy-1,2-naphthoquinone 2-oxime with an excess of sodium nitrite at 0°C

5-hydroxy-1,2-naphthoquinone 2-oxime (0.098 g, 0.518 mmol) was dissolved in methanol (30 cm^3). The solution was cooled to 0°C. To this solution, sodium nitrite (0.054 g, 0.783 mmol) was added followed by dropwise addition of conc. sulphuric acid (0.20 cm^3) over a period of 30 mins. The reaction mixture was stirred for 24 h at 20°C and concentrated to low volume then water was added. The mixture was allowed to stand and filtration afforded a brown solid which was washed with water and then dried at 0.1 mm/20°C to recover 5-hydroxy-1,2-naphthoquinone 2-oxime. The results of elemental analyses, melting point and comparative tlc with starting compound show the two compounds are identical and suggesting that no di-nitrosation reaction took place.

4.4.10 Reaction of 6-hydroxy-1,2-naphthoquinone 2-oxime with acetic anhydride

Acetic anhydride (3.50 cm^3, 37 mmol) was added to 6-hydroxy-1,2-naphthoquinone 2-oxime (0.500 g, 2.65 mmol) in acetone (100 cm^3) at 20°C. The mixture was stirred for 12 h and concentrated to dryness. Light petroleum ether (40–60°C) was added to the residue and after stirring the resultant mixture was filtered and dried at 0.1 mm/20°C to afford yellow *2-acetoxyimino-6-hydroxy-1,2-naphthoquinone* (0.457 g, 75%), m.p.164-165°C [Found C, 61.56; H, 3.77; N, 5.97%; M 231, $C_{12}H_9O_4N$ requires C, 62.34; H, 3.90; N, 6.06%; M 231].

4.4.11 Reaction of 7-hydroxy-1,2-naphthoquinone 1-oxime with acetic anhydride

Acetic anhydride (3.50 cm^3, 37 mmol) was added to 7-hydroxy-1,2-naphthoquinone 1-oxime (0.500 g, 2.65 mmol) in acetone (100 cm^3) at 20°C. The mixture was stirred for 12 h and concentrated to dryness. Light petroleum ether (40–60°C) was added to the residue and after stirring the resultant mixture was filtered and dried at 0.1 mm/20°C to afford brown *1-acetoxyimino-7-acetoxy-1,2-naphthoquinone* (0.578g, 80%), m.p.154-155°C [Found C, 60.48; H, 3.91; N, 5.01%; M 273, $C_{14}H_{11}O_5N$ requires C, 61.54; H, 4.03; N, 5.13%; M 273]

4.4.12 Reaction of 5-hydroxy-1,2-naphthoquinone 2-oxime with acetic anhydride

Acetic anhydride (0.70 cm^3, 7.50 mmol) was added to 5-hydroxy-1,2-naphthoquinone 2-oxime (0.100 g, 0.53 mmol) in acetone (50 cm^3) at 20°C. The mixture was stirred for 12 h and concentrated to dryness. Light petroleum ether (40–60°C) was added to the residue and after stirring the resultant mixture was filtered and dried at 0.1 mm/20°C to afford green *2-acetoxyimino-5-acetoxy-1,2-naphthoquinone* (0.114 g, 79%), m.p.158-159°C [Found C, 60.65; H, 3.95; N, 5.07%; M 273, $C_{14}H_{11}O_5N$ requires C, 61.54; H, 4.03; N, 5.13%; M 273].

4.4.13 Nitrosation of 1,6-dihydroxynaphthalene with sodium nitrite in the presence of nickel(II) nitrate

A solution of sodium nitrite (2.16 g, 31.30 mmol) in water (10 cm^3) was added dropwise with continuous stirring for 1 h to a cold mixture (0°C) of 1,6-dihydroxynaphthalene (4.0 g, 25 mmol) in methanol-water (3:2, 200 cm^3), acetic acid (9.50 cm^3), sodium acetate trihydrate (9.50 g) and nickel nitrate hexahydrate (3.63 g, 12.50 mmol) in water (20 cm^3).

The mixture was stirred for 2 h at room temperature. Filtration gave a brown solid, which was washed with water, ethyl acetate and diethyl ether, and then dried in air. Soxhlet extraction with diethyl ether afforded a brown residue *bis(6-hydroxy-1,2-naphthoquinone 2-oximato)nickel(II)* (3.86g, 71%), m.p. > 300°C [Found C, 55.38; H, 3.17; N, 6.39; Ni, 13.28%, $C_{20}H_{12}O_6N_2Ni$ requires C, 55.21; H, 2.76; N, 6.44; Ni, 13.50%]. The filtrate was rotary evaporated to afford a yellow solid of *6-hydroxy-1,4-naphthoquinone 4-oxime* (0.95g, 20%), m.p. 254-255°C [Found C, 63.72; H, 3.68; N, 7.46%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.14 Nitrosation of 1,6-dihydroxynaphthalene with sodium nitrite in the presence of copper(II) sulphate

A solution of sodium nitrite (2.16 g, 31.30 mmol) in water (10 cm^3) was added dropwise with continuous stirring for 1 h to a cold mixture (0°C) of 1,6-dihydroxynaphthalene (4.0 g, 25 mmol) in methanol-water (3:2, 200 cm^3), acetic acid (9.50 cm^3), sodium acetate trihydrate (9.50 g) and copper sulphate pentahydrate (3.12 g, 12.50 mmol) in water (20 cm^3). The mixture was stirred for 2 h at room temperature. Filtration gave a brown solid, which was washed with water, ethyl acetate and diethyl ether, and then dried in air. Soxhlet extraction with diethyl ether afforded a brown residue *bis(6-hydroxy-1,2-naphthoquinone 2-oximato)copper(II)* (4.17 g, 76%), m.p. > 300°C [Found C, 55.13; H, 2.80; N, 6.45; Cu, 14.31%, $C_{20}H_{12}O_6N_2Cu$ requires C, 54.60; H, 2.73; N, 6.37; Cu, 14.46%]. The filtrate was rotary evaporated to afford a yellow solid of *6-hydroxy-1,4-naphthoquinone 4-oxime* (0.91g, 19%), m.p. 254-255°C [Found C, 63.85; H, 3.65; N, 7.42%; M 189, $C_{10}H_7NO_3$ requires C, 63.49; H, 3.70; N, 7.40%; M 189].

4.4.15 Nitrosation of 2,7-dihydroxynaphthalene with sodium nitrite in the presence of nickel(II) nitrate

A solution of sodium nitrite (2.16 g, 31.30 mmol) in water (10 cm^3) was added dropwise with continuous stirring for 1 h to a cold mixture (0°C) of 2,7-dihydroxynaphthalene (4.0 g, 25 mmol) in methanol-water (3:2, 200 cm^3), acetic acid (9.50 cm^3), sodium acetate trihydrate (9.50 g) and nickel nitrate hexahydrate (3.63 g, 12.50 mmol) in water (20 cm^3). The mixture was stirred for 2 h at room temperature. Filtration gave a dark brown solid, which was washed with water, ethyl acetate and diethyl ether, and then dried in air. Soxhlet extraction with ethyl acetate afforded a dark brown residue *bis(7-hydroxy-1,2-naphthoquinone 1-oximato)nickel(II)* (4.94 g, 91%), m.p. > 300°C [Found C, 55.73; H, 3.24; N, 6.52; Ni, 13.34%, $C_{20}H_{12}O_6N_2Ni$ requires C, 55.21; H, 2.76; N, 6.44; Ni, 13.50%].

4.4.16 Nitrosation of 2,7-dihydroxynaphthalene with sodium nitrite in the presence of copper(II) sulphate

A solution of sodium nitrite (2.16 g, 31.30 mmol) in water (10 cm^3) was added dropwise with continuous stirring for 1 h to a cold mixture (0°C) of 2,7-dihydroxynaphthalene (4.0 g, 25 mmol) in methanol-water (3:2, 200 cm^3), acetic acid (9.50 cm^3), sodium acetate trihydrate (9.50 g) and copper sulphate pentahydrate (3.12 g, 12.50 mmol) in water (20 cm^3). The mixture was stirred for 2 h at room temperature. Filtration gave a dark brown solid, which was washed with water, ethyl acetate and diethyl ether, and then dried in air. Soxhlet extraction with ethyl acetate afforded a brown residue *bis(7-hydroxy-1,2-naphthoquinone 1-oximato)copper(II)* (5.05 g, 92%), m.p. > 300°C [Found C, 54.83; H, 2.78; N, 6.41; Cu, 14.51%, $C_{20}H_{12}O_6N_2Cu$ requires C, 54.60; H, 2.73; N, 6.37; Cu, 14.46%].

4.4.17 Nitrosation of 1,5-dihydroxynaphthalene with sodium nitrite in the presence of nickel(II) nitrate

A solution of sodium nitrite (2.16 g, 31.30 mmol) in water (10 cm^3) was added dropwise with continuous stirring for 1 h to a cold mixture (0°C) of 1,5-dihydroxynaphthalene (4.0 g, 25 mmol) in methanol-water (3:2, 200 cm^3), acetic acid (9.50 cm^3), sodium acetate trihydrate (9.50 g) and nickel nitrate hexahydrate (3.63 g, 12.50 mmol) in water (20 cm^3). The mixture was stirred for 2 h at room temperature. Filtration gave a dark brown residue which was washed with water, ethyl acetate and diethyl ether, and then dried in air. Soxhlet extraction with ethyl acetate gave an unidentifiable dark violet solid (2.53g)

4.4.18 Nitrosation of 1,5-dihydroxynaphthalene with sodium nitrite in the presence of copper(II) sulphate

A solution of sodium nitrite (2.16 g, 31.30 mmol) in water (10 cm^3) was added dropwise with continuous stirring for 1 h to a cold mixture (0°C) of 1,5-dihydroxynaphthalene (4.0 g, 25 mmol) in methanol-water (3:2, 200 cm^3), acetic acid (9.50 cm^3), sodium acetate trihydrate (9.50 g) and copper sulphate pentahydrate (3.12 g, 12.50 mmol) in water (20 cm^3). The mixture was stirred for 2 h at room temperature. Filtration gave a dark brown residue which was washed with water, ethyl acetate and diethyl ether, and then dried in air. Soxhlet extraction with ethyl acetate gave an unidentifiable dark violet solid (2.46g)

4.4.19 Interaction of bis(7-hydroxy-1,2-naphthoquinone 1-oximato)nickel(II) with hydrochloric acid at 20°C

Concentrated hydrochloric acid (10 cm^3) was added to a well suspended complex (0.50 g, 1.15 mmol) in water (10 cm^3) and the mixture was stirred for 1 h at 20°C. Filtration

afforded brown *7-hydroxy-1,2-naphthoquinone 1-oxime* (0.38 g, 87%) identified by comparative tlc and IR spectrum, which was washed with dilute hydrochloric acid and water and dried.

4.4.20 Interaction of bis(6-hydroxy-1,2-naphthoquinone 2-oximato)nickel(II) with hydrochloric acid at 20°C

Concentrated hydrochloric acid (10 cm^3) was added to a well suspended complex (0.50 g, 1.15 mmol) in water (10 cm^3) and the mixture was stirred for 1 h at 20°C. Filtration afforded brown *6-hydroxy-1,2-naphthoquinone 2-oxime* (0.39 g, 90%) identified by comparative tlc and IR spectrum, which was washed with dilute hydrochloric acid and water and dried.

4.4.21 Interaction of Ni complex derived from 1,5-dihydroxynaphthalene with hydrochloric acid at 20°C

Concentrated hydrochloric acid (10 cm^3) was added to a well suspended complex (0.50 g) in water (10 cm^3) and the mixture was stirred for 1 h at 20°C. Filtration afforded a dark brown solid, three components by tlc (0.29 g).

4.4.22 Synthesis of 7-hydroxy-1,2-naphthoquinone 1-oxime by ion exchange

A methanolic solution of bis(7-hydroxy-1,2-naphthoquinone 1-oximato)copper(II) (0.250 g, 0.57 mmol) was added to an ion exchange column (30 cm X 2 cm) (Dowex 50WX2 Cation Exchange Resin) and eluted with methanol/water (4:1). The solvent was removed under reduced pressure to obtain *7-hydroxy-1,2-naphthoquinone 1-oxime* (0.120 g, 56%), which was identified by comparative tlc.

4.4.23 Synthesis of 5-hydroxy-1,2-naphthoquinone 2-oxime by ion exchange

A methanolic solution of copper(II) complex (0.250 g) was added to an ion exchange column (30 cm X 2 cm) (Dowex 50WX2 Cation Exchange Resin) and eluted with methanol/water (4:1). The solvent was removed under reduced pressure to afford a dark brown solid, three components by tlc (0.056 g).

4.4.24 Reaction of 1,2-naphthoquinone 2-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in water (10 cm^3) was added to a mixture of 1,2-naphthoquinone 2-oxime (0.400 g, 2 mmol) and lithium hydroxide (0.055 g, 2 mmol) in water-methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a red solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate* (0.618 g, 82%), m.p. > 300°C.

4.4.25 Reaction of 1,2-naphthoquinone 1-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in water (10 cm^3) was added to a mixture of 1,2-naphthoquinone 1-oxime (0.400 g, 2 mmol) and lithium hydroxide (0.055 g, 2 mmol) in water-methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a dark brown solid which was washed with methanol and dried at 0.1 mm/20°C to obtain *bis(1,2-naphthoquinone 1-oximato)dioxouranium(VI) dihydrate* (0.639 g, 85%), m.p. > 300°C.

4.4.26 Reaction of 1,2-naphthoquinone 2-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in absolute methanol (10 cm^3) was added to a mixture of 1,2-naphthoquinone 2-oxime (0.400 g, 2 mmol) and triethyl amine (0.214 g, 2 mmol) in absolute methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a red solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate* (0.602 g, 80%), m.p. > 300°C [Found C, 37.20; H, 2.50; N, 4.35; U, 36.22%, $C_{20}H_{16}N_2O_8U$ requires C, 36.92; H, 2.46; N, 4.31, U, 36.62%].

4.4.27 Reaction of 1,2-naphthoquinone 1-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in absolute methanol (10 cm^3) was added to a mixture of 1,2-naphthoquinone 1-oxime (0.400 g, 2 mmol) and triethyl amine (0.214 g, 2 mmol) in absolute methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a dark brown solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(1,2-naphthoquinone 1-oximato)dioxouranium(VI) dihydrate* (0.615 g, 82%), m.p. > 300°C [Found C, 36.36; H, 2.40; N, 4.21; U, 36.47%, $C_{20}H_{16}N_2O_8U$ requires C, 36.92; H, 2.46; N, 4.31, U, 36.62%].

4.4.28 Reaction of 1,4-naphthoquinone 4-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in absolute methanol (10 cm^3) was added to a mixture of 1,4-naphthoquinone 4-oxime (0.400 g, 2 mmol) and triethyl amine (0.214 g, 2 mmol) in absolute methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a orange solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(1,4-naphthoquinone 4-oximato)dioxouranium(VI)*

dihydrate (0.625 g, 83%), m.p. > 300°C [Found C, 36.59; H, 2.48; N, 4.28; U, 36.38%, $C_{20}H_{16}N_2O_8U$ requires C, 36.92; H, 2.46; N, 4.31, U, 36.62%].

4.4.29 Reaction of 6-hydroxy-1,2-naphthoquinone 2-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in absolute methanol (10 cm^3) was added to a mixture of 6-hydroxy-1,2-naphthoquinone 2-oxime (0.400 g, 2 mmol) and triethyl amine (0.214 g, 2 mmol) in absolute methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a brown solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(6-hydroxy-1,2-naphthoquinone 2-oximato)dioxouranium(VI) dihydrate* (0.556 g, 77%), m.p. > 300°C [Found C, 35.04; H, 2.34; N, 4.06; U, 34.75%, $C_{20}H_{16}N_2O_{10}U$ requires C, 35.19; H, 2.35; N, 4.10, U, 34.89%].

4.4.30 Reaction of 7-hydroxy-1,2-naphthoquinone 1-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in absolute methanol (10 cm^3) was added to a mixture of 7-hydroxy-1,2-naphthoquinone 1-oxime (0.400 g, 2 mmol) and triethyl amine (0.214 g, 2 mmol) in absolute methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a dark brown solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(7-hydroxy-1,2-naphthoquinone 1-oximato)dioxouranium(VI) dihydrate* (0.572 g, 79%), m.p. > 300°C [Found C, 34.56; H, 2.30; N, 3.99; U, 34.68%, $C_{20}H_{16}N_2O_{10}U$ requires C, 35.19; H, 2.35; N, 4.10, U, 34.89%].

4.4.31 Reaction of 6-hydroxy-1,4-naphthoquinone 4-oxime with uranyl nitrate

A solution of uranyl nitrate hexahydrate (0.531 g, 1 mmol) in absolute methanol (10 cm^3) was added to a mixture of 6-hydroxy-1,4-naphthoquinone 4-oxime (0.400 g, 2 mmol)

and triethyl amine (0.214 g, 2 mmol) in absolute methanol (100 cm^3) at room temperature and stirred over night. Filtration afforded a brown solid which was washed with absolute methanol and dried at 0.1 mm/20°C to obtain *bis(6-hydroxy-1,4-naphthoquinone 4-oximato)dioxouranium(VI) dihydrate* (0.578 g, 80%), m.p. > 300°C [Found C, 35.40; H, 2.38; N, 4.12; U, 34.91%, $C_{20}H_{16}N_2O_{10}U$ requires C, 35.19; H, 2.35; N, 4.10, U, 34.89%].