SYNTHESES AND PROPERTIES OF TRANSITION METAL ION COMPLEXES OF A NOVEL BINUCLEATING EXTENDED-PORPHYRIN ANALOG

By

Ngala, J. K.

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.....Ngala.....

SUPERVISORS:

Dr. Acholla, F. V. .....

Dr. Ogur, J. A. .....

ABSTRACT.

The synthesis and characterisation of the uncomplexed ligand of a macrocyclic extended-porphyrin analog and its binuclear complexes with Zn^{2+}, Cu^{2+} and Co^{2+} has been undertaken. The dicobalt complex has displayed ability to bind dioxygen and hence activate it towards the oxidation of 2,6-Diisopropylphenol, which is otherwise a spin-forbidden process. This catalytic activity has been found to be superior to that of an analogous complex of smaller cavity size, following rate studies.

Multi-metal centred biomolecules as well as porphyrins have been found to play an important role towards the activation of oxygen.

Acknowledgements

I would like to thank the University of Nairobi for facilitating this research work by providing the research fund.

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I appreciate the assistance I received from my colleague, Ooko, in the computer operations. To him, also, I send my gratitudes.

Socially, I am sending my heartfelt thanks to the Dzombos, Munga, the Kombes and all others who made my life comfortable during the time span of my research.

Lastly, my deep appreciations goes to my family. Their moral support, as well as their patience, have been instrumental towards the success of this work. God bless us.

To my parents(Ngala and Mlongo),

brothers and sisters

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CHAPTER I

Literature Review

Nature posseses highly sophisticated ways of controlling the flexible stereochemistry of metal ions. This reason has been a source of a lot of interest in the metalloproteins of oxygenase and oxidase activity.

The design and synthesis of relatively low molecular weight compounds having similar structures and functions as the active sites of metalloproteins constitutes a traditional approach towards the understanding of the chemistry of these systems. In this light, the synthesis of transition metal complexes of macrocyclic ligands has been an area of major focus over the past four decades.

Metalloproteins[1-3] posses one or more metal ions as an essential constituent that is firmly bound to a protein. Hemoproteins constitutes a class of metalloproteins and their active sites are characterised by a heme; an iron atom in a porphyrin periphery. In this class are haemoglobin and myoglobin, responsible for O_2 transport and storage, respectively[4], found in all vertebrates and in some worms and insects. Also cytochromes[5-7] which serve as electron carriers, belong to this class. They mediate the oxidation of substrates with reduction of O_2. Cytochrome P - 450 generally catalyses the

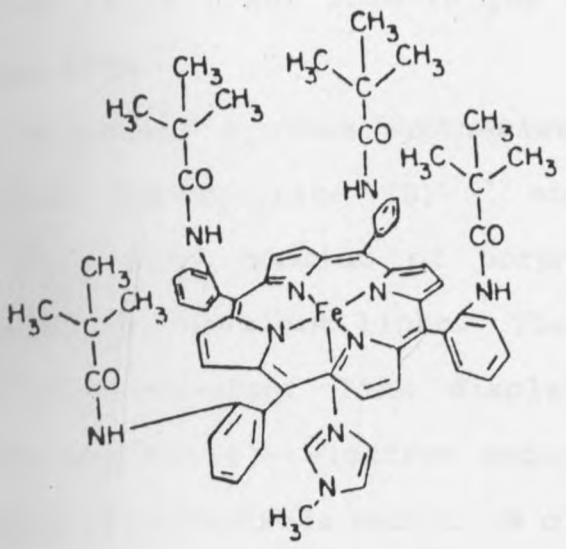
insertion of an oxygen atom in a C-H bond. Nature has devised an elegant way of manipulating the spin of oxygen hence effecting oxidation[8-10]. Independently, oxygen has a triplet ground state and its reaction with a singlet organic substrate is spin forbidden[8]. It is generally postulated that O_2 activation is accomplished by its binding to the metal ion in the active site, followed by formation of a complex intermediate with the substrate during oxidation[11].

Copper proteins consist of a binuclear copper active site and represent multicentered biomolecules. Hemocyanin, is responsible for the blue blood in lobsters[12], while tyrosinase catalyses hydroxylation of tyrosine, and the active sites for both bind dioxygen in a binuclear manner[13,14].

The synthesized compounds which mimic these natural systems can be categorized in two groups, namely: (i) Heme type (ii) Non-Heme type.

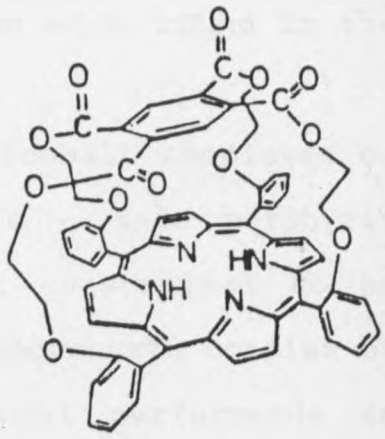
Heme type

A lot of attention has been directed towards probing haemoglobin and myoglobin[12,15,16,17], resulting in the synthesis of numerous compounds as their synthetic analogs. The most successful were the "picket fence" porphyrins (A) of Collman[18,19], "capped" porphyrins (B)[20] and bis pocket porphyrins (C)[21] of Baldwin and Suslick respectively, which reversibly bind O_2 at room temperature.



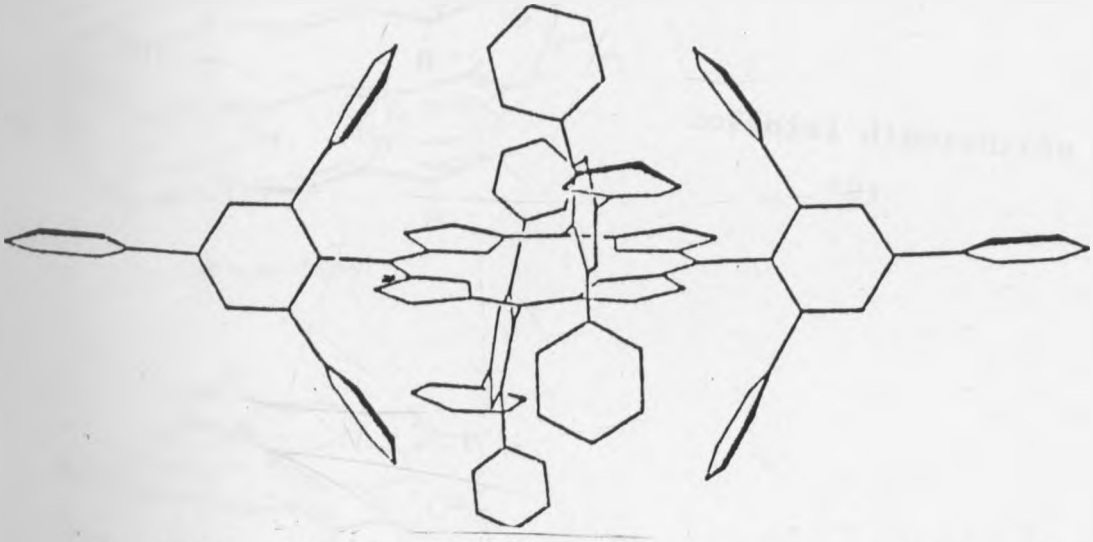
Collman's "picket fence" porphyrin

(A)



Baldwin's "capped" porphyrin

(B)

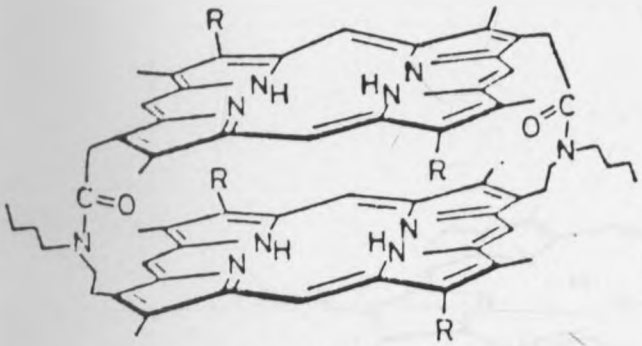


Suslik's "bis-pocket" porphyrin. Double bonds are omitted for clarity.

(C)

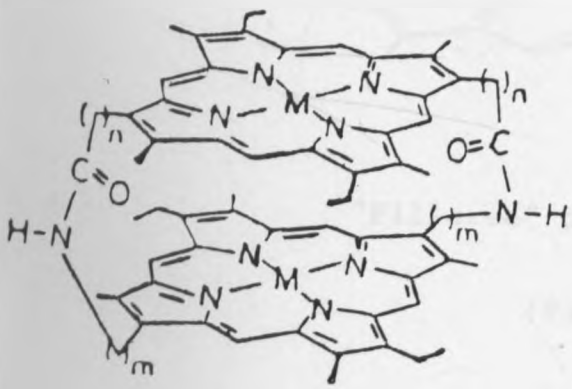
Following their synthesis, it was established[18-22] that steric control plays a key role in the stabilization of O_2 bound to the active site.

Binuclear systems synthesized include dicobalt complexes of cofacial diporphyrins (D)[23,24] and face - to - face porphyrin (E)[17,25]. They consist of porphyrin planes constrained to be parallel by covalent links. The cofacial diporphyrin complex of 4 - atom covalent link displayed exceptional performance in catalyzing the 4 - electron reduction of O_2 to H_2O[25-27] when coated on graphite electrode and it is cited as a model for multi - metal centered biomolecules[28]. The process was effected via protonation of the μ - peroxo dimer intermediate formed.



cofacial diporphyrin

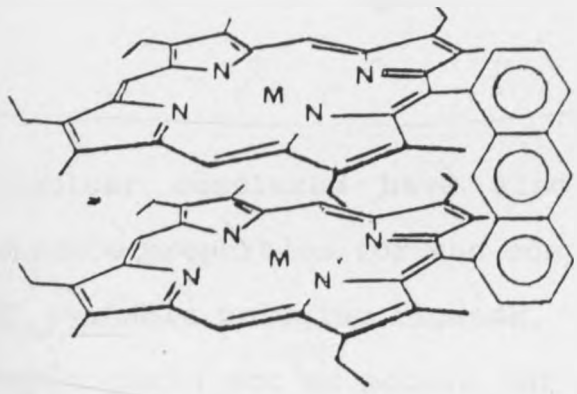
(D)



face-to-face porphyrin dimer

(E)

"pillared" cofacial diporphyrin (F)[29,30] comprising rigid separations between the porphyrin planes, that preclude lateral displacements of the planes, have been synthesized by Chang in studying the effect of separation of planes on the performance of the complex. The "pillars" employed were anthracene and biphenylene. Both complexes effectively catalyzed the electrode reduction of O_2 to H_2O[26,31]. It was proposed that the activity of the complex relies on its capability in producing the suitable conformation for the μ - peroxo complex.



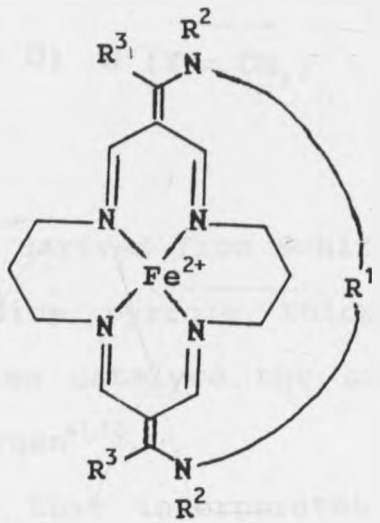
"Pillared" diporphyrin

(F)

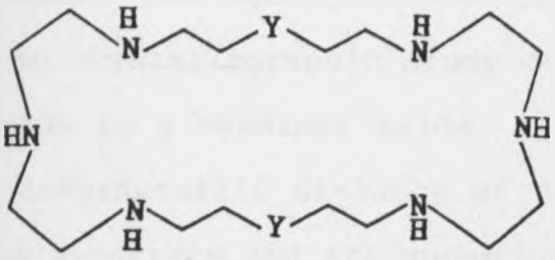
Non - Heme Type

Busch and coworkers[32-34] have synthesized complexes of lacunar macrobicyclic ligands shown in (G), of which the Fe(II)[35,36] and Co(II)[37] complexes exhibited outstanding capabilities in binding O_2 reversibly.

(G)



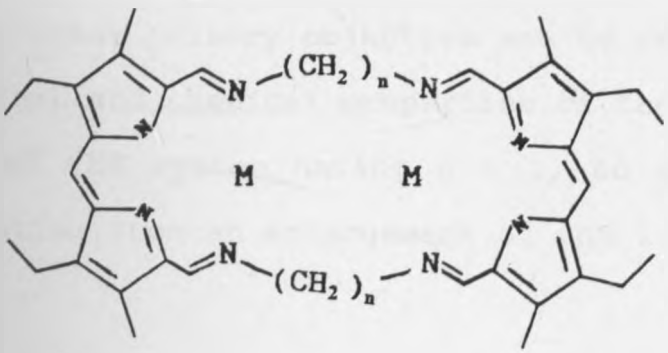
Numerous binuclear complexes have also been synthesized. Conveniently, desirable properties for the complexes are imposable by introduction of suitable bridging ligands. Among the binuclear copper complexes that could act as models for copper proteins are two types. One type are the macrocyclic inclusion complexes (H & H')[38,39]. For instance the μ-monohydroxy complexes reported by Lippard[40] share similar electronic and magnetic properties as the copper proteins.



H(Y = O) H'(Y = CH_2)

Other types have been derived from Schiff base condensation of carboxaldehydes of pyridine, pyrrole, thiophene and furan[41-51]. A number of these complexes catalyse the oxidation of organic substrates by molecular oxygen[41,52].

A hybrid system (I), that incorporates the two features; tetrapyrrolic framework, characteristic of porphyrins and coplanar metal atoms in proximity, has been synthesized[53].



(I) M = Co^{2+}, Cu^{2+}, Zn^{2+} etc.

The chloro - dicobalt(II) and azido - dicopper(II) complexes for n = 3 achieved the catalysis of oxidation of organic substrates. X - ray crystallographic study of the latter complex revealed, in addition to a terminal azide, an elliptical void at its centre and an intermetallic distance of 5Å. The void allows the approach of the substrate and its subsequent interaction with the metal atoms.

Systems for which n > 3 have not been studied. It was envisioned that an enlarged cavity size would create more room for interaction between a substrate and the metal atoms while the increased flexibility serves, more efficiently, any conformational demands. Larger cavity would permit bridge formation by a larger group ligand. Bridging ligands provide media for antiferromagnetic coupling in copper proteins.

Objectives:

It was the purpose of this work to synthesize the porphyrin - like bimetallic system (I) for n > 3, from its fundamental source. The other primary objective was to compare at least some of the physical and chemical properties of the synthesized system with those of the system having n = 3, so as to establish the effect emanating from an enlargement of the ligand cavity.

Major focus in n = 3, for comparison, was directed towards the azido - copper and the chloro - cobalt complexes, since they displayed catalytic activity[54].

Variation of the n value was affordable by way of utilizing different lengths of diamines in the Schiff base condensation with 5,5' - diformyldipyrromethane. In this work 1,6-hexamethylenediamine was employed, and synthesized were the free ligand, and complexes with Zn^{2+}, Cu^{2+} and Co^{2+} metal ions. The anions used were Cl^-, ClO_4^- and N_3^-. Properties of the synthesized compounds were elucidated with the aid of mass spectrometry, IR, ^1H NMR ^{13}C NMR, microanalysis and UV/VIS.

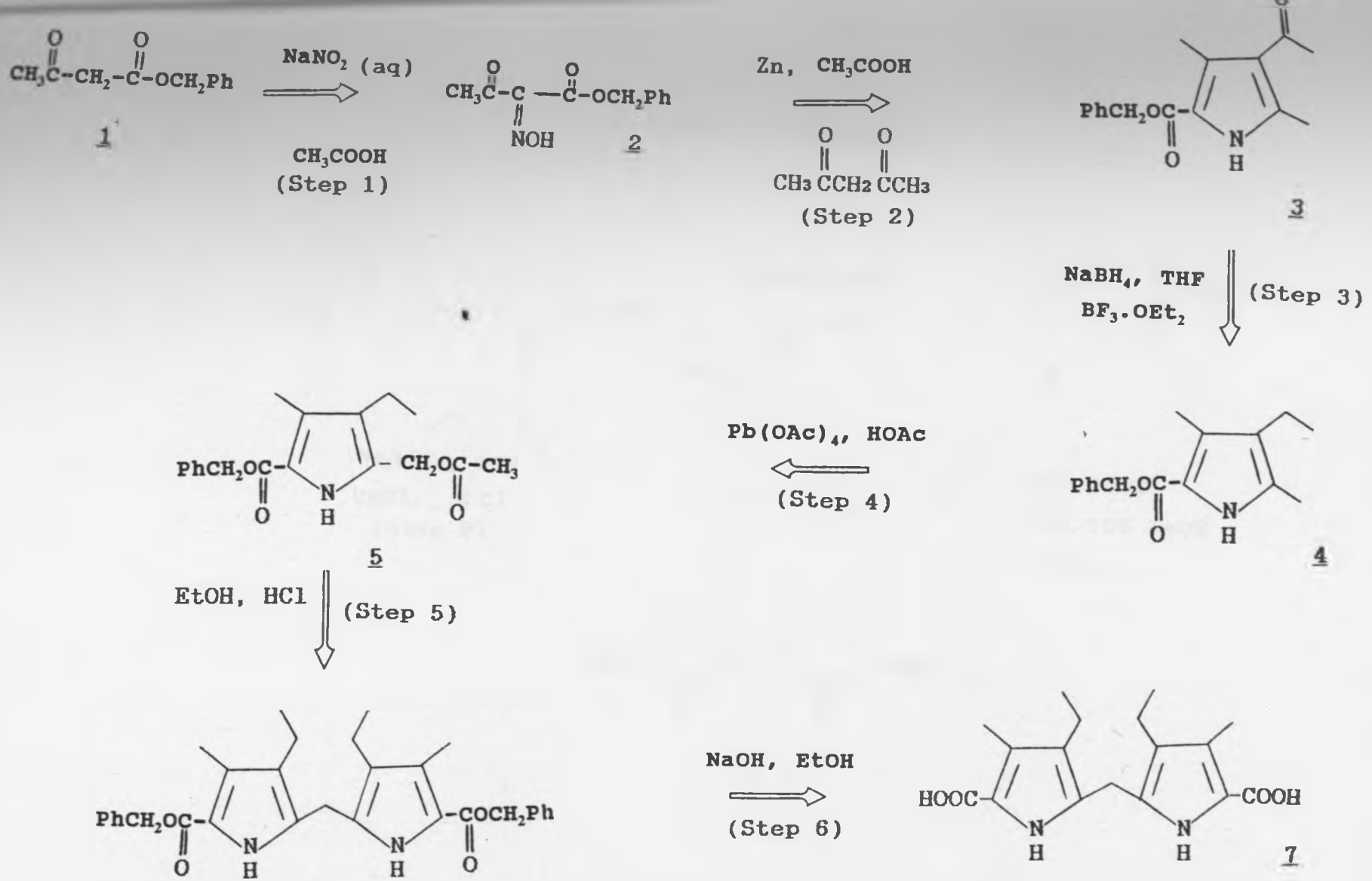
CHAPTER II

Results and Discussion

A.1. Synthesis: 3,3'-Diethyl-Diformyl-4,4'-Dimethyldipyrromethane (9)

The source of pophyrins and dipyrromethanes, in the laboratory, as well as in nature, are pyrroles. The pyrroles are synthesized from acyclic precursors via various pathways among which the Knorr reactions are the most established. Acholla[55] synthesized 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyrro- methane, employing an 8 - step synthetic scheme as shown in scheme 1. This scheme was implemented for the synthesis of the precursor molecule which is required for the synthesis of the binucleating macrocyclic ligand systems to be discussed later.

The first two steps are the Knorr[56] reactions which involve the initial formation of the oxime in situ and subsequently, the pyrrole. The oxime is reduced by the zinc dust in glacial acetic acid to obtain α - aminodiketone which undergoes Schiff base condensation in the presence of 2,4 - pentanedione followed by cyclisation of the Schiff's base to form the pyrrole. The mechanism for this reaction will be discussed later. An extensive treatise on synthesis of pyrroles from acyclic precursors has been furnished by Paine[57]. The third step is the reduction of the acyl group on the pyrrole by application of the diborane reduction technique.



Scheme 1. Synthesis of 3,3'-Diethyl-5,5'-Diformyl-4,4'-Dimethyldipyrromethane

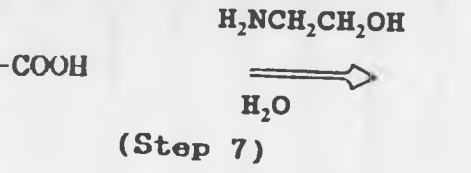
7

Na_2HPO_4, HCN

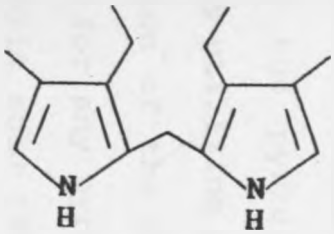
$CHCl_3$, H Cl

(Step 9)

Scheme 1 continued.



(Step 7)



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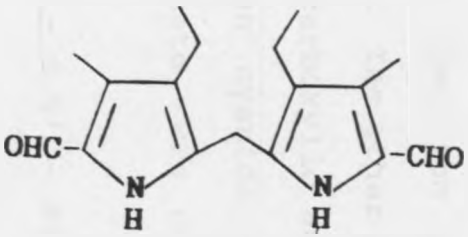
DMF, $POCl_3$

H_2O, 10% NaOH

(Step 8)



9

Acetoxylation of the α-methyl pyrrole (step 4) is effected by lead-tetraacetate in glacial acetic acid. In the fifth step, condensation of the pyrrole occurs to yield the symmetrical dipyrromethane by utilizing the acetoxylated sites. Step 6 entails the saponification of the diester functions, a process which is also achievable for any pyrrole ester function. Decarboxylation of the dicarboxylic acid (step 7) then follows by use of boiling 2 - aminoethanol as solvent. The last step in the synthesis is the formylation of the α-free sites by reaction with phosphorus oxychloride in N,N - dimethylformamide. The other method, in which dialdehyde is synthesized from the dicarboxylic acid by treatment with hydrogen chloride gas, hydrogen cyanide and an aqueous solution of disodium hydrogen phosphate, was not followed for reasons to be discussed later.

The synthesis of 3,3' - diethyl - 5,5' - diformyl - 4,4' - dimethyldipyrromethane (9) was undertaken without the investigation of the mechanisms involved. However, the mechanism of some of the steps in the scheme will be discussed in order to illuminate the rationalizations used in their procedures.

The benzylacetate moiety was selected in view of its readiness to cleave during the saponification[58], effected in step 6, in addition to its simplification of characterization. The benzyl-acetoacetate was prepared readily from the transesterification between ethylacetoacetate and benzylalcohol[59]. Attempts to

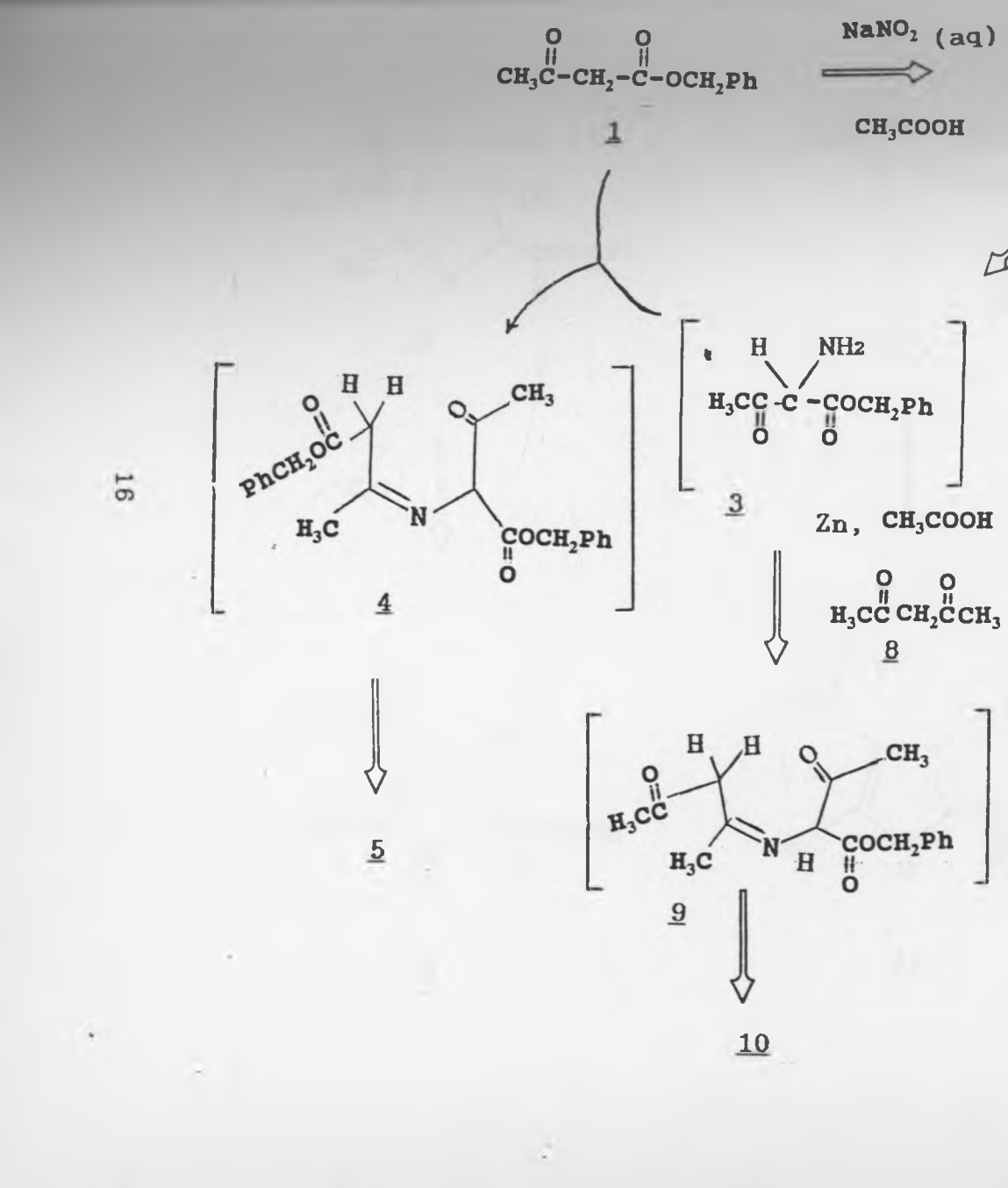
perform this reaction under acid catalysis resulted in instantaneous formation of whitish precipitate upon introduction of acid. During vacuum distillation, in the isolation of the product from the reaction mixture, some whitish precipitate appeared in the condenser, which was probably due to some decomposition as a result of the insufficiently low pressure employed. This may be attributed to the lower yields (70%) obtained versus those reported[55]. Steps 1 and 2 are the classical Knorr reactions[56]. In step 1 the ketoxime was prepared in situ with the treatment of aqueous sodium nitrite[58] on the benzylacetoacetate. Red nitrogen dioxide gas was observed in this reaction. Formation of the pyrrole in step 2, was effected by dropwise addition of the oxime plus small amounts of zinc dust to a solution of 2,4 - pentanedione, in glacial acetic acid. Initially, the zinc dust reduces the ketoxime to α-aminodiketone and subsequently the α-aminodiketone undergoes Schiff base condensation with any available ketones, in the reaction mixture. The mechanisms[60] are presumed to be as illustrated in fig. 1. With the reactants in the present system, the following are the alternative reactions of the α-aminodiketone:

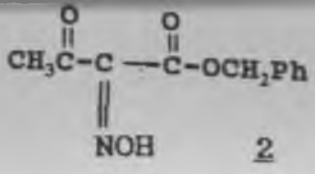
(a) condensation with substrate 1 to give the Schiff base intermediate 4 which cyclises and dehydrates to form compound 6.

(b) condensation with 2,4 - pentanedione, forming the intermediate compound 9 which undergoes two different modes of cyclisation. Upon dehydration, compounds 11 and 14 are formed, with the former predominating due to the highly unfavoured configuration of the latter's intermediate, 13

(c) Self - condensation, in the presence of oxygen to yield compound 7.

According to the strategy of the procedure, the concentrations of all reactants, except the desired substrate 8, are minimized, allowing the formation of the pyrrole 11 exclusively.


NaNO2 (aq)
CH3COOH
1
3
Zn, CH3COOH
8
4
5
9
10



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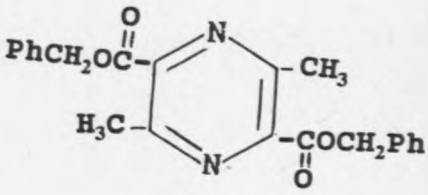
Zn, CH_3COOH

O_2



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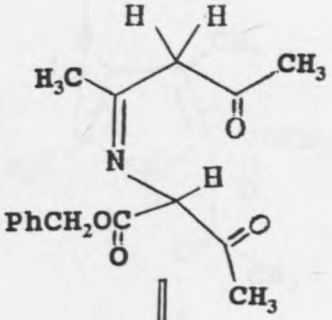

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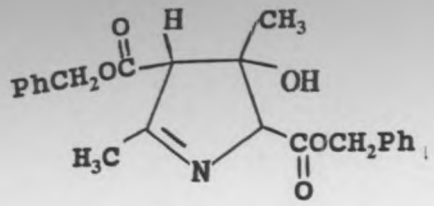
Figure 1 continued.



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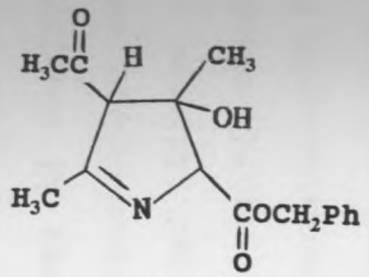

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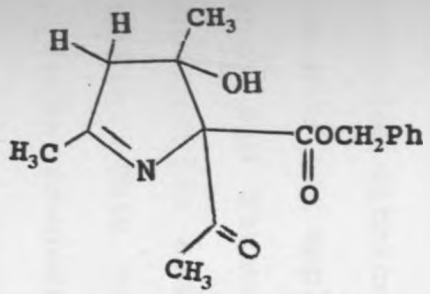
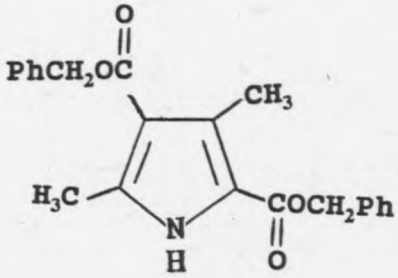


13

$-H_2O$

$-H_2O$

$-H_2O$



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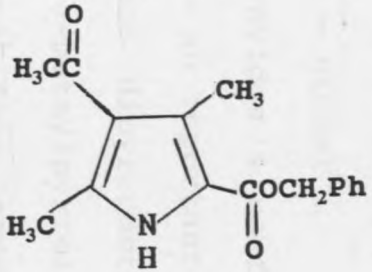

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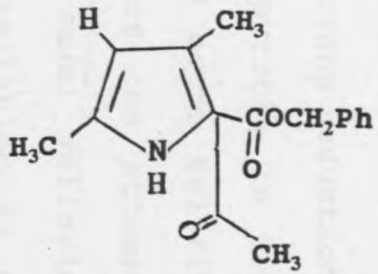
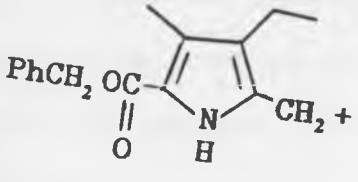


14

The reduction of the ketoxime by zinc dust in acetic acid is the most convenient procedure compared to others, such as sodium amalgam with carbondioxide buffering[61], catalytic hydrogenation[62] or buffered sodium dithionite[63]. Step 3 involves the reduction of the acyl group with the application of the diborane reduction technique of Whitlock and Hanauer[64], wherein the pyrrole is treated with sodium borohydride and freshly distilled boron tri-fluoride di-ethyletherate. This reaction, in some of the attempts gave a greenish crude product instead of the usual yellowish colour. However, recrystallization led to the isolation of pure white crystals, with the coloured impurities remaining in solution. The other reductive technique that could be used but gives less yield is the hydrogenation in presence of Ra - nickel[65].

Acetoxylation (step 4), which provides a useful source of pyrryl carbinyl cation (shown below) - an important intermediate in the condensation of pyrroles into dipyrromethanes[66] - is accomplished by the reaction of the α-methylpyrrole with lead-tetraacetate[67], in glacial acetic acid, at room temperature.



This reaction is monitored by adding water to a small amount of the reaction mixture, whereby the formation of a brown precipitate is indicative of unreduced Pb(IV) species. The extent of the reaction is established on tlc, by extracting the mixture into methylene chloride and developing with 2 - 3% ether in methylene chloride. The product was isolated by precipitation with water and recrystallized from acetone/water system of 50:50 ratio, giving a yield of 85.5%.

Worthy of mention procedures that furnish sources of pyrryl carbinyl cations are chlorination[68] and bromination[69];

Bromination.

This is achieved by the reaction of molecular bromine with the α-methylpyrrole, in diethylether or glacial acetic acid. Due to the electrophilic nature of the brominating agents, any β- free sites are attacked and β-acyl groups displaced, before the production of sufficient free radicals. The other drawback is the weakness and easy polarizability of the carbon - bromine bond and in moist atmosphere, the compound deliquesceses and subsequently decomposes due to the action of nucleophillic hydrogen bromide produced, which results in the loss of yield. Although bromination is more selective than chlorination, it has lost its popularity as a method for monooxidation.

chlorination.

Monochlorination is also prone to the same type of reactions undergone in bromination, though to a lesser degree, since the monochlorinating agents react more in the free radical sense than in the electrophilic sense. The product obtained in this case is also more stable than in bromination. This reaction is effected by the use of sulphurylchloride or t - butylhypochlorite. It is more useful for deactivated pyrroles or dipyrromethanes.

Acetoxylation is highly selective and provides an indefinitely stable product, under ordinary atmospheric conditions, in high yields.

Condensation, in step 5, serves to form the symmetrical dipyrromethane, by means of reflux of the acetoxylated pyrrole in ethanol, containing catalytic amount (1%) of hydrochloric acid[70,71]. The mechanism of this reaction which involves the liberation of formaldehyde[72] is shown in figure 2.

For the conversion of the diester into dicarboxylic acid (step 6), Abraham's procedure[73] was not followed in order to avoid the cumbersome crucial step of evaporation of the solvent under nitrogen leak. It has been found that the product decomposed under ordinary evaporation conditions in a rotary evaporator.

Saponification, first utilized by Chang in 1983 in the synthesis of pyrrolecarboxylic acid from a pyrrole ester, was undertaken, sodium hydroxide in ethanol being employed under vigorous reflux to give 88% yield.

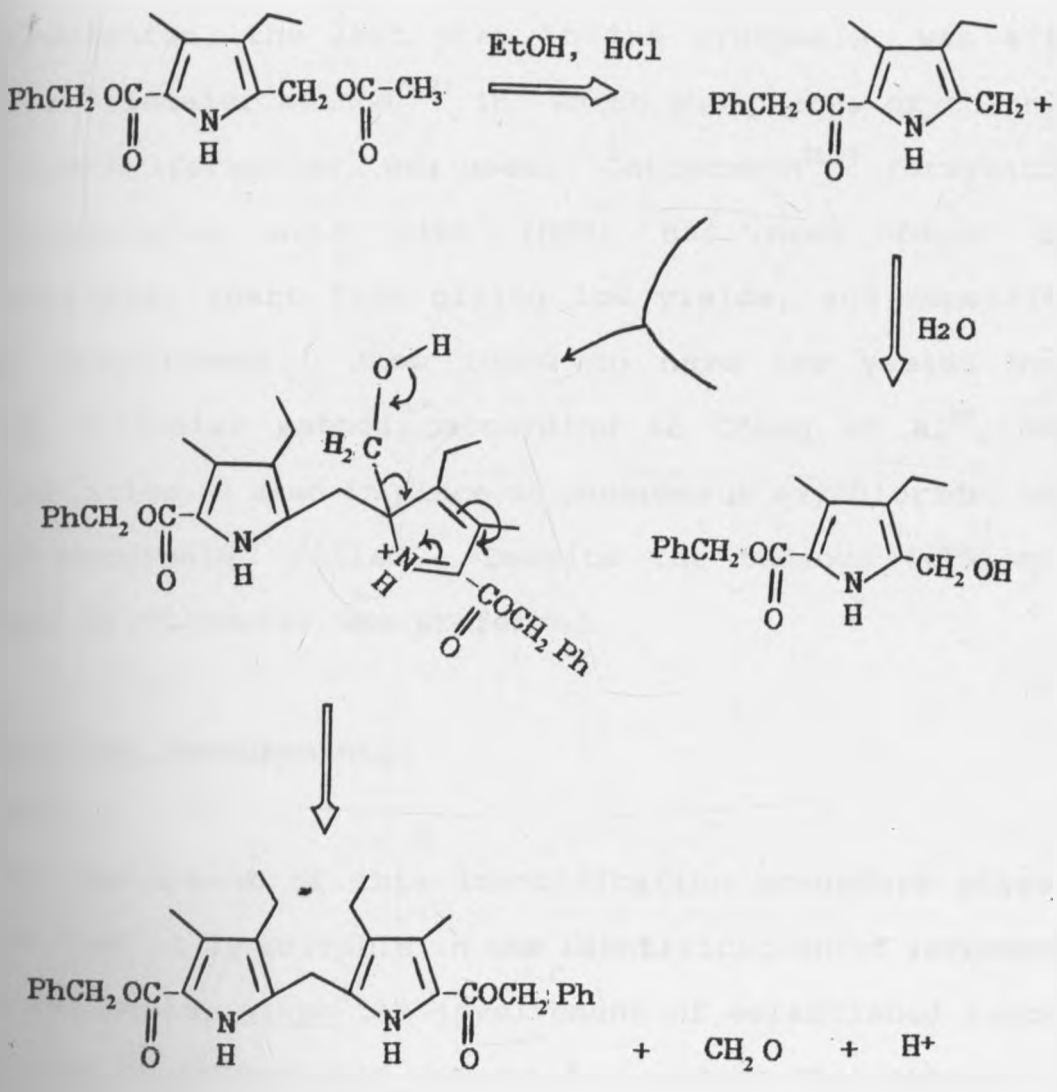


Figure 2. Mechanism for the formation of dibenzyl-3,3'-diethyl-4,4'-dimethyl-dipyrromethane-5,5'-dicarboxylate

The dicarboxylic acid was decarboxylated, in step 7, by its treatment with boiling 2 - aminoethanol[74]. Other solvents that have been used for the decarboxylation of dipyrromethane dicarboxylic acid or highly stable pyrroles are glycerine[69] and ethanolic hydrochloric acid[75].

Formylation, the last step in the synthesis, was effected using the Vilsmeier method[76,77] in which phosphorus oxychloride in N,N - dimethylformamide, was used. Gattermann[78,79] formylation of the dicarboxylic acid with (HCN) has been found to be irreproducible, apart from giving low yields, and necessitating special precautions. Also found to have low yields was the modified Vilsmeier method, according to Chang et al[80], wherein benzoylchloride is used in place of phosphorus oxychloride, whereas that of Macdonald[81] failed. Despite the tedious work up, the procedure of Vilsmeier was preferred.

A.2. Physical Measurements:

Infrared.

The employment of this identification procedure stems from the fact that it is suitable in the identification of intermediates in the synthesis, given the involvement of established functional groups with characteristic absorptions such as the carbonyl group. It also contributes in the identification of the synthesized compounds. The infrared spectral data for the starting raw materials and the final dialdehyde are as shown in table 1.

Infrared Spectral Data for compounds synthesised in scheme 1.

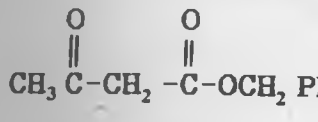
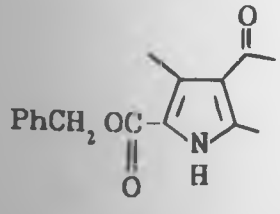
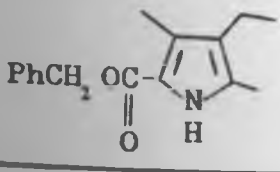
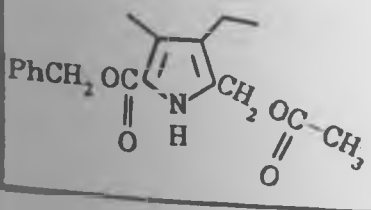
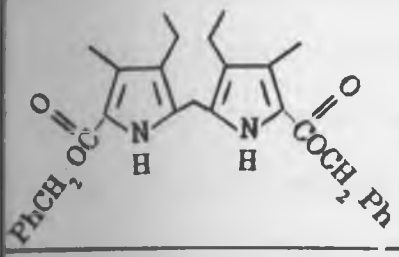
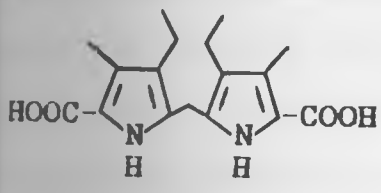
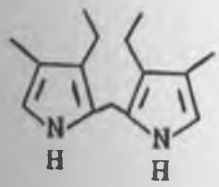
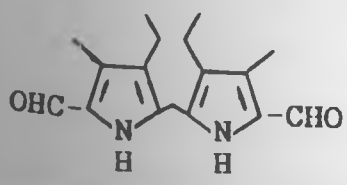
Compound	C-Hs	N-Hs	C=Os	Pyrrole Ring Vibrations
	2960(w)	-	1716, 1646	-
	3100, 3020, 2960	3160	1660, 1610	1410
	2940, 2920, 2860	3290	1640	1430
	2940, 2920, 2860	3300	1720, 1650	1440

Table 1

Table 1 continued

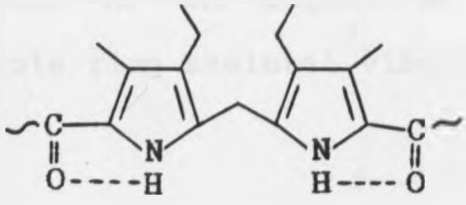
Compound	C-Hs	N-Hs	C=Os	Pyrrole Ring Vibrations
	2965, 2926, 2865	3327	1694	1448
	2963, 2930, 2872	3357	1682	1469
	2961, 2926, 2867	3364	-	1448
	2963, 2932, 2842, 2830.	3216	1617	1444

In the spectrum of benzylacetoacetate, the prominent peaks appear in the carbonyl stretching and the aromatic C-H bending regions; each region containing two peaks.

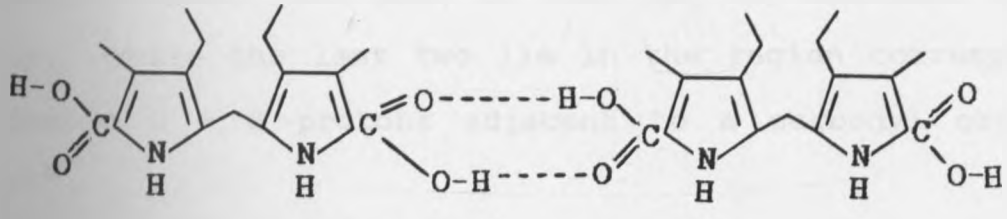
The synthesized pyrroles and dipyrromethanes give a sharp peak, within the range of 3200 - 3370 cm^{-1}, which is the region of heteroaromatic N-H stretching frequency. Three peaks are observed in the aliphatic C-H stretching region, except for the pyrrole 3 and dialdehyde dipyrromethane 9 (scheme 1). The spectrum of pyrrole 3 shows lower N-H, ν_{N-H}, together with increased C-H, ν_{C-H}, stretching frequencies, presumably due to the existence of high level of coplanarity between the ketone substituent and the ring, hence facilitating efficient delocalization, in turn depleting the electron density of the N-H bond. On the other hand, the electron withdrawal effect of delocalization, on the ring, will produce some inductive effects on the C-H bonds of the substituents, which acts to elevate their frequency. The resonance process is as depicted below:

The presence of the bulky benzyl group in the substituent imparts steric hindrance, causing some distortion of coplanarity and thus less resonance as is evidenced by the higher ν_{N-H} of the

dipyrromethane 6 (scheme 1) of 3327 cm^{-1} compared to the lower ν_{N-H} of the dialdehyde 9 of 3216 cm^{-1}. Intramolecular H - bonding between the proton on the nitrogen and oxygen on the 5th - carbon substituent also seems to play a role in the determination of ν_{N-H}, as shown in the following diagram:



In the dicarboxylic dipyrromethane 7 (scheme 1), the preferential polymerization via intermolecular H - bonding, presumably, distracts the above mentioned intramolecular H - bonding. As a result, a high ν_{N-H} of 3357 cm^{-1} is observed.



The polymerization is reflected in the broad peak due to O-H stretching near 3278 cm^{-1}.

The additional absorptions in the aliphatic C-H stretching zone that appear in the spectrum of the dialdehyde originate from the aldehydic C-H group. The characteristic carbonyl stretching peaks are observed in the region of 1600 - 1700 cm^{-1}, consistent

with aromatic carbonyls. The reduction of the ketone in step 3 (scheme 1) is manifested in the disappearance of one of the carbonyl peaks located at 1660 cm^{-1}. Similarly, decarboxylation, in step 7, is marked by the loss of the peak at 1682 cm^{-1} due to the carboxylic carbonyl group.

The absorptions in the region of 1400 - 1500 cm^{-1} are assignable to pyrrole ring skeletal vibrations[82].

^1H NMR

This spectral study was undertaken in order to establish the arrangement of the protons in the synthesized compounds and thus to facilitate identification. The spectral assignments for three important intermediates are presented in table 2.

The spectrum of benzylacetoacetate shows absorptions in the aromatic region. The peak at 4.8δ may be assigned to a $-CH_2-O$ group, while the last two lie in the region corresponding to aliphatic C - H protons adjacent to a carbonyl group (2.0 - 3.0δ)[82].

Pyrrole 3 (scheme 1) has three singlets in the aliphatic C-H region. Reduction of the carbonyl introduces adjacent protons to the methyl protons, in C - 3 substituent. The result is; concomitant with coupling, the methyl protons are shifted upfield and new absorption due to methylene protons occurs; a quartet due to - CH_2- appears at 2.38δ and a triplet for $-CH_3$, at 1.0δ.

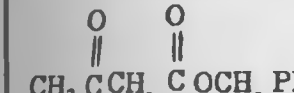
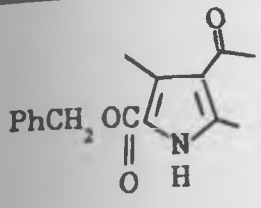
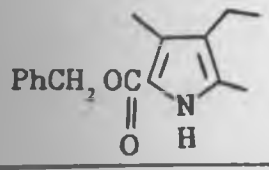
The characteristic broad peak for N-H is observed at 8.7δ. In pyrroles, the N-H group undergoes slow proton exchange, and thus coupling with nitrogen occurs but the electric quadruple moment of the nitrogen induces short half-lifes of the spins of its nucleus and the net effect is a broad peak[82].

Multiplets in the aromatic region are observed in the spectra of pyrroles 3 and 4 (scheme 1)

^{13}C NMR

This spectroscopy affords the observations of the carbon skeleton, by furnishing the number of non - equivalent carbon atoms and also allows the determination of proton count on each carbon, in the case of non- decoupled and off - resonance decoupled spectra. However, as a result of the large sweep width and the sharpness of the peaks, impurities are readily detected. In this spectroscopy, trends in chemical shifts are somewhat parallel to those of ^{1}H NMR. Shifts are related mainly to hybridization and substituent electronegativity; solvent effects are important in both spectra. Peak area ratios do not correlate to the number of carbon atoms, due to the difference in relaxation times of the different carbons. Furthermore, in the case of decoupled nuclei the nuclear overhauser effect is not the same for all nuclei.

^{1}H NMR Spectral Data for synthesized compds. in scheme 1.

Compound	Ar-H	$-CH_2-O$	$-CH_3$	$-CH_2-$	$-CH_2-CO-CH_3$
	7.0	4.8	-	-	1.7,3.1
	7.3	5.35	2.45, 2.55, 2.65	-	-
	7.4	5.3	2.2 2.3 1.0	2.4	

All spectra are reported in δ. The solvent used for benzylacetoacetate was CCl_4. $CHCl_3$ was used for the pyrroles.

Table 2

^{13}C NMR Spectral Data for Ethylpyrrole 4 in scheme 1.

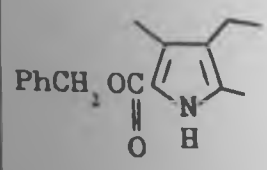
Compound	Aromatic	$-CH_2-O$	$-CH_3$	$-CH_2-$	Pyrrole Ring Carbons.
	128.21, 128.28, 128.74	65.58	10.78, 11.59 15.5	17.44	124.26, 129.71, 136.95, 150.10

Table 3

The assignment for the noise - decoupled spectrum for pyrrole 4 (scheme 1) is as shown in table 3. The three peaks in the region of 128 ppm are assigned to three sets of non - equivalent carbons in a substituted benzene. the low intensity peaks appearing within the range of 120 - 150 ppm are due to quaternary carbons and are assignable to the pyrrole ring carbons. The low intensities result due to the absence of directly attached protons which otherwise facilitate spin - lattice relaxations through dipole - dipole interactions.

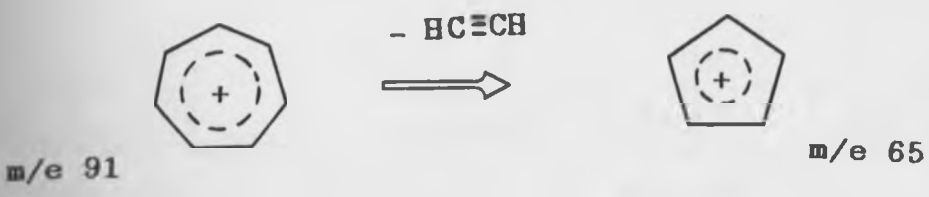
The peak at 65.58 ppm falls in the region corresponding to the group; $-CH_2-O$ (55 ppm - 75 ppm). The three peaks near 77 ppm are due to deuterated chloroform, which was used as the solvent. The deuterium atom, for which I=1, splits the carbon absorption into three peaks, in accordance with the formula: 2nI+1, where n is the number of the directly attached atoms.

Mass spectroscopy

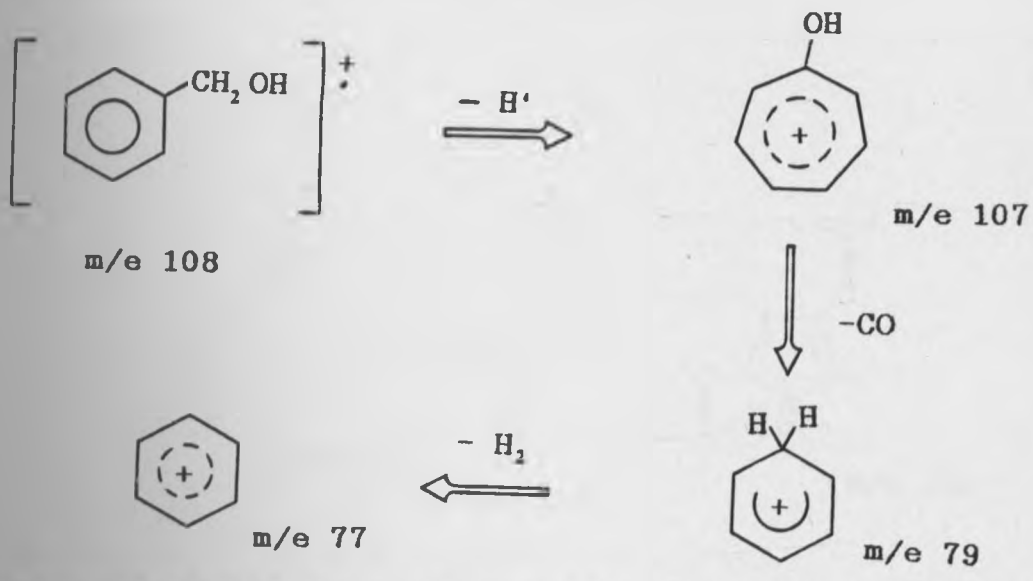
This study provides access to the molecular mass for numerous compounds for which the molecular ion (M^+) peak is prominent. By utilizing the natural abundance of isotopes, it is possible to determine the molecular formula from available tables[82].

The spectrum for benzylacetoacetate shows the M^+ peak at m/e 192. The base peak at m/e 91 is due to tropylium ion, which is indicative of presence of benzyl group. This ion loses acetylene

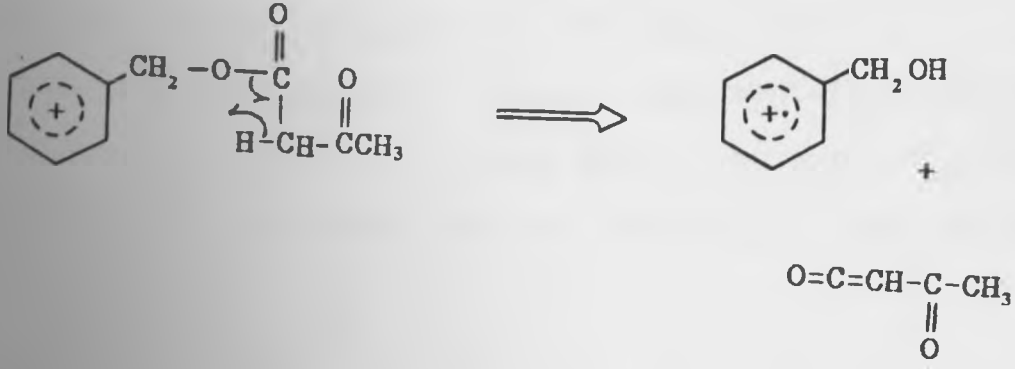
to form the 5 - membered ring cation which gives a peak at m/e 65, as depicted below:



The presence of the peak at m/e 108 suggests benzyl alcohol cation which undergoes a sequence of fragmentations; it expels H·, followed by neutral CO and H_2 as shown below:

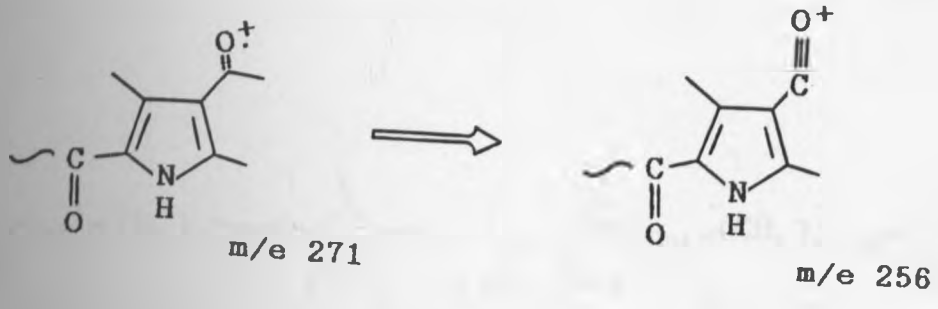


The benzylalcohol is most probably derived by the cleavage of the bond γ to the ring with H· abstraction as shown below:



The intense peak at m/e 43 is presumably due to the ion $CH_3-C\equiv O^+$ resulting from scission of the bond β to the methyl group.

In the spectrum of pyrrole 3, the molecular ion is seen as a prominent peak at m/e 271. Loss of the methyl group β to the pyrrole ring, from the C-3 substituent accounts for the peak at m/e 256, as shown below.



The ester portion undergoes cleavage at the bond adjacent to the carbonyl moiety, to give the peak at m/e 164.

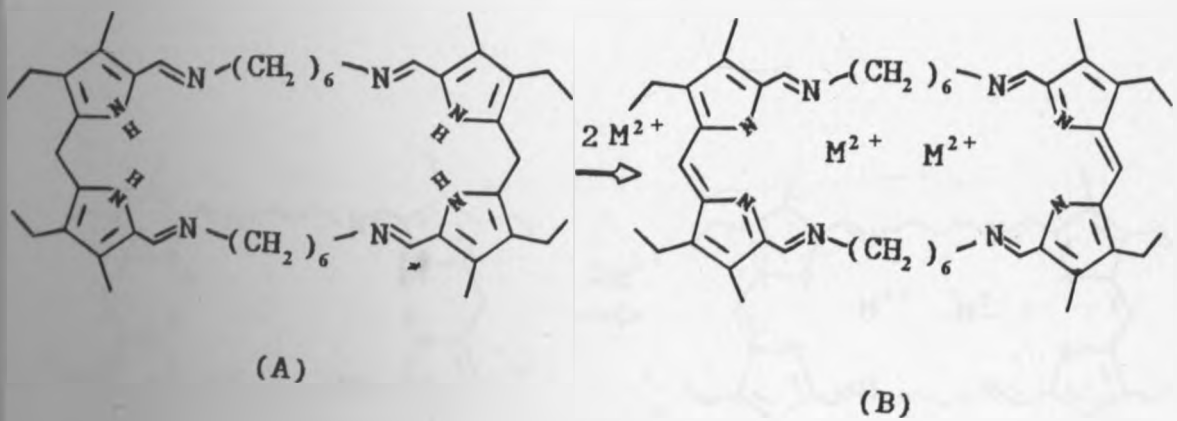
Pyrrole 4 also undergoes similar fragmentation patterns as pyrrole 3. The prominent M^+ peak appears at m/e 257, consistent with the removal of oxygen atom and addition of two H atoms, from pyrrole 3.

B.1 Synthesis: Ligand And Complexes

Introduction:

The quest into a suitable model for molecular oxygen activation in biological systems has led to the synthesis of a variety of complexes that incorporate desirable features. These complexes include the molecular A - frames[78,83] side - by - side macrocycles[79,84] macrocyclic inclusion complexes[38] and cofacial diporphyrins[23,29,85], which possess metals in proximity.

The binuclear complexes discussed herein consist of coplanar metals, that also enjoy a tetrapyrrolic environment. The synthesized ligand and complexes are shown in figure 3.



(A) (B)

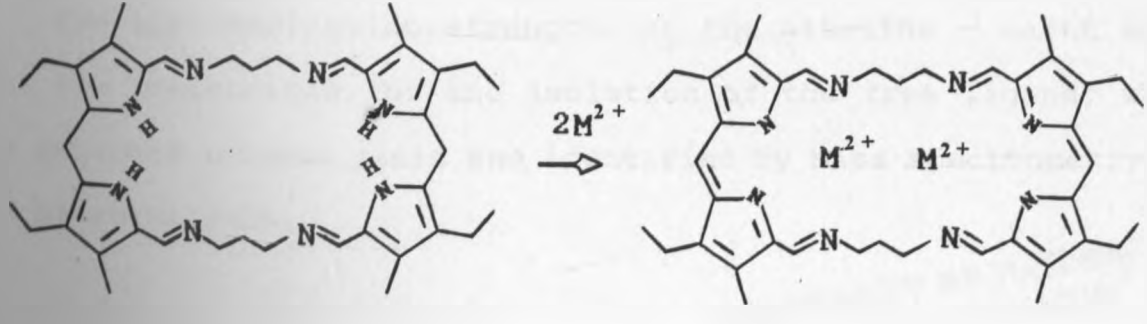
M^{2+} = Zn^{2+}, Cu^{2+}, Co^{2+} etc.

FIGURE 3.

The ligand system is conventionally known as 4,19,23,38-Tetraethyl-5,18,24,37-tetramethyl-8,15,27,34,39,40,41,42-octaazapentacyclo[34.2.1.1^{3,6}.1^{17,20}.1^{22,25}.]dotetraconta-3,5,7,15,17,19,22,24,26,34,36,38-dodecaene- hereafter referred to as Bi-dphmd.6H. This designation is derived as follows: Bi:- for two, dp :- dipyrromethane, hmd :- hexamethylenediamine, 6H :- six titrable protons.

(Bi-dphmd.6H)(A)

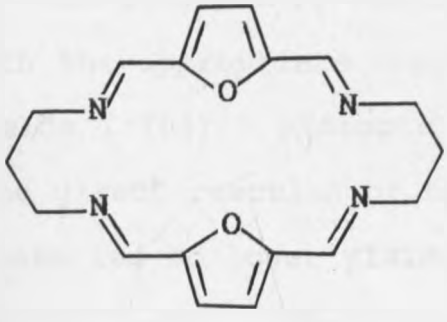
The Schiff base condensation of 1,6 - hexamethylenediamine, using barium chloride, calcium chloride or magnesium sulphate as templates, was utilized for the synthesis of the free ligand (A). The synthesis of the analogous free ligand derived from 1,3 - propanediamine as the diamine constituent, (Bi - dptmd.6H) (C), has also been accomplished by this procedure.



(C) (D)

Figure 3 continued.

The successful application of the alkaline - earth metal salts of Ba^{2+}, Ca^{2+} and Sr^{2+} except Mg^{2+} was reported by Drew[49] in the synthesis of the 1:1 complexes of macrocycle (1). However, noteworthy was the inclusion of the metal ions in the macrocycle, in contrast to the former case.



(1)

The low cordination strengths of the alkaline - earth metal ions are responsible for the isolation of the free ligand, which was obtained in good yield and identified by mass spectrometry, IR and microanalysis.

Zn_2(bi-dphmd)Cl_2

This complex was synthesized from Schiff base condensation, with $ZnCl_2$ as the template.

Here the complex, rather than the ligand, was isolated as opposed to when the alkaline-earth metal salts were used. This is attributed to the stronger cordination furnished by the Zn^{2+} ion, for the nitrogen donor atom.

Cu_2(bi - dphmd)$(X)_2$, figure 3 (B), X = ClO_4^-, Cl^-

These complexes were prepared by the metathetical reaction of the zinc complex with the appropriate Copper(II) salts, and were obtained in good yields (>70%). Attempts to synthesize Cu_2(bi - dphmd)$(ClO_4)_2$ from the direct reaction of the free ligand (A) with copper (II) perchlorate led to lower yields.

The preparation of Cu_2(bi - dphmd)$(ClO_4)_2$ necessitated the addition of lithium perchlorate, as revealed by the monitoring of the reaction through electronic spectroscopy. The lower coordination tendency of ClO_4^- as opposed to the Cl^- attributes to this observation, which is depicted in figure 4.

Cu_2(bi-dphmd)$(N_3)_2$

This complex was obtained from the reaction of Cu_2(bi-dphmd)$(ClO_4)_2$ with NaN_3, in 65% yield. It gave the characteristic strong peak at 2030 cm^{-1}, in the IR region, due to azide.

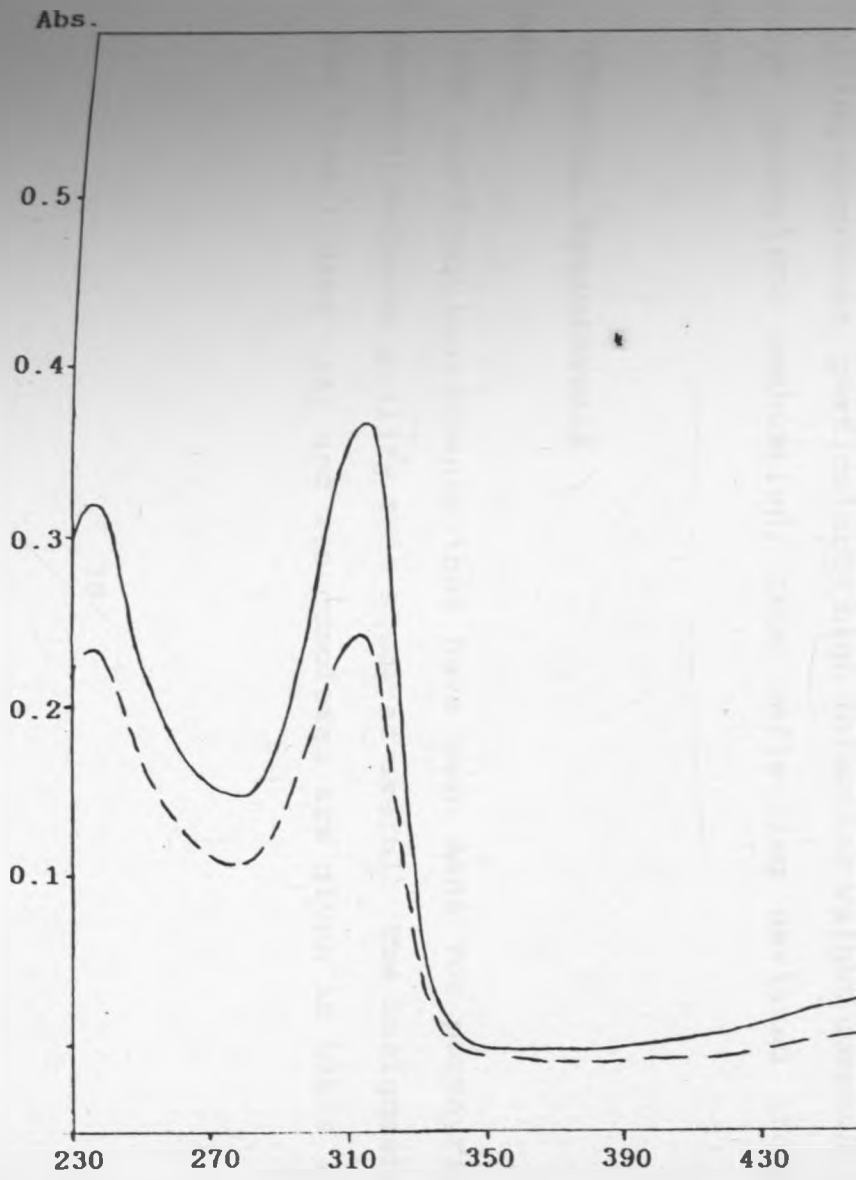
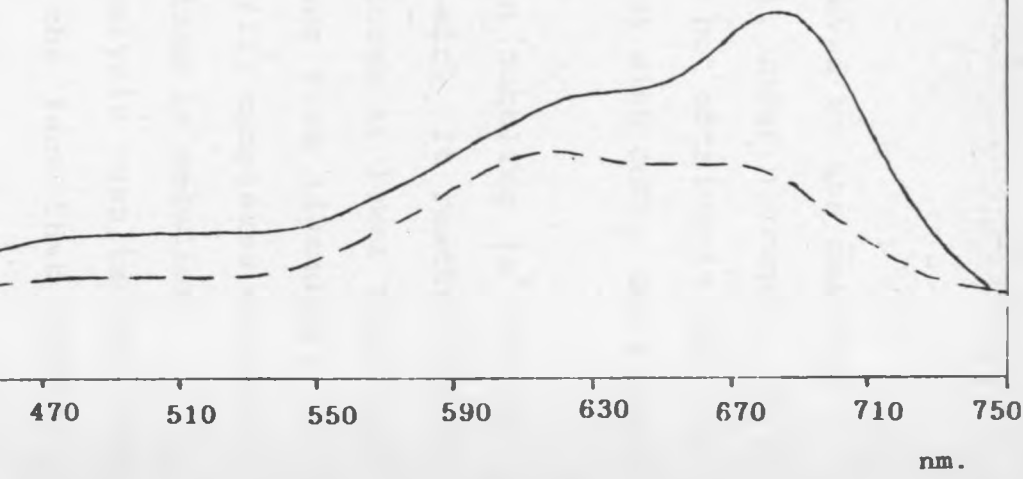

Abs.
0.5
0.4
0.3
0.2
0.1
230
270
310
350
390
430

Figure 4. Absorption Spectrum of Isolated Product, before(----) and after(——) addition of $LiClO_4$



Co_2(bi - dphmd)Cl_2

The synthesis of this complex was achieved by the reaction of the free ligand (A) with $CoCl_2$, in methanol, under nitrogen. Pure product was isolated in good yield. It was not obtainable from the metathetical reaction of Zn_2(bi-dphmd)Cl_2 (B) with $CoCl_2$, due to the higher stability of the former.

In this synthesis, thorough nitrogen bubbling is crucial, since the complex is readily oxidized by air. It reacts with O_2 in DMF, CH_3CN and methanol suspension although at lower rate than the dicobalt (II) complex of the analogous free ligand(C). It was interestingly observed that the cobalt(II) complexes were air-stable in the solid state but easily oxidized in solution.

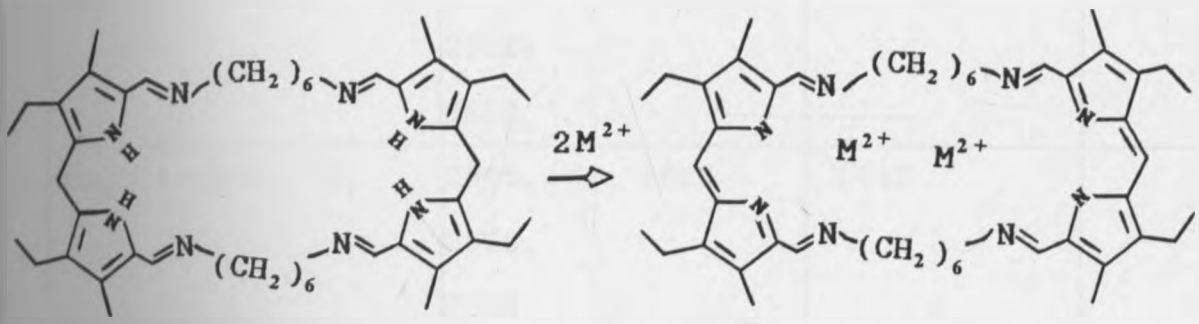
The somewhat off-the- mark microanalysis results obtained for the complexes were probably due to the fact that nitrogen containing compounds, particularly high molecular weight compounds, undergo incomplete combustion, thus reflecting deviated atomic contents.

B.2. Physical Measurements

Infrared.

The spectral assignments that have been made for porphyrins and porphodimethenes qualify this study as useful. The assignments for the free ligand (A) and its complexes are given in table 4.

The uncomplexed free ligand (figure 3) gives four peaks in the aliphatic C - H stretching zone. Upon complexation, the peak at 2820 cm^{-1} vanishes . This is ascribed to the conversion of the dipyrromethane fragment into dipyrromethene, concomitant with the insertion of the metal ions in the ligand, since a similar feature is observed with porphodimethenes (dihydropophyrins)[86]. The ensuing transformation is as shown below:



In the spectra of the complexes there exist additional features that are characteristic to analogous porphodimethenes[86] such as the absorptions in the regions of 1620 - 1550 cm^{-1} and 1400-1550 cm^{-1}, which may be correlated to methene stretching and pyrrole ring skeletal stretching, respectively.

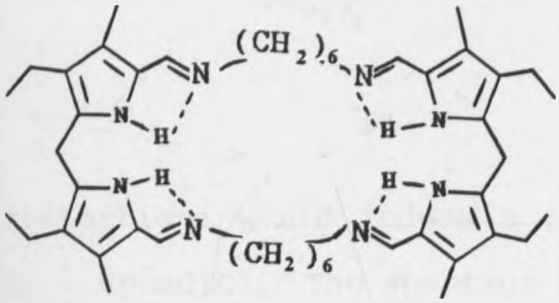
Infrared Spectral Data for the ligand and complexes

Compound	C-H	C=N	Pyrrole ring Vibrations.	Others
Bi - dphmd.6H	2940, 2900, 2840, 2810	1630	1430	
Zn_2(bi - dphmd)Cl_2	2961, 2928, 2868	1651(s)	1454	
Cu_2(bi-dphmd)Cl_2	2965, 2926, 2890	1628	1443	
Cu_2(bi-dphmd)$(ClO_4)_2$	2965, 2928, 2870	1636(w)	1450	1092[a]
Cu_2(bi-dphmd)$(N_3)_2$	2965, 2926, 2864	1636(m)	1447	2033[b]
Co_2(bi-dphmd)Cl_2	2930, 2900 2850	1655(s)	1458	

All spectra were taken in KBr pellets and frequencies are in cm^{-1} . [a] $[ClO_4]^-$, [b] N_3^-

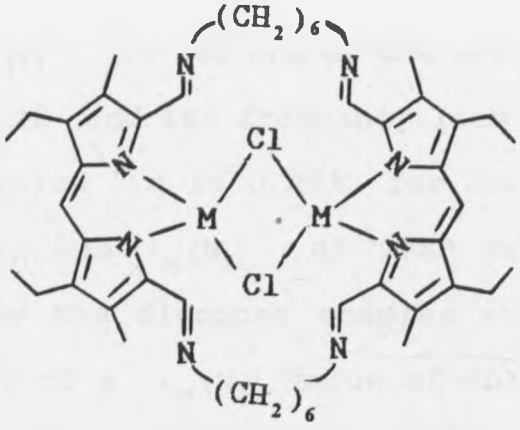
Table 4

The C=N stretching frequency, $\nu_{C=N}$, for the free ligand appears at 1630 cm^{-1}, the region for cordinated imine, as observed with free Schiff base[30] (1605 - 1640 cm^{-1}), whereas, generally, the complexes tend to have higher frequencies. This is explained in terms of the π - bonding that is present in the free ligand and which diminishes the bond order of the imine group, as illustrated below:



The zinc and dicobalt complexes consisting of chloride anions show $\nu_{C=N}$ at 1650 cm^{-1}, consistent with uncordinated imine as similar frequencies are to be found for other Schiff base complexes[87].

The propensity of Co^{2+} and Zn^{2+} ions to form tetrahedral geometries[88,89,90] and that of the chloride anion to bridge two metal ions point to the structure where the imine bonds are directed out of the cavity, as proposed for analogous complex derivatives of (C). The structure is as shown below:



Jahn Teller's distortions would induce a pseudo - tetrahedral geometry for Cu_2(bi - dphmd)Cl_2. The spectrum of Cu_2(bi-dphmd)$(N_3)_2$ complex exhibits an azide assymmetric stretching frequency, $\nu_{as}(N_3)$ of 2030 cm^{-1}. The modes of coordination of the azide anion to binuclear centre can be categorized with the representative structures[91] in fig. 5 as follows:

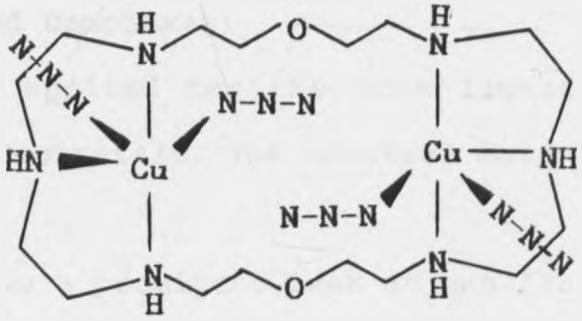
(a) cordination of separate azides for each metal ion (figure 5 (a))

(b) Bridging of the metal ions through the same nitrogen of an azide. A symmetrical configuration (1,1 μ azido) arises, as shown in figure 5 (b) ($l_1 = l_2$).

(c) Bridging via the end nitrogens of the azides resulting in an assymmetrical configuration (1,3 μ azido), as depicted in fig. 5 (c), where $l_1 \neq l_2$.

The position of $\nu_{as}(N_3)$ is governed, to a first approximation, by the difference in the N-N bond lengths, d_1 and d_2, given by Δd such that the larger the difference, the larger the $\nu_{as}(N_3)$. Taking the example of $Cu(N_3)_2$[92], Δd for one of the structurally independent azide anions is 0.12Å and its frequency lies at 2128 cm^{-1}, whereas $Cu(N_3)_2(NH_3)_2$[93] for which Δd is 0.05Å, for one of the structurally independent azides, has $\nu_{as}(N_3)$ of 2080 cm^{-1}. Consequently the observed $\nu_{as}(N_3)$ for the dicopper complex suggests a terminal azide, on the basis of a $\nu_{as}(N_3)$ value of 2033 cm^{-1} for $[Pd_2(N_3)_6]^{-2}$ (Δd=0.09Å), which bears a terminal azide[94].

(a)



(b)

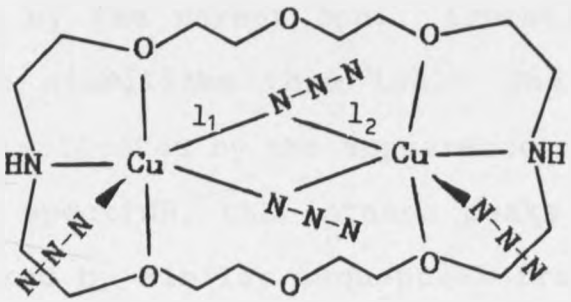
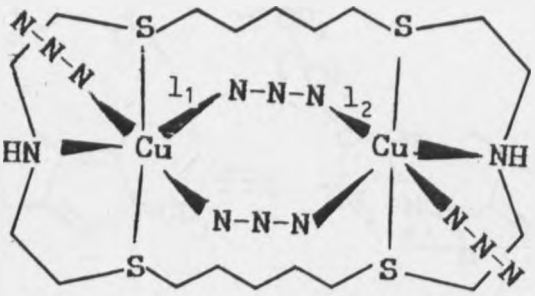


Figure 5

Figure 5 continued.



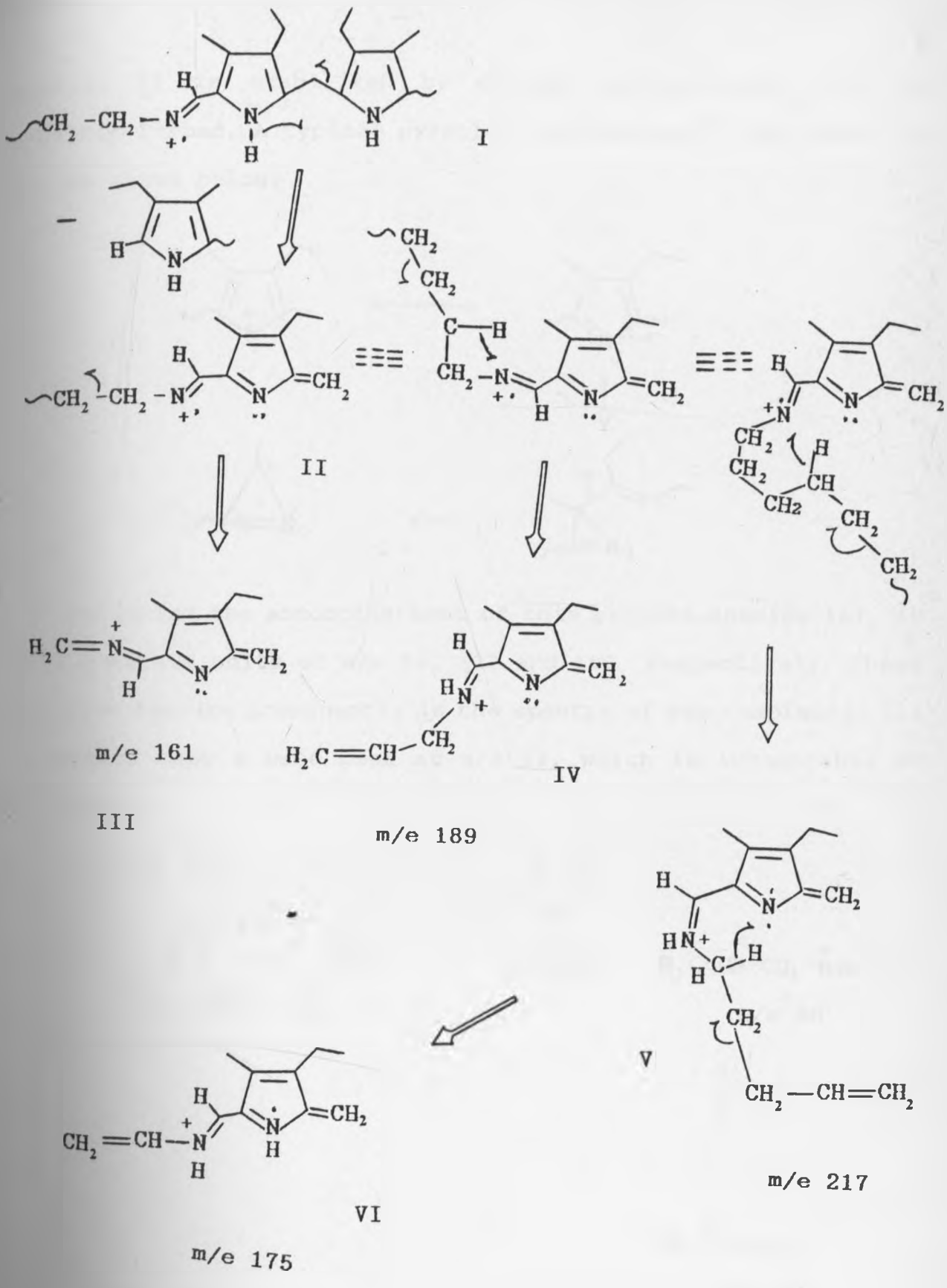
(c)

Mass Spectra (Free Ligand Complexes)

This technique was applied for the free ligand and chloro complexes with Zn and Cu as metals. The spectral data are given in chapter III.

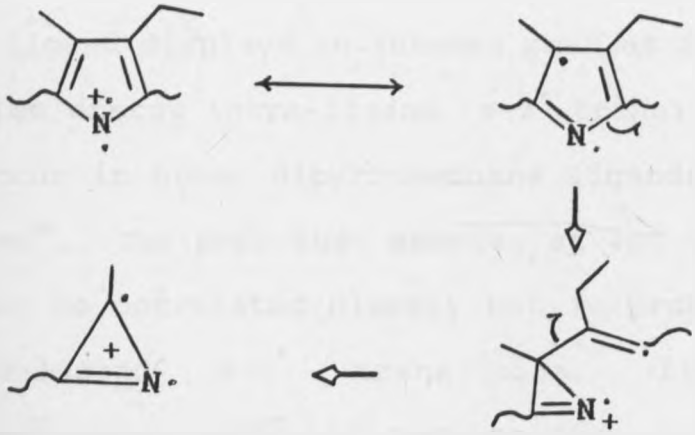
The free ligand shows a prominent peak at m/e 733 assigned as $(M+1)^+$ peak that arises from the abstraction of a hydrogen atom from a neutral molecule by the parent ion. Aromaticity of the dipyrromethane fragments stabilizes this ion. The macrocyclic nature of the ligand is implicated by the appearance of this peak.

In the free ligand spectrum, the intense peaks at m/e 217, 175, and 161 can be linked by similar sequential fragmentations. The peaks can be rationalized schematically as in scheme 2, which shows only portions of the macrocycle.

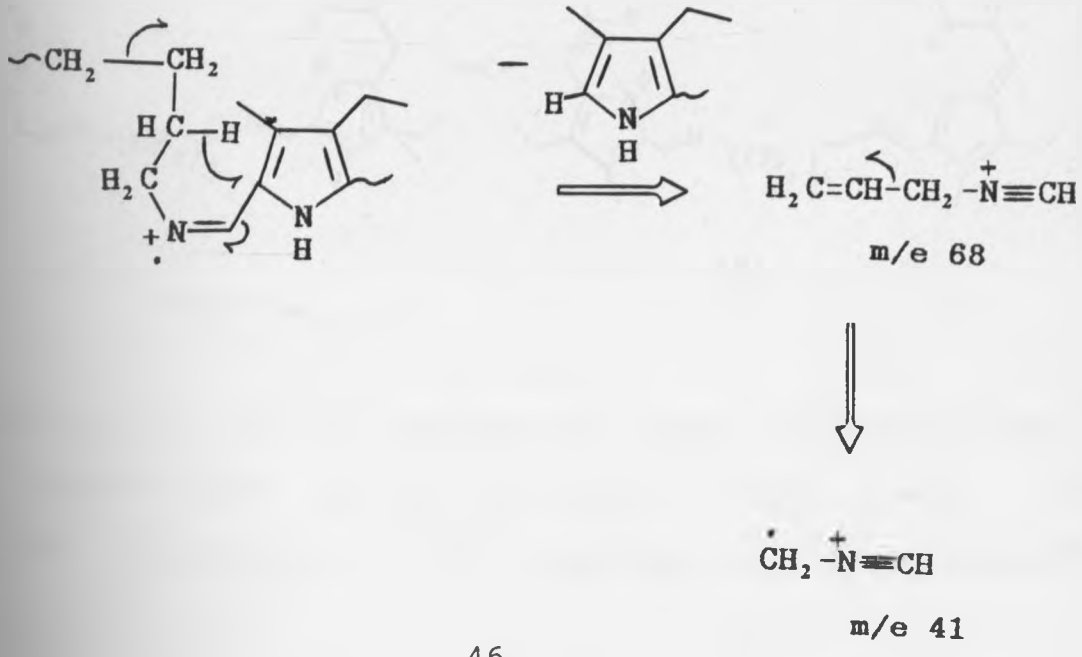


Scheme 2. Schematic Fragmentation Pattern For the Ligand

Species II is stabilized by charge delocalization and is favourably formed. A typical pyrrole ring cleavage[82] also seems to occur as shown below.



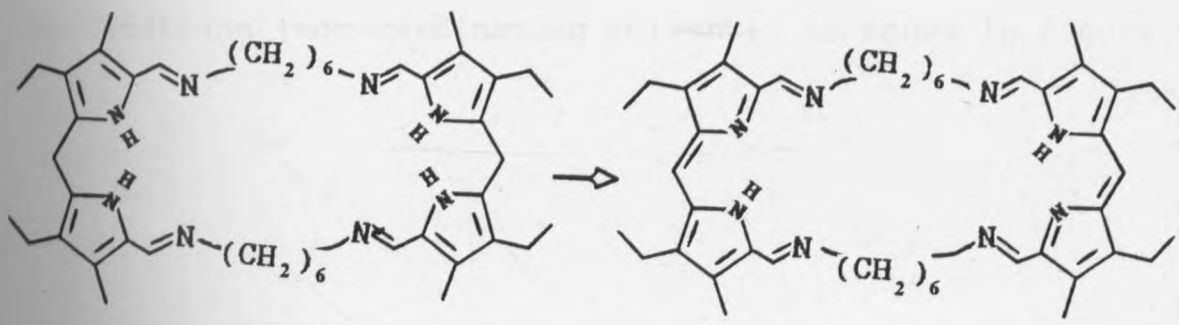
Following the accomplishment of this process species III, IV and VI generate units of m/e 94, 122 and 108, respectively. These peaks also feature prominently in the spectra of the complexes. All the spectra show a base peak at m/e 41, which is accountable as shown below.



ELECTRONIC SPECTRA

Electronic spectroscopic studies were undertaken in order to gain insight into the electronic properties of the ligand and complexes.

The free ligand displays an intense peak at 295 nm, which is assigned to high energy intra-ligand π-π^* transition, as similar absorptions occur in other dipyrromethane ligands, in the region of 259 - 275 nm[88]. The peak that emerges at 480 nm, after a few hours could not be correlated clearly but is probably due to low energy intra-ligand π-π^* transitions, like those of dipyrromethenes[88]. Presumably, it results from the transformation of the ligand to form the compound (2).



(2)

The spectrum of the zinc complex (d^{10}) shows two absorptions in the UV region which may be assigned to high energy π-π^* transitions, as observed for zinc complexes of dipyrromethenes[88].

The three low intensity broad peaks occurring in the visible region are attributed to M - L charge transfer absorptions. The complex being a d^{10} system, rules out d - d transitions.

The binuclear copper(II) complexes register spectra consisting of two intense bands in the UV region, which are probably due to high energy π-π^* transitions. They also show two bands within the range of 600 - 700 nm plus a shoulder at higher energy, which may be associated with low energy π-π^* transitions or M-L charge transfer absorptions. Similar correlations have been made by Fergusson et al[89]. The d-d transitions that may occur near 600 nm will be obscured by the other transitions. The copper(II) complexes with Cl^- and ClO_4^- anions show identical spectra in acetonitrile (cordinating solvent), implying the complexes to be isostructural. The reverse is true when the spectra is run in dichloromethane (non-cordinating solvent), as shown in figure 6.

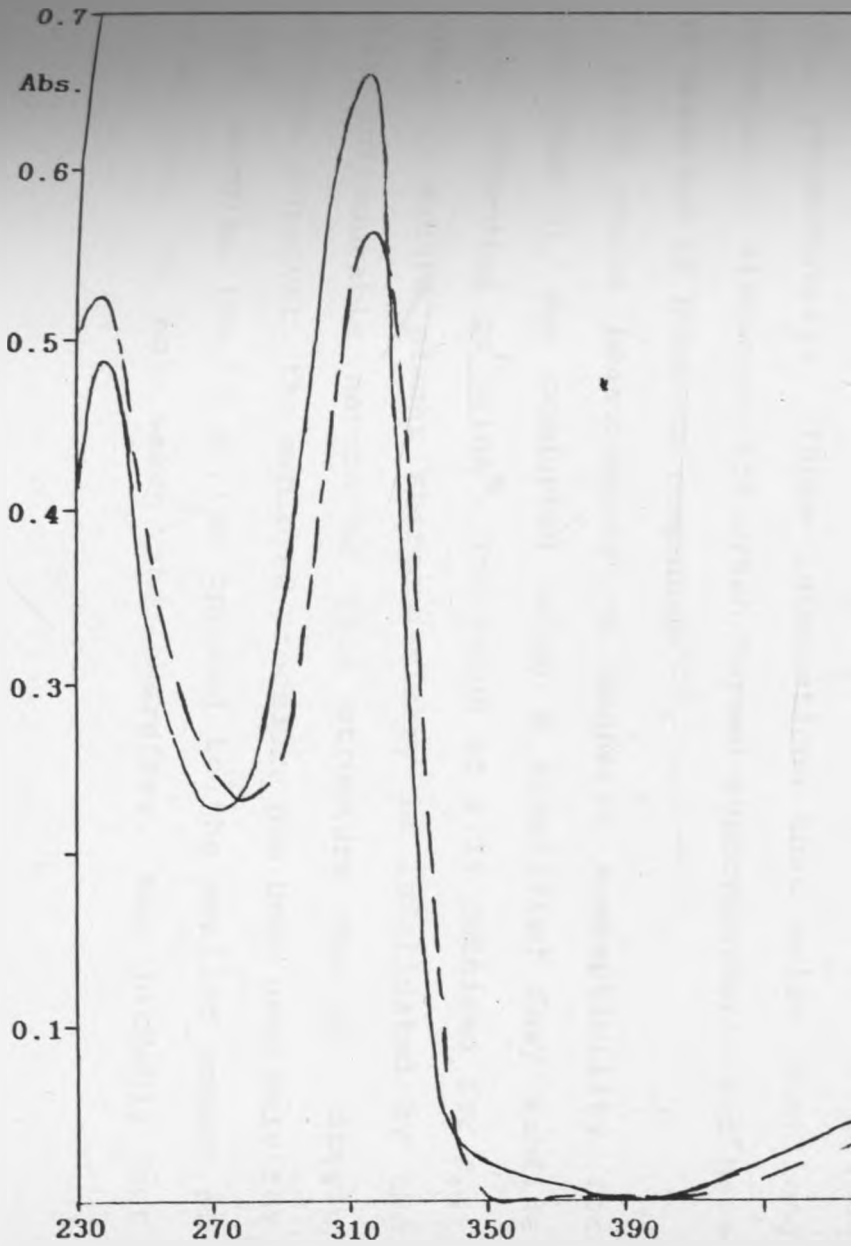
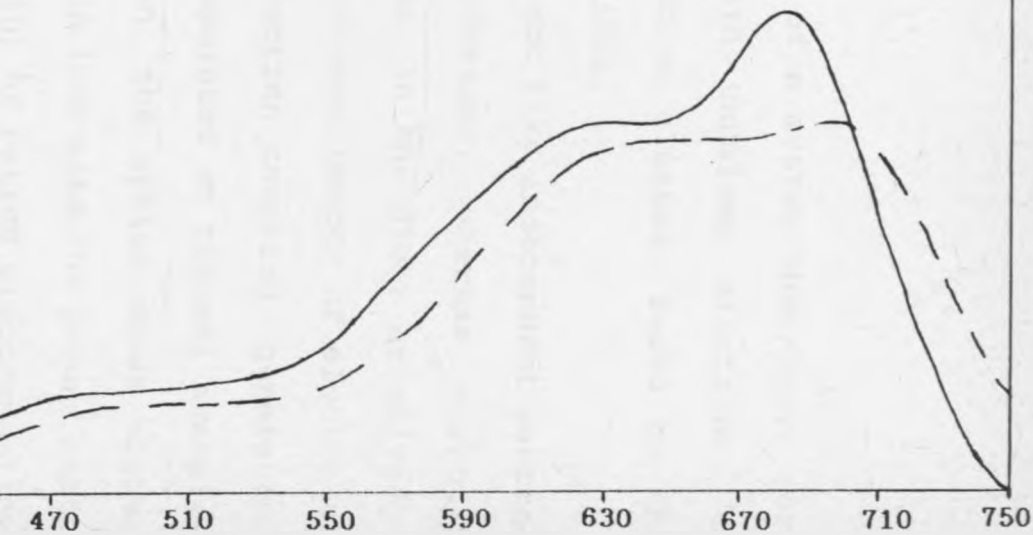

0.7
Abs.
0.6
0.5
0.4
0.3
0.1
230
270
310
350
390

Figure 6. Absorption Spectrum of $Cu_2(bi\text{-}dphmd)Cl_2$ in CH_3CN (——) and in CH_2Cl_2 (----)



Magnetic Susceptibility

The resultant magnetic property of a system that bears more than one transition metal ions with unpaired electrons, in vicinity, can be categorized into three classes, based on the degree of the inter-metallic interactions.

The non - interacting metal ions act like independent centres and hence exhibit paramagnetic behaviour, whereas strongly interacting ions, resulting from bonds, in the dimer or polymer, posses simple diamagnetic property, for even number of electrons. Weakly interacting ions experience electron coupling, generating low lying energy levels that can be populated at thermal energies ($\leq$1000 cm^{-1}). This being the case then, the system shows either ferromagnetism or antiferromagnetism, in line with the ground state comprising parallel electrons (high spin) or paired electrons (low spin), respectively. These interactions that arise from long intermetallic distances are often termed superexchange, and have been observed in numerous compounds[95-97].

Solid state measurements of magnetic susceptibility for Cc_2(bi-dphmd)Cl_2 was conducted using a simplified Gouy Rankine method, according to Irina[98]. The value of 2.83 obtained for μ_{eff}, suggesting square planar stereochemistry is invalidated by the highly unfavourable nature of this structure due to steric hindrance. Moreover, the employed procedure has been used only for larger samples (ca. 3 g), as opposed to the smaller amount of complex (ca. 70 mg) taken and therefore, was probably not

adequately sensitive. See appendix I for the computation of the μ_{eff} per cobalt centre.

Efforts to gain access to other methods of susceptibility measurements were fruitless.

C. Reaction of Co_2(bi - dphmd)Cl_2 with O_2

In the solid state, the complex is not air - sensitive. However, dissolution which was effected in the cordinating solvents: DMF, CH_3OH and CH_3CN, led to its reaction with O_2, as observed in the UV/VIS spectra of the respective fresh complex solutions. Practically, no dissolution was obtained with non-cordinating solvents such as dichloromethane. Figs. 7, 8, and 9 present the electronic spectra, as a function of time. The reaction was more apparent in MeOH, the spectrum of which apart from an isobestic point, showed two broad peaks; at 570 nm and 690 nm as monotonically rising in intensity with time. The rise is associated with the build - up of oxygen adduct of probably the 6 - coordinate μ- peroxo nature, since the same behaviour, in the same spectral region, had been observed in a cobalt(III) complex studied by Simandi[99].

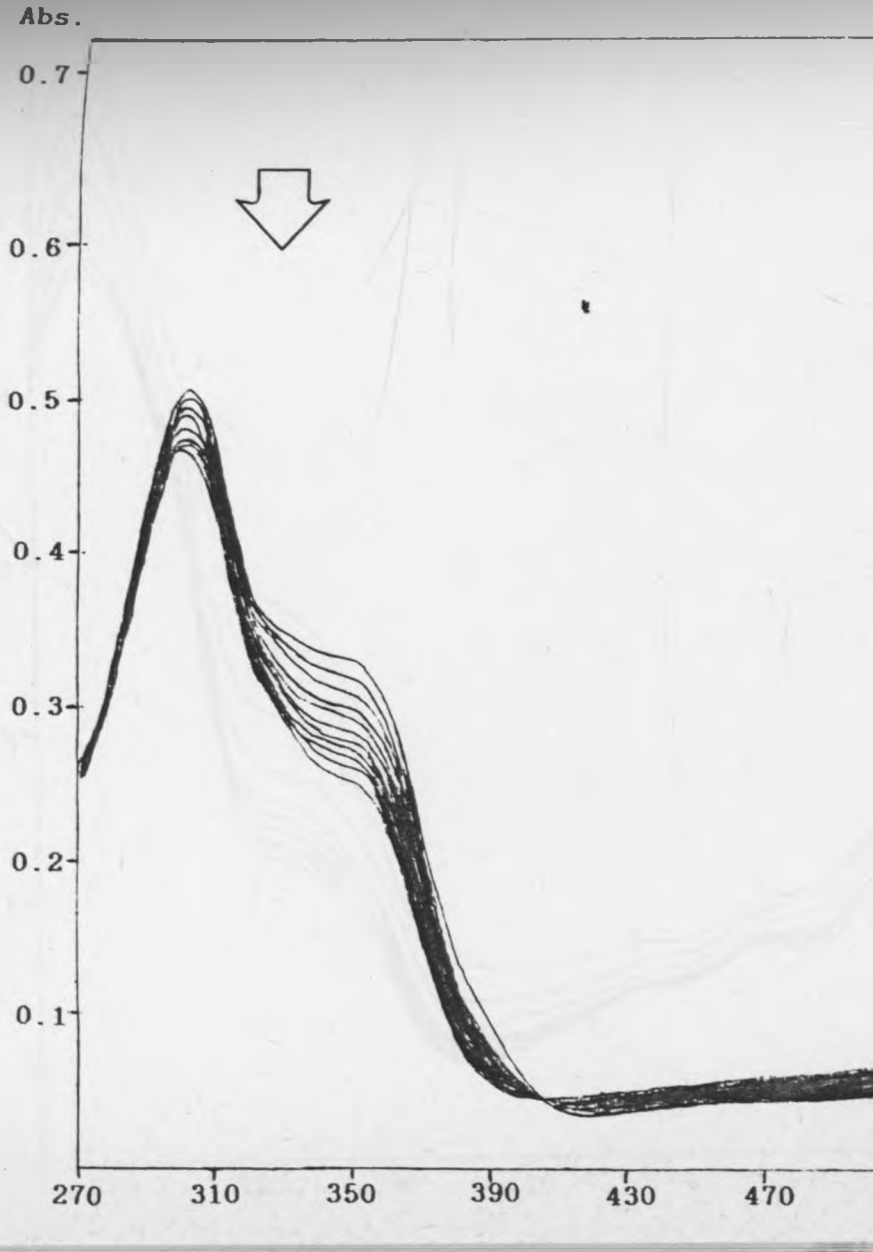
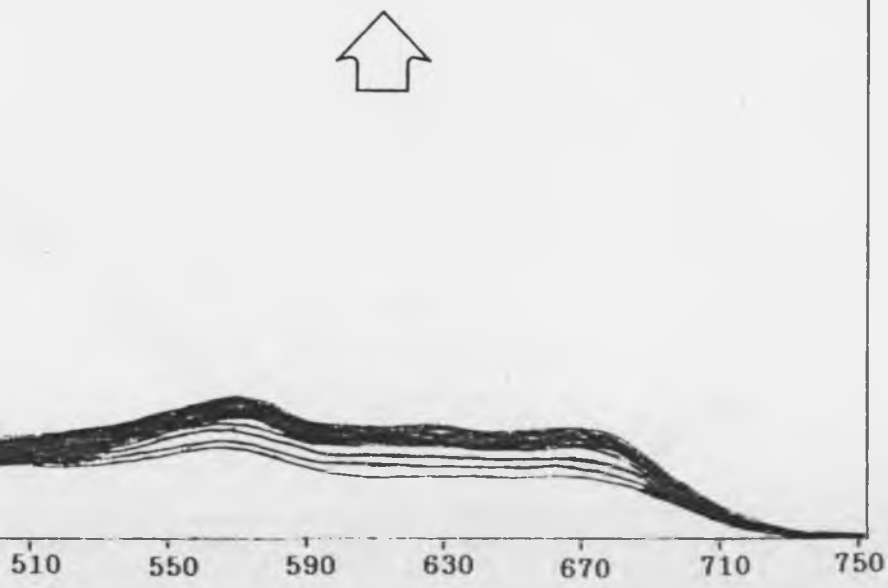

Abs.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
270
310
350
390
430
470

Figure 7. Oxygenation in CH_3OH



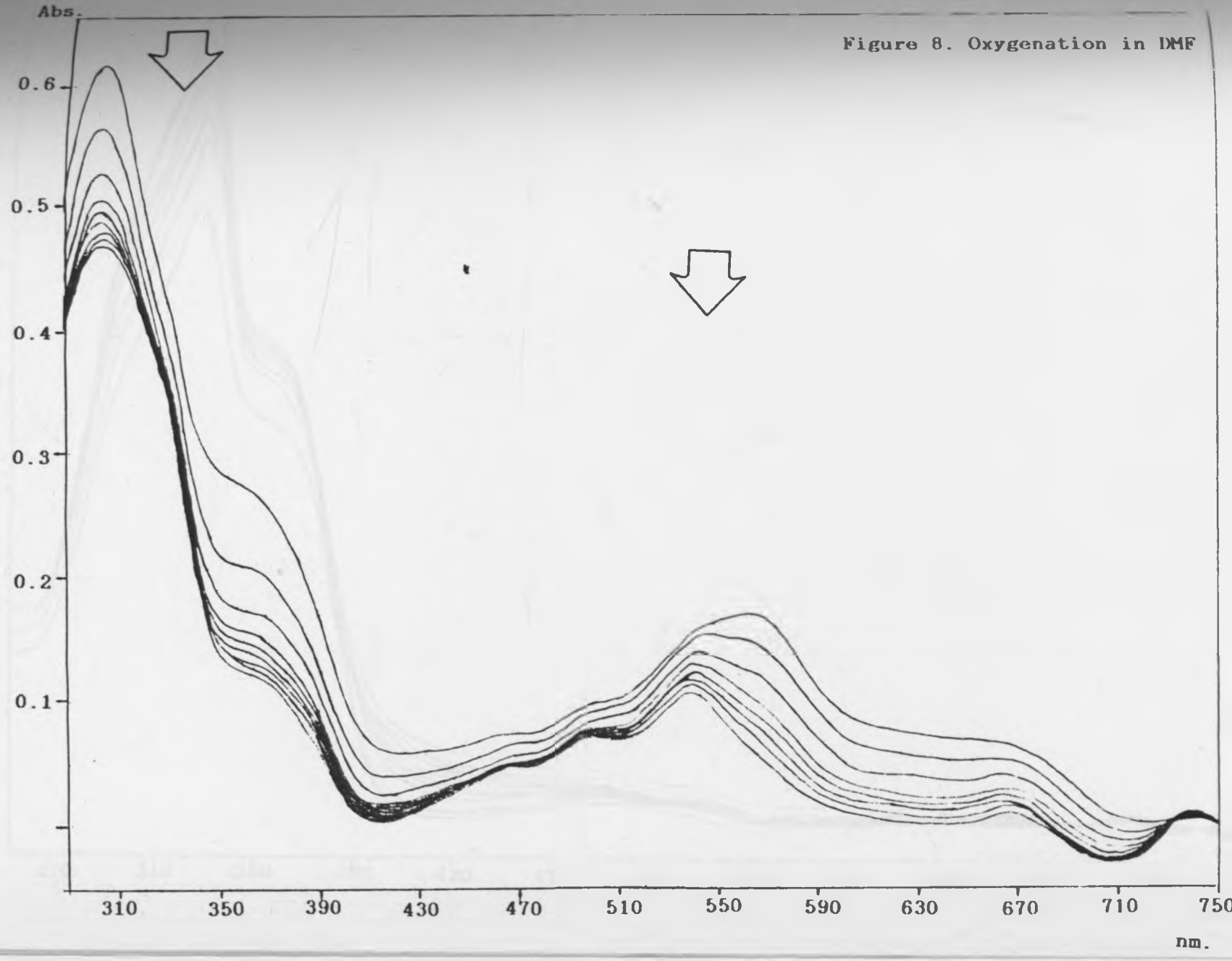


Figure 8. Oxygenation in DMF

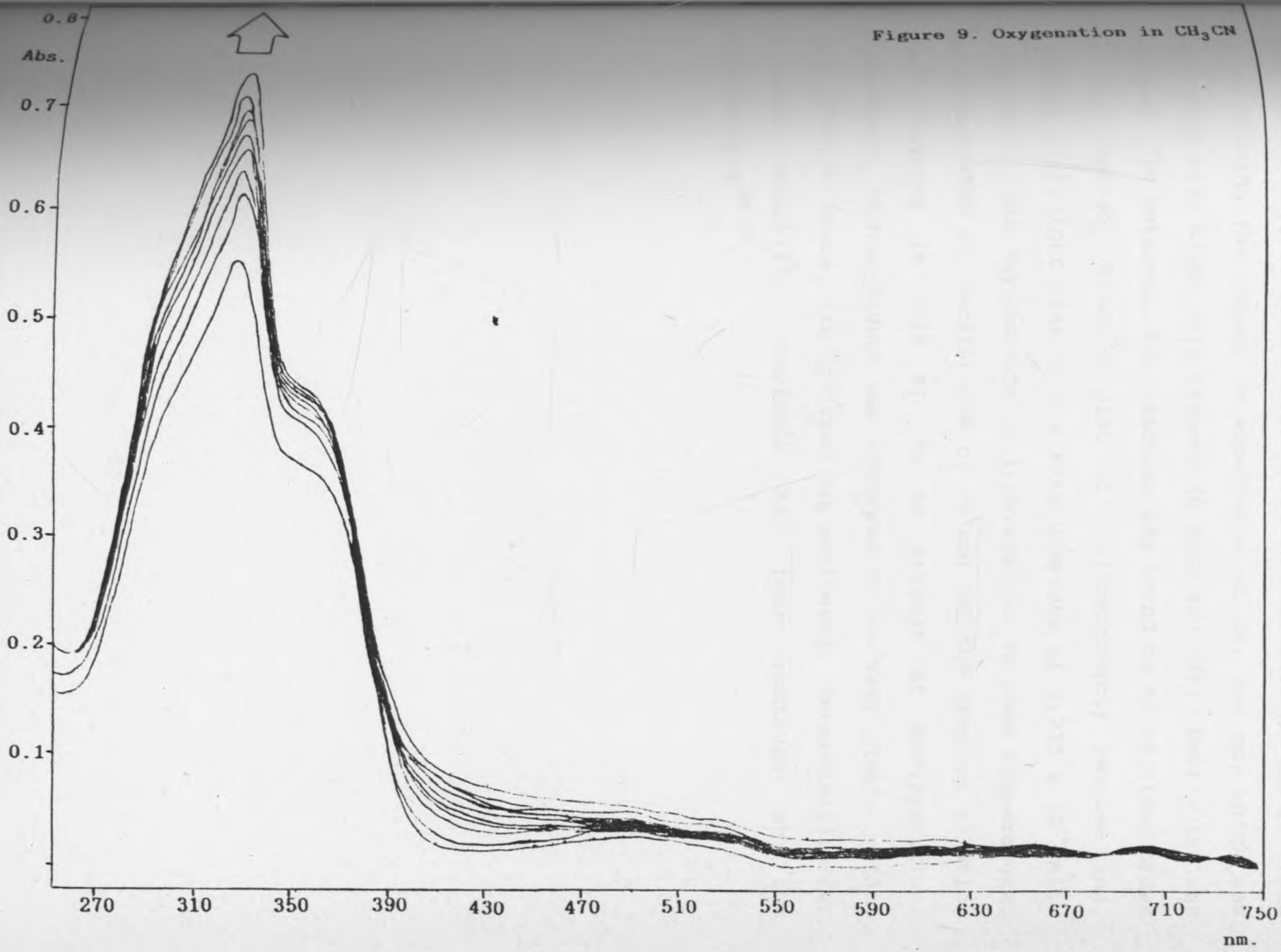


Figure 9. Oxygenation in CH_3CN

A rate study, at room temperature, in each solvent was afforded by monitoring the change in absorbance at ca. 300 nm, which was declining with time, with respect to MeOH and DMF. Beer's law was assumed. In methanol, the reaction was found to be of first order in the complex, since a plot of -In(Absorbance) versus time, yielded a straight line with a rate constant of 3.775×10^{-4} min^{-1} (fig. 10). The oxygenation is irreversible at room temperature, as illustrated by persistence of colour of the complex solution upon flushing it with N_2, as an attempt at deoxygenation. Conversely, the O_2-adduct was observed to be very stable, since even after 24 hours, its spectrum was unaltered. Reversibility for several cobalt(II) complexes has been achieved at low temperatures[100-102].

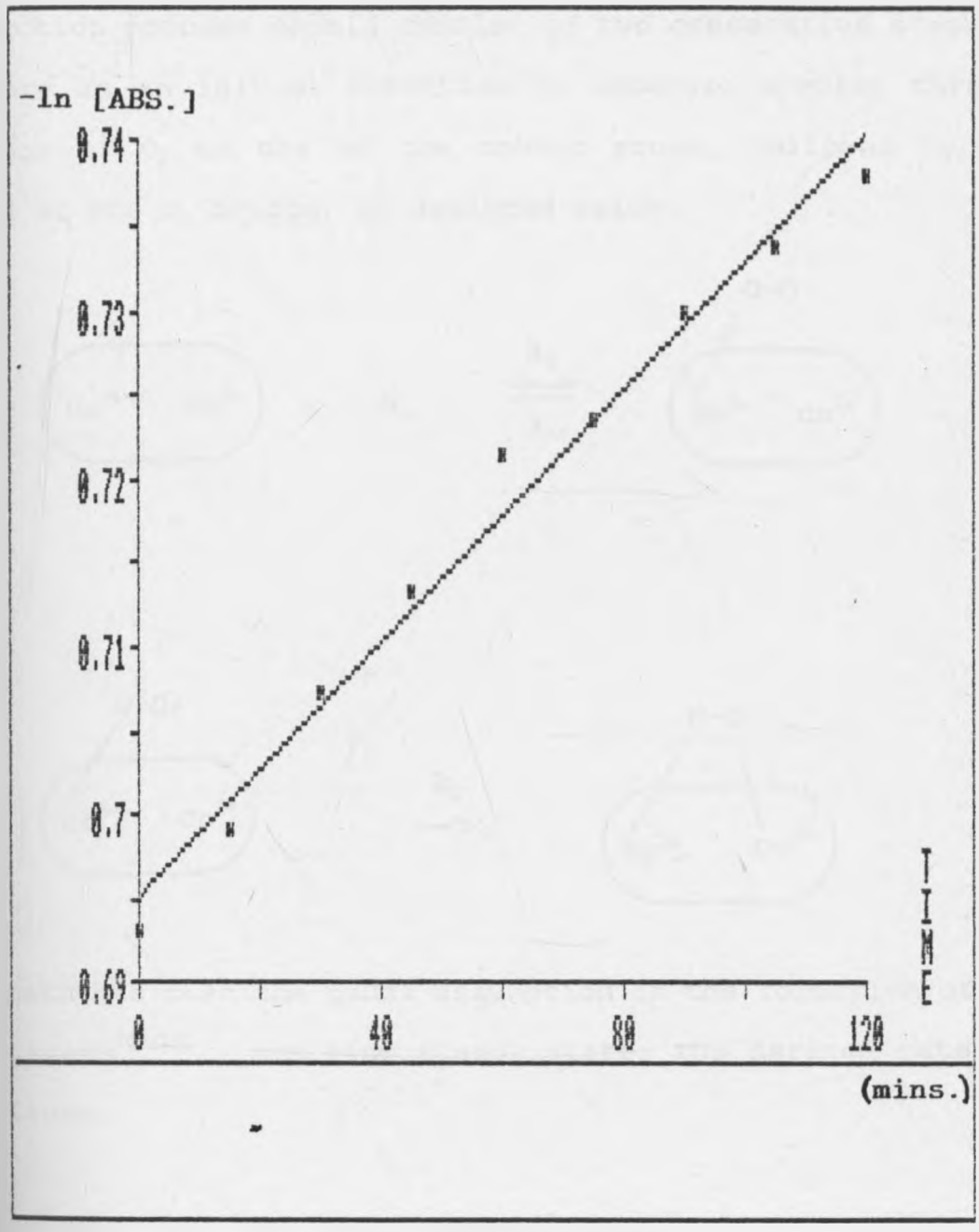
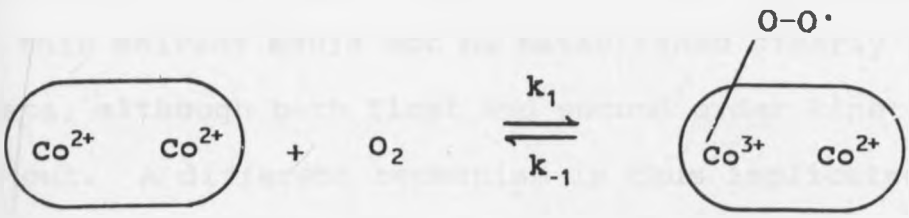


Figure 10. Plot of First Order Kinetics For the Oxygenation in Methanol

The reaction process should consist of two consecutive steps in which there is an initial formation of superoxo species through cordination of O_2 to one of the cobalt atoms, followed by the formation of the O_2 bridge, as depicted below.



This path has been the usual assumption in the formation of μ-peroxo systems[103-105]. Assuming steady state, the derived rate law is as follows.

$$dp/dt = k_1k_2/k_2+k_{-1}\ [Co_2\ (bi - dphmd)^{2+}][O_2]$$

where dp/dt = rate of formation of peroxo complex

In DMF, the complex shows a peak at 500 nm, associated with the O_2 - adduct, as in cobalt protoporphyrin IX dimethyl ester[101], while the oxygenation reaction is observed to go in a modified fashion, relative to what happens in MeOH, judging from the steady decline of the absorption in the region of 600 - 700 nm. The order of the reaction in this solvent could not be established clearly from the available data, although both first and second order kinetics seem to be ruled out. A different mechanism is thus implicated.

The reaction in acetonitrile is conveyed in a more complicated manner, in the electronic spectrum, with the visible region inhabited by low intensity peaks, and the intensity of the 300 nm peak exhibiting a rise, rather than a fall, with time. As with DMF the reaction seems to trace out a different mechanism.

The spectra of this complex differed with that of the analogous Co_2(bi - dptmd)Cl_2, indicative of structural difference in solution. Moreover, the oxygenation of the former is much slower than the latter, probably due to the time taken by larger size complex to orient itself into suitable configuration for oxygen binding.

A manomeric O_2 - uptake experiment conducted for the purpose of determining the stoichiometric ratio of the reactants could not yield any useful information due to the inadequate sensitivity of the procedure for the low concentrations of the complex used.

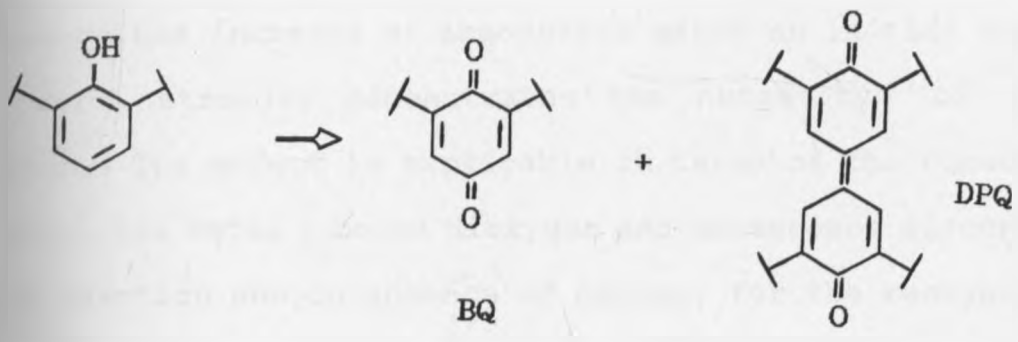
As regards the examination of the O_2 cordination, the ESR technique could not be employed due to the unavailability of this facility in our labs. Nevertheless, more efforts are in progress towards the elucidation of the mode of oxygen binding, as well as stoichiometric studies.

D. Oxidation of 2,6-Diisopropylphenol (2,6-DIPP)

One of the primary goals in this field of molecular oxygen activation studies involves the oxidation of substrates, and thus the oxidative capability of the dicobalt(III) complex was put under examination. Although models of oxidation catalysts generally involve the "end - on " σ- type complexes, because of their similarity to dioxygen complexes, μ - peroxo complexes are also to be enlisted in the membership of useful O_2 - adducts, in light of other biological systems such as tyrosinase and hemocyanin which were shown to bind oxygen in a binuclear fashion[13,14]. Martell and coworkers have oxidized 2,6 - ditertbutylphenol using a μ- peroxo complex of Co(III)[106].

2,6 - DIPP was taken as the substrate, since numerous reagents and catalysts oxidize phenols and these reactions have been reviewed extensively in the literature[107-109]. Generally, phenols can be oxidized to quinones, coupled products (diphenoquinones), or polymers depending on choice of catalyst or reagent.

Several dicobalt(II) complexes[110-112] realize the oxidation of hindered phenols towards the formation of diphenoquinone (DPQ) and benzoquinone (BQ) as shown below.



The substrate and the complex reacted in methanol with the instantaneous formation of a greenish - brown mixture which showed three spots on tlc, indicating the presence of more than one product. Orange crystals that were formed were isolated after concentrating the mixture and their subjection to UV/VIS spectroscopy, in CH_3OH, resulted in an absorption at ca. 420 nm. This suggests this product to be DPQ as a similar absorption for the same has been reported[113]. BQ was probably formed also.

As the 420 nm peak displayed a progressive build - up when the reaction was monitored by UV/VIS spectroscopy, the peak was thus used for rate studies,at room temperatures. Fig. 11 depicts the reaction in methanol, with time. Deaeration of the complex solution, with N_2, prior to the reaction, imposed a remarkable decline on the increase of absorbance after an initial surge (fig. 12), which strongly demonstrates the necessity of O_2 in the reaction. The effect is explicable in terms of the consumption of the available metal - bound dioxygen and subsequent discontinuation of the reaction due to absence of oxygen, for the reoxygenation of the complex. On performing the reaction with $CoCl_2$, in place of the complex, as control, no product formed within the standard durations employed, pointing to the nature of the active species as having O_2 bound to the dicobalt complex.

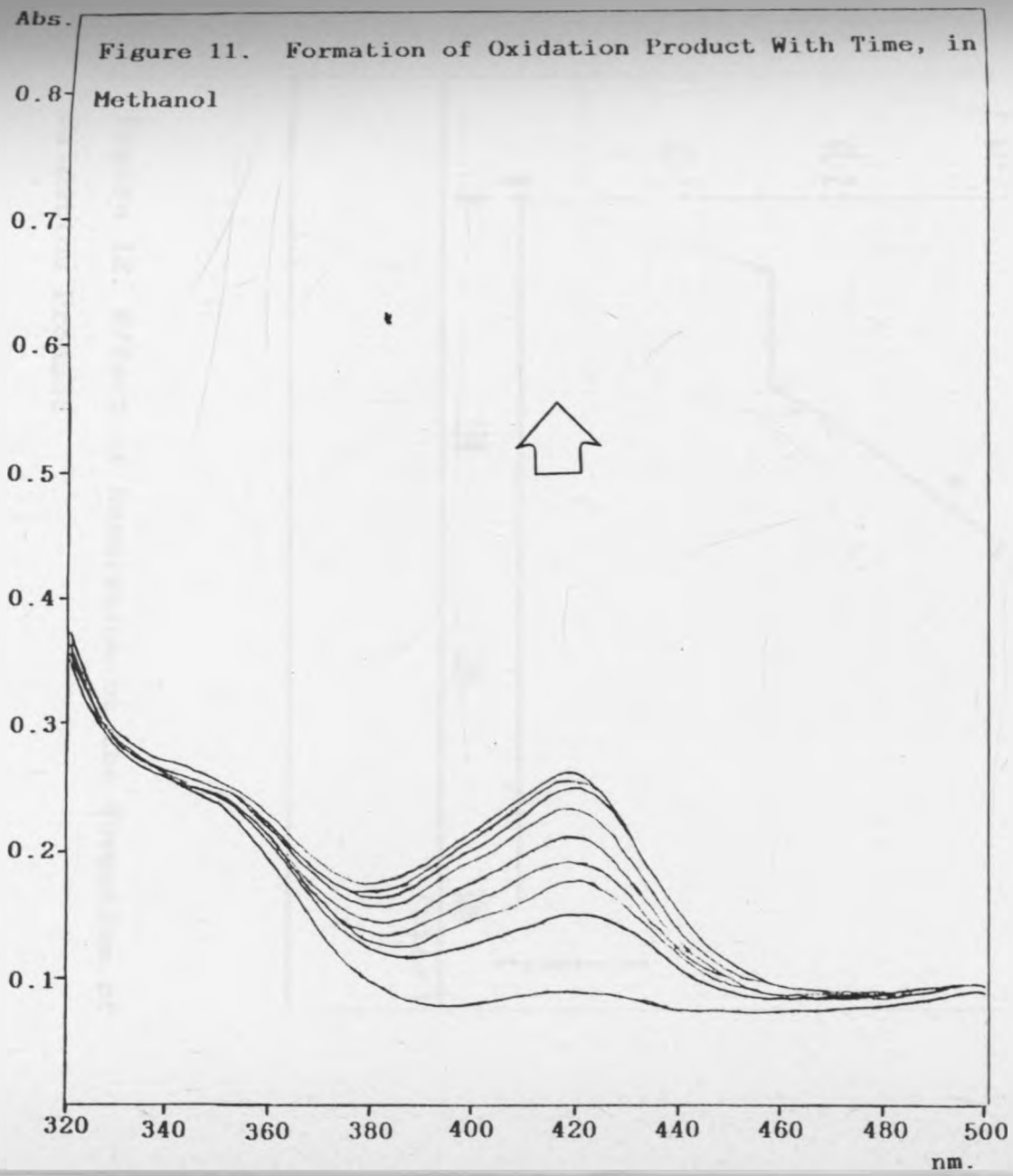


Figure 11. Formation of Oxidation Product With Time, in Methanol

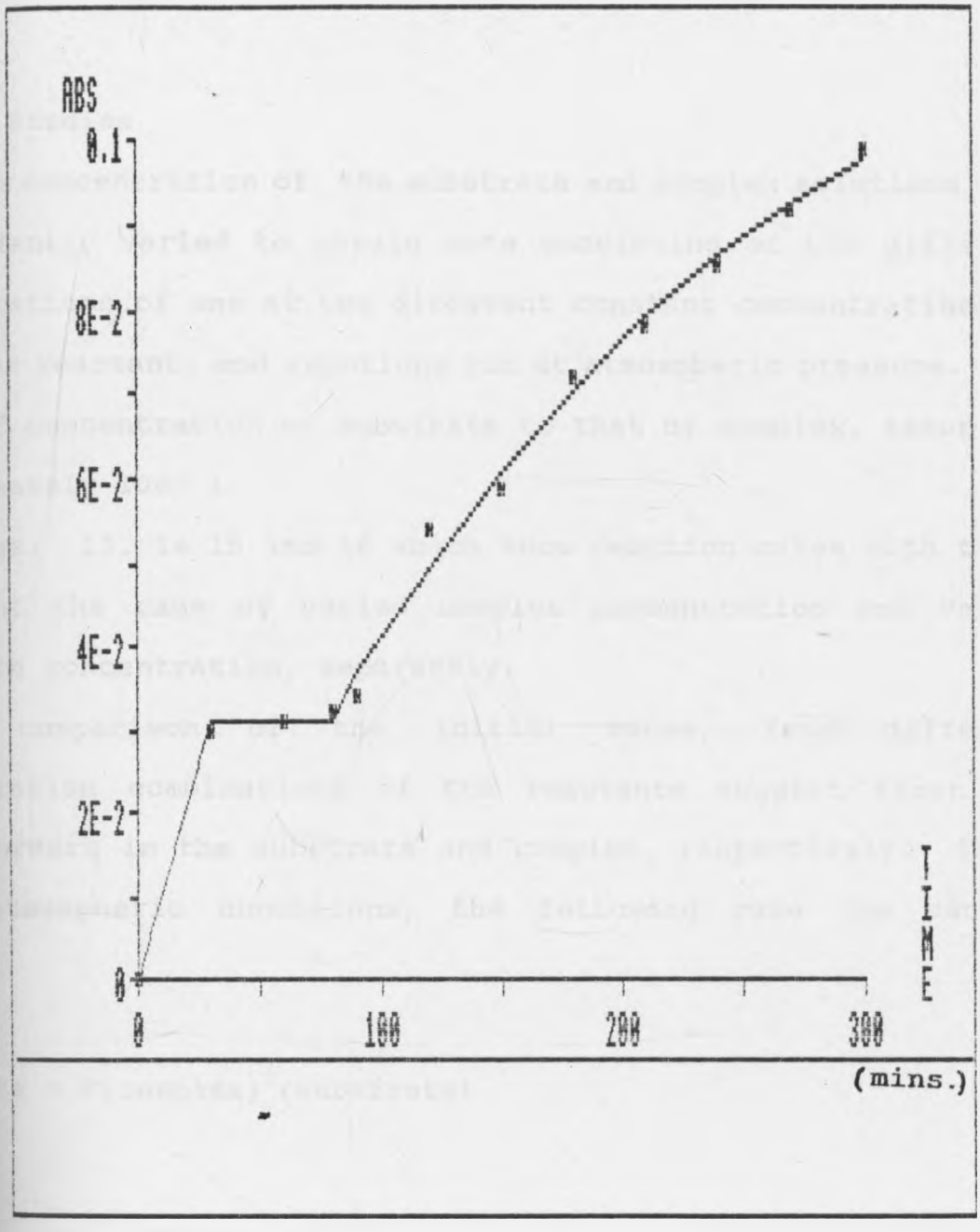


Figure 12. Effect of Deaeration on the Formation of Oxidation Product

Kinetic Studies

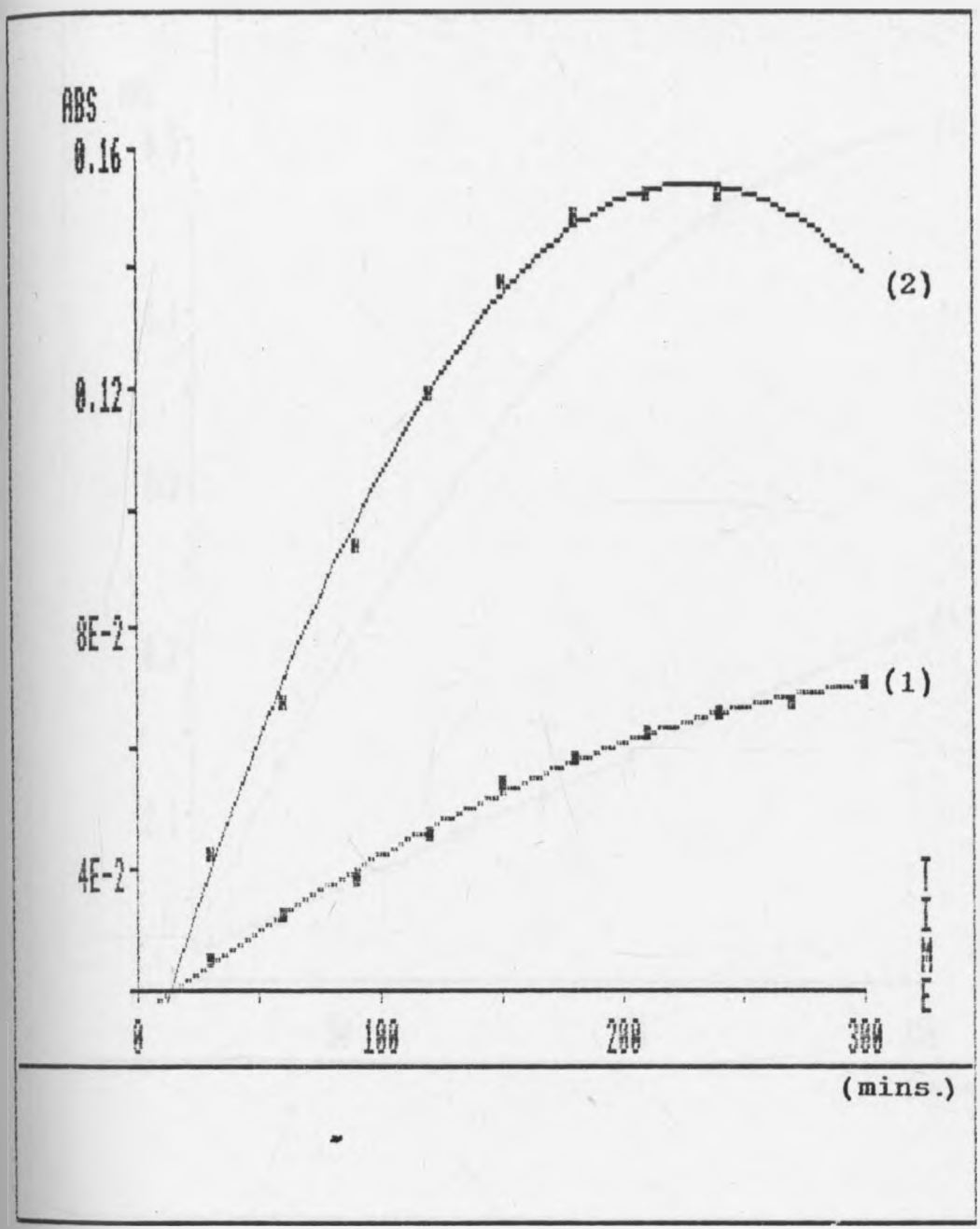
The concentration of the substrate and complex solutions were independently varied to obtain sets consisting of two different concentrations of one at two different constant concentrations of the other reactant, and reactions run at atmospheric pressure. The ratio of concentration of substrate to that of complex, taken was approximately 100: 1

Figs. 13, 14 15 and 16 which show reaction rates with time, represent the case of varied complex concentration and varied substrate concentration, separately.

A comparison of the initial rates, from different concentration combinations of the reactants suggest first and second orders in the substrate and complex, respectively. Thus, under atmospheric conditions, the following rate law can be written.

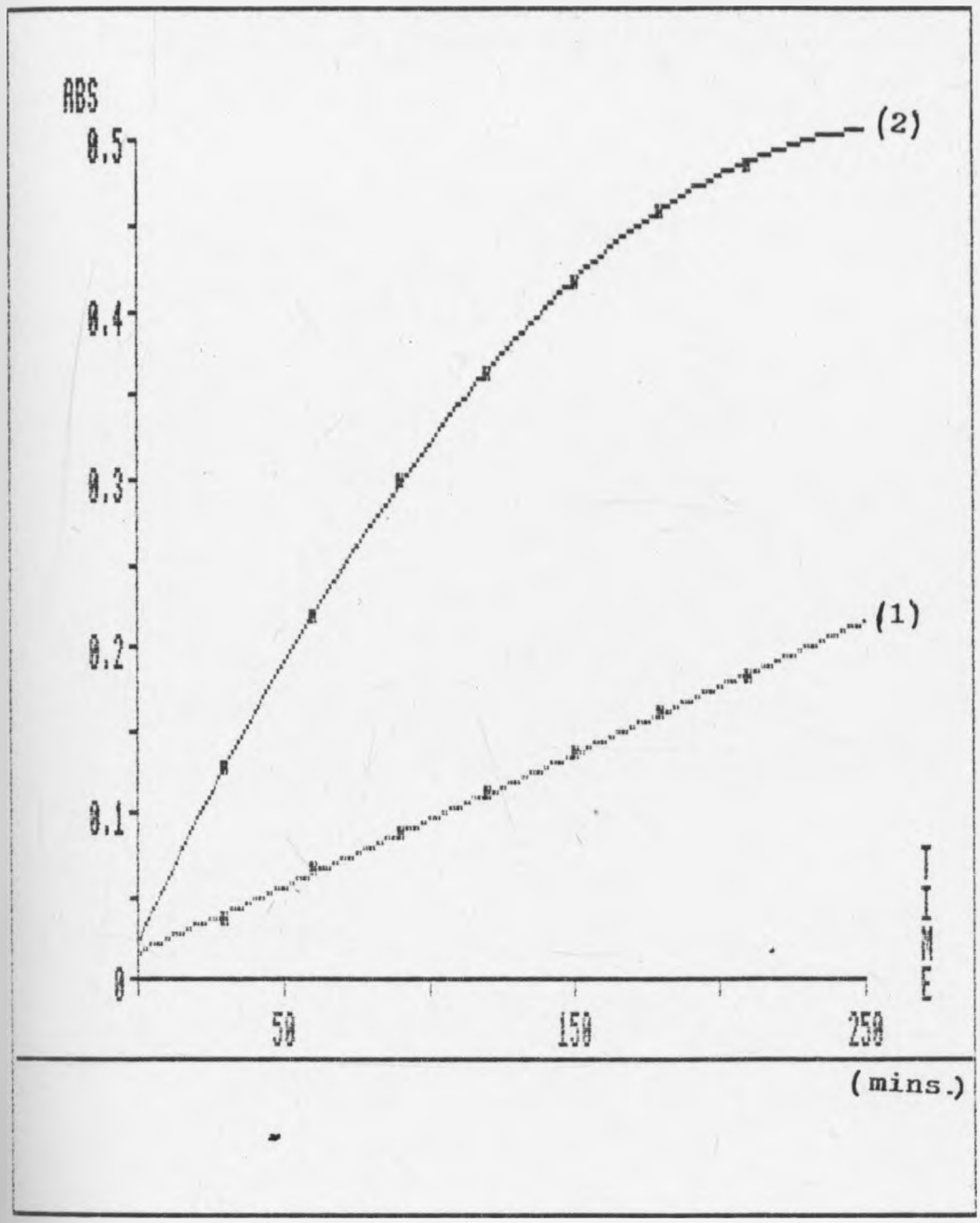
$$\text{Rate} = k(\text{complex})^2(\text{substrate})$$

Figures 13 and 14. Plots of Change of Absorbances versus Time Showing Rate Dependence on Complex Concentration



Curve	[S]	[C]	k (initial) (min^{-1})
1	2.695 X 10^{-3}M	7.1 X 10^{-6}M	3.17 X 10^{-4}
2	2.695 X 10^{-3}M	1.42 X 10^{-5}M	1.324 X 10^{-3}

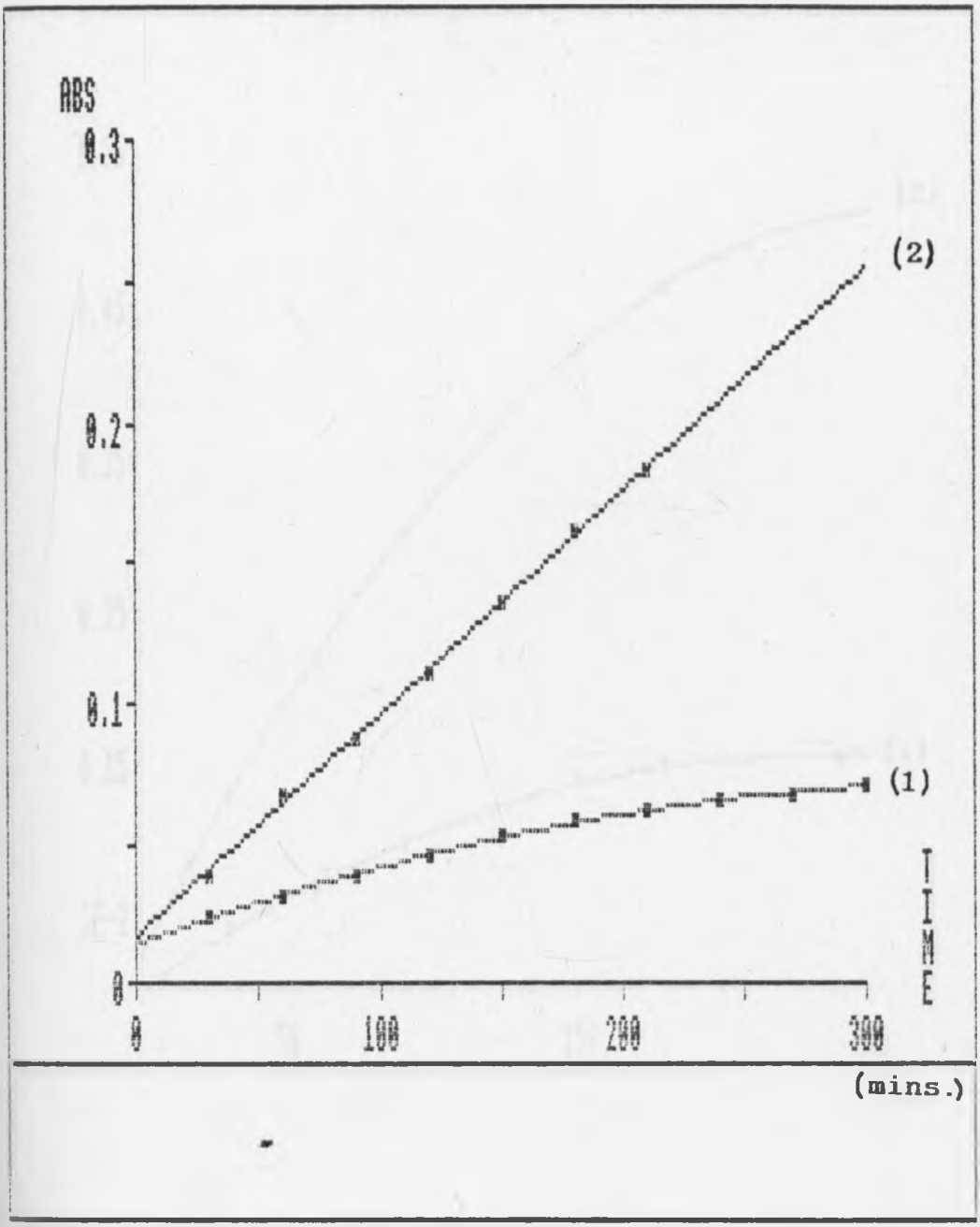
Figure 13



Curve	[S]	[C]	k (initial) (min^{-1})
1	5.39×10^{-3}M	7.1×10^{-6}M	7.929×10^{-4}
2	5.39×10^{-3}M	1.42×10^{-5}M	3.672×10^{-3}

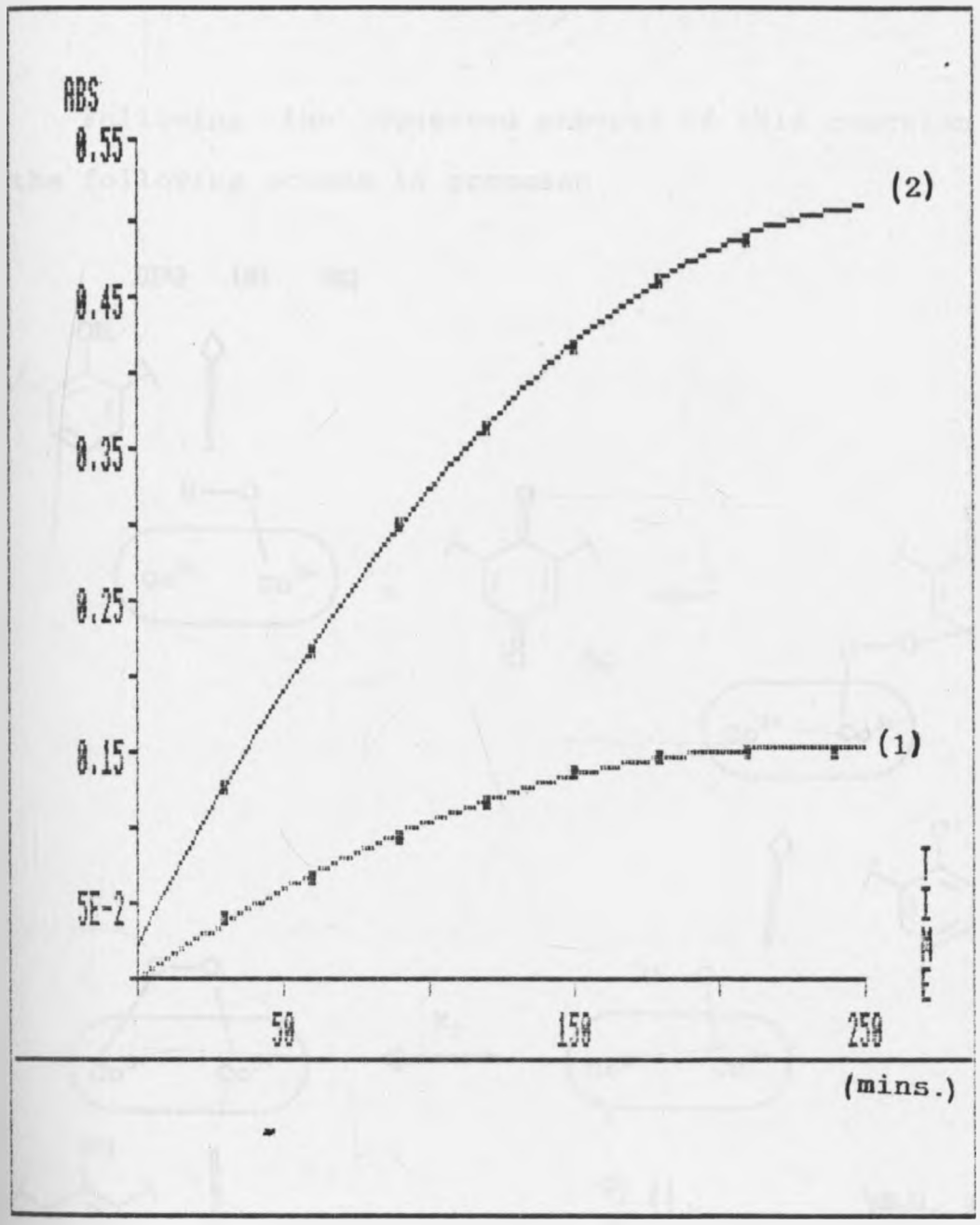
Figure 14

Figures 15 and 16. Plots of Change of Absorbances versus Time Showing Rate Dependence on Substrate Concentration



Curve	[S]	[C]	k (initial) (min^{-1})
1	2.695 X 10^{-3}M	7.1 X 10^{-6}M	3.17 X 10^{-4}
2	5.39 X 10^{-3}M	7.1 X 10^{-6}M	7.929 X 10^{-4}

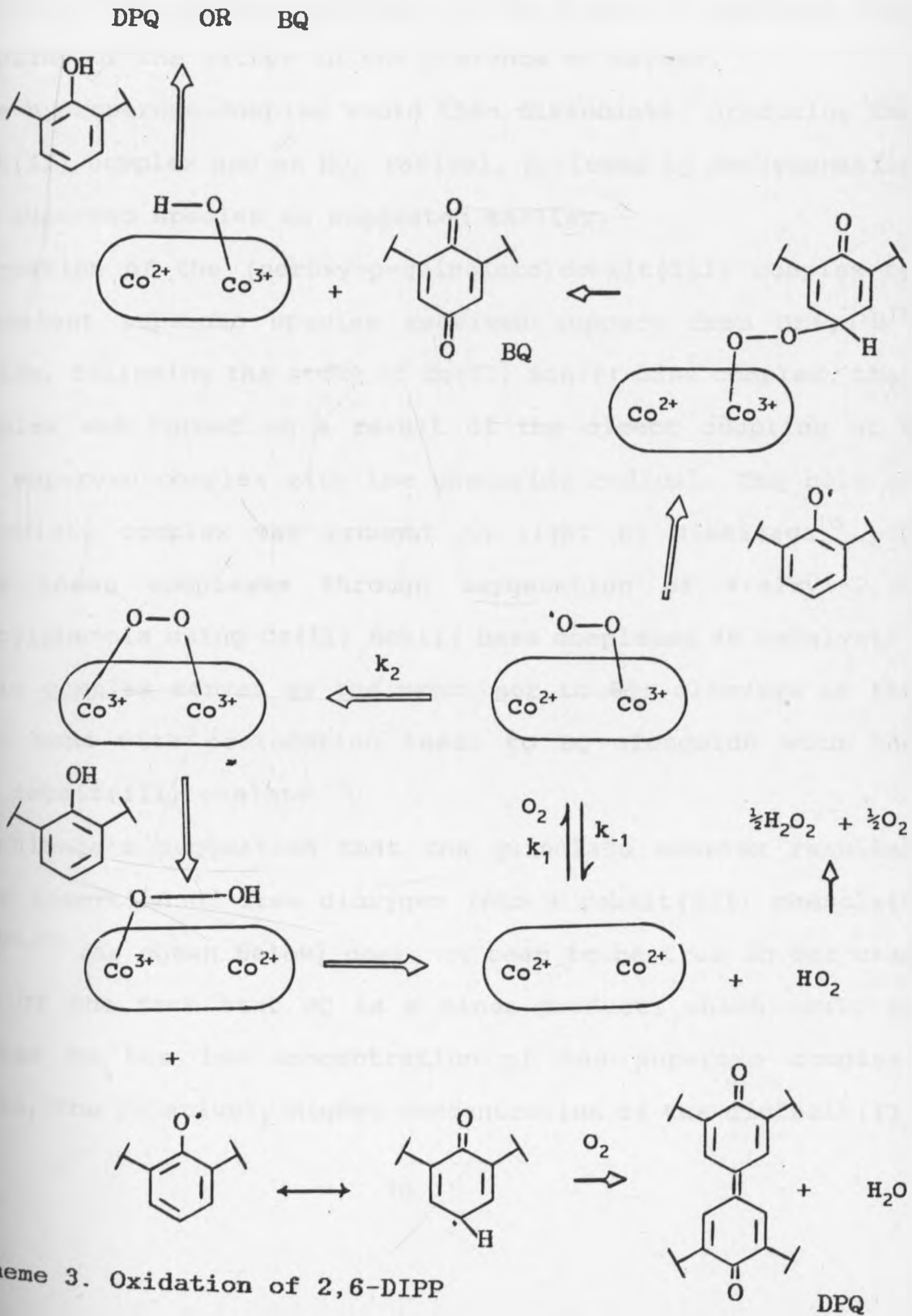
Figure 15



Curve	[S]	[C]	k (initial) (min^{-1})
1	2.695 X 10^{-3}M	1.42 X 10^{-5}M	1.324 X 10^{-3}
2	5.39 X 10^{-3}M	1.42 X 10^{-5}M	3.672 X 10^{-3}

Figure 16

Following the observed aspects of this reaction, the following scheme is proposed



Scheme 3. Oxidation of 2,6-DIPP

The first step in the proposed scheme involves H· abstraction from the phenol by the μ-peroxo dioxygen complex, forming phenoxy radical, and cobalt hydroperoxide as was suggested by Martell[106]. The presence of DPQ as a product may be considered as an implication of the phenoxy radical, as the former is obtained from the coupling of the latter in the presence of oxygen.

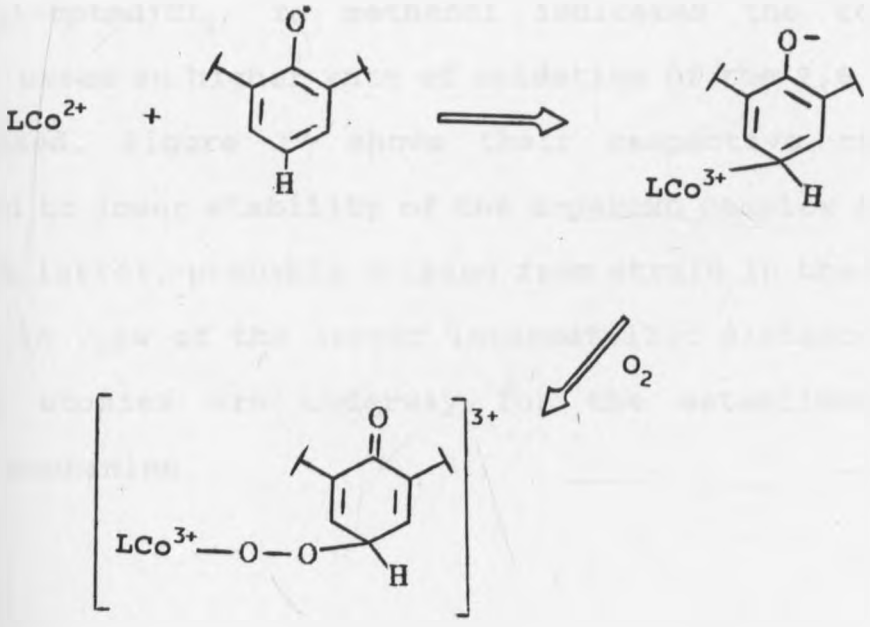
The hydroperoxo complex would then dissociate, producing the dicobalt(II) complex and an HO_2· radical, followed by reoxygenation via the superoxo species as suggested earlier.

Formation of the (peroxy-p-quinolato)cobalt(III) complex by the transient superoxo species receives support from Drago's[114] submission, following the study of Co(II) Schiff base complex, that the complex was formed as a result of the direct coupling of a Co(III) superoxo complex with the phenoxide radical. The role of the quinolato complex was brought to light by Nishinaga[115] who isolated these complexes through oxygenation of 4-alkyl-2,6-diterbutylphenols using Co(II) Schiff base complexes as catalysts.

This complex serves as the precursor to BQ; cleavage of the dioxygen bond with protonation leads to BQ alongside with the hydroxo cobalt(III) chelate.

Nishinaga's suggestion that the quinolato complex resulted from the insertion of free dioxygen into a cobalt(III) phenolate complex[116,117] (as shown below) does not seem to be true in our case in view of the fact that BQ is a minor product, which could be attributed to the low concentration of the superoxo complex. Otherwise, the relatively higher concentration of the dicobalt(II)

complex would have seen the production of correspondingly larger amount of BQ.



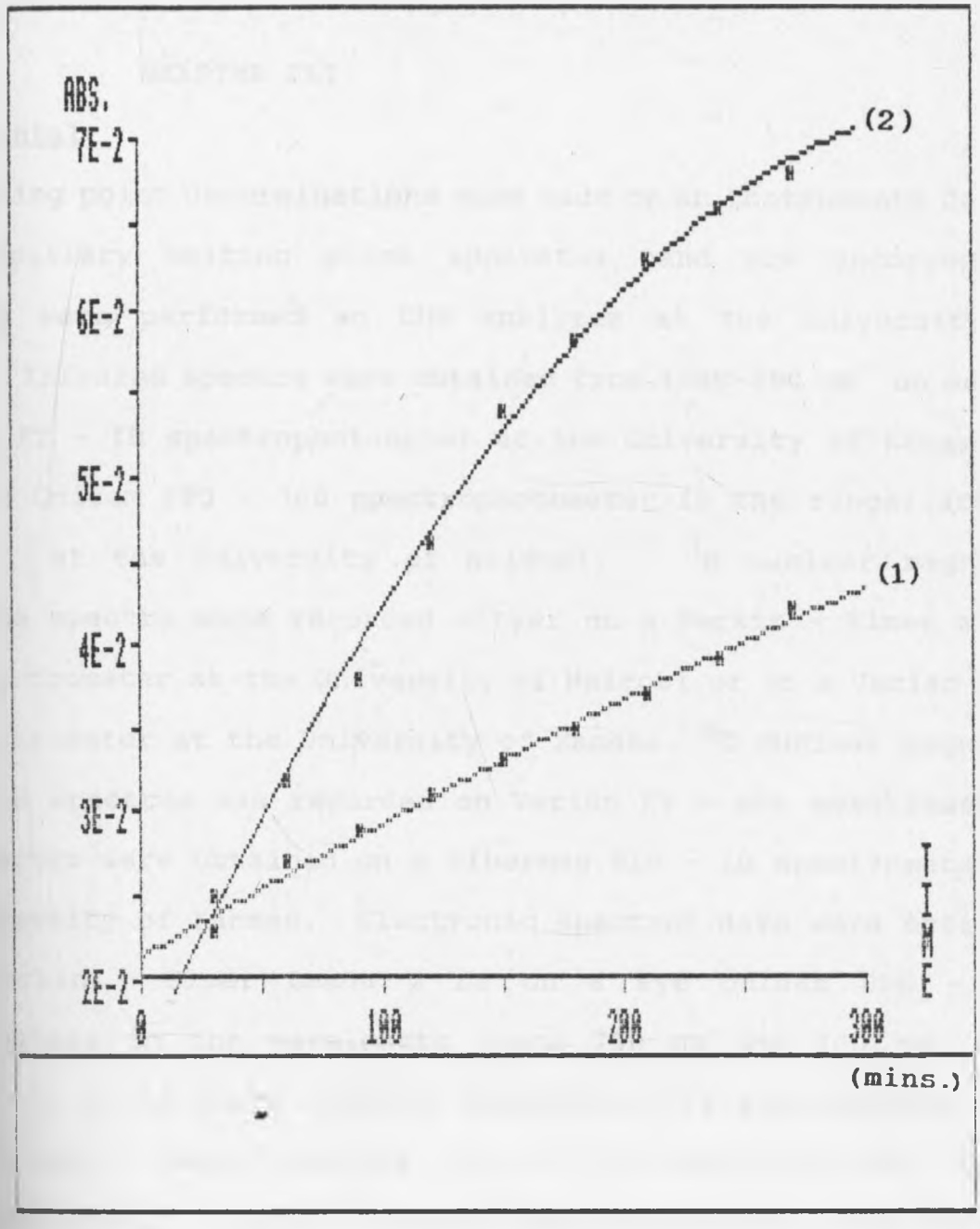
The hydroxo cobalt complex may serve as a proton abstractor hence contributing in the formation of phenoxy radicals, and in the process, regenerating the dicobalt(II) complex as traditionally speculated[106,114].

The fate of $HO_2^{\cdot}$ is most likely decomposition. Although the decomposition rate for $HO_2^{\cdot}$ is reported to approach diffusion controlled limit in non-polar solvents[118], a substantial rate is also expected in CH_3OH to render this process prominent.

Introduction of pyridine solution before the start, or in the course, of the reaction did not affect the reaction, as typical spectral behaviour was maintained, which further illustrates the stability of the O_2 - adduct formed.

A comparison of catalytic activity between Co_2(bi-dphmd)Cl_2 and Co_2(bi-dptmd)Cl_2, in methanol indicated the former to be superior, based on higher rate of oxidation of the 2,6 - DIPP, when it was used. Figure 17 shows their respective rates. This attributed to lower stability of the μ-peroxo complex in the former versus the latter, probably arising from strain in the bonds of the O_2 bridge in view of the larger intermetallic distance.

More studies are underway for the establishment of the reaction mechanism.



Curve	Complex	[S]	[C]
1	Co_2(bi-dptmd)Cl_2	2.695 X 10^{-3}M	9.025 X 10^{-6}M
2	Co_2(bi-dphmd)Cl_2	2.695 X 10^{-3}M	7.1 X 10^{-6}M

Figure 17. Comparison of the Catalytic Activities of the Dicobalt Complexes

CHAPTER III

Experimental

Melting point determinations were made on an Instruments Co.(P) Ltd. capillary melting point apparatus, and are uncorrected. Analyses were performed an CHN analyzer at the University of Kansas. Infrared spectra were obtained from 4000-600 cm^{-1} on an IBM IR - 32 FT - IR spectrophotometer at the University of Kansas or on a Pye Unicam SP3 - 300 spectrophotometer in the range; 4000 - 200 cm^{-1}, at the University of Nairobi. ^{1}H nuclear magnetic resonance spectra were recorded either on a Perkin - Elmer model R12B spectrometer at the University of Nairobi or on a Varian XL - 300 spectrometer at the University of Kansas. ^{13}C nuclear magnetic resonance spectrum was recorded on Varian FT - 80A spectrometer. Mass spectra were obtained on a Ribermag R10 - 10 spectrometer at the University of Kansas. Electronic spectral data were obtained on a Perkin - Elmer Lamda 3 or on a Pye Unicam SP8 - 150 spectrometers in the wavelength range 750 nm and 200 nm. Room temperature solid state magnetic susceptibility was measured by a modified Gouy - Rankine method (fig. 18) according to Prof. Irina at Moi University. Liquid Chromatography separations were done on a column packed with Riedel de Haën 230 - 400 mesh silica gel S. Oxygen uptake determinations were performed using a set up consisting of a manometer as shown in fig. 19.

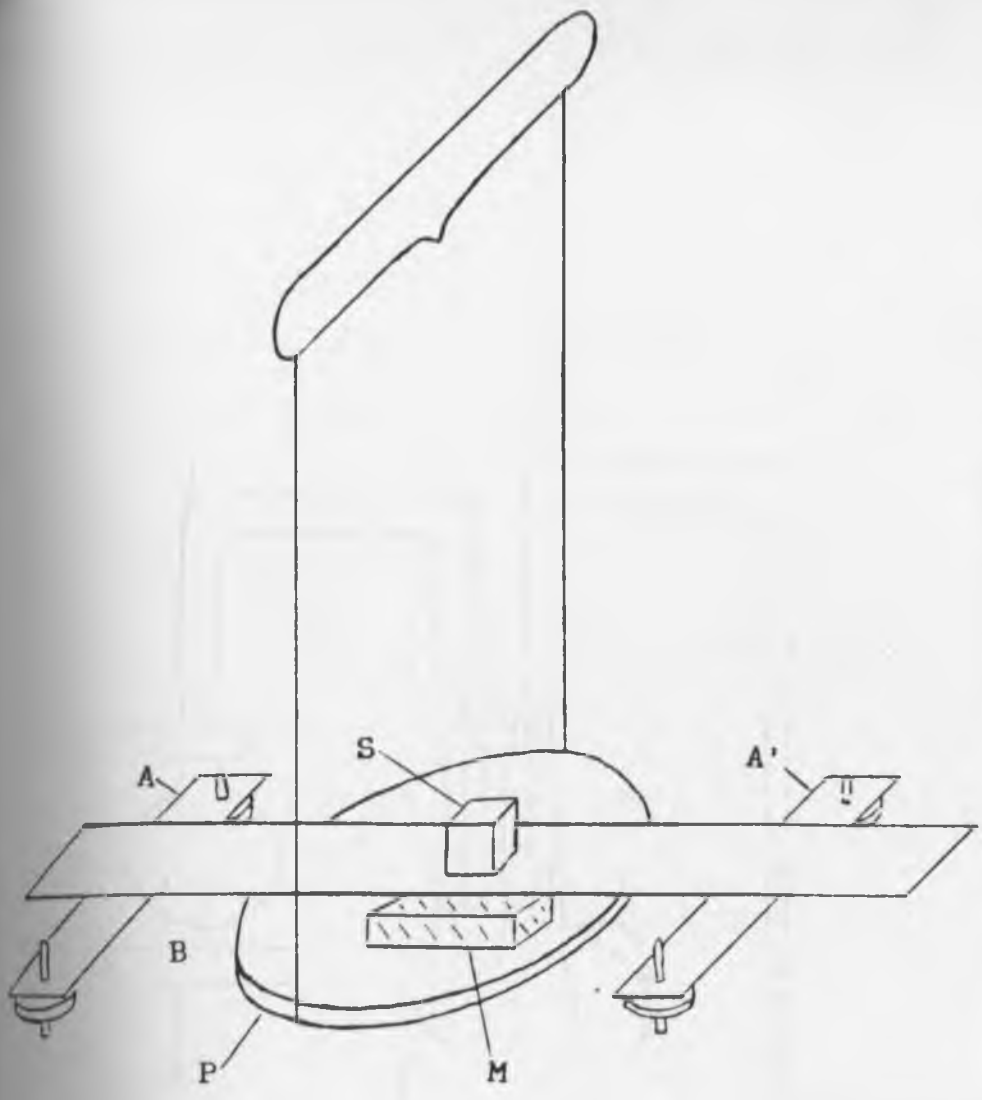
All salts used were hexahydrates, except barium chloride and zinc chloride which were dihydrate and anhydrous, respectively.

Physical Data:

Electronic absorbance taken during reactions are presented in tables 5 - 13.

Magnetic Measurements:

The diamagnetic corrections for the dicobalt(II) complex were approximated from Pascal's constants for the atoms.



AA'; adjusting plates

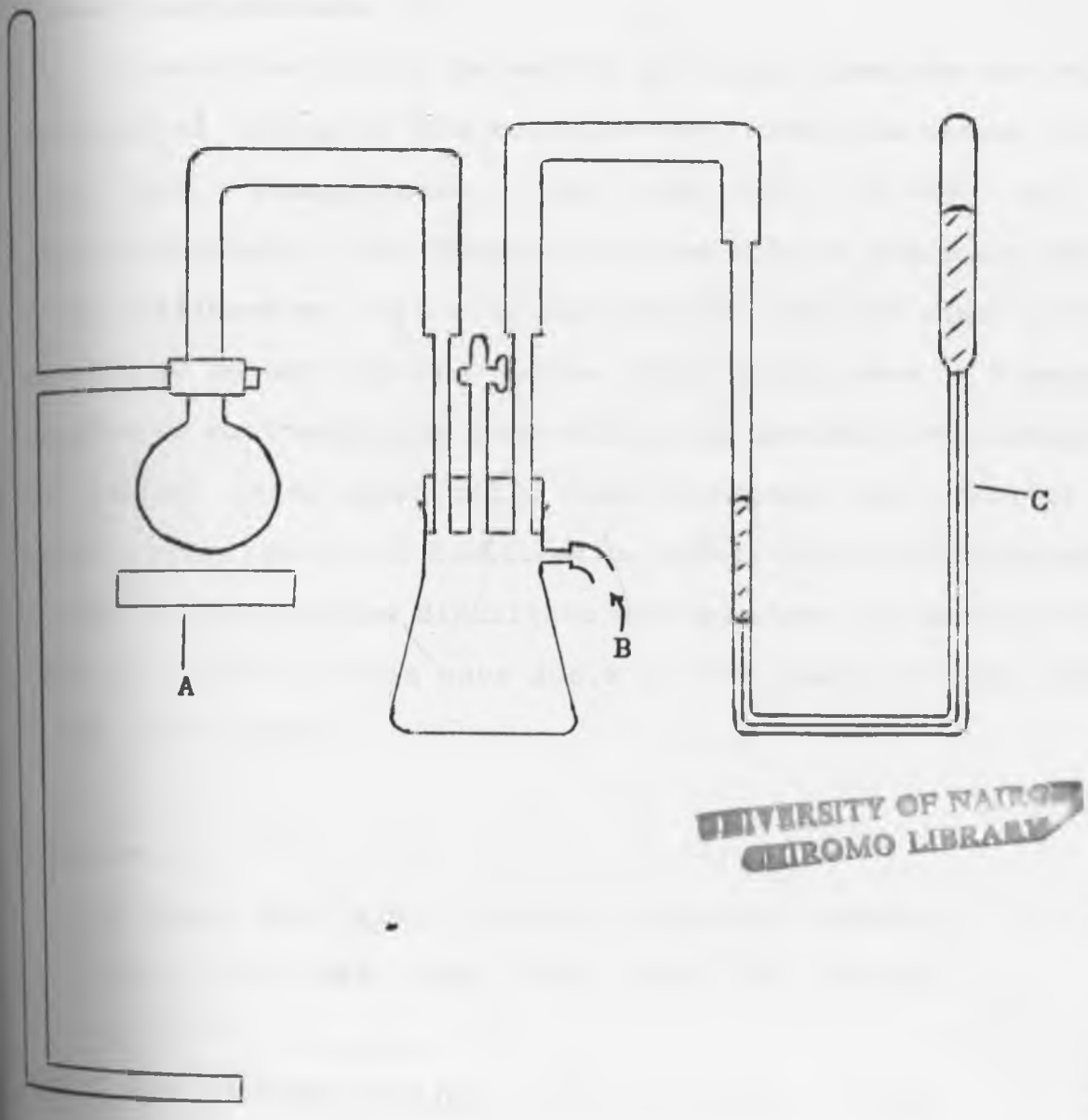
P; balance pan

B; supporting plate

M; magnet

S; sample

Figure 18. Set Up For Susceptibility Measurement



A; magnetic stirrer

B; gas inlet

C; manometer

Figure 19. Oxygen Uptake Set Up

A. Synthesis of 3,3' - diethyl - 5,5' - diformyl - 4,4' - dimethyldipyrromethane:

1. Benzylacetoacetate (1)

A modification of the method of Bader, Cummings and Vogel[119] was employed. In a 500 mls round bottom flask were placed 120 mls (1.11 mol) benzylalcohol and 240 mls (1.848 mol) of ethylacetoacetate. The flask was fitted with a condenser and the mixture refluxed at 130°C with the aid of a heating mantle, for 48 hours, its colour turning yellow from colourless. Occasional temperature monitoring was done with a thermometer. The mixture was then cooled, after which still head, condenser and receiver were fitted appropriately for distillation under vacuum at approximately 10 mmHg. A light yellow distillate was obtained in the temperature range 140 - 170°C. This gave 206.8 g (70% yield) of pure product of bpt. 145 - 150°C.

Analysis:

1. IR (neat, NaCl disc): 3450(b), 3030(w), 2960(w), 1742, 1716, 1646, 1559, 1456, 1265, 749, 698 cm^{-1}

2. ^1H NMR ($CHCl_3$); δ 7(m), 4.8(s), 3.1(s), 1.75(s).

3. Mass Spec. (m/e): 192(M^+), 64, 108, 107, 91, 79, 65, 58, 43.

Elemental analysis for this compound was not obtainable.

2. **Benzyl -α - oximinoacetoacetate (2)**

The procedure of Johnson et al[58] was followed. To a solution of 48 g (0.25 mol) benzylacetoacetate (1) in 100 mls glacial acetic acid, in a flask, was added, in small amounts, a solution obtained from dissolving 20 g sodium nitrite in 40 mls water, during 15 minutes at a temperature less than 10°C. An exothermic reaction occurred, with the formation of a yellow solution. Red colouration of the reaction solution results later. Stirring was conducted at the same temperatures for 4 hours. The solution was then left, stirring, overnight, at room temperature, after which it was used for the subsequent reaction without characterization.

3. **2,4 - dimethyl - 3 - ethoxy - 5 - carbobenzoxypyrrole (3):**

The followed procedure was of a typical Knorr reaction[56,120]. 30 mls (0.3 mol) of 2,4 - pentanedione was placed in a 3 - neck 500 mls round bottom flask, fitted with a mechanical stirrer and a thermometer, and two volumes of glacial acetic acid was added. 65 g (1 mol) of zinc dust was taken and a small amount of it was added, initially, followed by dropwise addition of the oxime solution, with powerful stirring. The addition of small amounts of both zinc dust and oxime was continued at such rates as to ensure the maintenance of the temperature between 75 - 85°C, as an exothermic reaction ensued.

At these low temperatures, precipitation of zinc acetate occurs, which impedes stirring and suitable amounts of sodium or ammonium acetate were added to keep it in solution. A greenish - brown mixture was obtained from the reaction. High temperatures have been shown to be unfavourable to starting materials[121]. After the addition of all the reactants, stirring was continued for 2 hrs. with the temperature maintained at 75- 85°C, by thermostatical heating, to maximize yield. The hot reaction mixture was decanted from the zinc sludge before zinc acetate or product could crystallize out. The residual zinc dust was rinsed with glacial acetic acid and discarded through reaction with conc. HCl in the hood (due to its pyrrophoric nature). After this 4 - 6 volumes of water were added to the reaction mixture to enhance crystallization. The white precipitate obtained was separated by filtration and washed thoroughly with water, discarding all of the aqueous filtrates. To separate the product from remaining zinc dust, the precipitate was dissolved and washed through a Buchner funnel with methylene chloride. The filtrate obtained was concentrated leaving the crude product which was recrystallized from methanol. Pure product of yield; 22.72 g (33.5%) and mpt. 134 - 136°C was obtained.

Analysis:

IR (KBr) ; 3160, 3100, 3020, 2960, 1660, 1610, 1550, 1460, 1410, 1370, 1265, 1170, 1090, 1060 cm^{-1}

^1H NMR ($CHCl_3$); δ 7.5 (m, 5H), 5.4(s, 2H), 2.6(3s, 9H)

Microanalysis:

Cald.;	Found;
C,70.84	C,70.68
H,6.27	H,6.30
N,5.16	N,5.41

4. 2,4 - dimethyl - 3 - ethyl - 5-carbobenzoxypyrrole (4)

The procedure of Whitlock and Hanauer[64] was used, for the reduction step. 15 g (0.0558 mol) of 2,4 - dimethyl- 3 - ethoxy - 5 - cabobenzoxypyrrole (3) was added, under nitrogen, to 150 mls of freshly purified THF[122] in a 500 mls 3 - neck round bottom flask, fitted with mechanical stirrer, dropping funnel and nitrogen inlet. The solution was stirred and its temperature initially lowered to 5°C, by means of an ice bath, and upon dissolution of all the solid, 5.8 g (0.15 mol) of fresh sodium borohydride was added. Distilled boron tri-fluoride di-ethyletherate (29.8 mls, 0.21 mol) was added slowly during 30 minutes, with temperature regulated at near 10°C, resulting in the formation of a white solution. The mixture was heated to 25°C and stirring continued for 1 hour, after which duration the temperature was lowered to 15°C and 150 mls 5% HCl cautiously added, giving a short - lived exothermic reaction, while the temperature was kept at below 35°C. The mixture was stirred overnight at room temperature (12 hours). Two layers (the

top one being yellowish) were observed at the end of the stirring. The reaction mixture was added to 75 mls of water in a separatory funnel and the aqueous layer extracted with ether several times. The combined extracts were washed with saturated salt solution (aqueous NaCl) and dried over potassium carbonate. After the evaporation of the solvent under reduced pressure, the crude product was in form of a high boiling yellow liquid that solidified on standing. Recrystallization from methanol produced white needle - like crystals with a melting point range of 99 - 100°C. 9.56 g (67.2% yield) of pure product was obtained.

Analysis:

IR (KBr); 3290(s, sh), 2940, 2900, 2860, 1630(s), 1490(w), 1420(s), 1250(s), 1200(m), 1160, 1110, 1070 cm^{-1}

^{1}H NMR ($CDCl_3$); δ 8.7(b, 1H), 7.4(m, 5H), 5.3(s, 2H), 2.38(q, 2H), 2.3(s), 2.18(s, 3H), 1.0(t, 3H)

$^{13}CNMR$ ($CDCl_3$); ppm 0.2326, 10.7863, 11.5935, 15.5446, 17.4393, 65.5818, 124.2661, 128.2157, 128.2855, 128.740, 129.7173, 136.9534, 150.1022.

Mass spec. (m/e): 257, 242, 166, 150, 134, 123, 91, 77, 65, 41.

Microanalysis:

Calcd.;	Found;
C,74.71	C,74.87
H,7.39	H,7.98
N,5.45	N,5.98

5. Benzyl - 5 - acetoxymethyl - 4 -ethyl - 3 - methylpyrrole - 2 - carboxylate (5)

The procedure of Johnson et al[70] was followed. A solution of 11.6 g (0.0452 mol) benzyl - 4 - ethyl - 3,5-dimethylpyrrole - 2 - carboxylate (4) in 200 mls glacial acetic acid was prepared and to it added, in small amounts, 20 g (4.6×10^{-4} mol) of lead-tetraacetate, with stirring during 10 minutes. The lead - tetraacetate had low solubility. A yellow solution was obtained whose colour deepened to brown with further additions of lead-tetraacetate. Stirring was continued for 12 hrs., after which, only a small amount of precipitation resulted. 200 mls of water was added to the mixture to promote precipitation. The white precipitate obtained was filtered, washed thoroughly with water and recrystallized from acetone. The recrystallized fluffy whitish material was separated by filtration and rinsed with 50% acetone/water mixture to obtain 12.15 g (85.5% yield) of product of melting point range 120 - 121°C.

Analysis:

IR (KBr); 3300(s,sh), 2940, 2920, 2860, 1720(m), 1650(s), 1440, 1270, 1230, 1160, 1110, 980, 950, 910, 690 cm^{-1}

Microanalysis

Calcd.;	Found;
C,68.57	C,68.78
H,6.67	H,6.78
N,4.40	N,4.44

6. **Dibenzyl - 3,3' - diethyl - 4,4' - dimethyl-dipyrromethane - 5,5' - dicarboxylate (6)**

The procedure of Johnson et al[119] was employed. Benzyl - 5 - acetoxymethyl - 3 - ethylpyrrole - 2 - carboxylate (5) (9.6 g, 0.03 mol) was placed in 300 mls ethanol containing 7 mls conc. HCl, in a flask. A condenser was fitted to the flask and the mixture heated under reflux for 2 hrs., during which dissolution occured with the formation of a yellow solution whose colour intensified to brown with time. The solution was then concentrated by evaporating some of the solvent, and cooled. The formed light brown crystalline material was separated by filtration, rinsed with ethanol and dried. The yield was 7.13 g (94%) and the melting point range: 127 - 128°C

Analysis:

IR (KBr): 3327(s), 2965, 2926, 2865, 1694(s), 1646(s), 1506, 1464, 1448(s), 1315, 1279(s), 1256, 1057 cm^{-1}.

Microanalysis:

Calcd.;	Found;
C,74.7	C,74.60
H,6.83	H,6.90
N,5.62	N,5.50

7. 3,3' - diethyl - 4,4' - dimethyldipyrromethane dicarboxylic acid (7)

The followed procedure was similar to that of Chang and Abdalmuhdi[29]. 4.8 g (9.6×10^{-3} mol) of dibenzyl - 3,3' - diethyl-4,4' - dimethyldipyrromethane - 5,5' - dicarboxylate (6) was dissolved in 120 mls of hot ethanol in a 250 mls round bottom flask. Sodium hydroxide solution (7.4 g, 0.185 mol) in 20 mls water was added cautiously with an immediate orange colour appearing. The mixture was refluxed for 8 hrs., forming a yellow solution in the process. The solvent was then evaporated and the light orange residue redissolved in 200 mls of water and acidified with acetic acid. Precipitation of a pink solid resulted after 20 minutes of ageing. The product was separated by filtration and washed with 40 mls water. It was air - dried

for 5 hrs., then kept in a descicator, under reduced pressure, for 2 days. Melting of the product occured with effervescence at 163 - 166°C. The yield was 2.71 g (88%)

Analysis:

IR (KBr): 3357, 3278, 3132, 3065, 2963,2930,2872, 1682(s), 1470, 1264,1246 cm^{-1}.

Microanalysis:

Cald.;	Found;
C,64.15	C,64.00
H,6.92	H,6.86
N,8.81	N,8.72

8. **3,3' - diethyl - 4,4' - dimethyldipyrromethane (8)**

The employed procedure was similar to that of Chang and Abdalmuhdi[29]. To 20 mls of ethanolamine in a 100 mls flask, equipped with a condenser, was added 3.6 g (0.11) of 3,3' - diethyl-4,4'-dimethyldipyrromethane - 5,5'- dicarboxylic acid (7) and the mixture heated to boiling for 10 minutes. A brown mixture was formed. The mixture was poured into a suitable amount of ice - water, while still hot and left to stand for several hours. The resulting brown solid was filtered, washed with water and dried in a vacuum, to obtain a yield of 2.4 g (85%). The melting point of the product was 52 - 54°C.

Analysis:

IR (KBr): 3374(s, sh), 3364, 2961, 2926, 2867, 1448, 1304, 1088, 1061, 739,553, 536 cm^{-1}.

9. 3,3' - diethyl - 5,5' - diformyl - 4,4' - dimethyl-dipyrromethane(9)

The procedure of Vilsmeier[77] was employed. 2.2 g (9.6×10^{-3} mol) of 3,3' - diethyl - 4,4' - dimethyldipyrromethane (8) was dissolved in 77.5 mls of N,N - dimethylformamide in a 100 mls flask equipped with a magnetic stirrer, condenser and an ice - bath. To the cold stirring solution, phosphorus oxychloride (1.8 mls, 0.0192 mol) was added dropwise using a dropper, at temperatures of 0-5°C. Stirring was conducted for a further 24 hrs., followed by the transference of the reaction mixture to 40 mls of water in a separatory funnel. Extraction of the solution was carried out several times with methylene chloride until an almost colourless organic layer was obtained. To the aqueous layer, 10% NaOH was added dropwise until complete precipitation was accomplished and the mixture was left to stand at room temperature for 24 hrs. the brown crystalline material was separated by filtration and recrystallized twice from 95% ethanol, leaving out the dark brown solid that had settled at the bottom of the beaker. The latter was also collected by filtration, rinsed with water and recrystallized twice from 95% ethanol. The combined yield was 1.1 g (40.2%), melting point = 197 - 199°C.

Analysis:

IR(KBr): 3216, 3119, 3075, 3052, 2982, 2970, 2963, 2932, 2917, 2842, 2830, 1617(s), 1609(s), 1445, 1340, 1308, 1240, 874, 777 cm^{-1}.

Microanalysis:

Cald,;	Found;
C,71.33	C,70.69
H,7.69	H,7.69
N,9.79	N,9.99

B. **Synthesis: Free Ligand And Complexes**

(Bi - dphmd).6H

235.4 mg (0.823 mmol) of 3,3' - diethyl - 5,5'- diformyl - 4,4'- dimethyldipyrromethane was weighed and introduced into a 100 mls flask, containing 70 mls methanol and provided with a magnetic stirrer and condenser. Also added were barium chloride (378.2 mg, 1.548 mmol) and 1,6 - hexamethylenediamine (2 - fold in excess of the dialdehyde). The mixture was then heated under reflux for 12 hrs. An orange solution was obtained whose colour intensified with time. A whitish precipitate started forming after about 3 hrs. of reflux. After the reflux period, the mixture was concentrated under pressure to enhance precipitation and upon cooling, the product was collected by filtration, rinsed with a little methanol and dried. The yield was 264.8 mg (87.9%) and decomposition temperature; 198 - 200°C. The free ligand was also obtainable in the same manner,

using calcium chloride and magnesium sulphate.

Analysis:

IR (KBr): 3391, 3362, 3304, 3244, 2940, 2940 2900, 2840, 2810, 1630, 1430 cm^{-1}.

Mass spec. (m/e): (M+1)733, 484, 366, 322, 239, 217, 161, 149, 135, 122, 108, 94, 56, 41.

UV/VIS (in CH_2Cl_2); 295 nm (ϵ, 2.2692 X $104M^{-1}$)

Microanalysis:

Compd.;	(bi-dphmd). $6H.2H_2O$
Calcd.;	Found;
C,71.88	C,71.05
H,9.37	H,9.39
N,14.58	N,13.10

$Zn(II)_2$(bi - dphmd)Cl_2

In a flask equipped with a magnetic stirrer and a condenser, 249.0 mg(0.87 mmol) of 3,3' - diethyl - 5,5' - diformyl - 4,4'-dimethyldipyrromethane was dissolved in 80 mls methanol. Zinc chloride (119,6 mg, 0.877 mmol) and 101 mg of 1,6-hexamethylenediamine were added with stirring. Formation of a white precipitate occured instantaneously. The mixture was refluxed overnight with stirring. The mixture turned brown, its

colour intensifying with heat and after 5 hrs. of reflux a brick reddish precipitate appeared that deepened in colour. A pinkish red pure product of yield 167.9 mg (41.5%) was obtained after it was separated by filtration, rinsed with methanol and dried.

Analysis:

IR (KBr); 3200, 2940, 2920, 2850, 1630(s), 1440, 1300, 1120, 1100, 960, 720 cm^{-1}.

Mass spec.(m/e): 856, 430, 341, 239, 225, 213, 122, 108, 94, 68, 41.

UV/VIS (in $CHCl_3$) nm; 310(ϵ, 1.743 X 10^4M^{-1}), 342(ϵ, 2.964 X 10^4M-1), 366(ϵ, 1.898 X 10^4M^{-1}), 550(ϵ, 8.523 X 10^2M-1)

Microanalysis:

Compd.; $Zn(II)_2$(bi - dphmd)$Cl_2.3H_2O$

Calcd.;	Found;
C,56.46	C,54.05
H,6.95	H,5.78
N,11.45	N,9.70

$Cu(II)_2$(bi - dphmd)Cl_2

$Zn(II)_2$(bi-dphmd)Cl_2 (90 mg, 0.0969 mmol) was added to 70 mls methanol, with stirring, in a flask equipped with a magnetic stirrer and a condenser. 53 mg (0.394 mmol, 4 - fold in excess) of copper chloride was also added, resulting in the instantaneous colour change of solution from pink to blue. The mixture was refluxed for 3 hrs., with stirring. After 2 hrs. of reflux all the zinc complex had dissolved forming a dark blue solution and some dark blue precipitate. The solution was then refluxed for another 1 hour and left to cool overnight. The product was collected by filtration, rinsed with methanol and dried. The yield was 68.3 mg (76.2%).

Analysis:

IR (KBr); 3260, 3180, 2930, 2900, 1600, 1360(s), 1260, 1235, 1070 cm^{-1}.

Mass spec. (m/e); 539, 257, 134, 123, 108, 94, 91, 41.

UV/VIS (in CH_2Cl_2) nm; 698(ϵ, 1.1125 X 10^4M^{-1}), 650(ϵ, 1.06 X 10^4M^{-1}), 510(ϵ, 2.587 X 10^3M^{-1}), 314(ϵ, 2.92 X 10^4M^{-1}), 235(ϵ,2.7165 X 10^4M^{-1})

Electronic spectrum in CH_3CN was same as for Cu_2(bi - dphmd)$(ClO_4)_2$

Microanalysis:

Compd.: $Cu(II)_2(bi - dphmd)Cl_2.6H_2O$

Calcd.;	Found;
C,53.48	C,49.48
H,6.98	H,5.80
N,10.80	N,9.68

$Cu(II)_2(bi - dphmd)(ClO_4)_2$

Into a 100 mls flask containing a solution of $Zn_2(bi - dphmd)Cl_2$ (167 mg, 0.18 mmol) in 50 mls methanol and equipped with a magnetic stirrer and a condenser, was added 183.8 mg (0.7 mmol) (4 - fold excess) of copper perchlorate. Instantly, a blue solution was formed. The mixture was refluxed, with stirring for 2 hrs., during which precipitation of blue solid material results. After 1 hr. of reflux, lithium perchlorate was added. The product was collected by filtration, rinsed with methanol and dried. The yield was 129.5 mg (71%).

Analysis:

IR (KBr) : 3400(b), 2920, 2890, 2850, 1550, 1410, 1260, 1210, 1080, 1040, 980, 890 cm^{-1}.

UV/VIS (in CH_3CN); 682(ϵ, 1.649 X 10^4M^{-1}), 630(ϵ, 1.266 X 10^4M^{-1}), 314(ϵ, 3.887 X 10^4M^{-1}), 238(ϵ, 2.886 X 10^4M^{-1}), 490 nm.

$Cu(II)_2$(bi - dphmd)$(ClO_4)_2$ From The Free Ligand.

33.1 mg (0.0452 mmol) of free ligand was added to approximately 50 mls of methanol in a 100 mls round bottom flask equipped with a condenser and a magnetic stirrer. 32.6 mg (0.124 mmol) of copper perchlorate (in excess of 2 equivalents of free ligand) was added to the suspension, causing the formation of a deep blue solution. The mixture was heated under reflux for 2 hrs., at the end of which a blue precipitate was separated by filtration and rinsed with methanol and dried. The yield was 15.9 mg (12.28%).

Analysis:

IR (KBr) ;3400(b), 2920, 2890, 2850, 1550, 1410, 1260, 1210, 1080, 1040, 980, 890 cm^{-1}.

UV/VIS (in CH_3CN); 682, 630, 490, 314, 238 nm

$Cu(II)_2$(bi - dphmd)$(N_3)_2$

A solution of 50 mg (0.0474 mmol) of $Cu(II)_2$(bi - dphmd)$(ClO_4)_2$ in 50 mls acetonitrile was prepared in flask, provided with a magnetic stirrer and a condenser. A solution containing 6.5 mg (ca. 2 - fold excess) of sodium azide in 20 mls methanol was introduced and the mixture refluxed for 2 hrs. The solution remains dark blue with the formation of a blue precipitate which was filtered off, rinsed with methanol and dried, after the

concentration of the solution and cooling. The yield was 29.1 mg (65%).

Analysis:

IR (KBr) ;3400, 3370(sh), 2920, 2880, 2080(s), 2010(s), 1210, 1110, 1080, 890, 630 cm^{-1}.

UV/VIS (in CH_2Cl_2); nm 670(ϵ, 1.095 X 10^4M^{-1}), 626(ϵ, 1.374 X 10^4 M^{-1}), 314(ϵ, 2.926 X 10^4M^{-1}), 242(ϵ, 2.568 X 10^4M^{-1}), 490

$Co(II)_2$(bi-dphmd)Cl_2

A suspension of 83.9 mg (0.1146 mmol) free ligand in approximately 70 mls methanol, in a 3-neck 100 mls flask, that was provided with a magnetic stirrer, a condenser and a nitrogen inlet, was bubbled with nitrogen, thoroughly, for effective deaeration.72 mg (0.303 M) of cobaltous chloride (two-fold in excess of free ligand) was added, with stirring, and colour development of the mixture, towards green, occured. The mixture was refluxed for 5 hrs., with nitrogen supply maintained. A bluish precipitate was formed, which was collected by filtration and rinsed with methanol, under nitrogen to obtain pure product of yield; 86.6 mg (82.4%). The filtrate obtained turned purple instantaneously.

Analysis:

IR (KBr) ; 3448, 3210, 2930, 1655(s), 1560, 1458, 1400, 1312, 1128, 980 cm^{-1}.

UV/VIS (in CH_3OH); 670 (ϵ, 6.152 X 10^3M^{-1}), 570(ϵ, 8.202 x 10^3M^{-1}), 350(ϵ, 2.409 X 10^4M^{-1}), 302(ϵ, 4.358 X 10^4M^{-1}) nm.

c. **Magnetic Susceptibility Measurement for $Co(II)_2(bi - dphmd)Cl_2$**

The method of Irina[96], was employed. Initially, the weights of the standard and the sample were taken. A plastic plate was placed on the cradles, above and close to the magnet that was on the balance pan, to act as a support for samples under study. The weight of the magnet was first zeroed and then taken with:

(a). empty cuvette on the plate.

(b). standard on the plate.

(c). sample on the plate.

The measurements obtained were as follows:

ΔW_e = 0.0000 g; $\Delta W_{ref.}$ = - 0.0101g; ΔW_s = -0.0028 g;

$W_{ref.}$ = 0.2318 g; W_s = 0.0782 g, where:

ΔW_e: change in weight of the magnet with empty cuvette on the plate.

ΔW_{ref}: change in weight of the magnet with the standard on the plate

ΔW_s: change in weight of the magnetic with the sample on the plate.

W_s: weight of the sample.

W_{ref}: weight of the standard.

The standard used was $Hg(Co(CNS)_4)$

D. **Reaction of Co_2(bi - dphmd)Cl_2**

(a) **Oxygenation of Co_2(bi - dphmd)Cl_2**

(i) **Stock solution:**

A solution of concentration 2.84×10^{-5}M was prepared. 1.3 mg of the dicobalt(II) complex was placed in 50 mls volumetric flask. A little amount methanol was added to it to allow effective shaking. The complex showed low solubility, accompanied by slow colour change towards blue. After the dissolution of all the complex, more methanol was added upto the 50 mls mark and the solution shaken again.

(ii) **Reaction:**

The stock solution was diluted by factor 2, by taking equal amounts of stock solution and methanol in a test-tube, using a pipette. The solution was then put in a cuvette, filling it partially so as to allow some aeration, and its electronic spectrum run at 15 mins. intervals, in the presence of oxygen.

During the intervals, the cuvette was opened occasionally to effect some aeration. The spectrum displayed changes in intensities throughout the entire range. The intensities in the regions; 665 nm, 570 nm and 620 nm increased whereas those at 345 nm and 300 nm decreased, with time. After two days, the spectrum was run again at intervals of 30 mins. and there were no variations of intensities.

(b). **Effect of Solvent on Oxygenation Rate.**

(i). **Rate in Methanol:**

A stock solution of the dicobalt(II) complex of concentration 2.818×10^{-5}M, was prepared by dissolving 1.0 mg of the complex in 50 mls of methanol in a volumetric flask as described earlier. Two - fold dilution of the stock solution was made and the electronic spectrum of the resulting solution run at 15 mins. intervals in the presence of oxygen. Sufficient aeration was ensured. The absorbance readings at 302 nm were recorded as shown in table 5.

Time (mins.)	Absorbance
0	0.500
15	0.497
30	0.493
45	0.490
60	0.486
75	0.485
90	0.482
105	0.480
120	0.478

Table 5

(ii). **Rate in Dimethylformamide:**

A 1.96 X 10^{-5}M complex solution (0.9 mg complex) in dimethylformamide (50 mls) was prepared in 50 mls. volumetric flask. The complex shows a high solubility, forming a deep blue solution. The electronic spectrum for this solution was run, in presence of oxygen and the absorbance readings at 300 nm taken, at 15 mins. intervals as in table 6.

Time (mins.)	Absorbance
0	0.673
15	0.649
30	0.635
45	0.626
60	0.620
75	0.615
90	0.612
105	0.609
120	0.607

Table 6

(iii) **Rate in Acetonitrile:**

0.4 mg of the dicobalt (II) complex was dissolved in 25 mls acetonitrile, in a volumetric flask to form a 1.745×10^{-5}M solution. A high solubility was observed with the formation of a blue solution. Its electronic spectrum was run, in presence of oxygen, with the absorbance readings at 328 nm recorded, at 15 mins. intervals. The results were as in table 7.

Time (mins.)	Absorbance
0	0.595
15	0.655
30	0.670
45	0.690
60	0.705
75	0.715
90	0.722
105	0.730
120	0.738

Table 7

(c). Oxygen Uptake:

Methanol (ca. 5 mls) was placed in a 10 mls flask that was equipped with a magnetic stirrer and a mercury manometer. Positive oxygen pressure was applied, with the stirrer on. The pressure was monitored, through the manometer, and recorded at 10 mins. intervals. No significant change was registered. A small amount of the dicobalt(II) complex (0.4 mg or less) was introduced in the flask and the above procedure repeated, whereupon there was a markable change in pressure in the initial 10 minutes, as in table 14.

Time (mins.)	Upper Reading	Lower Reading	Pressure (cm)
0	74.0	5.5	68.5
10	71.8	7.7	64.1
20	71.6	7.8	63.8
30	71.5	7.9	63.6
40	71.5	7.9	63.6
50	71.4	8.0	63.4

Table 14

(d). **Reaction of Co_2(bi - dphmd)Cl_2 Complex with 2,6 - Diisopropylphenol (2,6 - DIPP) in the Presence of Oxygen**

2,6 - DIPP was purified by silica gel column chromatrography using Pet - Ether (40 - 60°) as the solvent. To a 100 mls flask, equipped with a magnetic stirrer, was a placed a methanol solution (25 mls) of 2,6 - DIPP (0.216M). 25 mls of Co_2(bi - dphmd)Cl_2 (5.68 x 10^{-5}M) was added, with stirring and instantaneously the mixture turned greenish - brown. Stirring was continued for 12 hrs. Some solid particles started forming after about 2 hours. The solid material was separated by decantation, then the reaction mixture

as passed through a silica gel column for separation, using pet - ether (40 - 60°)/dichloromethane (2:1) as the solvent system. A road yellow band (R.f. = 0.77) and a red narrow band (R.f. = 0.28) ere separated out. The complex remained at the top of the column. he products were identified by electronic spectroscopy whereby he crystals and the yellow product were found to be the same and re characterised by a band at 420 nm. For the red product; there as a broad band in the region of 500 nm.

(ii) **Control reaction:**

A solution (2.1 X 10^{-3}M) of cobaltous chloride (0.5 mg in 25 mls methanol) was prepared in a volumetric flask by thorough shaking. Equal volumes (1.3 mls each) of substrate (1.078 X 10^{-2} M) and the cobalt salt solution were mixed in a cell. The electronic spectrum was run at 15 mins. intervals and the 420 nm absorbance monitored. An almost constant absorbance was observed.

(a) **Concentration Effect On the Rate of Reaction Between Co_2(bi - dphmd)Cl_2 and 2,6 - DIPP, in Presence of Oxygen**

(i) **Substrate Stock Solution:**

A solution of concentration 2.156 X 10^{-2}M was prepared. 0.1 mls of substrate (density = 0.96 gml^{-1}) was measured in a pipette and introduced into a 50 mls volumetric flask. Methanol as added to make a 50 mls solution which was then shaken.

(ii) **Complex Stock Solution:**

A 2.84 X 10^{-5}M solution was prepared. 1.3 mg of the dicobalt(II) complex was dissolved in methanol and its 50 mls solution made, in a volumetric flask.

(iii) **Rate Studies:**

The concentrations of the stock solutions were varied and rates studied each time. The combinations taken were:

(a) both stock solutions diluted two fold.

(b) 4 - fold diluted substrate stock solution with 2 - fold diluted complex stock solution.

(c) 4 - fold diluted substrate stock solution with undiluted complex solution.

(d) 2 - fold diluted substrate stock solution with undiluted complex stock solution.

The reactions were conducted in a cuvette. For each combination, equal amounts of substrate and complex solutions (1.3 mls) were put in the cell, effectively diluting each solution concentration by factor 2, and the absorbance reading at 420 nm recorded at 30 mins intervals. Tables 8 - 11 show the results.

Time(mins.)	Absorbance	Change in Absorbance
0	0.108	0.000
30	0.147	0.039
60	0.176	0.068
90	0.196	0.088
120	0.220	0.112
150	0.244	0.136
180	0.269	0.161
210	0.291	0.183

substrate concentration in the cell [S] = 5.39 X 10^{-3}M

complex concentration in the cell , [C]= 7.1 X 10^{-6}M

Table 8

Time(mins.)	Absorbance	Change in Absorbance
0	0.073	0.000
30	0.098	0.025
60	0.105	0.032
90	0.111	0.038
120	0.119	0.046
150	0.127	0.054
180	0.131	0.058
210	0.136	0.063
240	0.139	0.066
270	0.141	0.068
300	0.144	0.071

[S] = 2.695 X10^{-3}M, [C] = 7.1 X 10^{-6}M

Table 9

Time(mins.)	Absorbance	Change in Absorbance
0	0.110	0.000
30	0.152	0.042
60	0.178	0.068
90	0.204	0.094
120	0.229	0.119
150	0.248	0.138
180	0.259	0.149
210	0.262	0.152
240	0.262	0.152
270	0.259	0.149
300	0.259	0.149

[S] = 2.695 X 10^{-3}M, [C] = 1.42 X 10^{-5}M

Table 10

Time(mins.)	Absorbance	Change in Absorbance
0	0.129	0.000
30	0.257	0.128
60	0.347	0.218
90	0.428	0.299
120	0.493	0.364
150	0.545	0.416
180	0.587	0.458
210	0.614	0.485

[S] = 5.39 X 10^{-3}M, [C] = 1.42 X 10^{-5}M

Table 11

(f) Role of Oxygen in the Reaction:

1.3 mls of 1.42 X 10^{-5}M complex solution was placed in a vial and deaerated by bubbling nitrogen through it. After 10 minutes of deaeration the vial was immediately sealed with a rubber septum and with the aid of a syringe, 1.3 mls of substrate solution (1.078 X 10^{-2}M) was injected. The 420 nm peak absorbances were taken at 30 mins intervals. During each interval, the reaction mixture was deaerated. After 1½ hrs., aeration was done for 1½hrs., then followed by deaeration. Table 12 potrays the behaviour.

Time(mins.)	Absorbance	Change in Absorbance
0	0.078	0.000
30	0.108	0.030
60	0.109	0.031
90	0.112	0.034
120	0.132	0.054
150	0.137	0.059
180	0.150	0.072
210	0.156	0.078
240	0.163	0.085
270	0.170	0.092
300	0.177	0.099

[S] = 5.39 X 10^{-3}M, [C] = 7.1 X 10^{-6}M

Table 12

(g) **Effect of Pyridine**

(i) **Stock solution:**

A stock solution of pyridine of 0.1M concentration was prepared by placing 0.2 mls pyridine (density = 0.9 gml^{-1}) in a 25 mls solution and shaking done.

(ii) **Reaction:**

A pyridine solution of 0.002M concentration was made by taking 10 mls of the stock solution and diluting to 50 mls with methanol.

The separate electronic spectra of the pyridine and dicobalt(III) complex (1.42 X 10^{-5}M) solutions were taken. A drop of pyridine solution was introduced to the complex solution in the cell and mixed, by shaking. The spectrum of the mixture was run at ½ hour intervals, for 2 hrs., and it registered no changes in the intensities in the spectrum. A suitable amount of substrate solution (1.078 X 10^{-2}M) was added and the spectrum monitored for 1 hour at ½ hour intervals. There was the usual growth of the intensity at 420 nm and no effect on the pyridine peaks was observed.

(i) **Effect of Pyridine on Proceeding Reaction**

Substrate (1.078 X 10^{-2}M) and 1.42 X 10^{-5}M complex solutions were mixed in the cell in the ratio of 1:1 by volume and the electronic spectrum run at ½ hr. intervals for 1½ hrs. A drop of pyridine solution (2 X 10^{-2}M) was added and monitoring of the spectrum continued. No effect on the reaction was observed and the 420 nm peak intensity grew as usual.

E. Comparison of Catalytic Activities Between Co_2(bi - dphmd)Cl_2 and Co_2(bi - dptmd)Cl_2 on Oxidation of 2,6-DIPP

A stock solution of $Co(III)_2$(bi - dptmd)Cl_2 of concentration 3.61×10^{-5}M (1.5 mg complex in 50 mls methanol) was prepared, in a volumetric flask. It was diluted by factor 2 and 1.3 mls placed in a cell. An equal volume of substrate solution (5.39×10^{-3}M) was added and the 420 nm absorbance monitored. The results (table 13) were compared to those in table 9.

Time(mins.)	Absorbance	Change in Absorbance
0	0.082	0.000
30	0.105	0.023
60	0.109	0.027
90	0.111	0.029
120	0.113	0.031
150	0.115	0.033
180	0.117	0.035
210	0.119	0.037
240	0.121	0.039
270	0.124	0.042

[S] = 2.695×10^{-3}M, [C] = 9.025×10^{-6}M

Table 13

F. Reaction of Cu_2(bi - dphmd)Cl_2 With 2,6 - DIPP in Presence of Oxygen

A 1.138 X 10^{-5}M solution of Cu_2(bi - dphmd)Cl_2 (0.3 mg) in 25 mls of methanol was prepared, by thorough shaking, in a volumetric flask. Equal volumes (1.3 mls each) of the complex and the substrate (1.078 X 10^{-2}M) solutions were mixed in a cell and the electronic spectrum of the mixture was run in presence of oxygen at 15 mins. intervals for 1¼ hrs, during which changes in intensities in the different regions of the spectrum were exhibited. At 686, 630 and 310 nm positions, the intensities decreased whereas at 370 nm, it increased. There was no peak growth at 420 nm.

conclusions:

The synthesis of the free ligand and complexes that incorporate Zn^{2+}, Cu^{2+}, and Co^{2+} as metal ions and Cl^-, ClO_4^-, N_3^- as anions has been achieved although the employment of X - ray crystallographic studies which could have lent more support to the structural elucidation was not attempted because of lack of X-ray facilities.

The dicobalt(II) complex reacted with O_2 in solution in a generally less rapid manner than the analogous Co_2(bi-dptmd)Cl_2. Conversely, the order reversed in their catalytic activities. More elaborate techniques would be of help in the kinetic studies for the oxidation of 2,6 - DIPP. Preliminary studies of Cu_2(bi - dphmd)Cl_2 indicated catalytic activity and further work on the dicopper complexes is necessary.

Other investigations that need to be undertaken for this system (n=6) are EPR and electrochemical studies. The former would provide information on magnetic properties whereas the latter would do the same on redox properties of the system and the potentials at which the system is reduced or oxidized.

The system for which n=4 has been focussed on, at a preliminary level. In fact the electrochemistry of some of its complexes has shown interesting behaviour. Further work employing this system is in progress.

The study of these systems holds a lot in terms of activity and industrial catalysts.

Appendix I

The measurement of magnetic susceptibility for Co_2(bi - dphmd)Cl_2 was perfomed by using $Hg(Co(NCS)_4)$ as the standard, for which $X_g = 10.44X10^{-6}$ egs at 20°C. Computation of the magnetic susceptibility was done using the following formula.

$$X_s(g) = \frac{\Delta W_s - \Delta W_e}{W_s} X \frac{W_{ref}}{\Delta W_{ref} - \Delta W_e} X \; X_{ref}(g)$$

where X_s (g) = gram susceptibility of the sample

ΔW_s = change in weight of the magnet with the sample above it.

ΔW_e = change in weight of the magnet with empty container above it.

ΔW_{ref} = change in weight of the magnet with the standard above it.

W_s = weight of the sample.

W_{ref} = weight of the standard.

$X_{ref}(g)$ = gram susceptibility of the standard.

The obtained X_s (g) was converted to molar susceptibility ($X_s(M)$) by multiplication with the molecular weight of the sample (complex). The $X_s(M)$ was corrected for diamagnetism by the addition of the diamagnetic corrections values of the Pascal's constants tables, upon which the effective magnetic moment per cobalt atom (μ_{eff}/Co) was calculated by the application of the following expression.

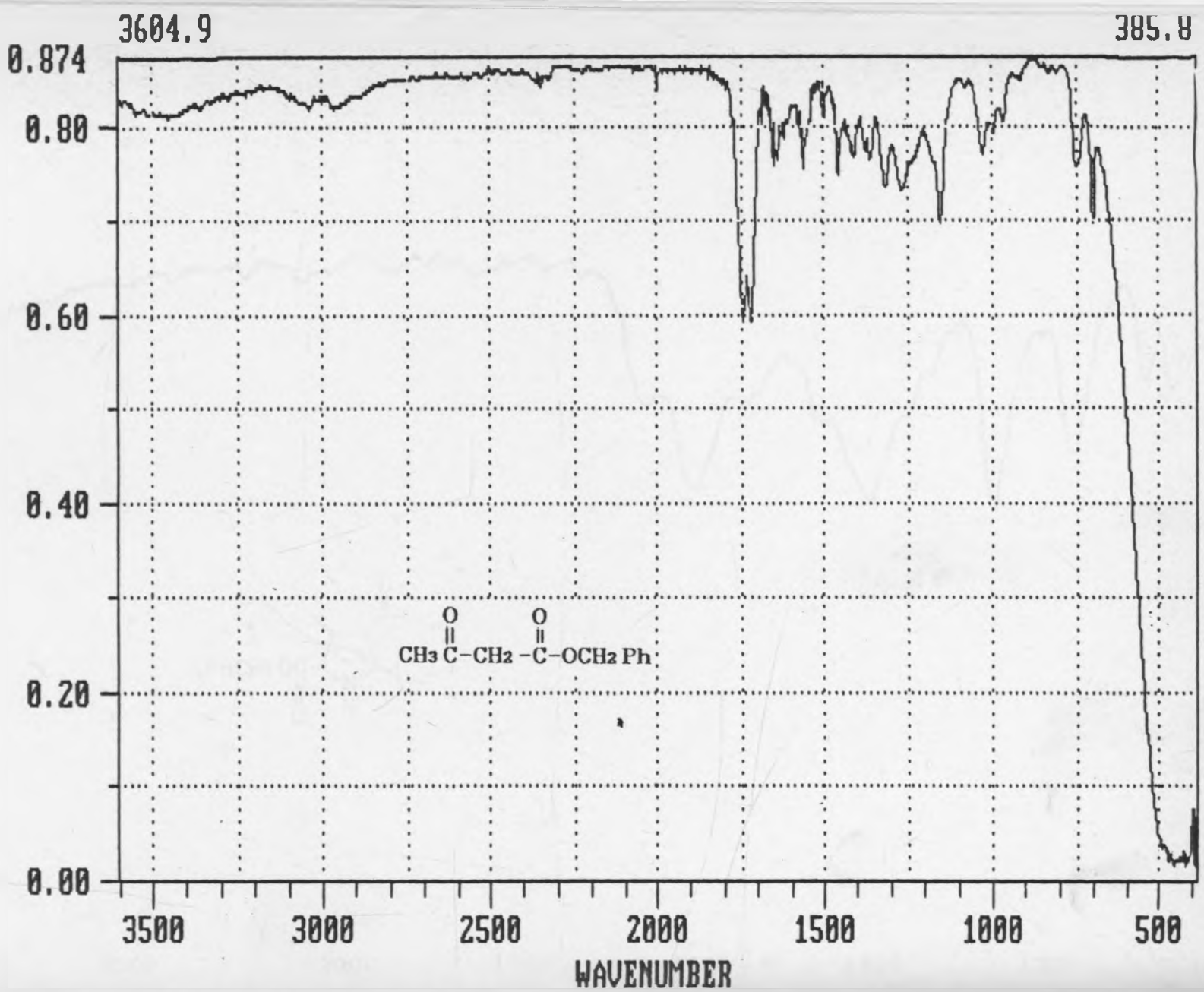
$$\mu_{eff}/Co = \sqrt{(\mu_{calc.})^2/_2}$$

where $\mu_{calc.} = 2.83\ X_s(M)\ X\ T$

$T = {}^{o}K$

$X_s(M)$ = molar susceptibility for sample.

Appendix II. Infrared Spectra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385.8
0.874
0.80
0.60
0.40
0.20
0.00
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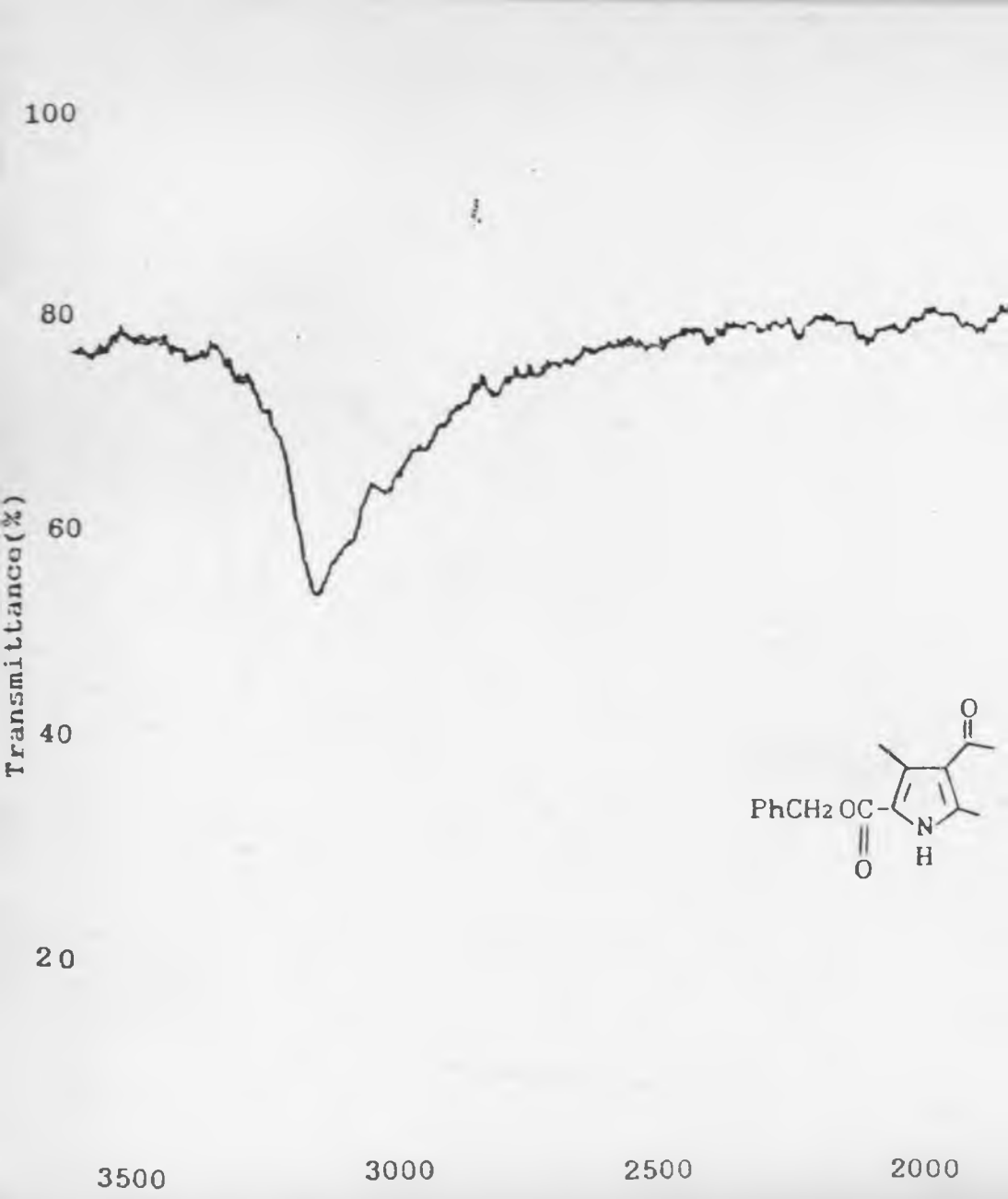
3000
2500
2000
1500
1000
500
WAVENUMBER
O
O
CH3 C–CH2 –C–OCH2 Ph


100
80
60
40
20
Transmittance(%)
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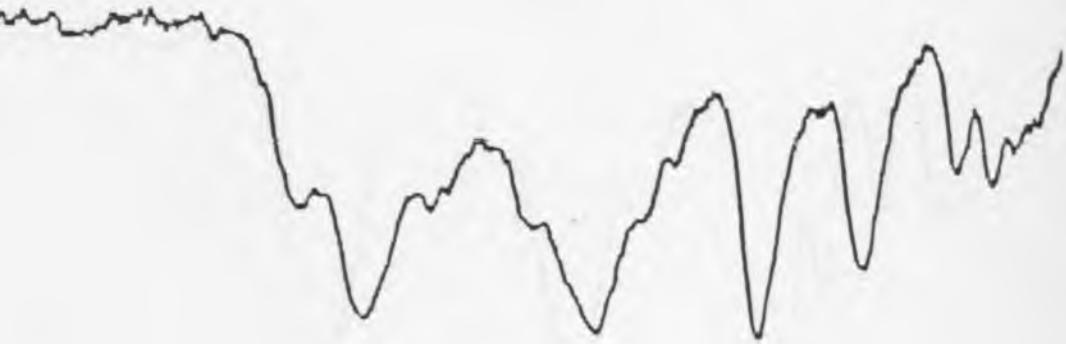
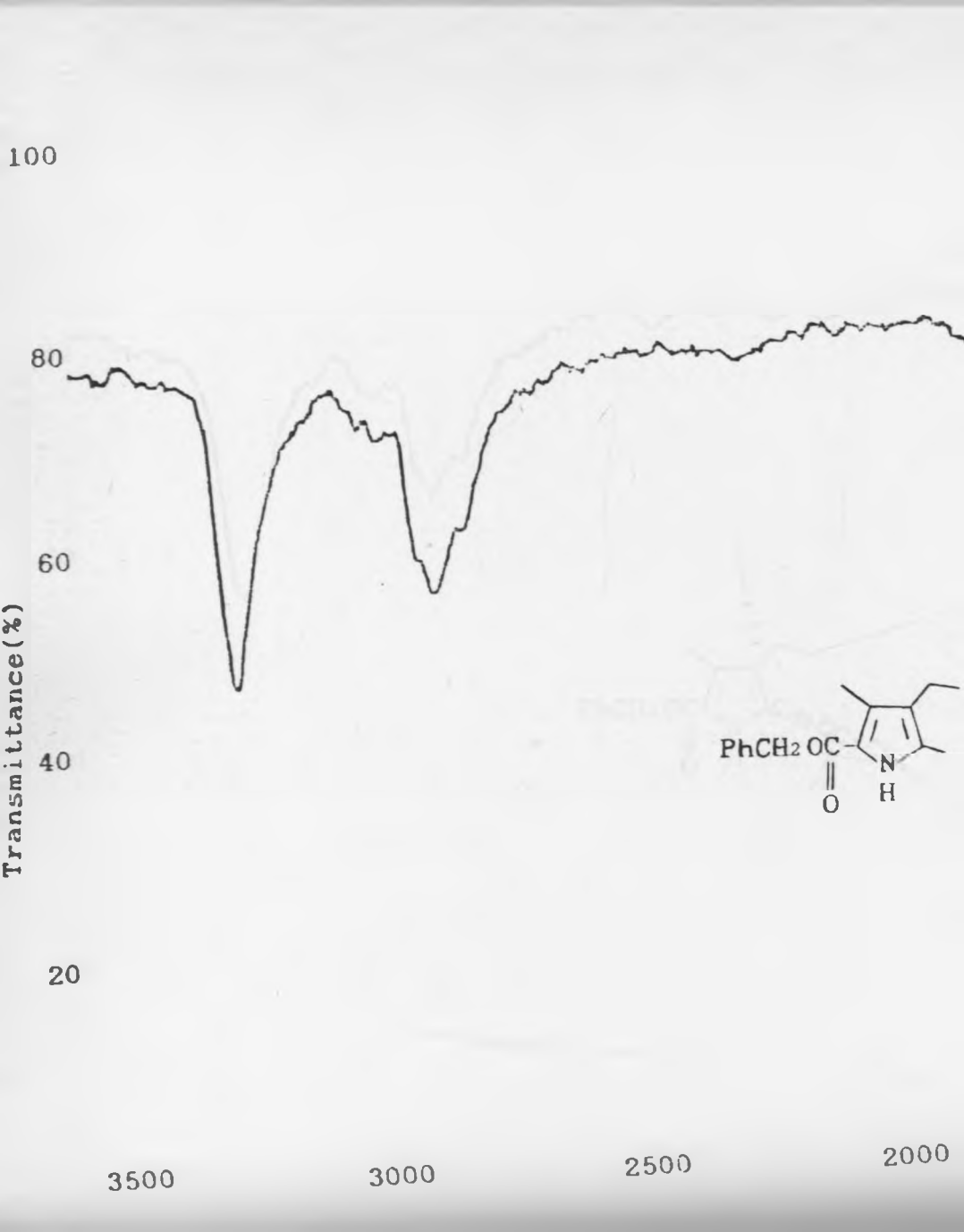
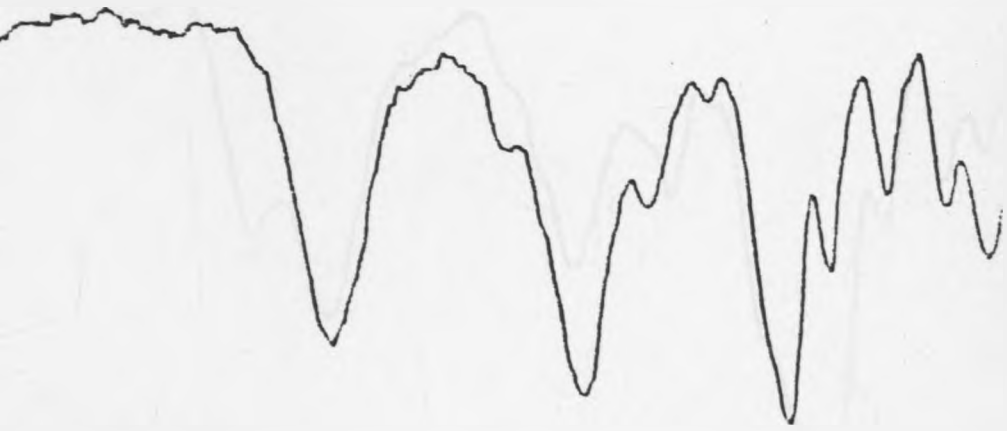
3000
2500
2000
PhCH2 OC-
O
N
H
O
O



114

1800 1600 1400 1200 cm-1 10


100
80
60
40
20
Transmittance(%)
3500
3000
2500
2000
PhCH2 OC
O
N
H



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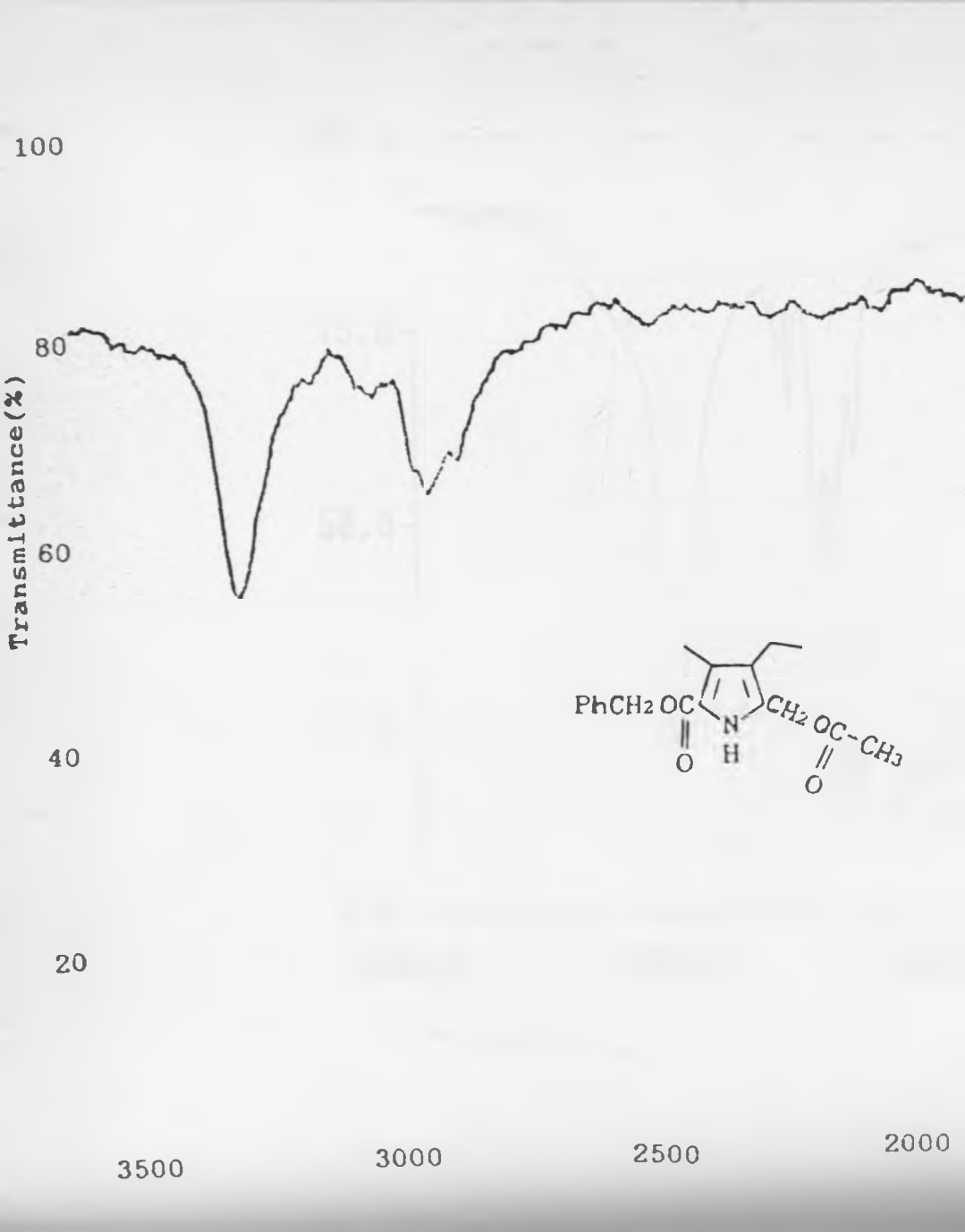
1800 1600 1400 1200 cm-1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80
60
40
20
Transmittance(%)
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3000
2500
2000
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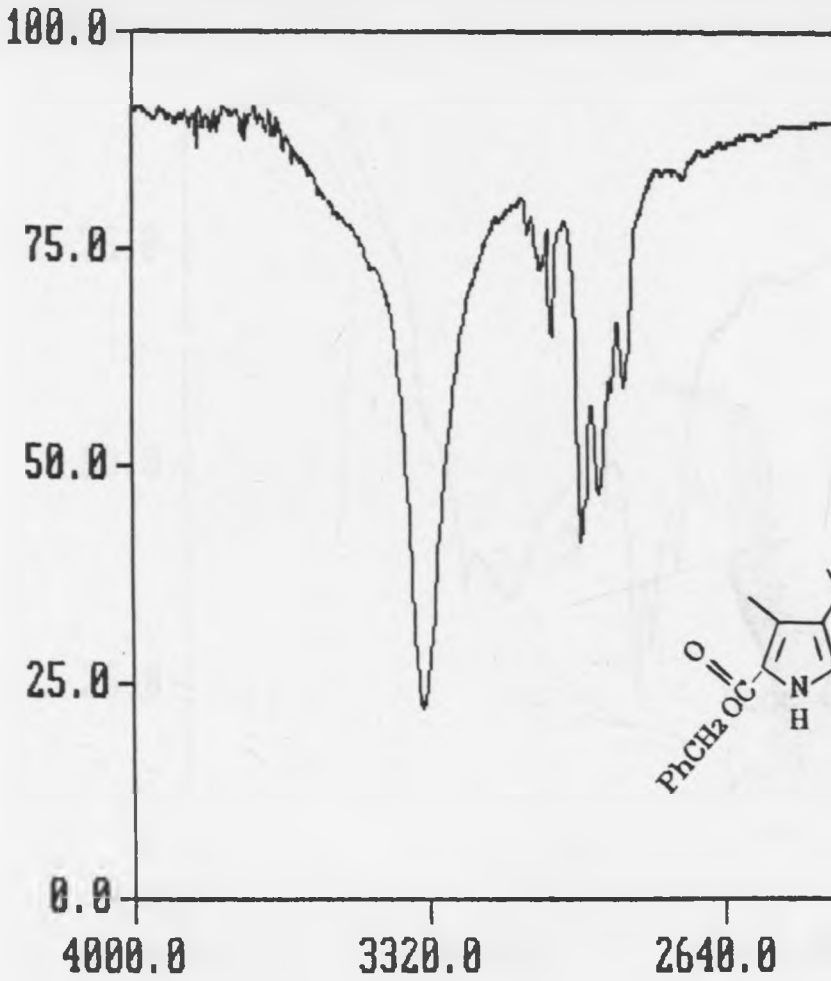
CH2 OC-CH3
N
H
O
O
O

116

1800 1600 1400 1200 cm^{-1} 10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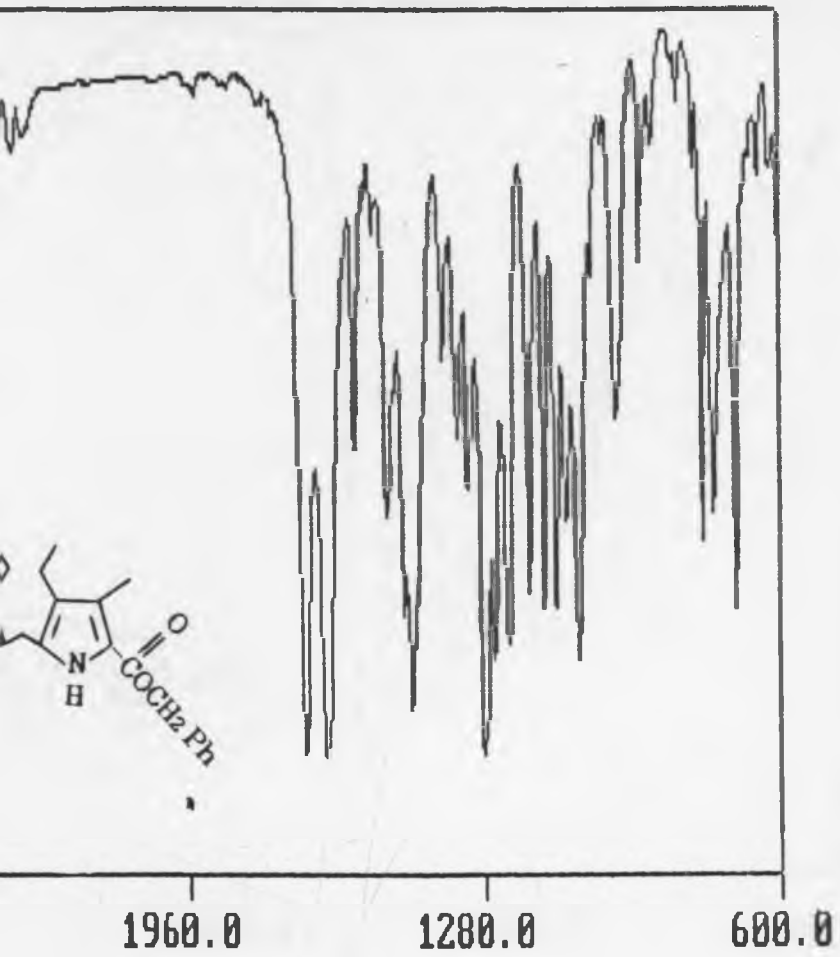
PhCH2 OC
N
H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COCH2 Ph
N
H
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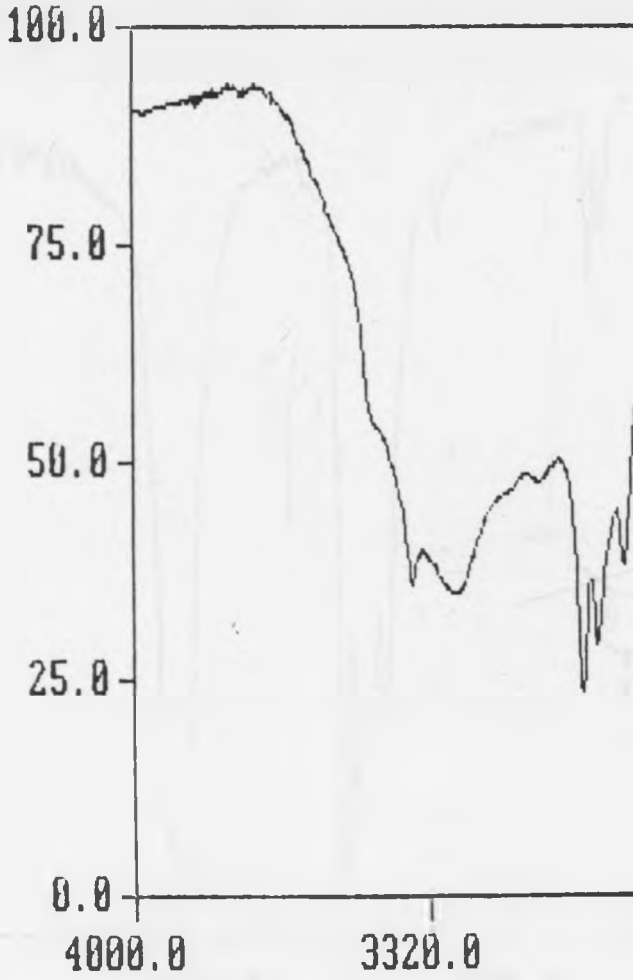
1280.0
600.0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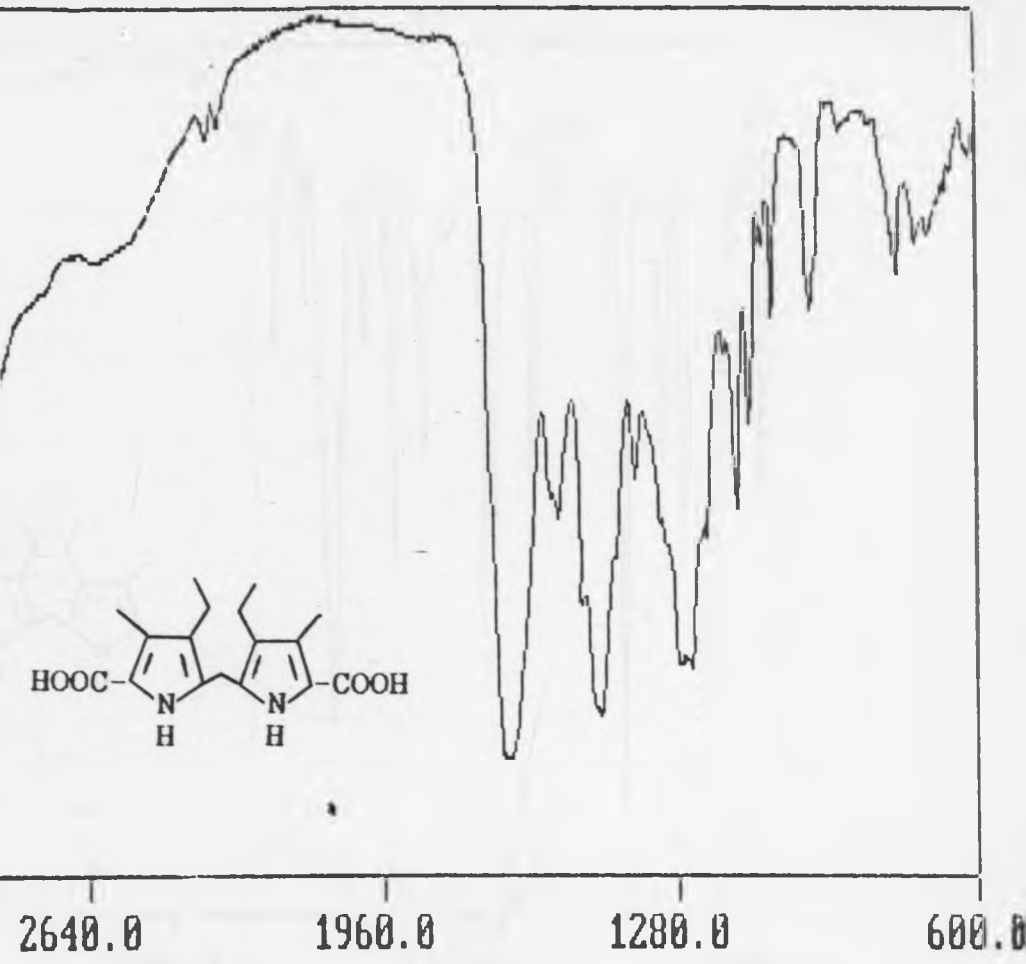
50.0
25.0
0.0
4000.0
3320.0


HOOC-
N
H
N
H
-COOH
2640.0
1960.0
1280.0
600.0

100.0
75.0
50.0
25.0
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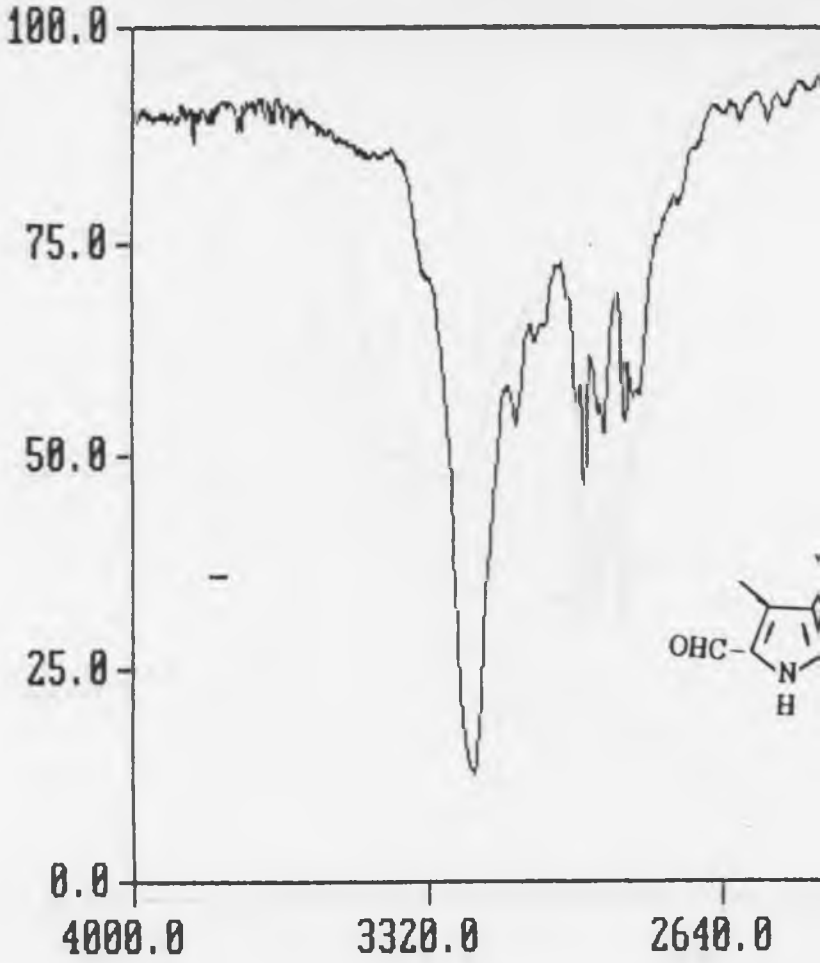
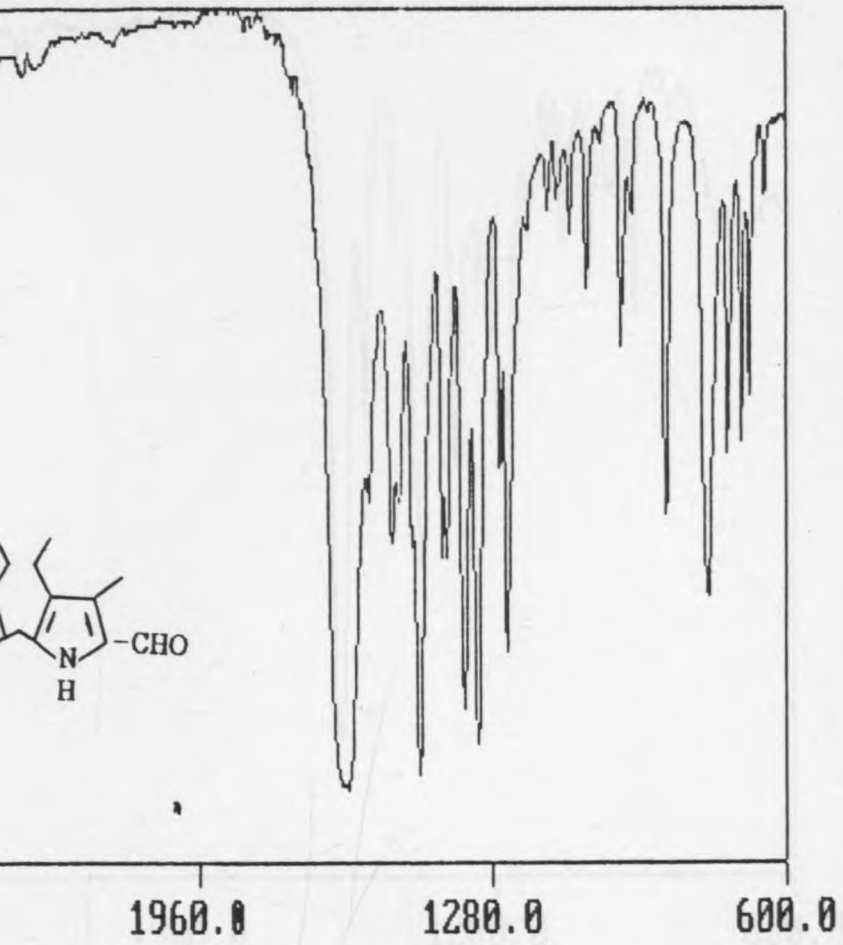
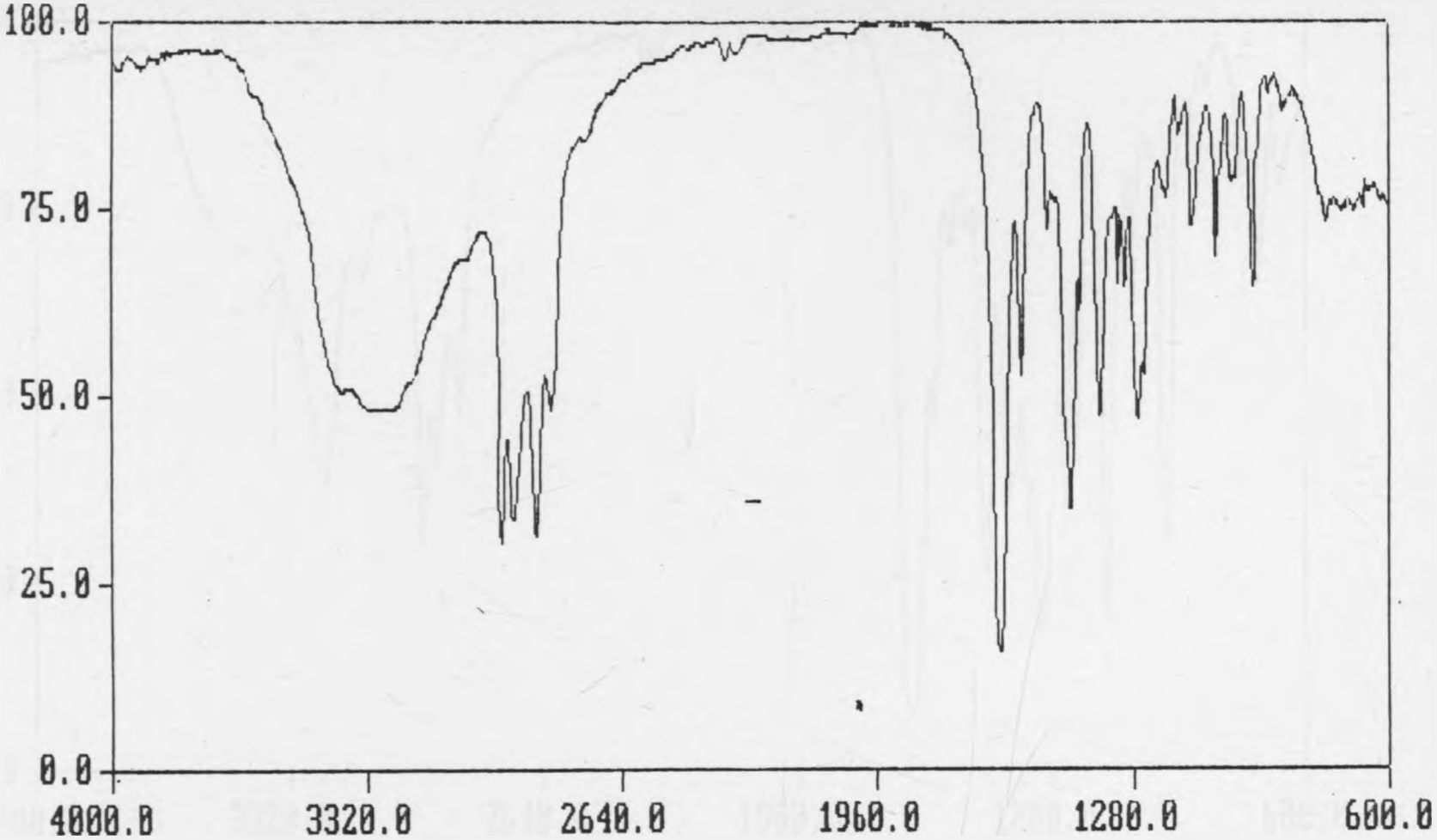
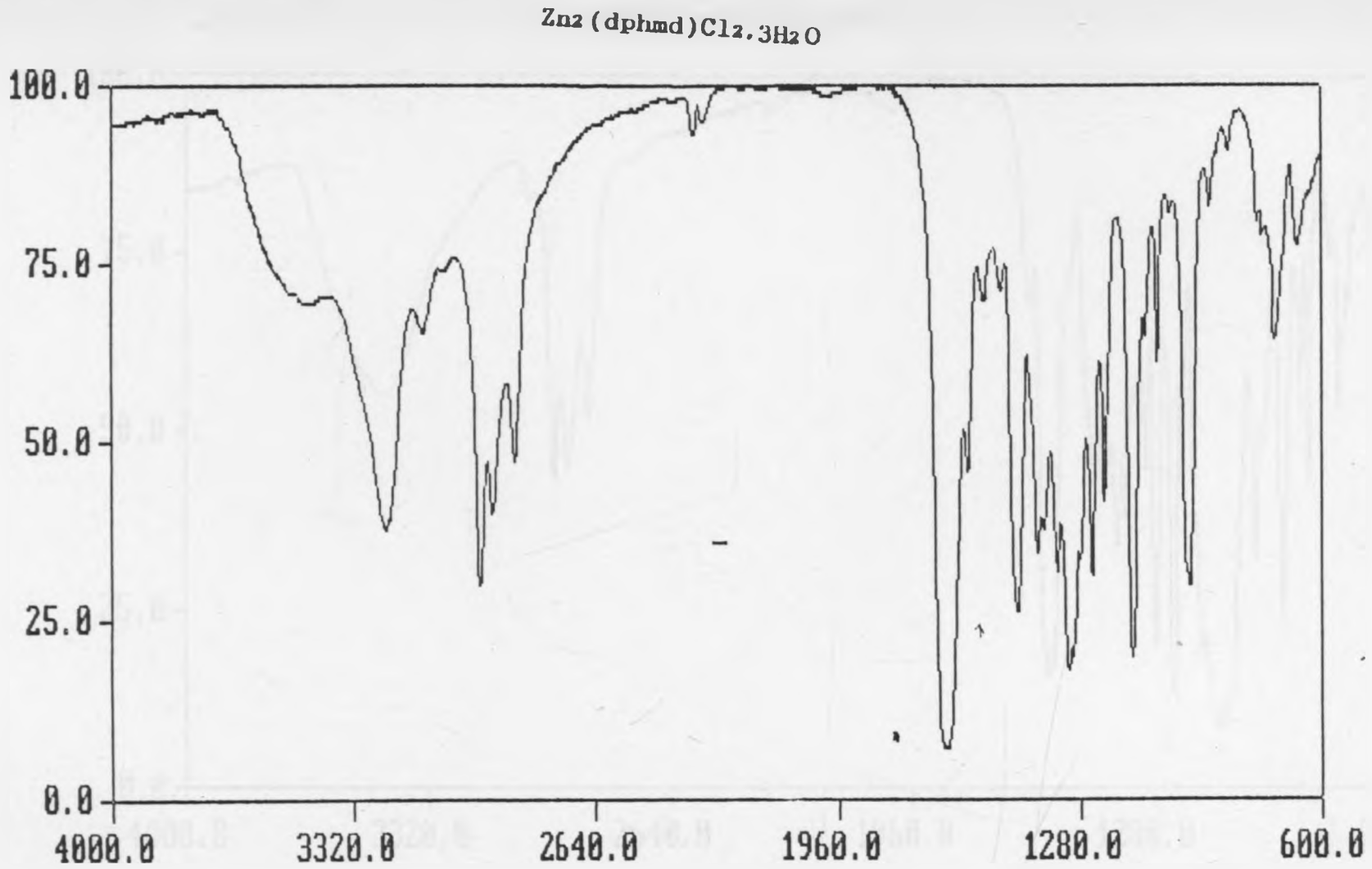
H
N
H
N





(Bi-dphmd).6H.2H$_2$O




Zn2 (dphmd)Cl2.3H2O
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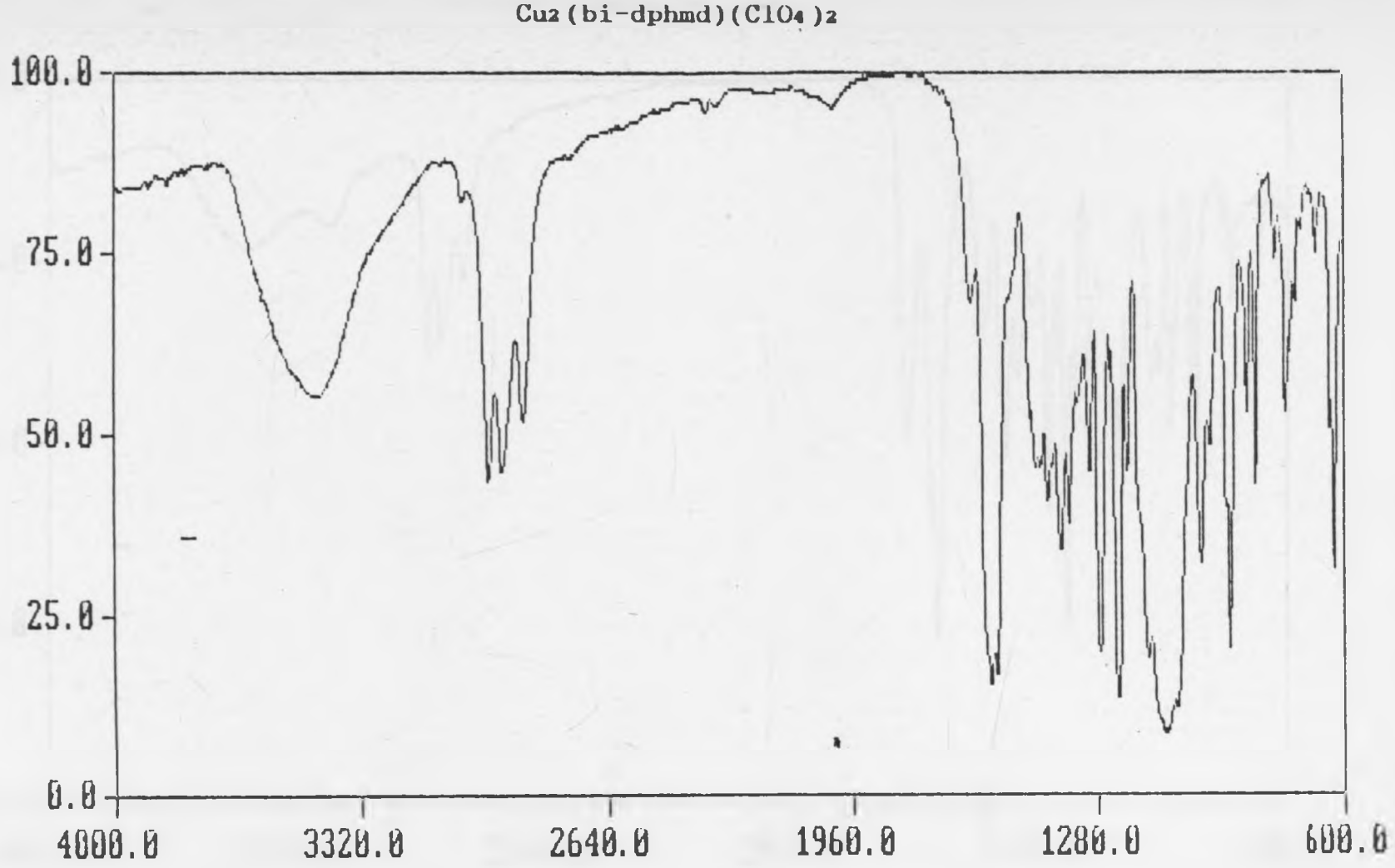
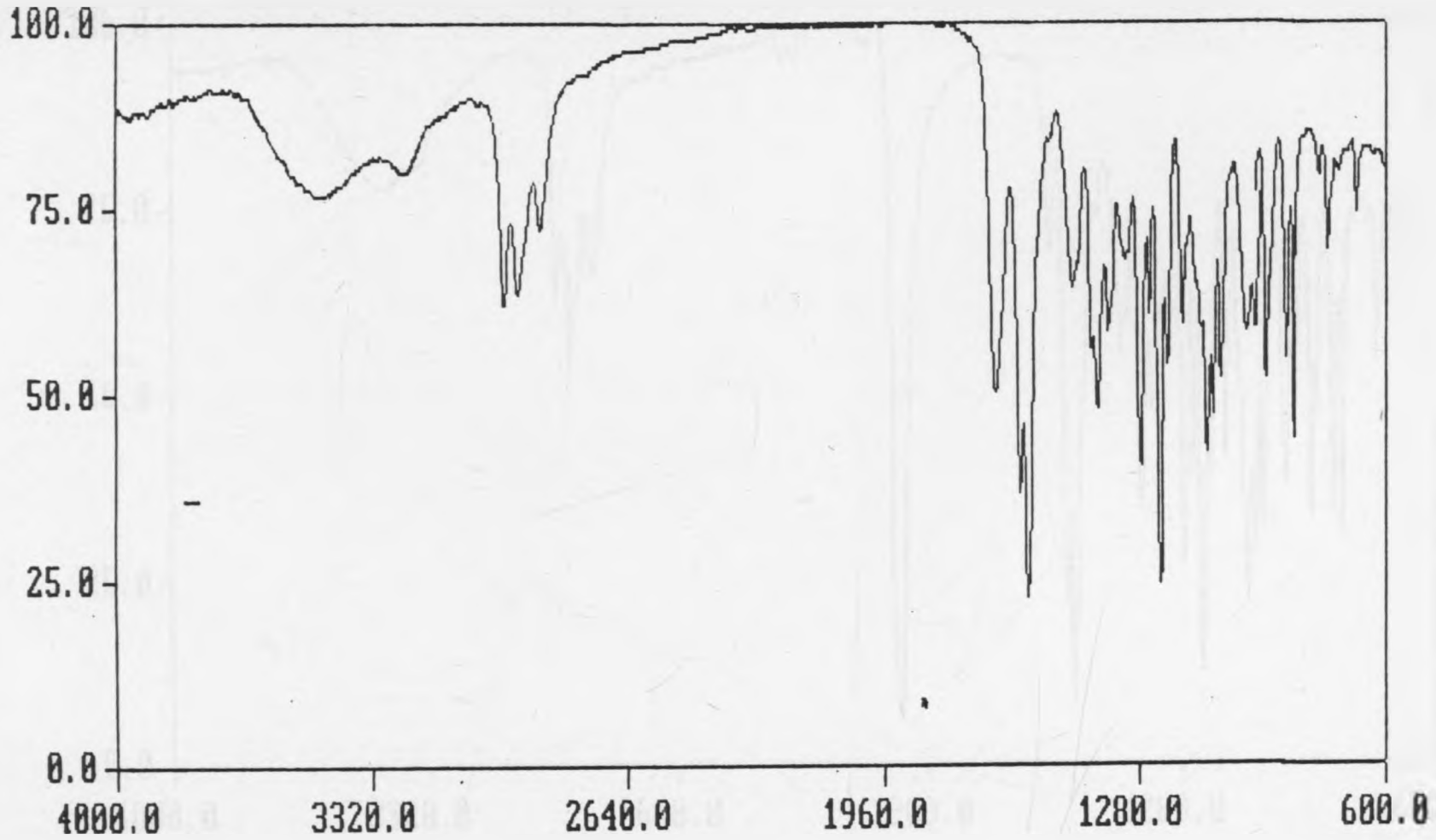
50.0
25.0
0.0
4000.0
3320.0
2640.0
1960.0
1280.0
600.0

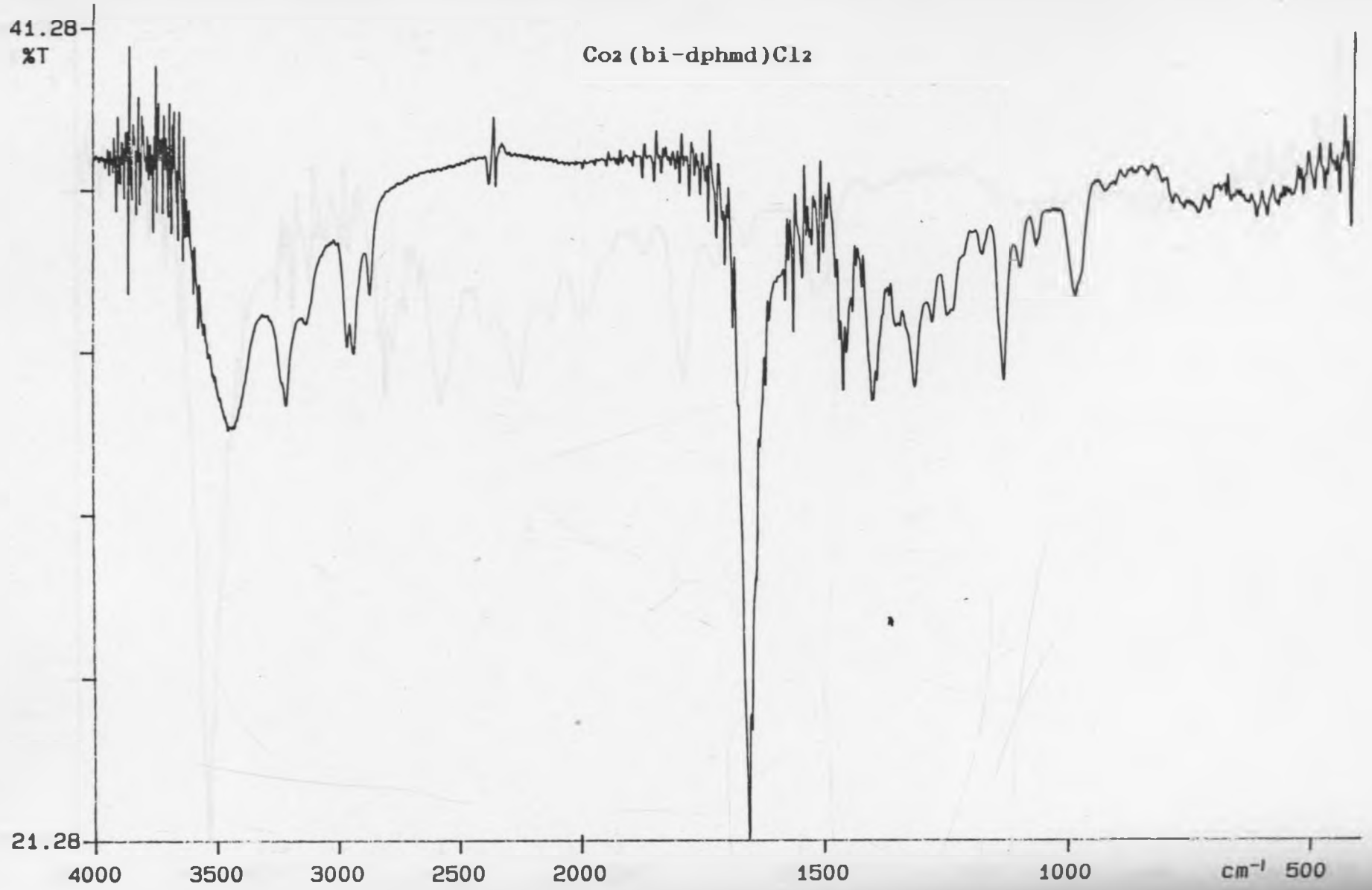

Cu2(bi-dphmd)(ClO4)2
100.0
75.0
50.0
25.0
0.0
4000.0
3320.0
2640.0
1960.0
1280.0
600.0

$Cu_2(bi\text{-}dphmd)(Cl)_2.6H_2O$

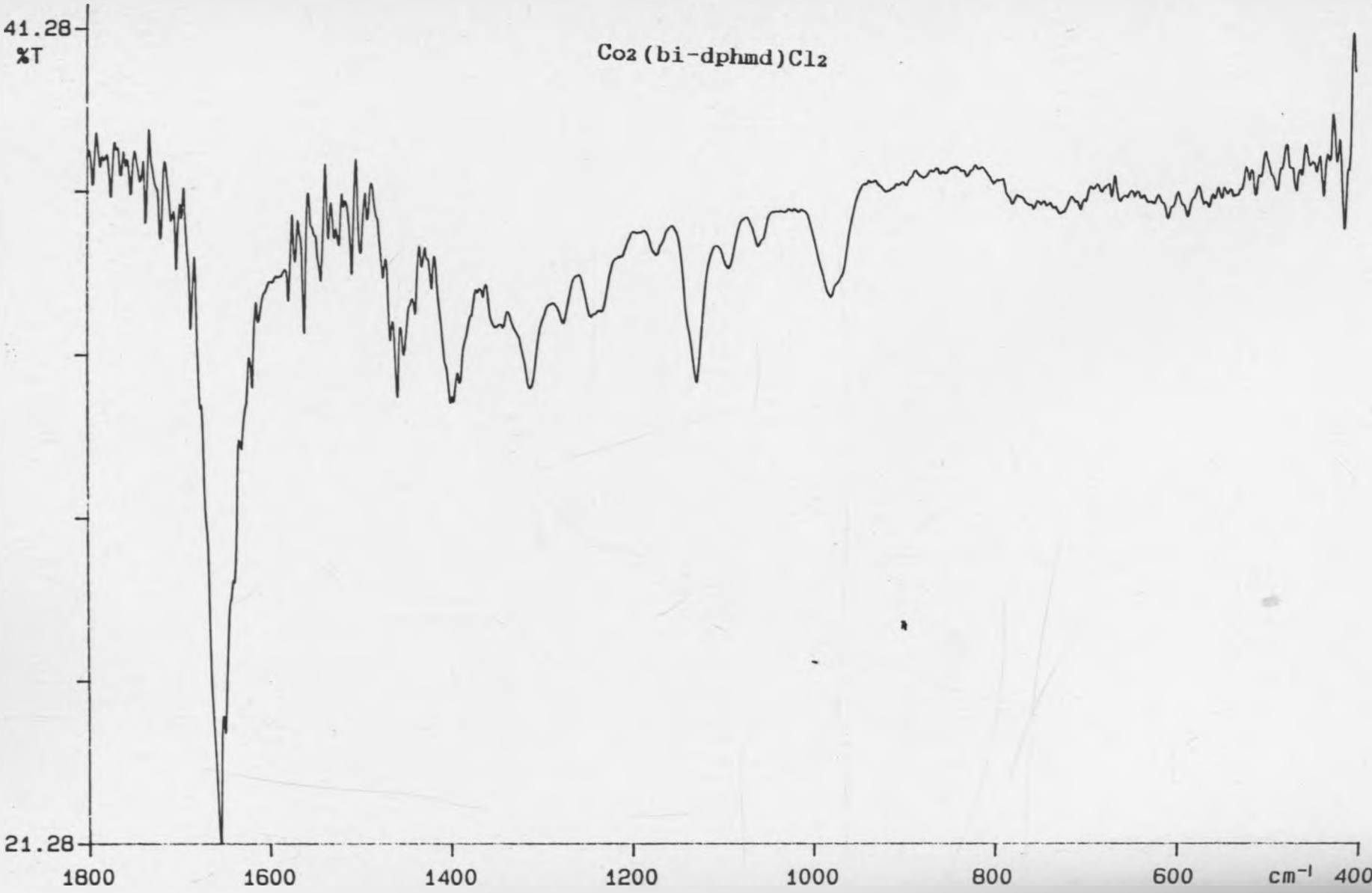


$Cu_2(bi\text{-}dphmd)(N_3)_2$

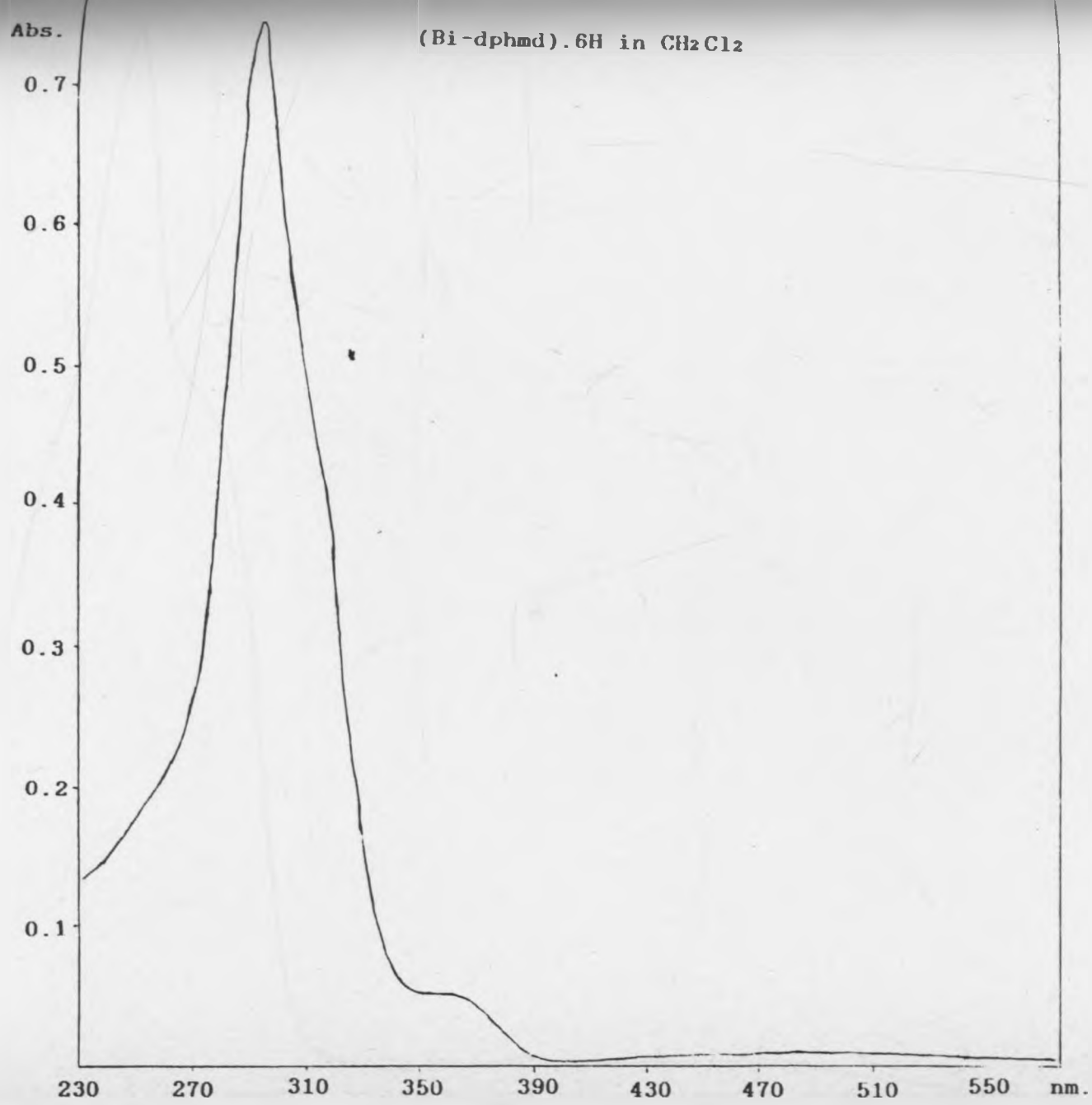
PERKIN ELMER



PERKIN ELMER



Appendix III. UV/Vis. Spectra


(Bi-dphmd).6H in CH2Cl2
Abs.
0.7
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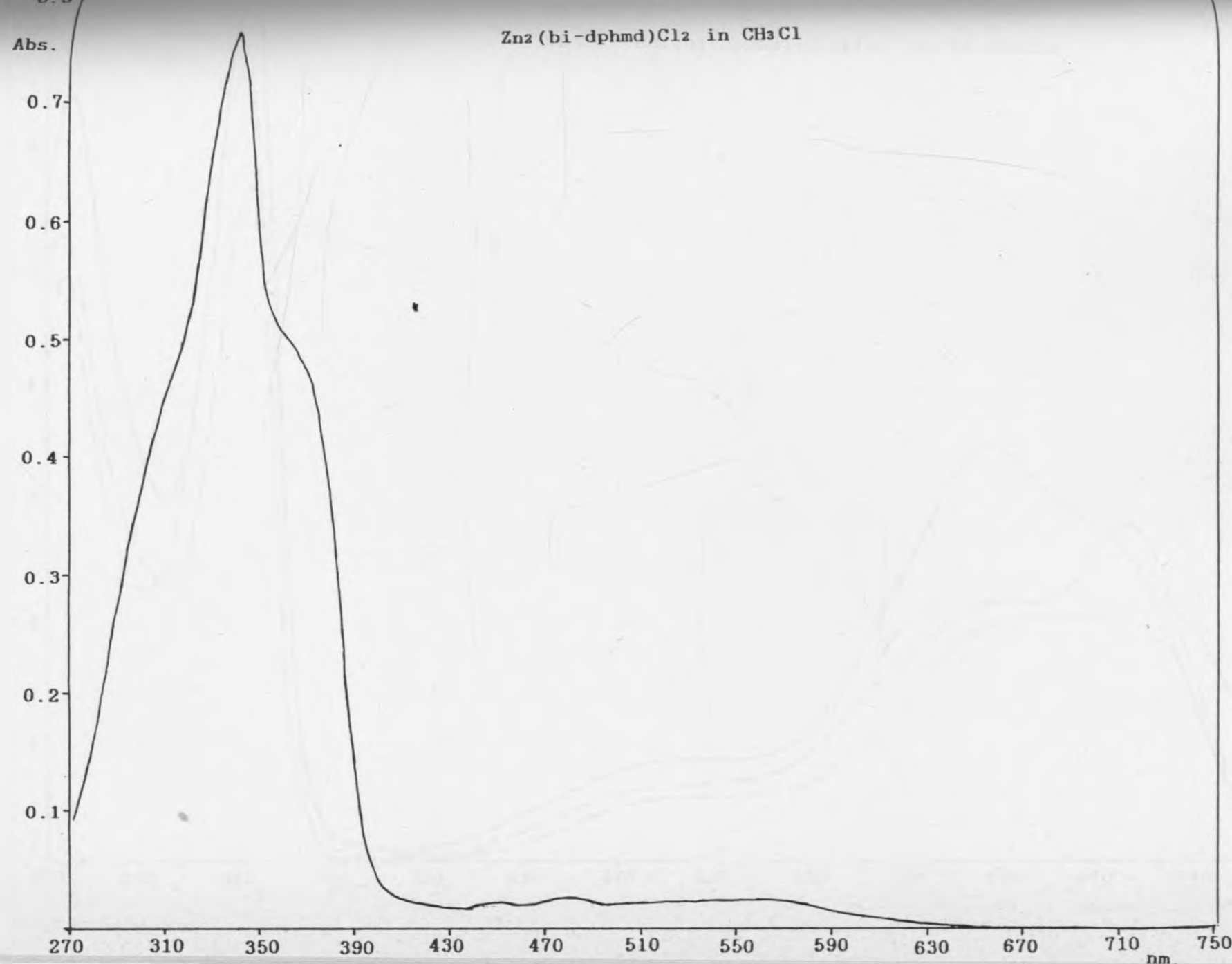
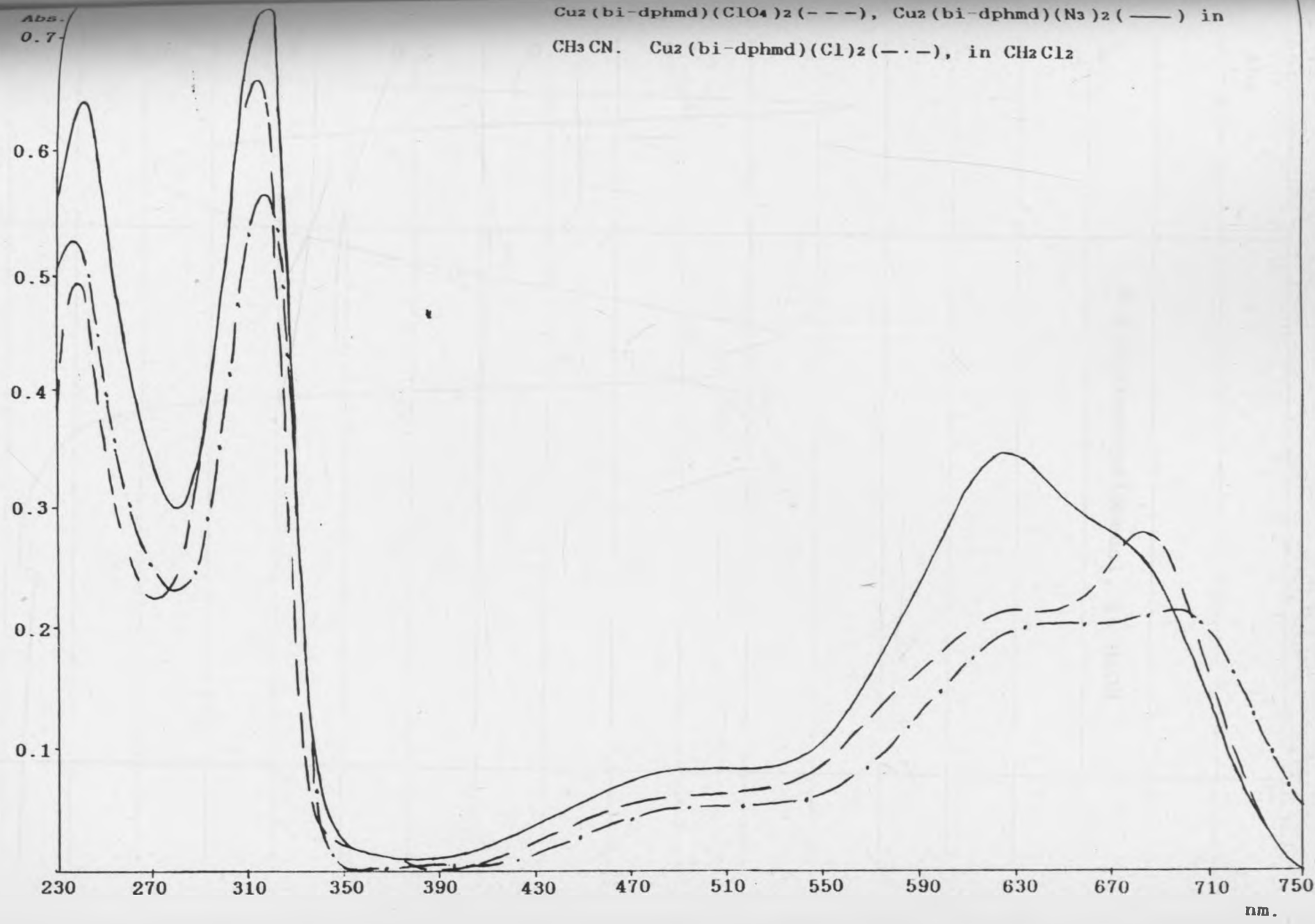
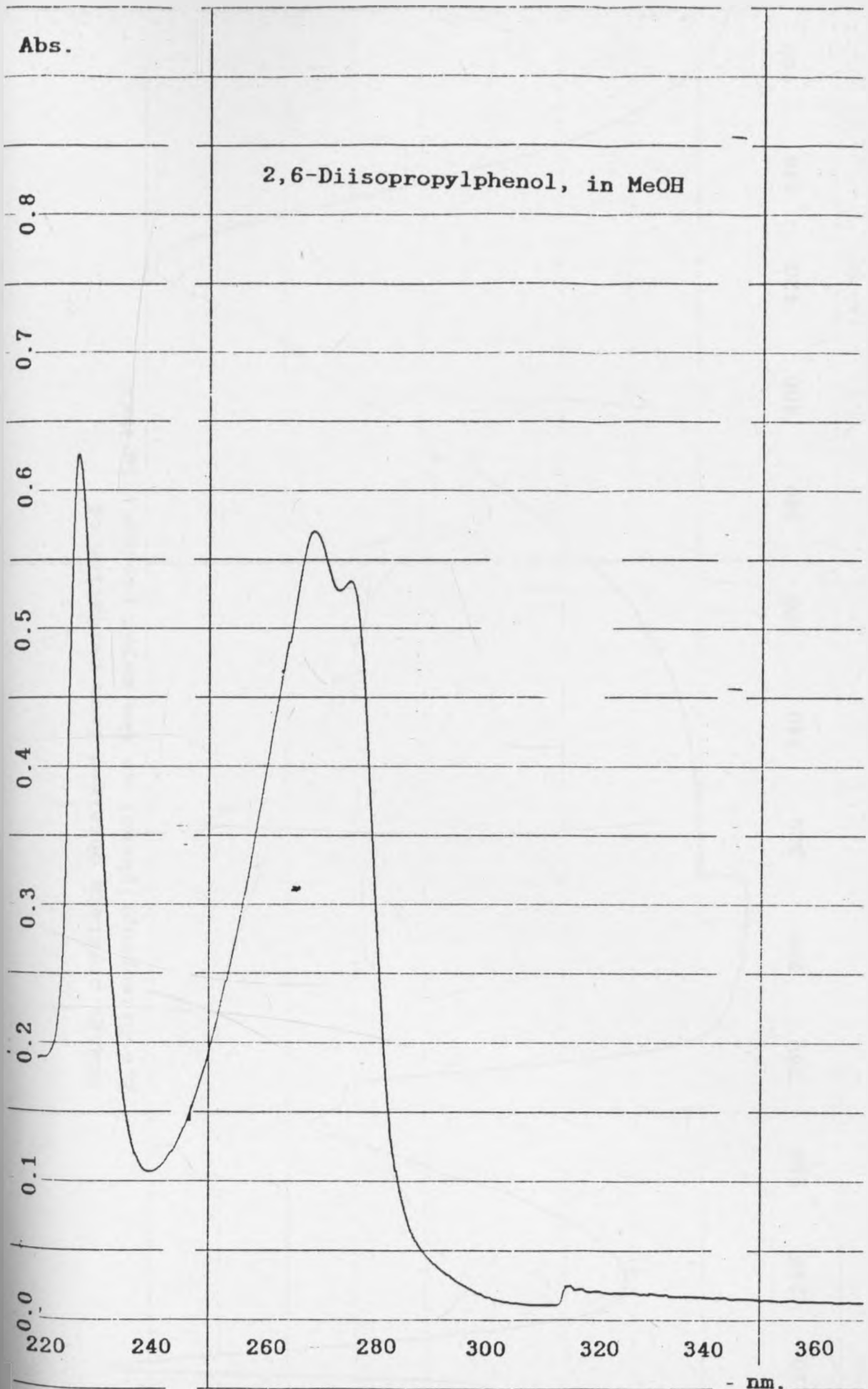
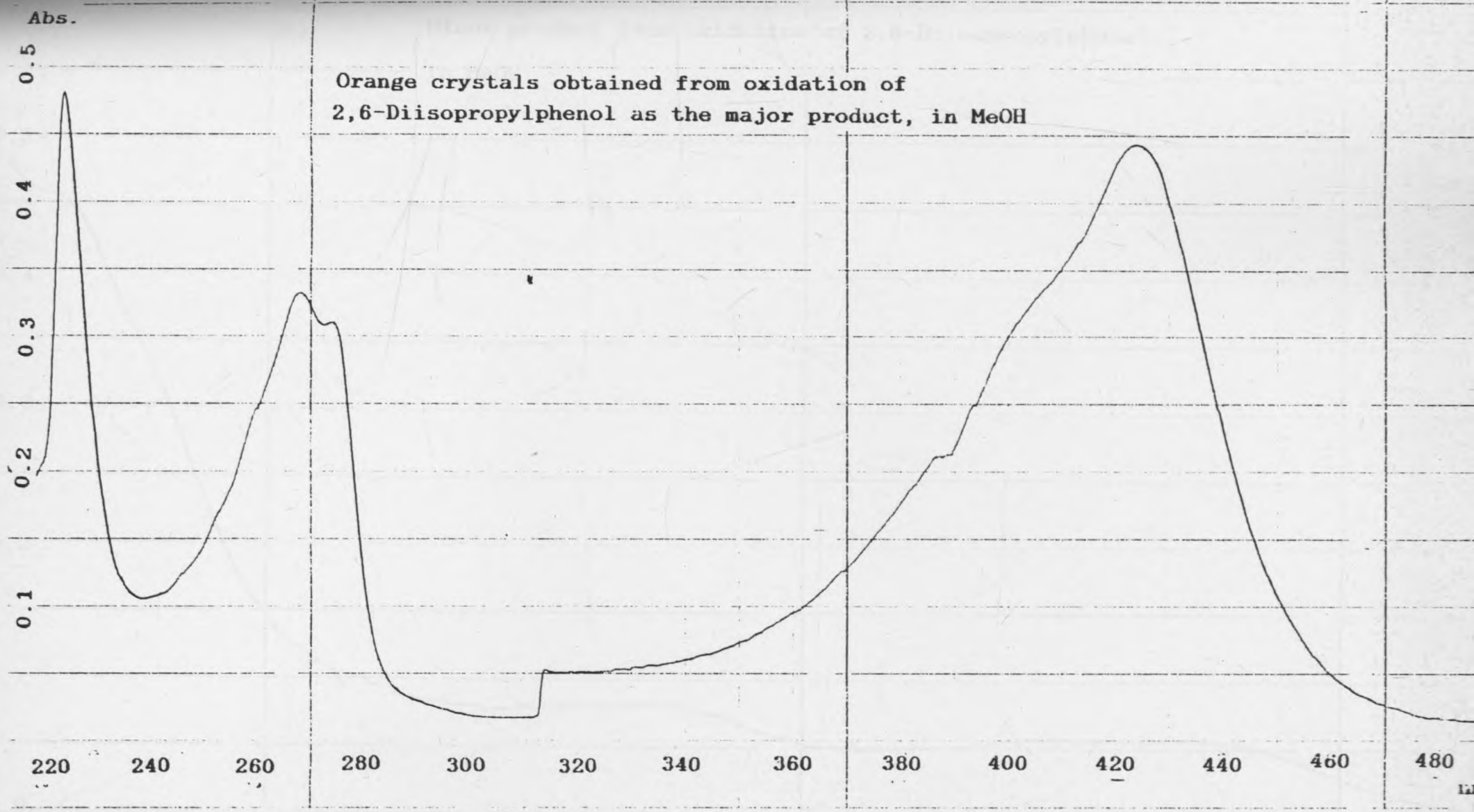
0.5
0.4
0.3
0.2
0.1
230
270
310
350
390
430
470
510
550
nm.


Zn2(bi-dphmd)Cl2 in CH3Cl
Abs.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
270
310
350
390
430
470
510
550
590
630
670
710
750
nm.

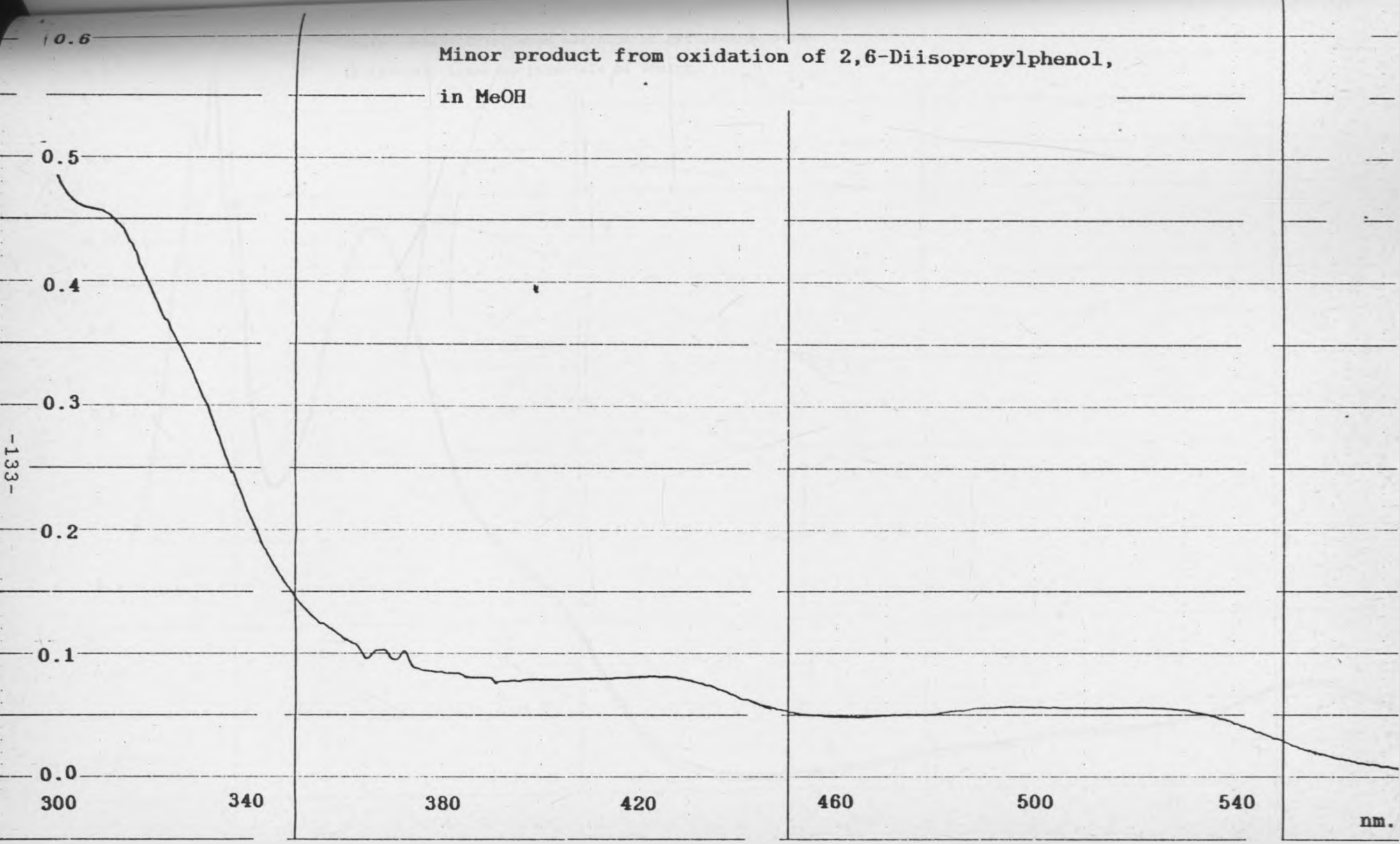


$Cu_2(bi\text{-}dphmd)(ClO_4)_2$ (– – –), $Cu_2(bi\text{-}dphmd)(N_3)_2$ (——) in CH_3CN. $Cu_2(bi\text{-}dphmd)(Cl)_2$ (— · —), in CH_2Cl_2


Abs.
2,6-Diisopropylphenol, in MeOH
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
220
240
260
280
300
320
340
360
nm.

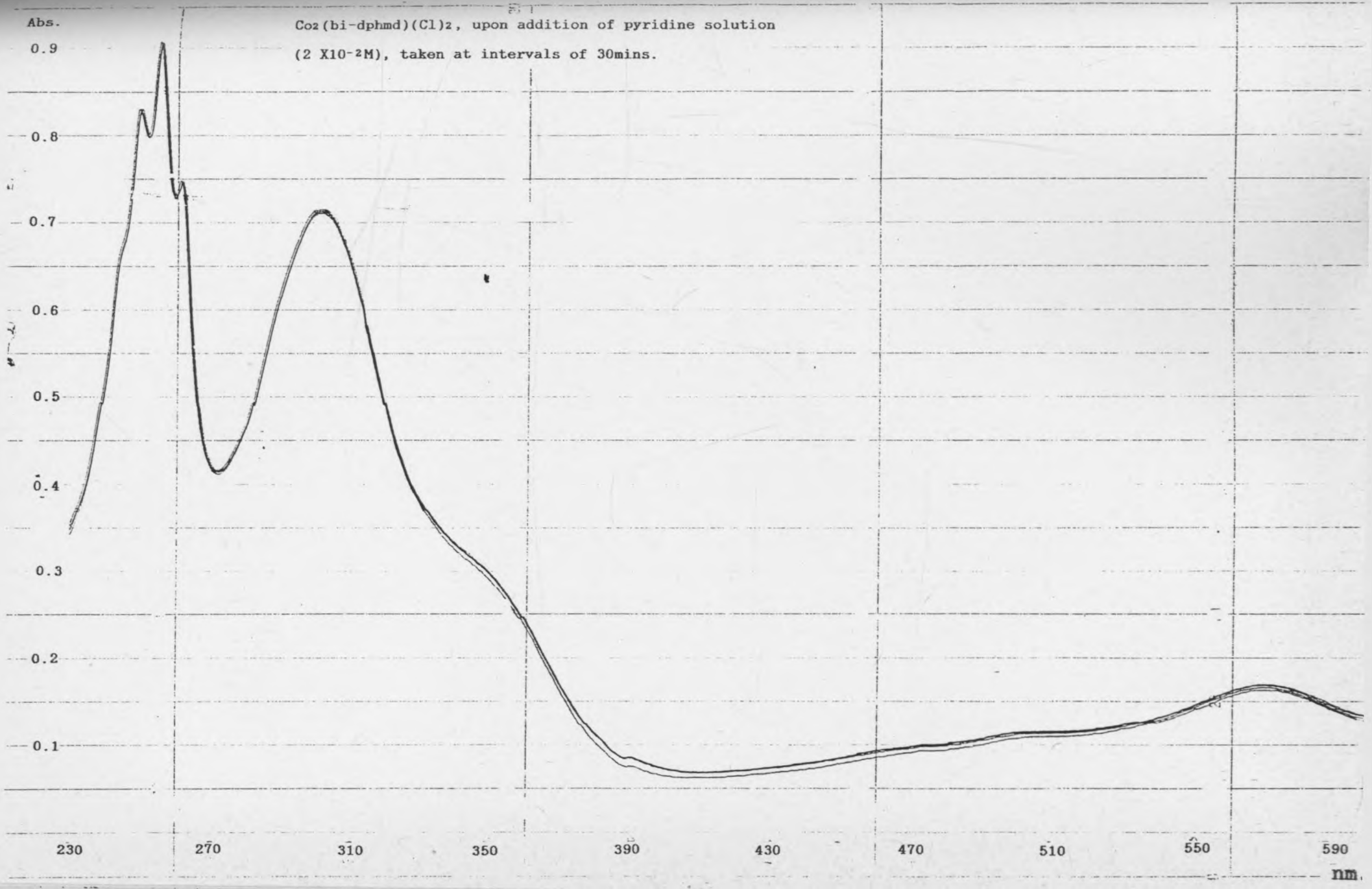


Orange crystals obtained from oxidation of
2,6-Diisopropylphenol as the major product, in MeOH



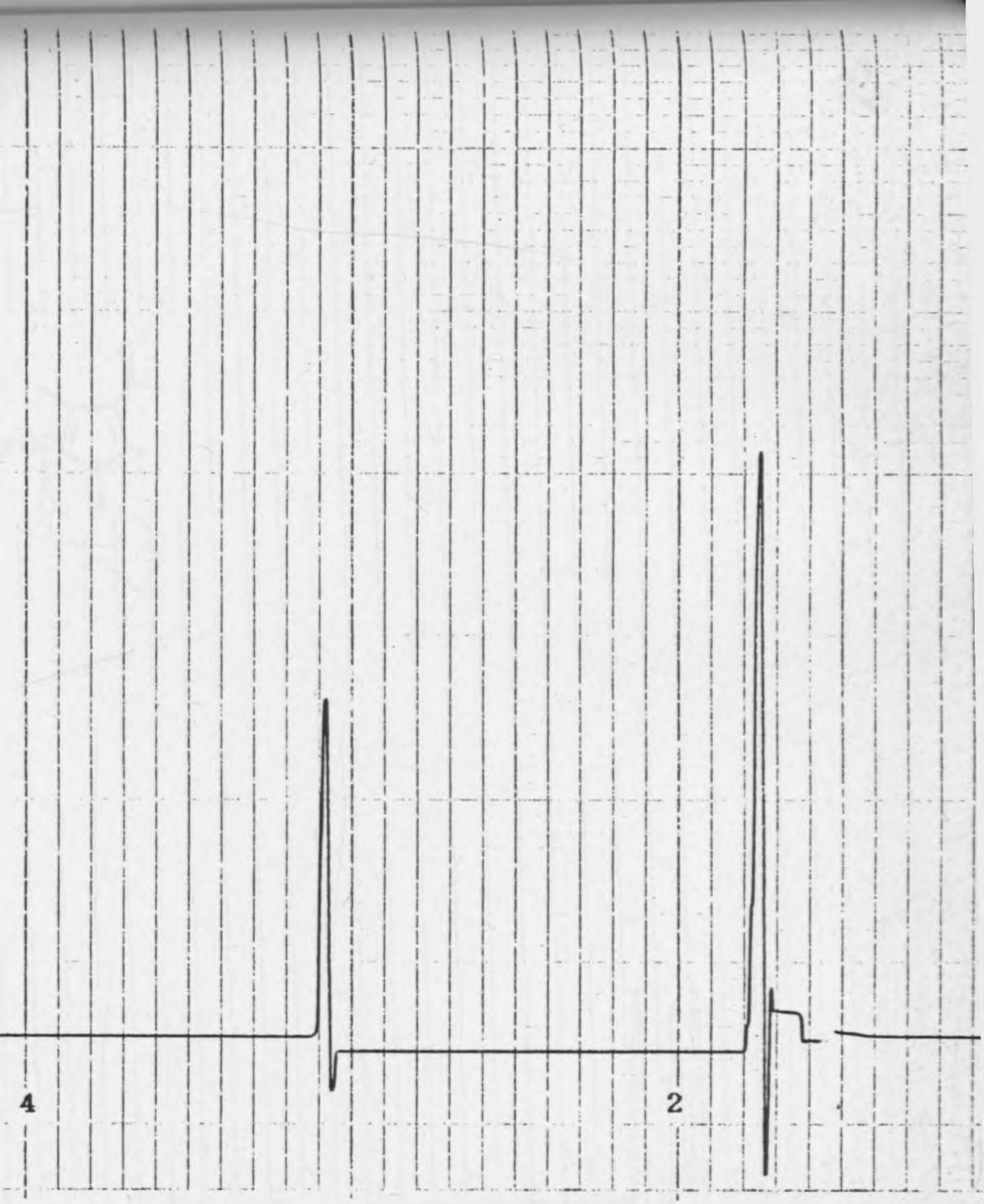
159-1003

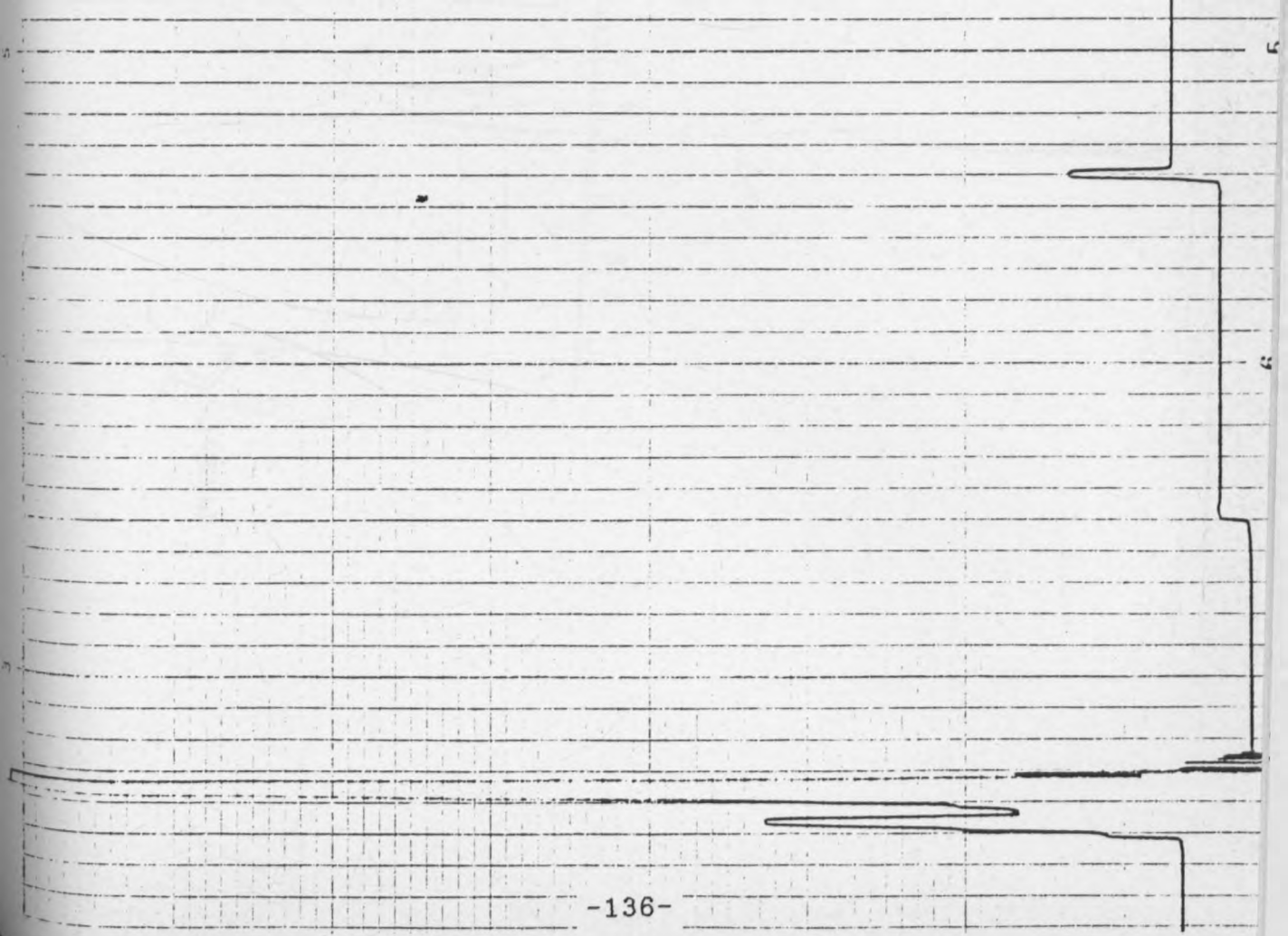
159-1003

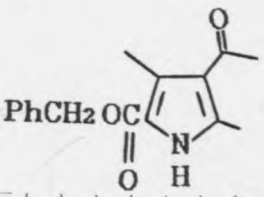

Abs.
Co2(bi-dphmd)(Cl)2, upon addition of pyridine solution
(2 X10-2M), taken at intervals of 30mins.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
230
270
310
350
390
430
470
510
550
590
nm.

Appendix IV. ^{1}HNMR and ^{13}CNMR Spectra

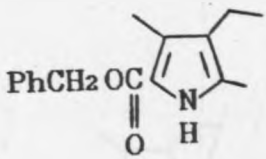

O O
CH3 C–CH2 –C–OCH2 Ph
7
6

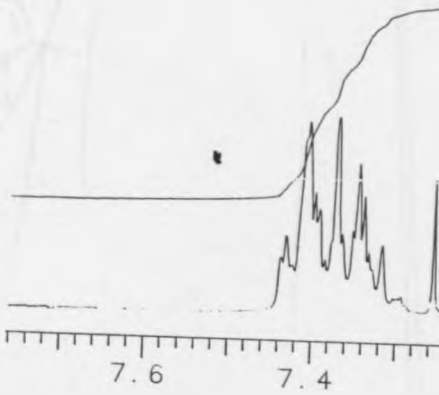

4
2

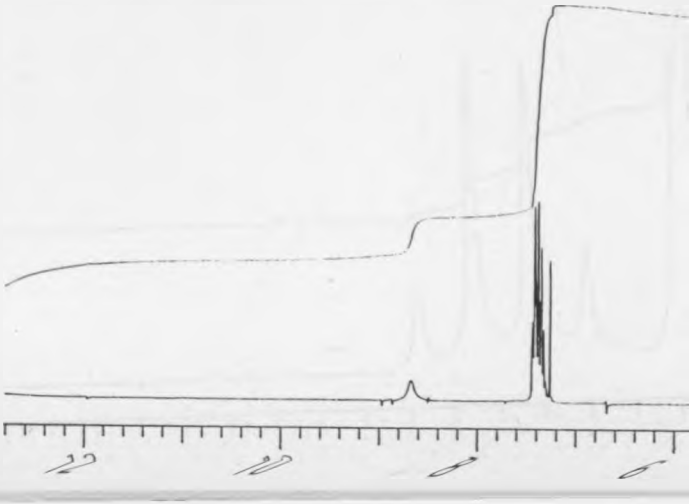



O
PhCH2 OC
N
O H

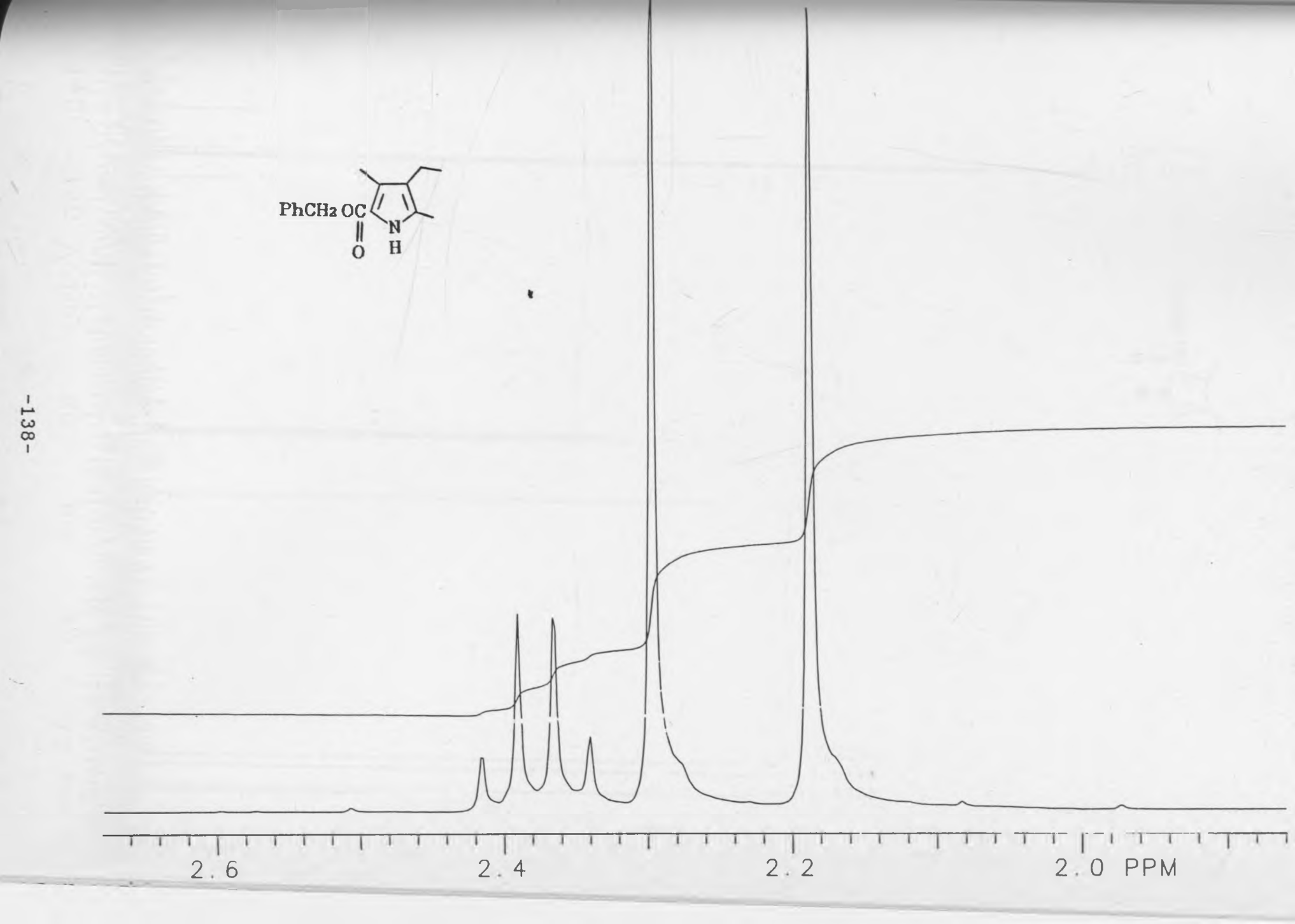

4
3
2


PhCH2 OC
O
N
H


7.6
7.4

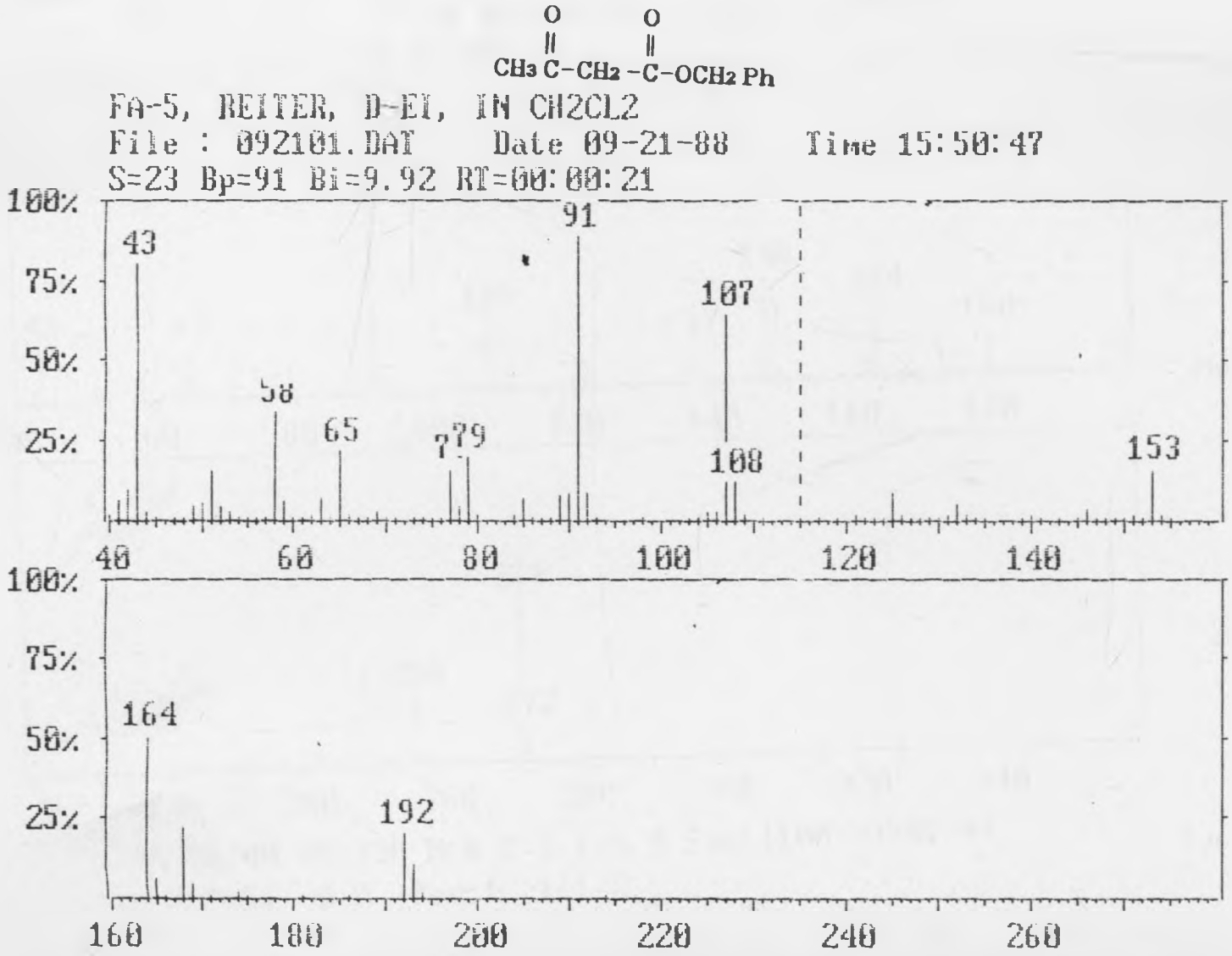


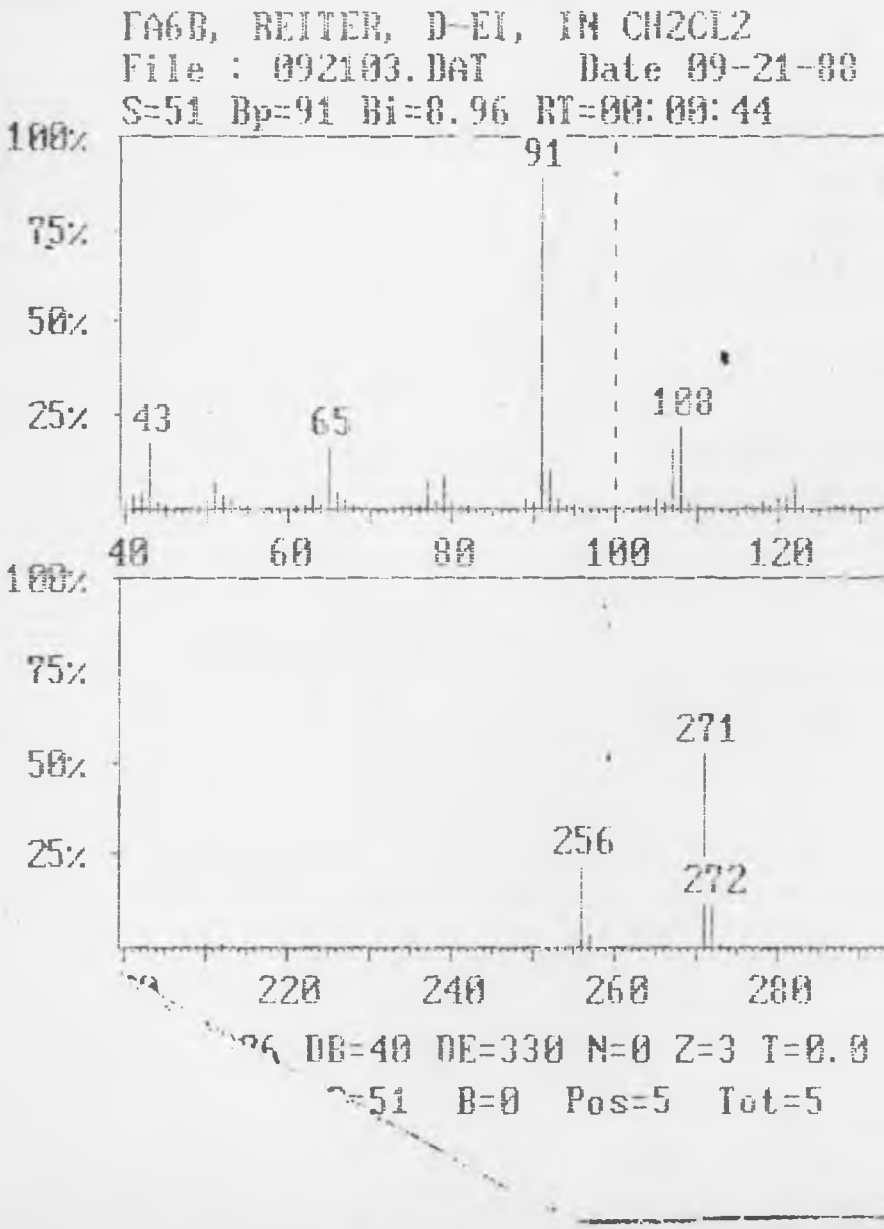

7.2


PhCH2 OC
O
N
H
2.6
2.4
2.2
2.0 PPM

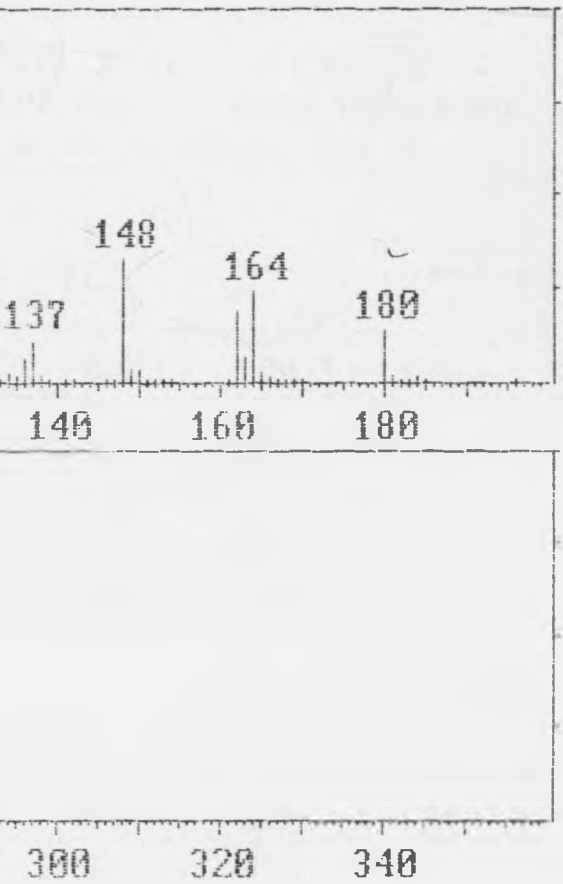
PhCH2 OC
O
N
H
128.740:
128.2855
122.2157
150.1022
136.9534
129.7173
124.2661
17.4393
15.5446
11.5935
10.7865
0.2326
140
120
100
80
60
40
20
PPM 0

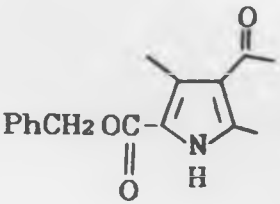
Appendix V. Mass Spectra


O O
CH3 C-CH2 -C-OCH2 Ph
FA-5, REITER, D-EI, IN CH2CL2
File : 092101.DAT Date 09-21-88 Time 15:50:47
S=23 Bp=91 Bi=9.92 RT=00:00:21
100%
75%
50%
25%
43
91
107
58
65
79
108
153
40
60
80
100
120
140
100%
75%
50%
25%
164
192
160
180
200
220
240
260
SB=40 SE=259 DB=40 DE=260 N=0 Z=4 T=0.0 Fact[115->270] *8
Scan List > S=23 B=0 Pos=2 Tot=2


ГА6В, REITER, D-EI, IN CH2CL2
File : 092103.DAT Date 09-21-00
S=51 Bp=91 Bi=8.96 RT=00:00:44
100%
75%
50%
25%
91
43
65
108
40
60
80
100
120
100%
75%
50%
25%
271
256
272
220
240
260
280
DB=40 DE=330 N=0 Z=3 T=0.0
=51 B=0 Pos=5 Tot=5

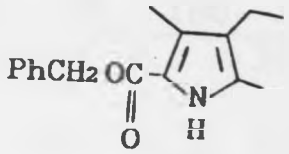
Time 16:00:31



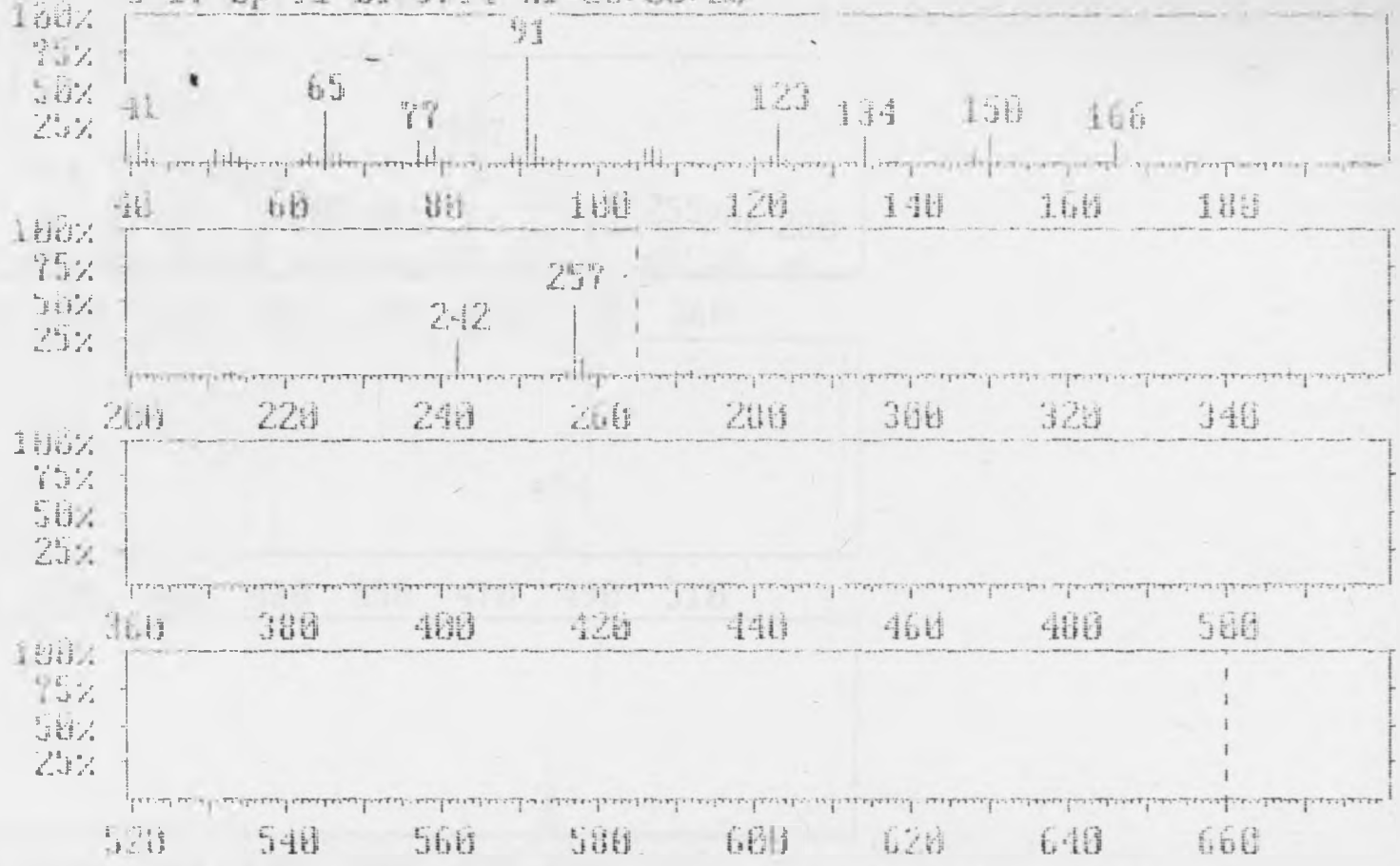


Fact [100->350] *4

350 0.0000

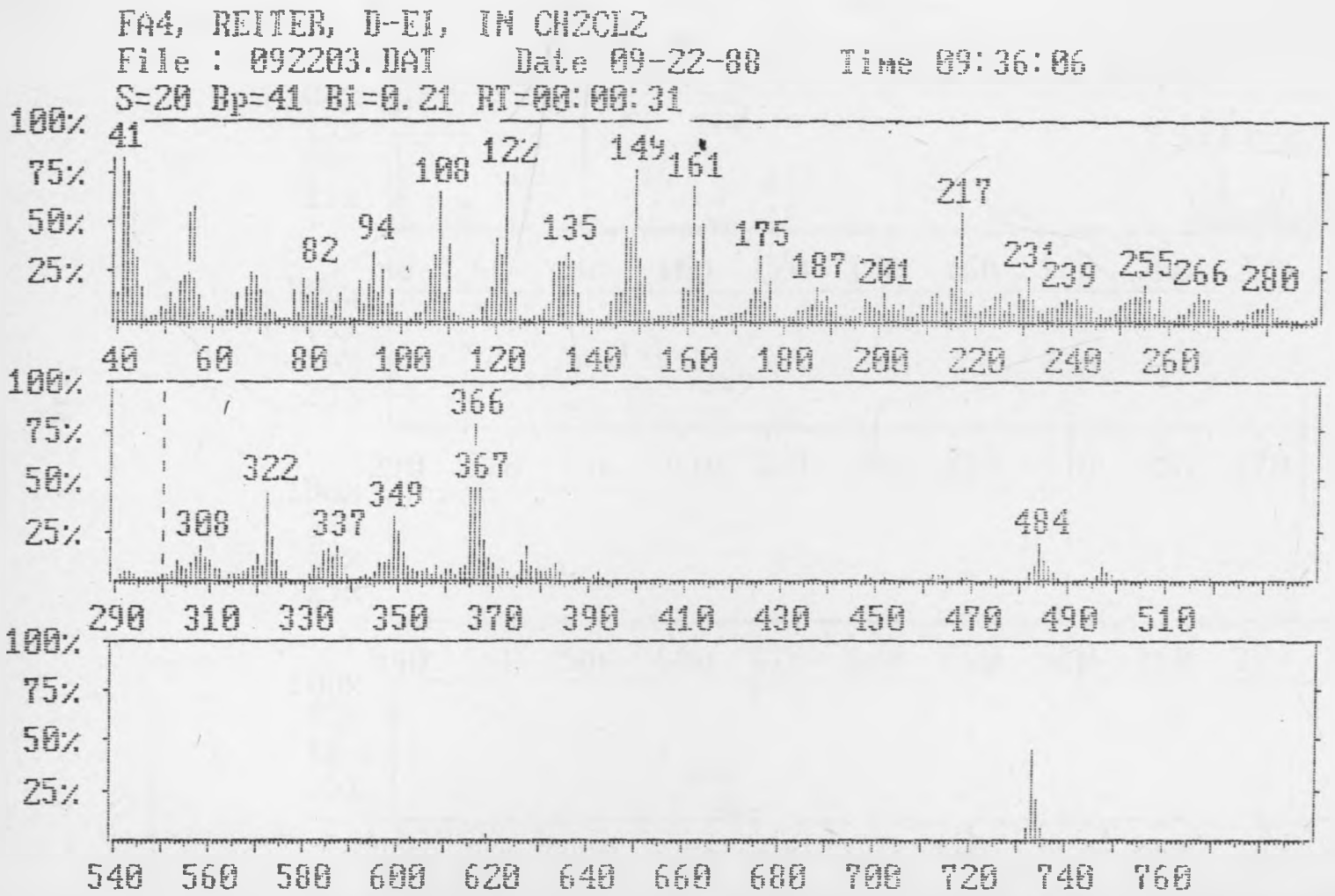


FA-16, REITER, 0 EI, In CH2Cl2
File : 021311.DAT Date 02-13-89 Time 13:43:26
S=17 Bp=91 Bi=9.91 RI=00:00:26



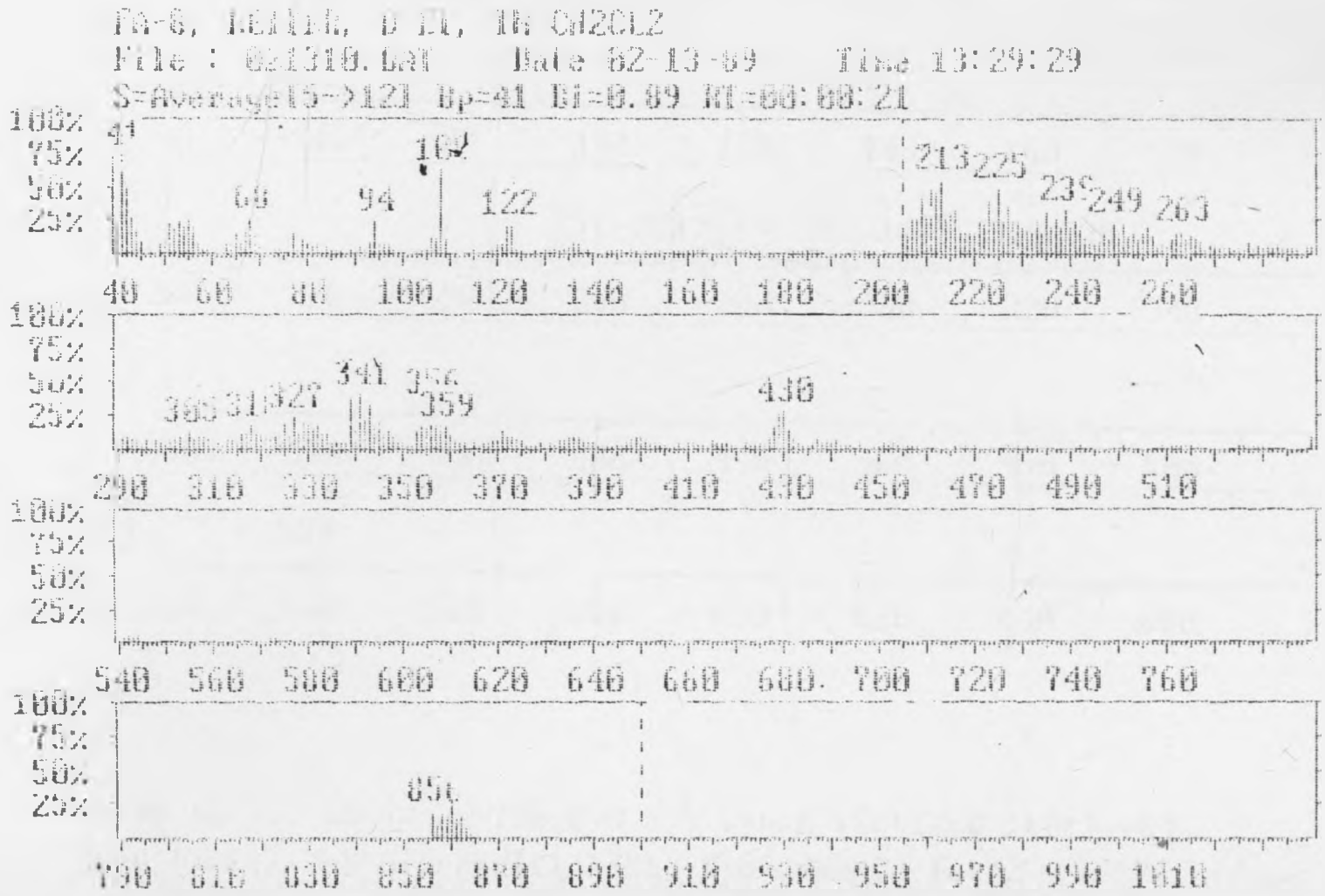
SB=40 SE=340 DB=40 DE=620 M=0 Z=3 T=0.0 Fac(1265->660) =64
Scan List > S=17 B=0 Pos=1 Tot=1

(Bi-dphmd).6H

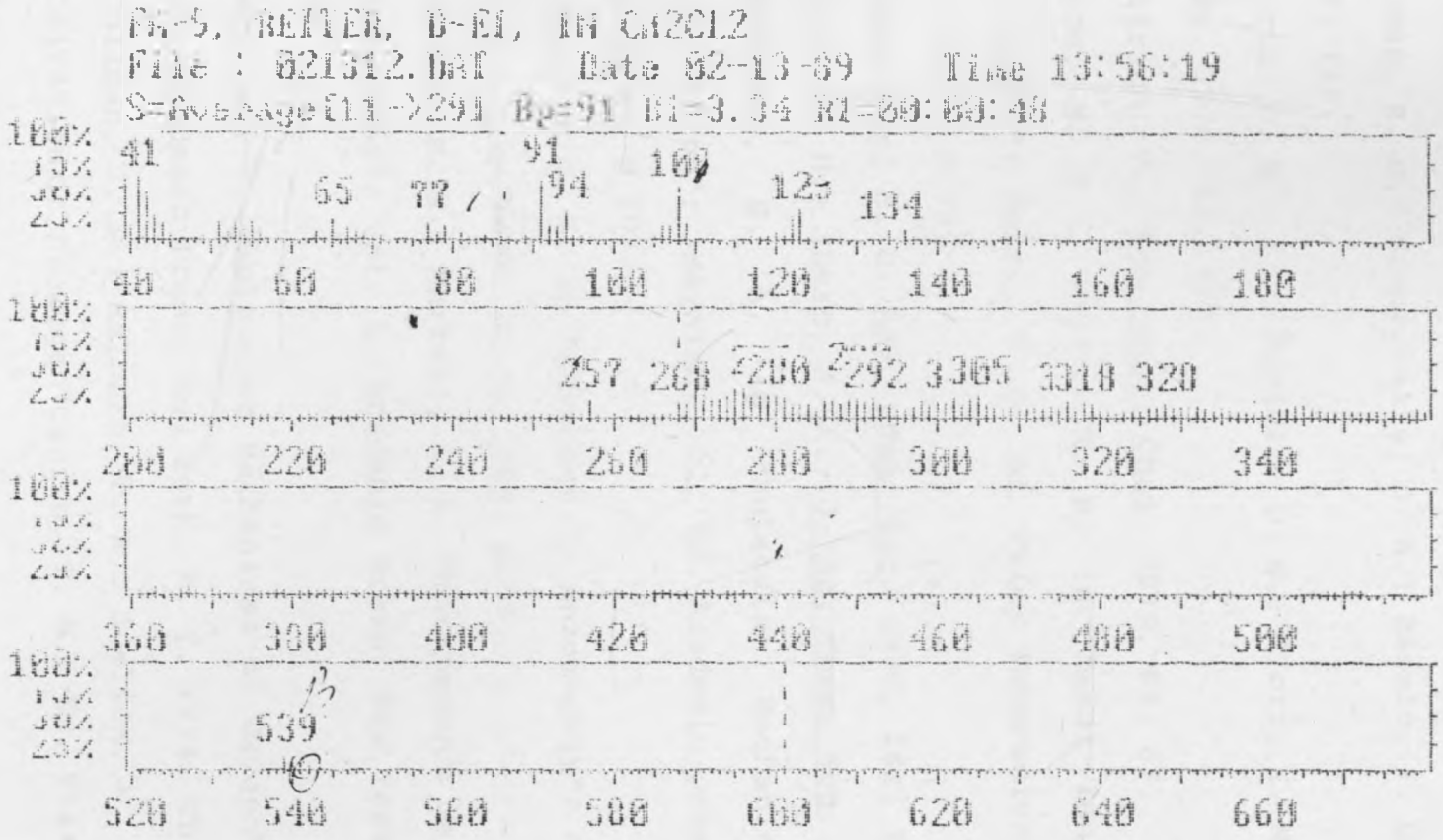


SB=40 SE=735 DB=40 DE=740 N=0 Z=2 T=0.0 Fact[300->770] *4

$Zn_2(dphmd)Cl_2$



$Cu_2(bi\text{-}dphmd)(Cl)_2$



SB=40 SI=552 DB=40 DE=700 N=0 Z=1 T=0.0 Fact[268 >601] *64

Scan List > S=Average[11->29] B=0 Pos=2 Tot=2

601 0.0000

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