CHAPTER TWO

PART A : EXPERIMENTAL WORK

PART B : SPECTRAL INTERPRETATION OF THE COMPOUNDS

PART A : Experimental work has been divided into three parts :

Part I : consists of synthesis of substituted 4(hydrazido) 1,4-benzoxazin-3(2H)-ones. The strategy employed in the synthesis of title compounds is described as follows:

The substituted phenoxy acetic acids were converted into their corresponding amides which further undergo base catalysed cyclisation to form 1,4-benzoxazin-3(2H)-ones. These on refluxtion with ethyl chloroformate in presence of triethylamine and methanol for about 18 hours gave corresponding carboethoxy derivative. The purified sample of carboethoxy derivative on heating with hydrazine hydrate in ethanol formed their respective hydrazides.

Part II : consists of synthesis of N-dialkyl derivatives of substituted 4-(hydrazido)-1,4-benzoxazin-3(2H)-one:

Various N-dialkyl derivatives of different 4-(N-dialkyl hydrazido)-1,4-benzoxazin-3(2H) one have been prepared by condensing 4-(hydrazido) 1,4-benzoxazin-3(2H) one with dimethyl sulphate.

Part III : consists of synthesis of triazolo derivatives of substituted 4(hydrazido)-1,4-benzoxazin-3(2H) one:

The acid catalysed cyclodehydration of substituted 4(hydrazido) 1,4-benzoxazin-3(2H)-one in methanol afforded the targetted tricyclic triazole in 70 to 80 % yield.

The above experimental work has been represented by Scheme 1.

General remarks :

i) Yield percentage, physical constants (MP/BP elemental analysis (found and required) and spectral characteristics of the derivatives have been reported.

ii) MP/BP were determined by open capillary method and are uncorrected.

iii) PMR spectra were recorded on "Perkin-Elmer Varian-90" using T.M.S. as an internal reference using CCl_4, $CHCl_3$ or $CDCl_3$, and $CD_3-\overset{O}{\overset{\|}{C}}-CD_3$ as solvents. The chemical shifts (δ-values) are reported in PPM.

iv) IR spectrum was recorded on "Beckman-20" instrument in KBr/Nujol pallet. The values of stretching frequencies are reported in cm^{-1}.

v) The purity of the compounds were checked by T.L.C. using silica gel as adsorbent.

vi) UV spectrum was recorded on "Beckman DK-1" spectrophotometer in 95 % ethanol.

EXPERIMENTAL PROCEDURE

Part I : Synthesis of substituted 4(hydrazido)-1,4-benzoxazin -3(2H)-ones.

The general method followed for the preparation of arloxy acetic acid (IIa-d) from their corresponding phenols (Ia-d) and the preparation of substituted arloxy amides (IIIa-d) from their corresponding arloxy acetic acid as per method described in vogel[56] and Tarapure et al.[57]

1:4-benzoxazin-3(2H)-ones were prepared as follows as per Scheme 1.

Synthesis of 6-methyl 1,4-benzoxazin-3(2H)-one (IVb) :

2-Bromo-4-methyl-aryloxamide (7.0 g, 0.043 mol) and triethyl amine (2.0 g, 0.02 mol) in 30 ml of dry methanol was refluxed on water bath for about six hours, cooled. The solvent was removed under reduced pressure. The residue extracted with ether and concentrated. The white solid obtained was recrystallized from ethanol.

The physical constant (M.P.) yield, percentage yield, elemental analysis (found and calculated) have been reported in Table 1.

Table 1

Compd	M.P. °C	Yield in gm	% yield	Molecular Formula	Elemental Analysis					
					Found(%)			Required(%)		
					C	H	N	C	H	N
IVa	168	5.00	80	$C_8H_7NO_2$	64.00	4.1	9.2	64.43	4.69	9.39
IVb	110	5.49	90	$C_9H_9NO_2$	65.8	5.2	8.48	66.25	5.52	8.59
IVc	120	5.50	78.5	$C_9H_8NO_2Cl$	54.56	3.9	6.9	54.68	4.05	7.08
IVd	118	10.00	75	$C_{10}H_{11}NO_2$	67.73	6.11	7.8	67.79	6.21	7.9

The structures of compouhds (IVa-d) have been confirmed by IR and PMR spectra.

IR(Nujol) compd IVb : 3200 - 3300 cm^{-1} (NH), 2900 cm^{-1} (C-H stretch),
1695 cm^{-1} (δ-Lactam ketone),
1600 cm^{-1} (phenyl), Fig. 1.

Compd No.	PMR ($CD_3-\overset{O}{\overset{\|}{C}}-CD_3$) δ, PPM	Fig. No.
IVa	4.6 (2H, s, $-OCH_2$), 7.25 (1H, d, J_{ortho} = 9.0 Hz, C_8-H), 7.4 (1H, dd, J_{ortho} = 9 Hz, J_{meta} = 3 Hz, C_7-H), 7.5 (1H, dd, J_{ortho} = 9 Hz, J_{meta} = 3 Hz, C_6-H), 7.7 (1H, d, J_{ortho} = 9 Hz, J_{meta} = 3 Hz, C_5-H), 8.4 (1H, s, br-NH, exchangeable with D_2O).	2
IVb	2.05 (3H, s, $-CH_3$), 4.52 (2H, s, $-OCH_2$), 6.8 (1H, d, J_{ortho} = 9 Hz, C_8-H), 6.95 (1H, dd, J_{ortho} = 9 Hz, J_{meta} = 2.5 Hz, C_7-H), 7.3 (1H, d, J_{meta} = 2.5 Hz, C_5-H), 8.4 (1H, s, br, NH exchangeable with D_2O).	3
IVc	2.57 (3H, s, C_7-CH_3), 4.60 (2H, s, $-OCH_2$), 6.8 (1H, s, C_8-H), 7.6 (1H, s, C_5-H), 8.1 (1H, s, br, -NH).	8
IVd	2.3 (3H, s, C_8-CH_3), 2.38 (3H, s, C_6-CH_3), 4.62 (2H, s, $-OCH_2$), 6.82 (1H, s, C_7-H), 7.97 (1H, s, C_5-H), 8.15 (1H, br, -NH).	

Synthesis of N-(carboethoxy)-1,4-benzoxazin-3(2H)-ones Vb :

Compound IVb (5.9, 0.031 mol) and ethylchloroformate (7.5 g, 0.07 mol) and triethylamine (2.0 g, 0.02 mol) in 20 ml of dry methanol was refluxed for about 18 hours, on oil bath at 110°, cooled and the solvent is removed under reduced pressure. The heavy oil obtained was purified by distillation.

Physical constants (B.P.) yield, percentage yield elemental analysis (found and required) have been reported in Table 2.

Table 2

Compd No.	B.P.	Yield in gm	% yield	Molecular Formula	Elemental Analysis					
					Found (%)			Required (%)		
					C	H	N	C	H	N
Va	280	7.00	70.00	$C_{11}H_{11}NO_4$	59.00	4.70	6.20	59.72	4.97	6.33
Vb	303	5.29	70.00	$C_{12}H_{13}NO_4$	61.20	5.33	5.90	61.27	5.53	5.95
Vc	315	6.00	69.5	$C_{12}H_{12}NO_4Cl$	53.40	4.59	5.12	53.43	4.44	5.19
Vd	308	7.00	75.5	$C_{13}H_{15}NO_4$	62.60	6.15	5.56	62.65	6.00	5.62

Structures of Va-d compounds have been confirmed by PMR spectra.

Compd No.	PMR (CCl_4), δ, PPM	Fig. No.
Va	1.3 (3H, t, $-CH_3$), 4.2 (2H, q, $-CH_2$), 4.55 (2H, s, $-OCH_2$), 6.9 (1H, d, J_{ortho} = 8 Hz, C_8-H), 7.1 (1H, dd, J_{ortho} = 8 Hz, J_{meta} = 2.5 Hz, C_6-H), 7.3 (1H, d, J_{meta} = 2.5 Hz, C_5-H).	4
Vb	1.3 (3H, t, $-CH_3$), 2.25 (3H, s, C_6-CH_3), 4.2 (2H, q, $-CH_2$), 4.55 (2H, s, $-OCH_2$), 6.75 (1H, d, J_{ortho}= 8.5 Hz, C_8-H), 6.9 (1H, dd, J_{ortho} = 8.5 Hz, J_{meta} = 3 Hz, C_7-H), 7.35 (1H, d, J_{meta} = 3 Hz, C_5-H).	5
Vc	1.5 (3H, t, $-CH_3$), 2.55 (3H, s, C_7-Ar-CH_3), 4.40 (2H, t, $-CH_2$), 4.78 (2H, s, $-OCH_2$), 6.8 (1H, s, C_8-H), 7.65 (1H, s, C_5-H).	6
Vd	1.05 (3H, t, $-CH_3$), 2.3 (3H, s, C_8-Ar-CH_3), 2.38 (3H, s, C_6-CH_3), 4.30 (2H, q, $-CH_2$), 4.6 (2H, s, $-OCH_2$), 7.3 (1H, s, C_7-H), 7.4 (1H, s, C_5-H).	7

Synthesis of 6-methyl-4(hydrazido)-1,4-benzoxazin-3(2H)-one (VIb) :

A mixture of compound Vb (4.5 g, 0.019 mol) and hydrazine hydrate (4.5 g, 0.09 mol) in 10 ml ethanol was heated on water bath for about 15 minutes, cooled, the white needle shaped crystals separated which were recrystallized from ethanol.

Physical constants (M.P.), Yield, percentage yield, elemental analysis (found and required) have been reported in Table 3.

Table 3

Compd No.	M.P.	Yield in gm	% yield	Molecular Formula	Elemental Analysis					
					Found (%)			Required (%)		
					C	H	N	C	H	N
VIa	120	5.00	85.60	$C_9H_9N_3O_3$	52.10	4.25	20.23	52.17	4.34	20.28
VIb	115	3.50	82.30	$C_{10}H_{11}N_3O_3$	54.20	4.90	18.95	54.30	4.97	19.00
VIc	187	4.50	82.00	$C_{10}H_{10}N_3O_3Cl$	46.80	3.85	16.25	46.96	3.91	16.43
VId	162	5.00	83.12	$C_{11}H_{13}N_3O_3$	55.40	6.27	17.65	55.70	6.33	17.72

The structures of compound VIa-d have been confirmed by UV, IR and PMR spectra.

(Compound VIb), UV (ethanol) : λ_{max} 280 nm Fig.8.

IR (nujol) : 3280 cm^{-1} ($NH-NH_2$ stretch),

1690-1700 cm^{-1} (δ-lactam ketone) Fig.9.

Compd No.	PMR ($CDCl_3$); δ, PPM	Fig. No.
VIa	4.6 (2H, s, $-OCH_2$), 4.8 (2H, s, br, $-NH_2$), 6.91 (1H, d, J_{ortho} = 9 Hz C_8-H). 7.12 (1H, dd, J_{ortho} = 9 Hz, J_{meta} = 2.5 Hz, C_7-H), 7.2 (1H, dd, J_{ortho} = 9 Hz, J_{meta} = 2.5 Hz, C_6-H), 7.3 (1H, d, J_{ortho} = 9 Hz, J_{meta} = 2.5 Hz, C_5-H), 8.9 (1H, s, br, -CONH).	-
VIb	2.2 (3H, s, $C_6-Ar-CH_3$), 4.0 (2H, s, br, $-NH_2$ exchangeable with D_2O), 4.55 (2H, s, $-OCH_2$), 6.85 (1H, d, J_{ortho} = 8 Hz, C_8-H), 6.95 (1H, dd, J_{ortho} = 8 Hz, J_{meta} = 3 Hz, C_7-H), 7.3 (1H, d, J_{meta} = 3 Hz, C_5-H).	10
VIc	2.58 (3H, s, C_7-CH_3), 4.59 (2H, s, $-OCH_2$), 6.81 (1H, s, C_8-H), 7.6 (1H, s, C_5-H).	-
VId	2.3 (3H, s, $C_8-Ar-CH_3$), 2.38 (3H, s, $C_6-Ar-CH_3$), 4.62 (2H, s, $-OCH_2$) 7.4 (1H, s, C_7-H), 7.60 (1H, s, C_5-H).	11

Part II :

Synthesis of 4 (N-dialkyl hydrazido)-1,4-benzoxazin-3(2H)-ones:

Various N-dialkyl derivatives of different 4(hydrazido)-1,4-benzoxazin-3(2H)-one have been prepared by condensing 4(hydrazido)-1,4-benzoxazin-3(2H)-one with dimethyl sulphate in methanol. The structures of these compounds were confirmed by IR and PMR spectra.

The general method followed for the synthesis of the compounds is described below. Scheme 2

Synthesis of 4(N-dialkyl hydrazido)1,4-benzoxazin-3(2H)-ones (VIIa-d):

The compound 4(hydrazido)-1,4-benzoxazin-3(2H)-one (VIb) (0.241 g, 0.001 mole) was dissolved in dry methanol, 0.1 ml dimethyl sulphate was added at room temperature and refluxed for about 30 minutes, cooled, separated solid was filtered and recrystallised from methanol. The M.P., analytical data and PMR spectral studies are given in Table 4.

All the compounds gave satisfactory, carbon, hydrogen and nitrogen analysis.

UV absorption spectra in 95 % ethanol with λ_{max} = 285 nm.

IR (nujol) : a band at 1600 cm^{-1} (phenyl), 1670-1690 cm^{-1} (δ-lactam ketone), 2880-2900 cm^{-1} (methylene stretch) and 3160 cm^{-1}, broad singlet (-NH-). Fig.12.

PMR (CDCl$_3$) : δ, 1.9 (3H, s, -CH$_3$), 2.05 (3H, s, -CH$_3$), 4.65 (2H, s, -OCH$_2$), 6.8 (1H, d, J_{ortho} = 9 Hz C$_8$-H), 7.05 (1H, d, J_{ortho} = 9 Hz, J_{meta} = 2.0 Hz, C$_7$-H), 7.1 (1H, d, J_{ortho} = 9 Hz, J_{meta} = 2.0 Hz, C$_6$-H), 7.3 (1H, d, J_{ortho} = 9 Hz, J_{meta} = 2 Hz, C$_5$-H). Fig. 13.

Table 4

Compd	M.P. °C	Yield in gms	% yield	Molecular formula	Found (%) C	H	N	Required (%) C	H	N
VIIa	210	1.20	80.00	$C_{11}H_{13}N_3O_3$	56.00	5.40	17.30	56.20	5.53	17.86
VIIb	231	1.25	83.00	$C_{12}H_{15}N_3O_3$	57.50	5.80	16.70	57.80	6.02	16.87
VIIc	233	1.30	78.00	$C_{12}H_{14}N_3O_3Cl$	50.20	4.80	14.68	50.4	4.93	14.80
VIId	228	1.10	82.00	$C_{13}H_{17}N_3O_3$	59.00	6.35	15.85	59.30	6.46	15.97

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Part III :

Synthesis of some new tricyclic triazoles derived from 4(hydrazido)-1,4-benzoxazin-3(2H)-ones :

The acid catalysed cyclisation of substituted 4(hydrazido)-1,4-benzoxazin-3(2H)-ones provided a new route for the synthesis of 4H-[1,2,4]-triazolo-3-oxo-[3,4-c]-benzoxazines. Strategy employed for the synthesis of desired compounds is as shown in Scheme 2.

Synthesis of 6-methyl-4H-(1,2,4)-triazolo-3-oxo-[3,4-c]-benzoxazine (VIIIa-d) :

To the solution of 6-methyl-4(hydrazido)-1,4-benzoxazin-3(2H)-one (VIb)(0.75 g, 0.033 mole) in 10 ml of methanol, hydrochloric acid is added till the solution becomes just acidic and heated on water bath for about three hours. The separated solid was recrystallised from ethanol. The M.P., analytical data and IR spettral studies are given in Table 5.

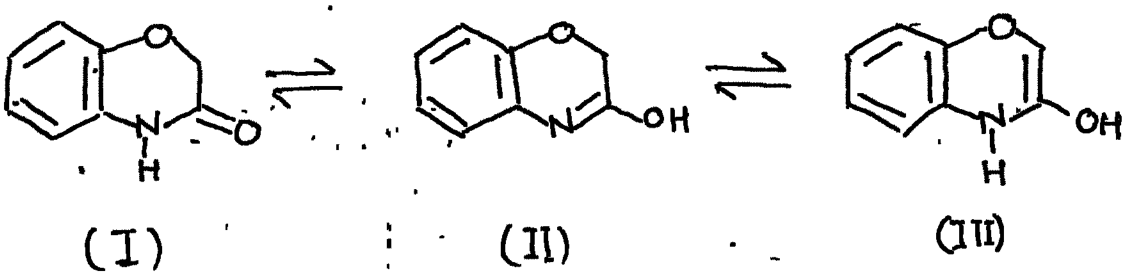
Table 5

Compd	M.P.	Yield in gm	% yield	Molecular formula	Elemental Analysis					
					Found (%)			Required (%)		
666					C	H	N	C	H	N
VIIIa	150	0.50	80.50	$C_9H_7N_3O_2$	57.14	3.70	22.20	57.20	3.75	22.00
VIIIb	227	0.75	80.00	$C_{10}H_9N_3O_2$	59.10	4.40	20.60	59.11	4.43	20.68
VIIIc	196	0.60	83.15	$C_{10}H_8N_3O_2Cl$	50.50	3.30	17.40	50.53	3.36	17.70
VIIId	207	0.80	82.15	$C_{11}H_{11}N_3O_3$	60.18	5.68	18.78	60.30	5.90	19.18

[VIIIb] IR(Nujol) : 3200-3300 cm^{-1} (-NH), 1640 cm^{-1} (C=O), 1620 cm^{-1} (-C=N-), 1600 cm^{-1} (phenyl), Fig. 14.

Part B : Spectral interpretation of the compounds :

Earlier studies on UV, IR, PMR of the compound 1,4-benzoxazin-3(2H)-one reveal that the compound exists in three different potential lactim-lactam tautomers, where mobile hydrogen atom can move from ring nitrogen to adjacent hetero-atom oxygen or keto-enol tautomers I to III.



Out of these tautomers, the predominant tautomer is (I) as evident from their UV, IR, PMR spectra.

UV Spectra :

The UV spectral data of 3-oxo and substituted-1,4-benzoxazine* exhibit an absorption pattern very similar to that of compound (I) [λ_{max} = 256.4 nm]. Similarly 2-methyl, N-methyl and 2,4-dimethyl-2H-1,4-benzoxazin-3-one show the UV absorption in 95 % ethanol with λ_{max} = 254.6 nm, 256.4 nm and 254.5 nm respectively.

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* Mazhuruddin M. and Thyagarajan G., Tetrahedron, vol. 25, 517-525 (1968).

IR Spectra :

Sullivan and Sadler studied the IR of 3,4-dihydro-2H-1,4-benzoxazin-3-one (compound I) in solid and solution states. Based on the carbonyl absorption in the 1700 cm^{-1} region and NH-absorption around 3200 cm^{-1} in solid state and 3400 cm^{-1} in solution supported the Lactam structure.

PMR Spectra :

The PMR spectra are useful to confirm the structure and also to establish the predominant tautomer in the potentially tautomeric system.

The presence of the 'sharp singlet' in the region 4.5 - 5.0, δ (ppm) fixes the position of the C_2-methylene protons.

The aromatic protons are observed around 7.0 δ (ppm) as 'singlet' or 'multiplet' depending upon the substituent atom or group present on benzene ring of 1,4-benzoxazine molecule.

Compound (IVb) :

6-Methyl1,4-benzoxazin-3(2H)-one :

[Fig. 1]

The IR studies of various substituted 1,4-benzoxazin-3(2H)-ones (compound IVa-d), in solid state in nujol show NH-stretching band around 3200 cm^{-1}, C-H stretching at 2900 cm^{-1}. The presence of δ-lactam carbonyl group is indicated by the absorption at 1695 cm^{-1} as observed in case of 6-methyl-1,4-benzoxazin-3(2H)-one (compound IVb) that supports the lactam structure (I).

PMR Spectra :

Compound (IVa) :

1,4-Benzoxazin-3(2H)-one :

[Fig. 2]

The presence of 'sharp singlet' integrating to two protons at 4.5 - 5.0, δ (ppm) indicate the presence of C$_2$-methylene protons (-OCH$_2$) which fixes the position of C$_2$-methylene protons in the compound IVa and eliminate the possibility of methylene proton participating in keto-enol tautomerism.

The four aromatic protons are not representing 'singlet' around 7.0, δ (ppm), the 'doublet' appeared at 7.25, δ (ppm) with J_{ortho} = 9Hz; indicates the ortho coupling of C_8-proton which is highly shielded due to the presence of oxygen at position one in benzoxazine ring. The C_7-proton splits as 'doublet-doublet' at 7.4, δ (ppm) with J_{ortho} = 9Hz; due to ortho coupling with C_8-proton and J_{meta} = 3Hz; due to meta coupling with C_5-proton. The doublet at 7.7, δ (ppm) with J = 3Hz, corresponds to C_5-proton which is meta coupled with C_7-proton.

The secondary imido proton appeared as 'broad singlet' integrating to one proton at 8.4, δ (ppm) corresponding to NH proton of (CO-NH) group. This establishes the structure of the compound IVa.

Compound (IVb) :

6-Methyl-1,4-benzoxazin-3(2H)-one :
[Fig. 3]

Sharp singlet at 2.05, δ (ppm) integrating to three protons indicates methyl group attached to aromatic ring. The two magnetically equivalent protons of C_2-methylene are observed as a 'singlet' at 4.52, δ (ppm) indicates two C_2-methylene protons. The aromatic splitting pattern of the compound shows 'doublet' at 6.8, δ (ppm) having J_{ortho} = 9.8Hz.

Corresponding to C_8-proton while 'doublet-doublet' at 6.95 δ (ppm) (J_{ortho} = 9Hz; J_{meta} = 2.5Hz), represents C_7-proton. The presence of C_5-proton is indicated by the presence of 'doublet' at 7.3, δ (ppm) with J_{meta} = 2.5 Hz. The NH proton of amide group appears in the form of a 'broad singlet' exchangeable with D_2O.

Similarly, the structures of compound IVc and IVd have been confirmed by PMR.

PMR Spectra :

Compound (Va) :

4-Carboethoxy-1,4-benzoxazin-3(2H)-one :

[Fig. 4]

The presence of a 'triplet' integrating to three protons in the region 1.2 - 1.4 δ (ppm) indicates methyl-protons of an ester. The observed splitting pattern is due to adjacent methylene protons. A 'quartet' is encountered between 4.1 - 4.3 δ (ppm) integrating to two protons of methylene group of an ethyl ester. A 'sharp singlet' corresponding to two protons observed at 4.6, δ (ppm) indicates the presence of methylene protons of $-OCH_2$ group. This peak appeared at down field region due to the presence of vicinal electronegative oxygen atom. A 'doublet' is observed between 6.7 - 6.8, δ (ppm) with J = 8.0 Hz indicating that the ortho coupling of C_8-proton with C_7-proton. Two 'doublets' encountered between 7.05 - 7.15, δ (ppm) (J_{ortho} = 8.0 Hz and J_{meta} = 3.0 Hz) indicates the presence of C_7-proton ortho coupled with C_8-proton and meta coupled with C_5-proton in the benzoxazine ring. A 'doublet' with J_{meta} = 3 Hz appeared at 7.35, δ (ppm) proved the presence of meta coupling of C_5-proton with C_7-proton. Thus PMR study proves the structure assigned to the compound Va in Scheme-1.

<u>Compound (Vb)</u> :

<u>6-Methyl-4-carboethoxy-1,4-benzoxazin-3(2H)-one</u> :

[Fig. 5]

A 'triplet' encountered at 1.3,   (ppm) integrating to three protons due to ester methyl group and a 'singlet' observed at 2.25, δ (ppm) corresponding to protons of aromatic C_6-CH_3 group. A quartet at 4.2, δ (ppm) is due to two protons of CH_2 group of an ethyl ester. The PMR signal observed at 4.55 δ (ppm) corresponds to two protons of $-OCH_2$ group. The aromatic splitting pattern of this compound shows a 'doublet' at 6.75, δ (ppm) (J_{ortho} = 8.5 Hz), 'doublet-doublet' at 6.9, δ (ppm) (J_{ortho} = 8.5 Hz, J_{meta} = 3 Hz) and a 'doublet' at 7.35, δ (ppm) corresponding to C_8-H, C_7-H and C_5-H respectively.

Compound (Vc) :

6-Chloro-7-methyl-4-carboethoxy-1,4-benzoxazin-3(2H)-one :

[Fig. 6]

The presence of 'triplet' at 1.5, δ (ppm) integrating to three protons indicates methyl proton of an ester group. A 'sharp singlet' at 2.55 δ (ppm) is due to aromatic methyl group attached to C_7-carbon atom. The 'quartet' encountered at 4.40, δ (ppm) is due to methylene protons of ester group. The PMR signal of $-OCH_2$ group is observed at down field region 4.75δ(ppm) due to the presence of electron withdrawing chlorine substituent at C_6. The two aromatic protons, one observed at 6.8 δ (ppm), C_8-H and another at 7.65, δ (ppm) C_5-H.

Compound (Vd) :

6,8-Dimethyl-4-carnoethoxy-1,4-benzoxazin-3(2H)-one :

[Fig. 7]

The presence of 'triplet' at 1.05, δ (ppm) is indicative of an ester methyl gfoup. The two 'sharp singlets' integrated to three protons observed at 2.3 and 2.38, δ (ppm) are due to C_8-Ar-CH_3 and C_6-Ar-CH_3 respectively. The usual OCH_2-methylene signal is observed at 4.6, δ (ppm). The two aromatic protons C_7-H and C_5-H are observed at 7.3 and 7.4, δ (ppm) respectively.

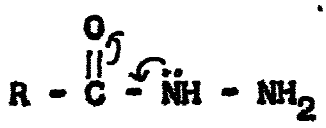
6-Methyl-4(hydrazido)-1,4-benzoxazin-3(2H)-one :

UV Spectrum :

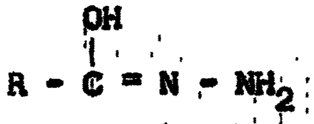
Compound (VIb) :

[Fig. 8]

The UV spectrum was recorded in 95 % ethanol. The observed λ_{max} = 280 nm of this compound indicates that the presence of a chromophoric group which shifts the absorption maxima of corresponding parent 1,4-benzoxazin-3-one from 256.4 nm towards longer wavelength.



$R - \overset{\overset{\Large O}{||}}{C} - \ddot{N}H - NH_2$



$R - \overset{\overset{\Large OH}{|}}{C} = N - NH_2$

[R = 6-methyl-4(N-substituted)-1,4-benzoxazin-3(2H)-one]

IR Spectrum :

Compound (VIb) :

[Fig. 9]

A doublet is observed at 3280 cm^{-1} indicating the presence of $-NHNH_2$ group in the compound. The presence of a band at 2880-2900 cm^{-1} indicates the C-H stretching frequency. The peak at 1690-1700 cm^{-1} indicates the δ -lactam carbonyl function. A band at 1600 cm^{-1} indicates the presence of phenyl ring in the compound.

PMR Spectrum :

Compound (VIb) :

[Fig. 10]

The 'singlet' at 2.2, δ(ppm) integrating to three protons is due to the presence of aromatic methyl group at C_6. The broad 'singlet' observed at 4.0, δ(ppm) and is exchangeable with D_2O is due to NH_2 group. The 'broad singlet' observed may be due to possibility of hydrogen bonding. A 'singlet' observed at 4.55, δ(ppm) is due to the presence of methylene proton of $-OCH_2$ group. The aromatic splitting pattern is clearly distinguishable. A doublet at 6.85, δ(ppm), (J_{ortho} = 8 Hz), a 'doublet-doublet' at 6.95, δ (ppm) (J_{ortho} = 8 Hz, J_{meta} = 3 Hz) and a 'doublet' at 7.3, δ (ppm) (J_{meta} = 3 Hz) are due to C_8-H, C_7-H and C_5-H protons respectively.

Compound (VId) :

6,8-Dimethyl-4(hydrazido)-1,4-benzoxazin-3(2H)-one :

[Fig. 11]

PMR Spectrum :

Two 'sharp singlets' encountered at 2.3 and 2.38, δ(ppm) corresponding to two aromatic methyl groups attached to C_8 and C_6 carbon atoms of benzoxazine ring. The protons of 'OCH_2' group are observed as a 'sharp singlet' at 4.62, δ(ppm).

The two aromatic protons observed as two separate singlets at 7.4 and 7.6, δ (ppm) corresponding to C_7-H and C_5-H respectively.

Compound (VIIa) :

4(N-dimethyl hydrazido)-1,4-benzoxazin-3(2H)-one :

UV Spectrum :

UV spectrum of compound VIIa in 95 % ethanol shows λ_{max} = 285 nm. The shift of absorption maxima of 1,4-benzoxazin-3(2H)-one from 256.0 nm to 285.0 nm is due to the presence of N-dimethyl hydrazido group attached to nitrogen atom at position 4 in the 1,4-benzoxazin-3(2H)-one.

Compound (VIId) :

6,8-Dimethyl, 4(N-dimethyl hydrazido)-1,4-benzoxasin-3(2H)-one :

[Fig. 12]

IR Spectrum :

A band at 1600 cm^{-1} is due to C=C stretching of the phenyl ring. The δ-lactam ketone is observed as a band between 1670 - 1690 cm^{-1}. The methylene stretch and broad singlet due to (-NH-) are observed at 2900 cm^{-1} and 3160 cm^{-1} respectively in IR spectrum.

Compound (VIIa) :

4-N-dialkyl hydrazido-1,4-benzoxazin-3(2H)-one :

[Fig. 13]

PMR Spectrum :

The PMR spectrum of N-dialkyl derivative of VIa i.e. compound VIIa is interesting because two methyl groups bonded to same nitrogen atom are observed as two 'sharp singlets' at 1.9 and 2.05, δ (ppm) each integrating to three protons, which indicates that nonequivalence of two methyl groups. The methylene signal of $-OCH_2$ group is observed at 4.65, δ (ppm). The aromatic pattern of the compound is distinguishable. Four doublets observed at 6.8, 7.05, 7.1 and 7.3 δ (ppm) are due to C_8-H, C_7-H, C_6-H and C_5-H protons respectively.

Compound (VIIIb) :

6-Methyl-2H-(1,2,4)-triazolo-3-oxo-[3,4-c]-benzoxazine :

[Fig. 14]

IR Spectrum :

The presence of NH in the compound is ascertained by the presence of a broad band in the region 3200-3300 cm^{-1}. The presence of carbonyl group ($>C=O$) and cyno group ($-C=N-$) in the compound have been confirmed by the presence of IR bands at 1660 cm^{-1} and 1620 cm^{-1} respectively. The band at 1600 cm^{-1} is due to phenyl ring.

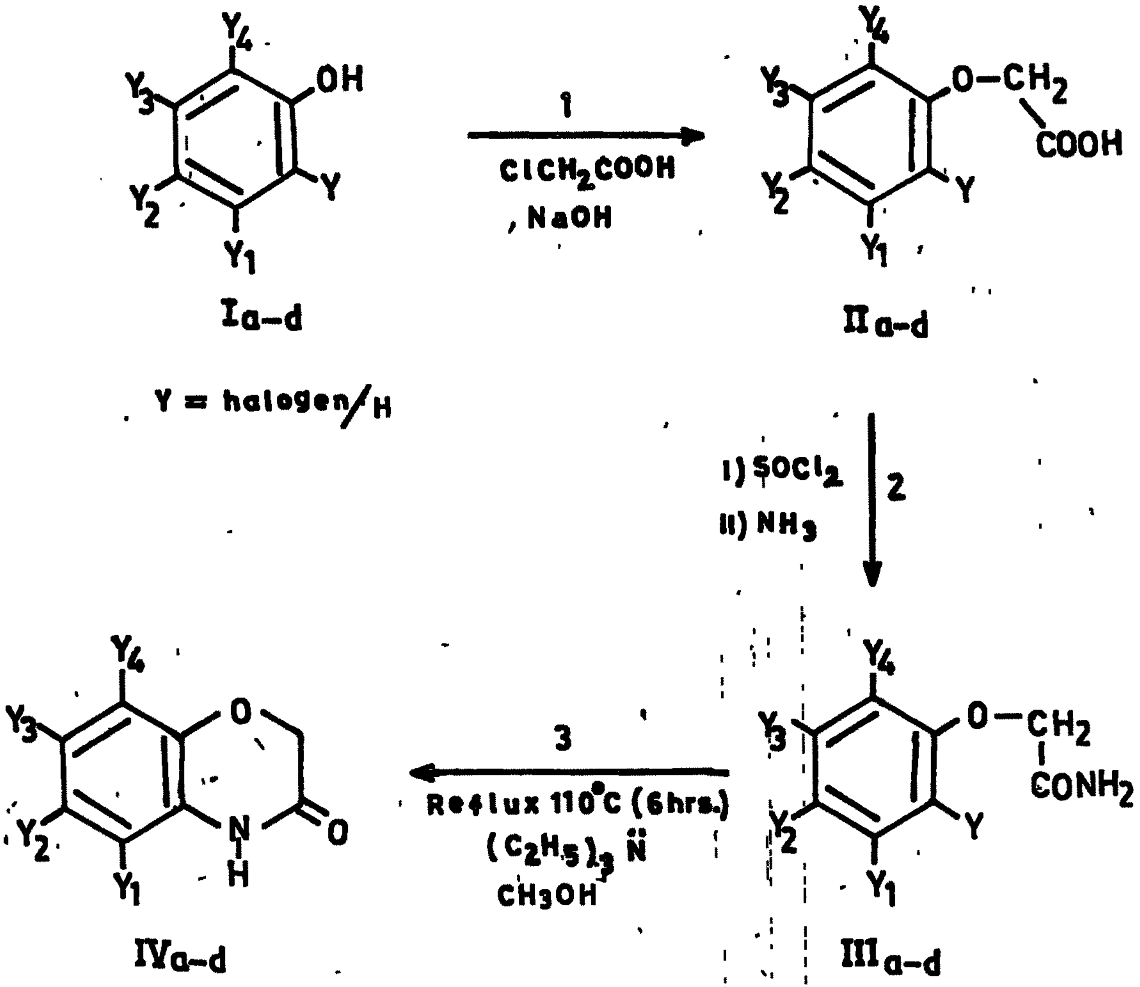
Thus the structures of the above compounds were confirmed.

Scheme 1

Scheme 2

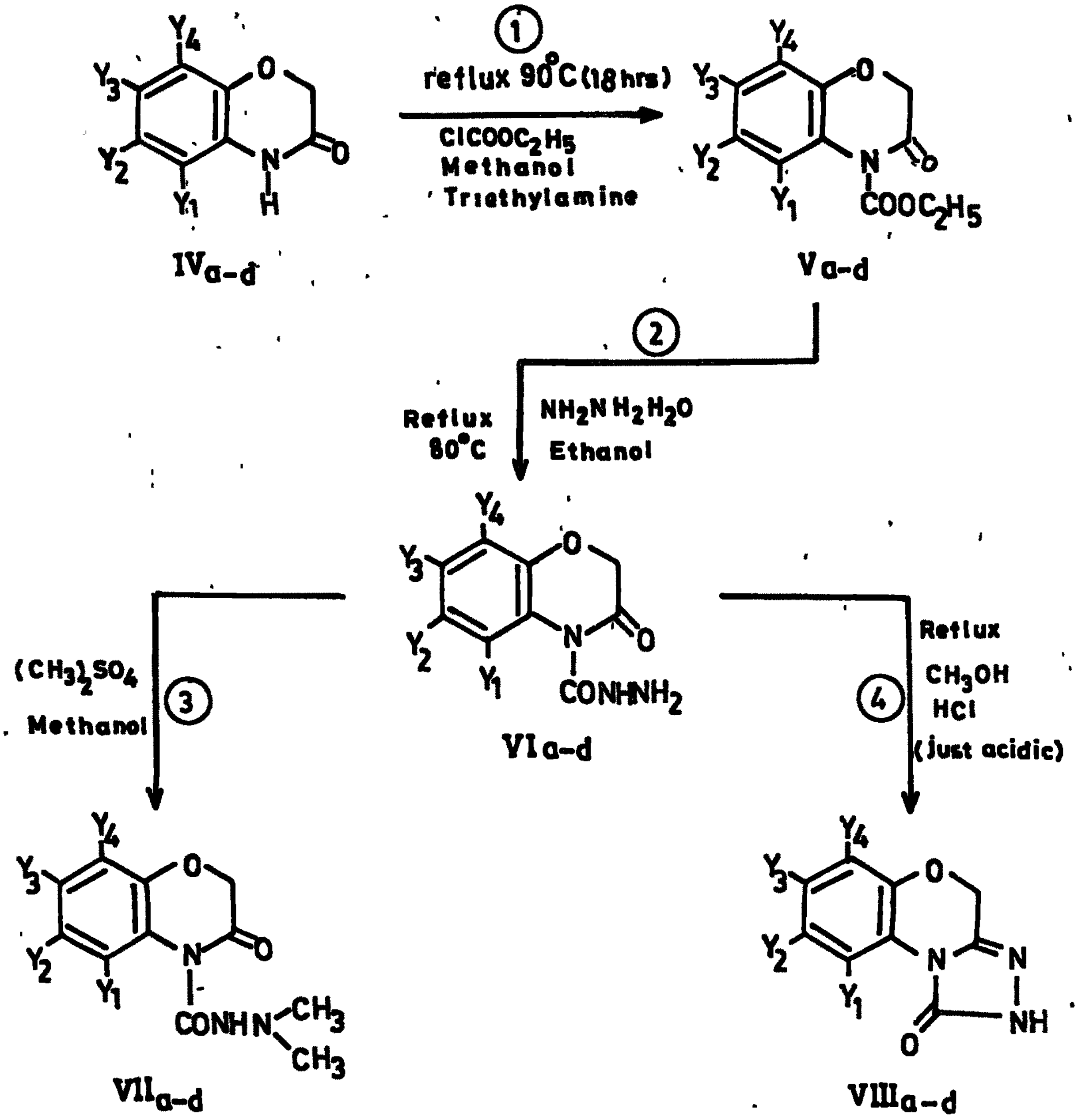
Spectra

SCHEME-1



Comp.d I–IV	Y_1	Y_2	Y_3	Y_4
a	H	H	H	H
b	H	CH_3	H	H
c	H	Cl	CH_3	H
d	H	CH_3	H	CH_3

SCHEME-2



Comp^d IV–VIII	Y_1	Y_2	Y_3	Y_4
a	H	H	H	H
b	H	CH_3	H	H
c	H	Cl	CH_3	H
d	H	CH_3	H	CH_3

IR Spectrum of 6-Methyl-1,4-benzoxazin-3(2H)-one, (IV_b).

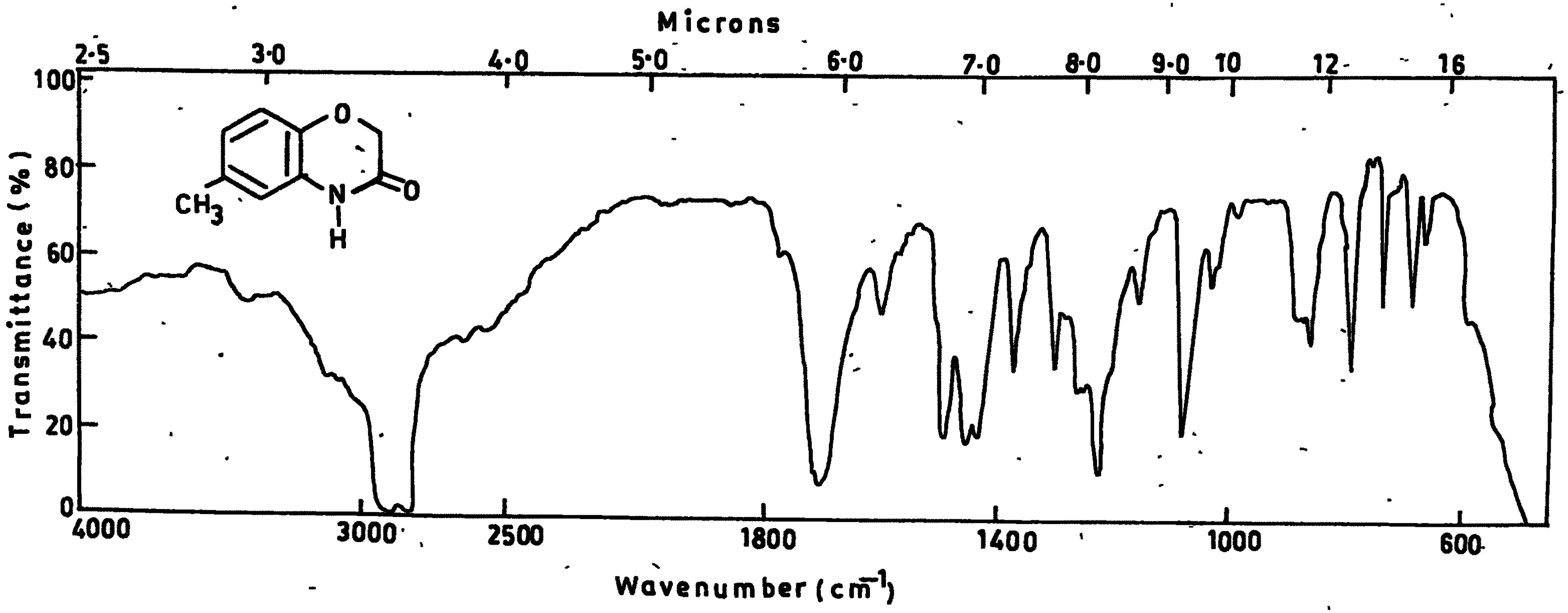


Fig. 1

PMR Spectrum of 1,4-benzoxazin-3(2H)-one, (IVa).

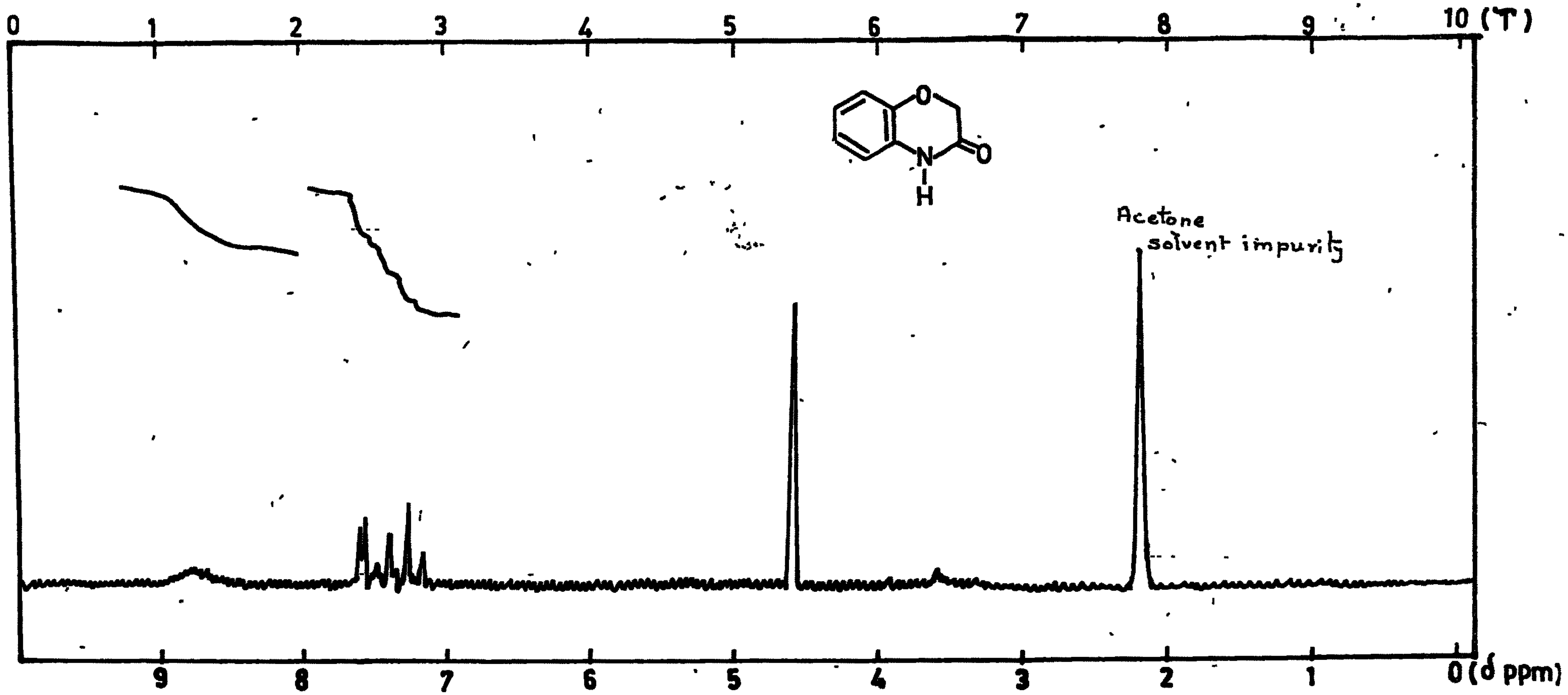


Fig. 2

PMR Spectrum of 6-Methyl-1,4-benzoxazin-3 (2H)-one ,(IV$_b$) .

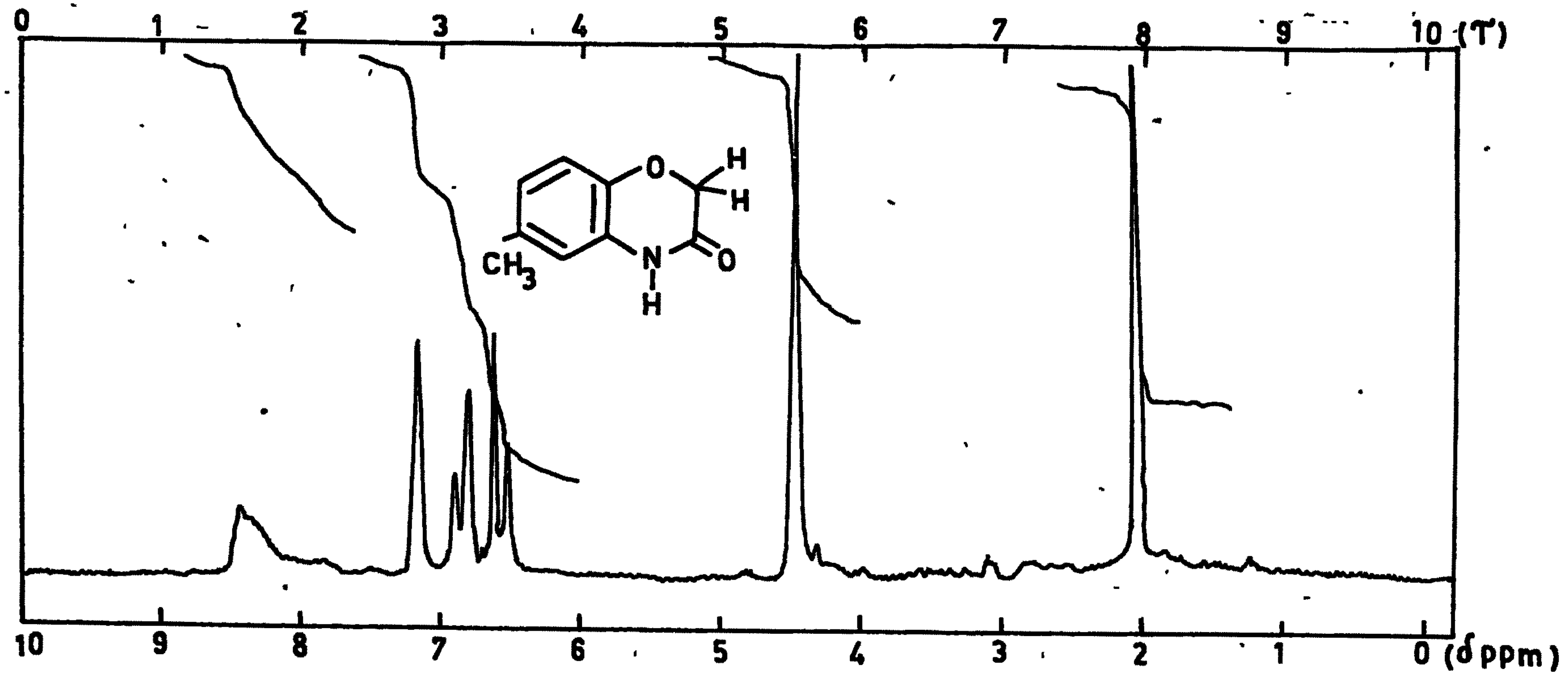


Fig. 3

PMR Spectrum of 4-Carboethoxy-1,4-benzoxazin-3(2H)-one ,(Va).

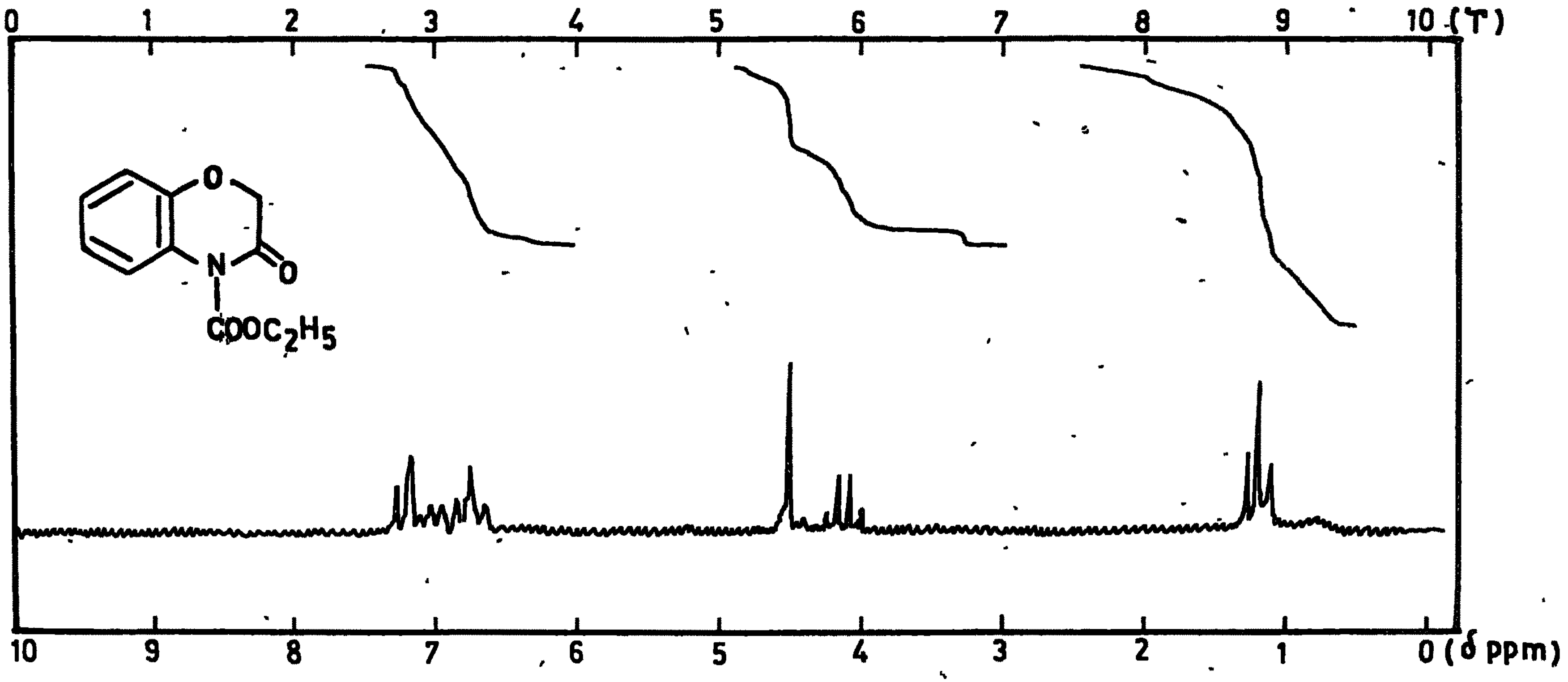


Fig. 4

PMR Spectrum of 6-Methyl-4-carboethoxy-1,4-benzoxazin-3(2H)-one, (V_b).

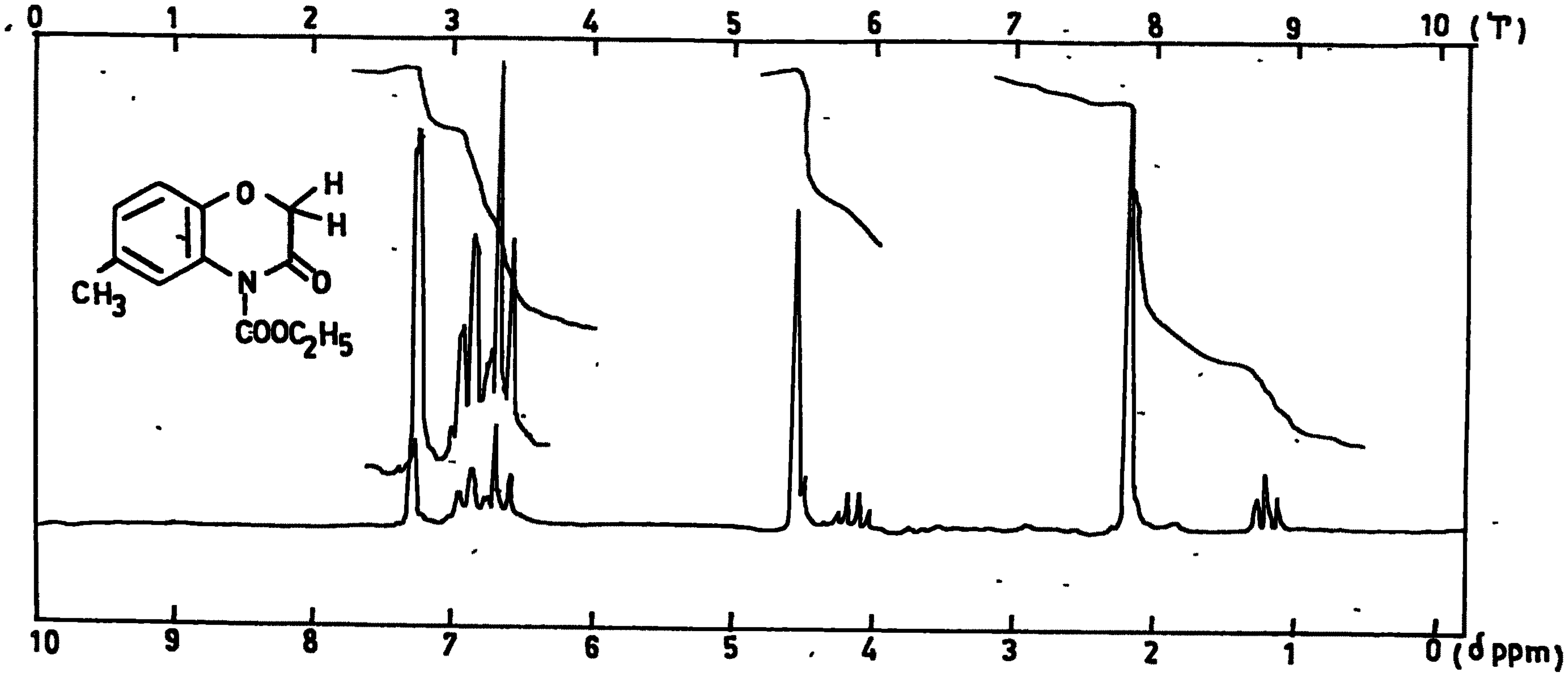


Fig. 5

PMR Spectrum of 6-Chloro-7-Methyl-4-carboethoxy-1,4 benzoxazin-3(2H)-one,(Vc).

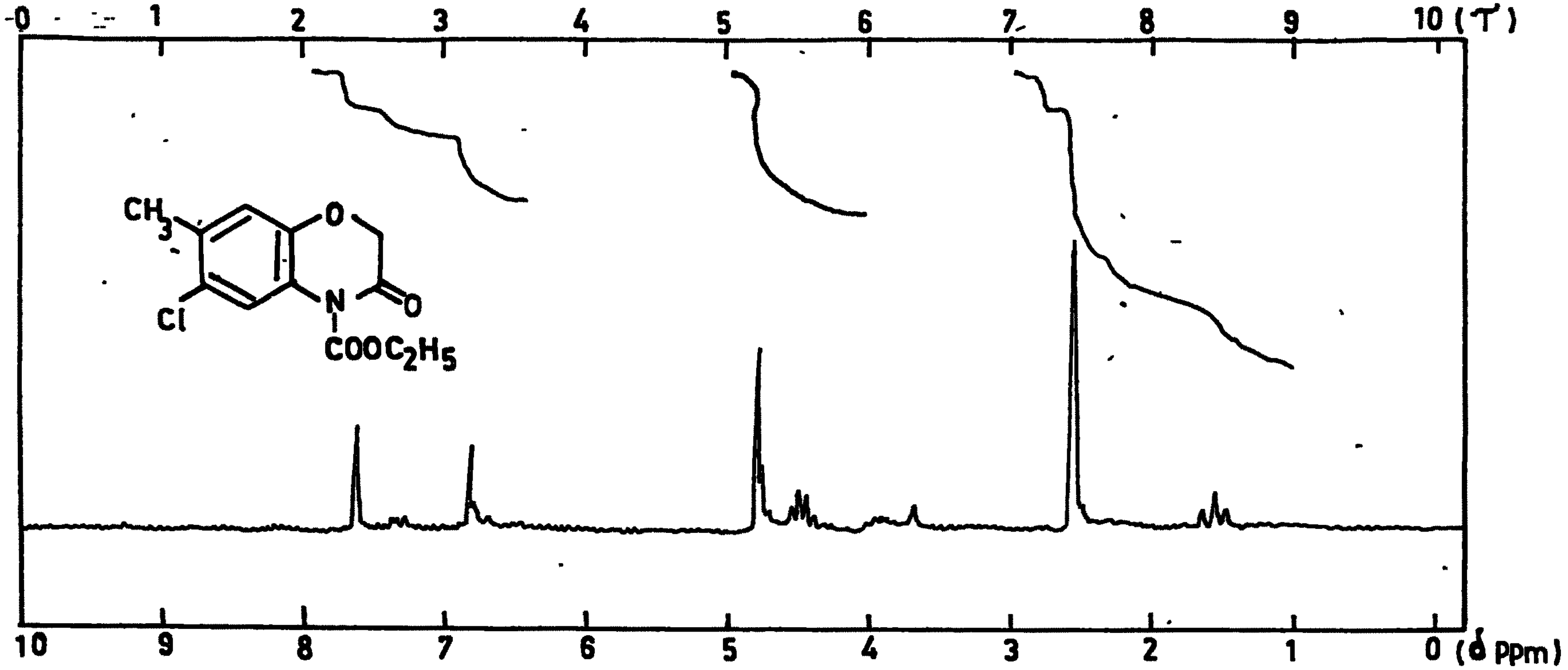


Fig. 6

PMR Spectrum of 6,8-Dimethyl-4-Carboethoxy-1,4-benzoxazin-3(2H)-one, (Vd).

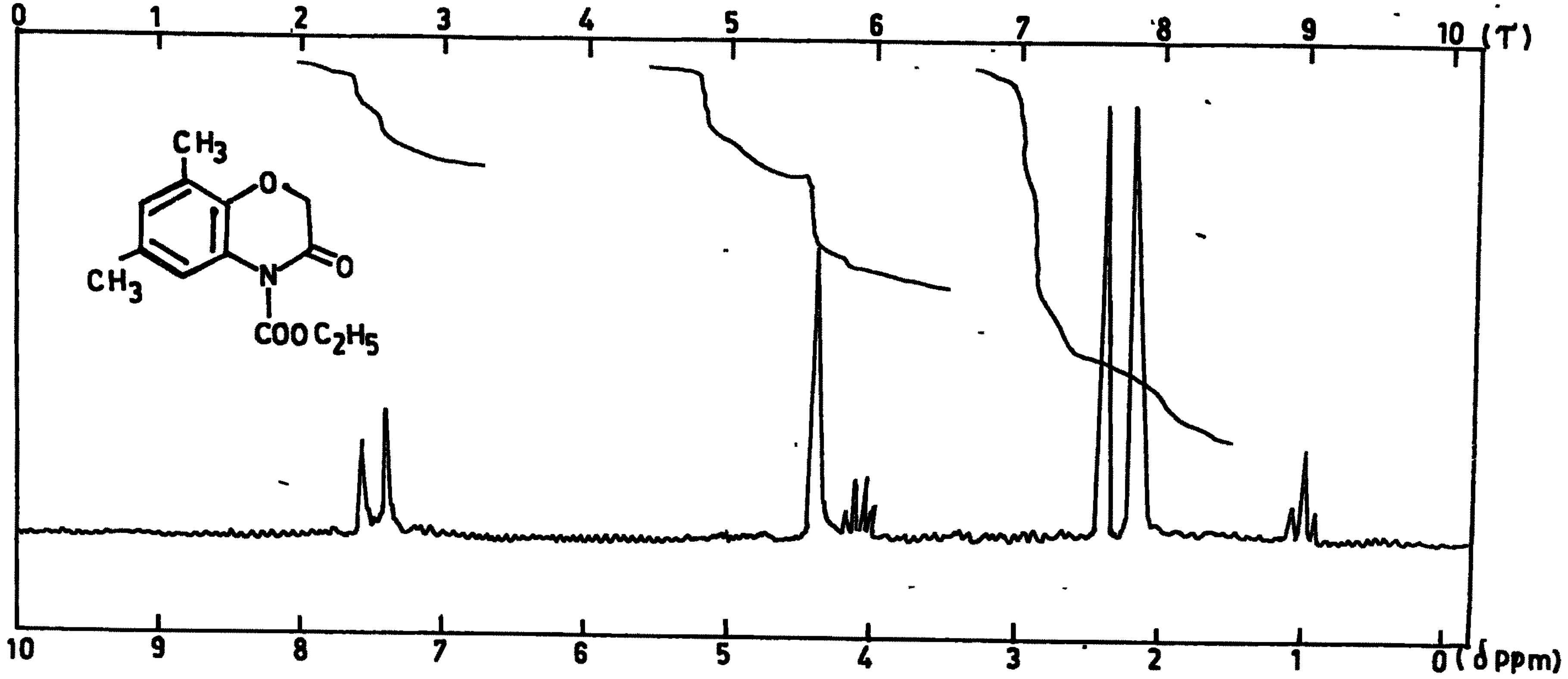


Fig. 7

U.V Spectrum of 6 Methyl-4-hydrazido-1,4-benzoxazin-3(2H)-one ,(VI_b).

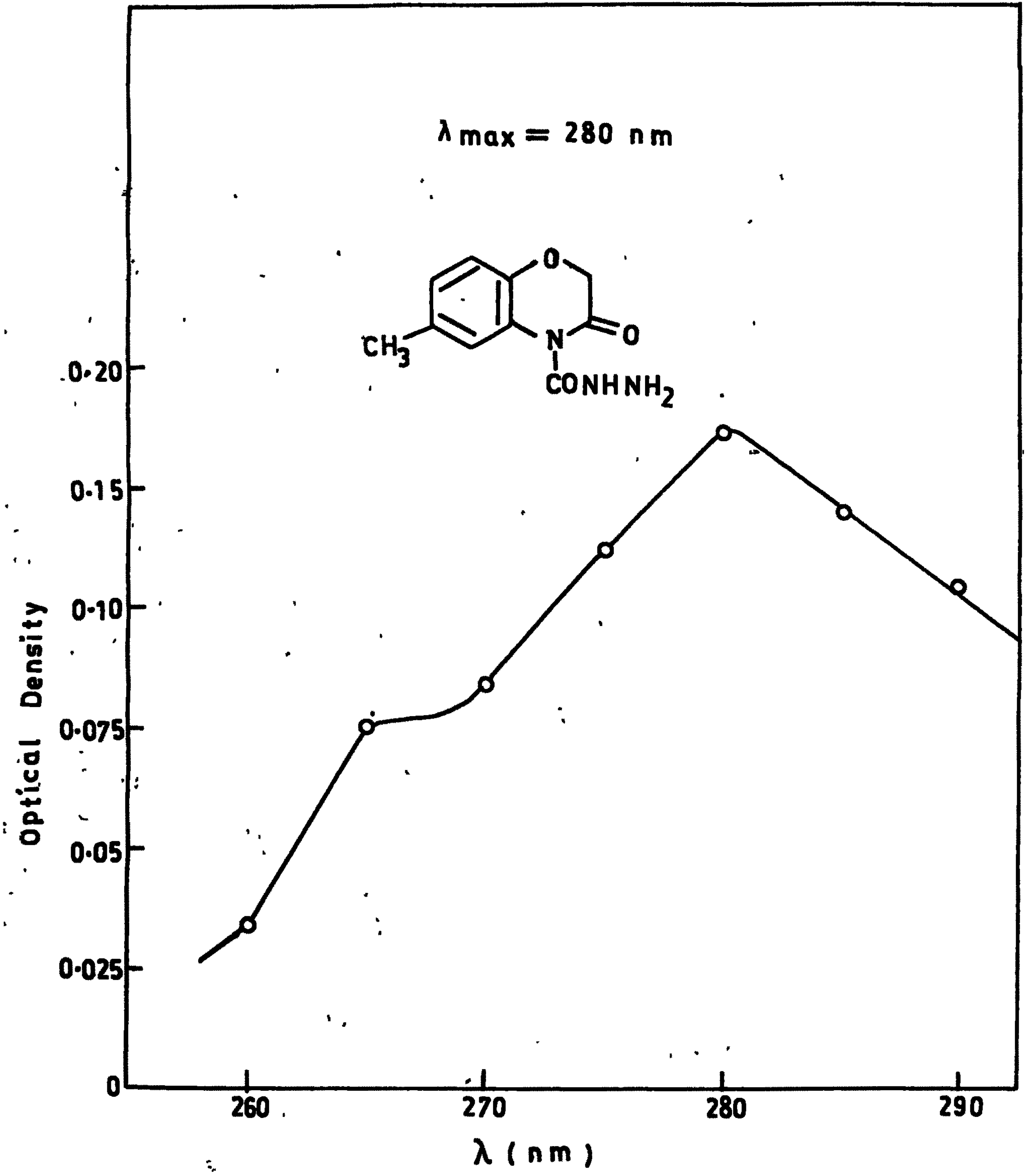


Fig. 8

IR Spectrum of 6-Methyl-4-hydrazido-1,4-benzoxazin-3(2H)-one,(VI$_b$).

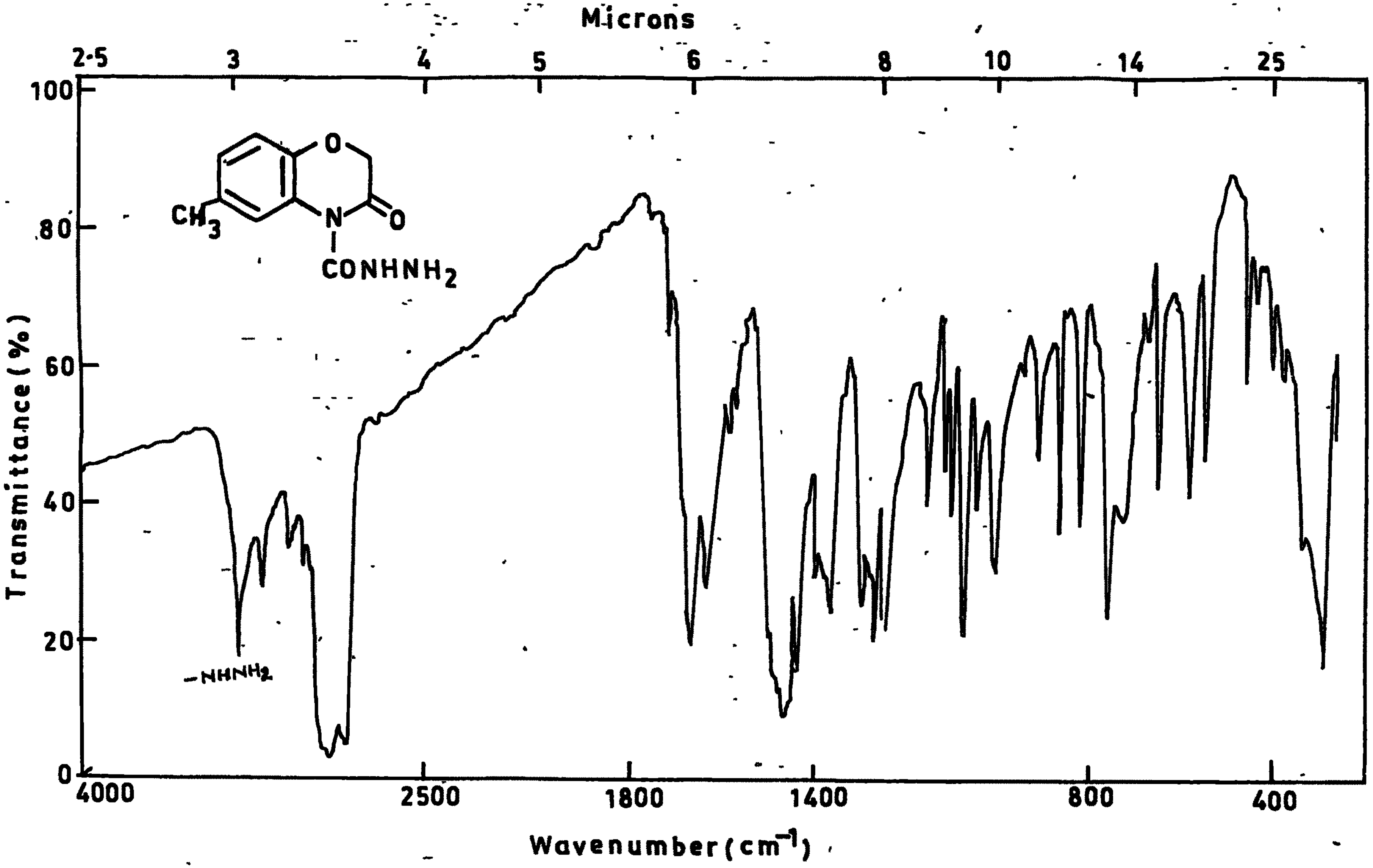


Fig. 9

PMR Spectrum of 6-Methyl-4-hydrazido-1,4-benzoxazin-3 (2H)-one, (VI b).

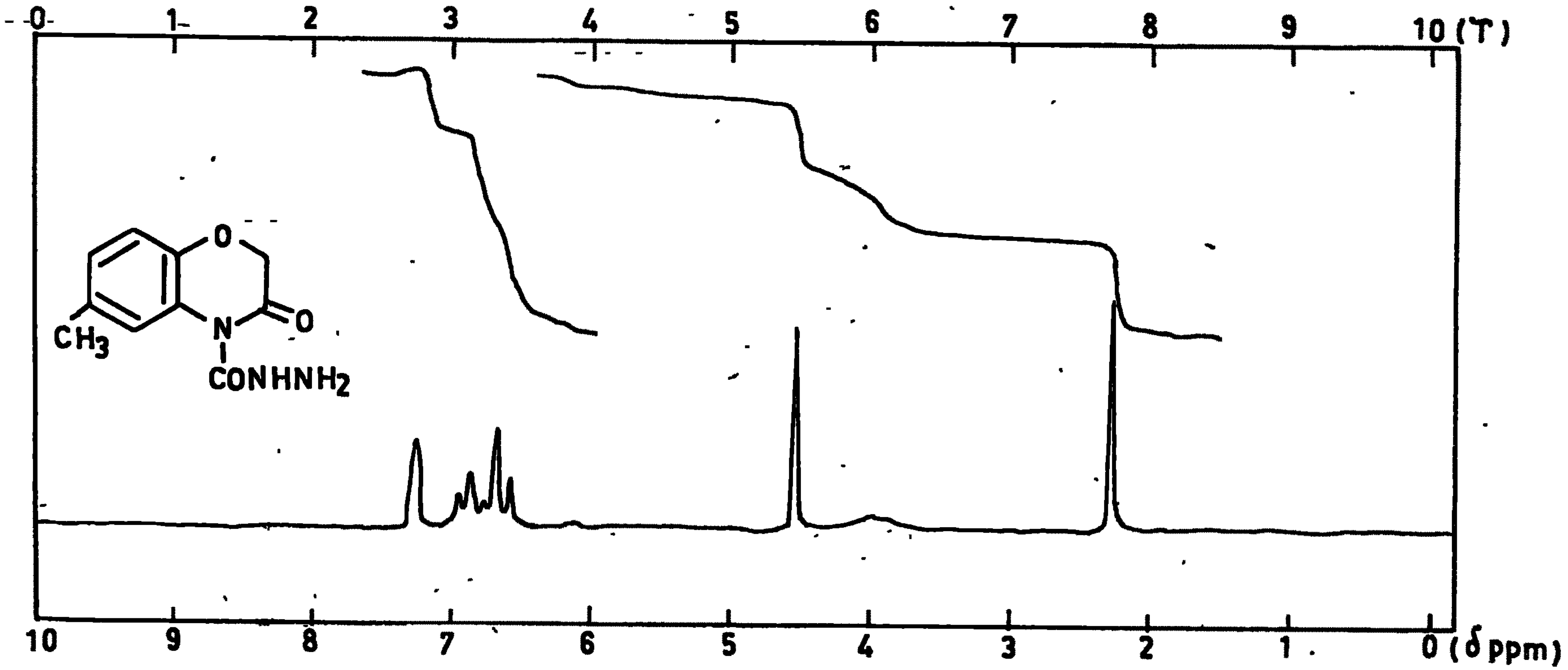


Fig. 10

PMR Spectrum of 6,8-Dimethyl-4-hydrazido-1,4-benzoxazin-3(2H)-one (VI$_d$).

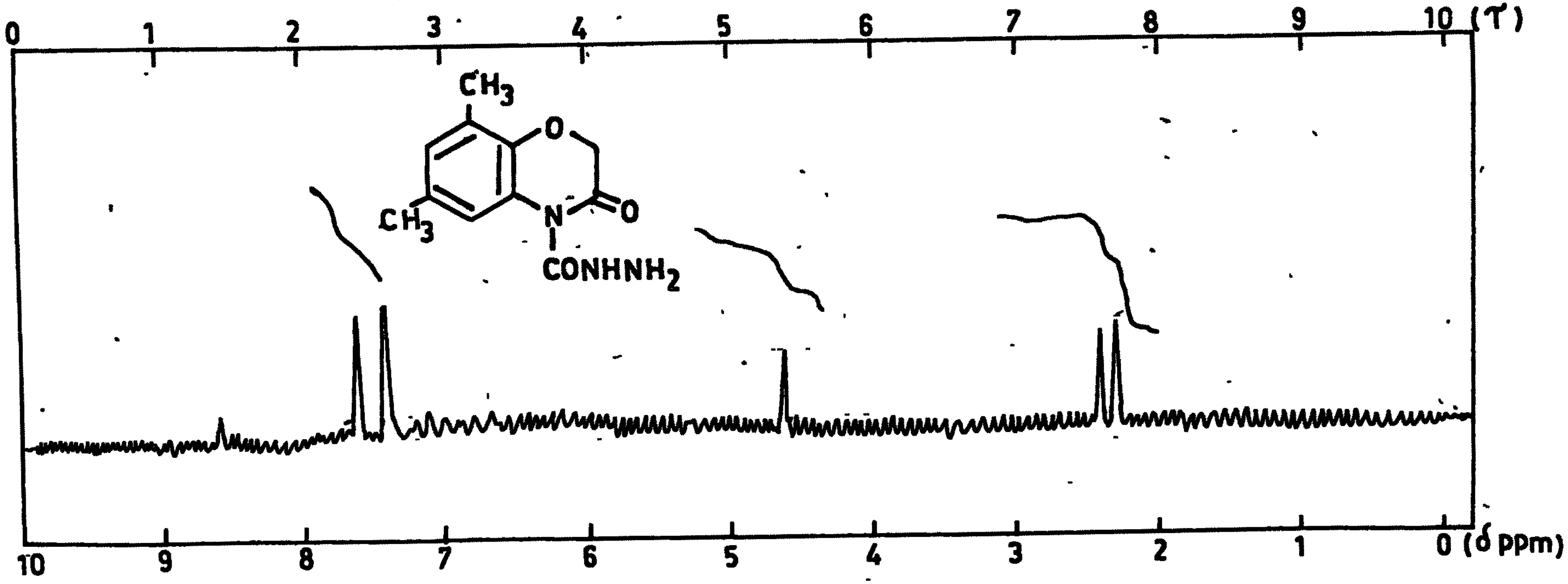


Fig. 11

IR Spectrum of 6,8-Dimethyl,4 (N-dimethyl hydrazido)-1,4-benzoxazin-3(2H)-one ,(VII_d).

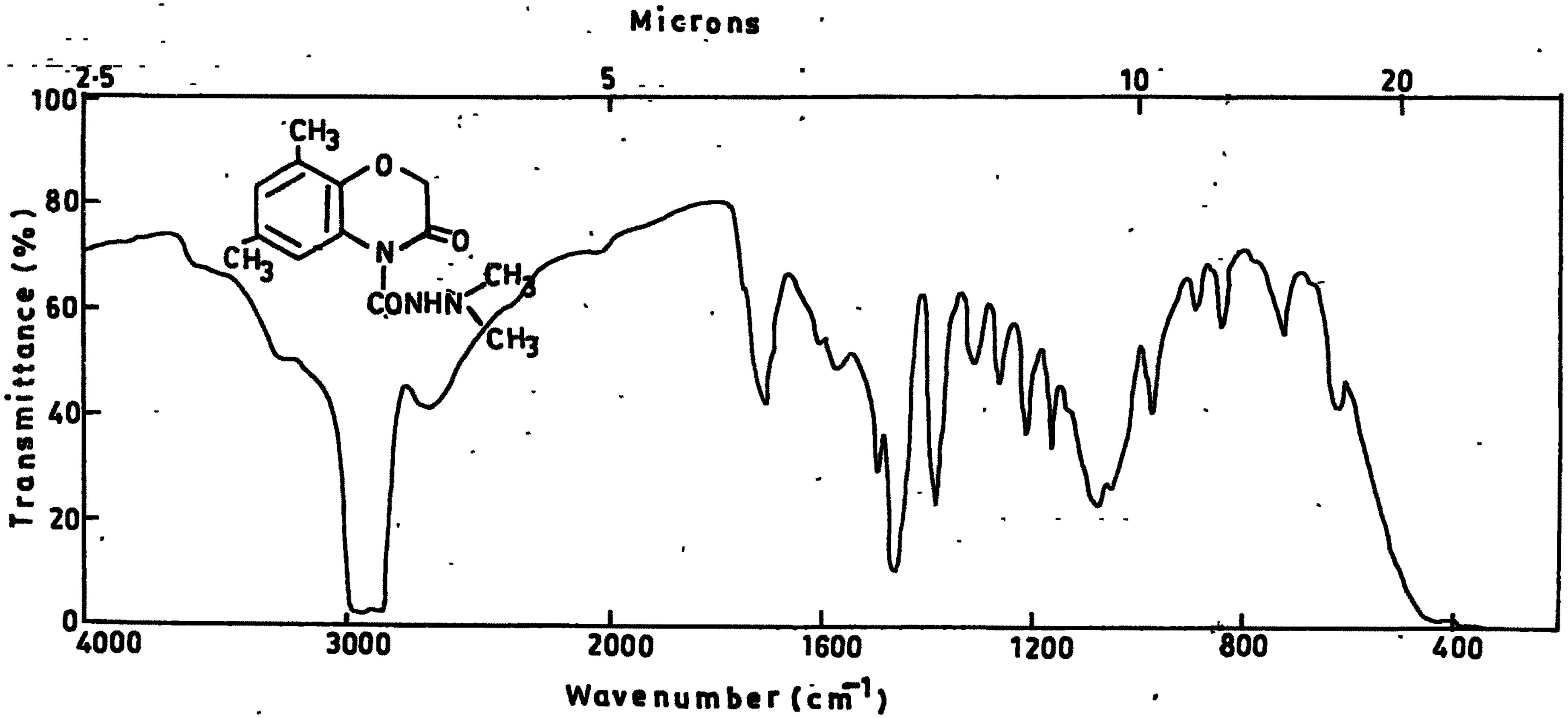


Fig. 12

PMR Spectrum of 4-(N-dialkyl hydrazido)-1,4-benzoxazin-3(2H)-one,(VIIa).

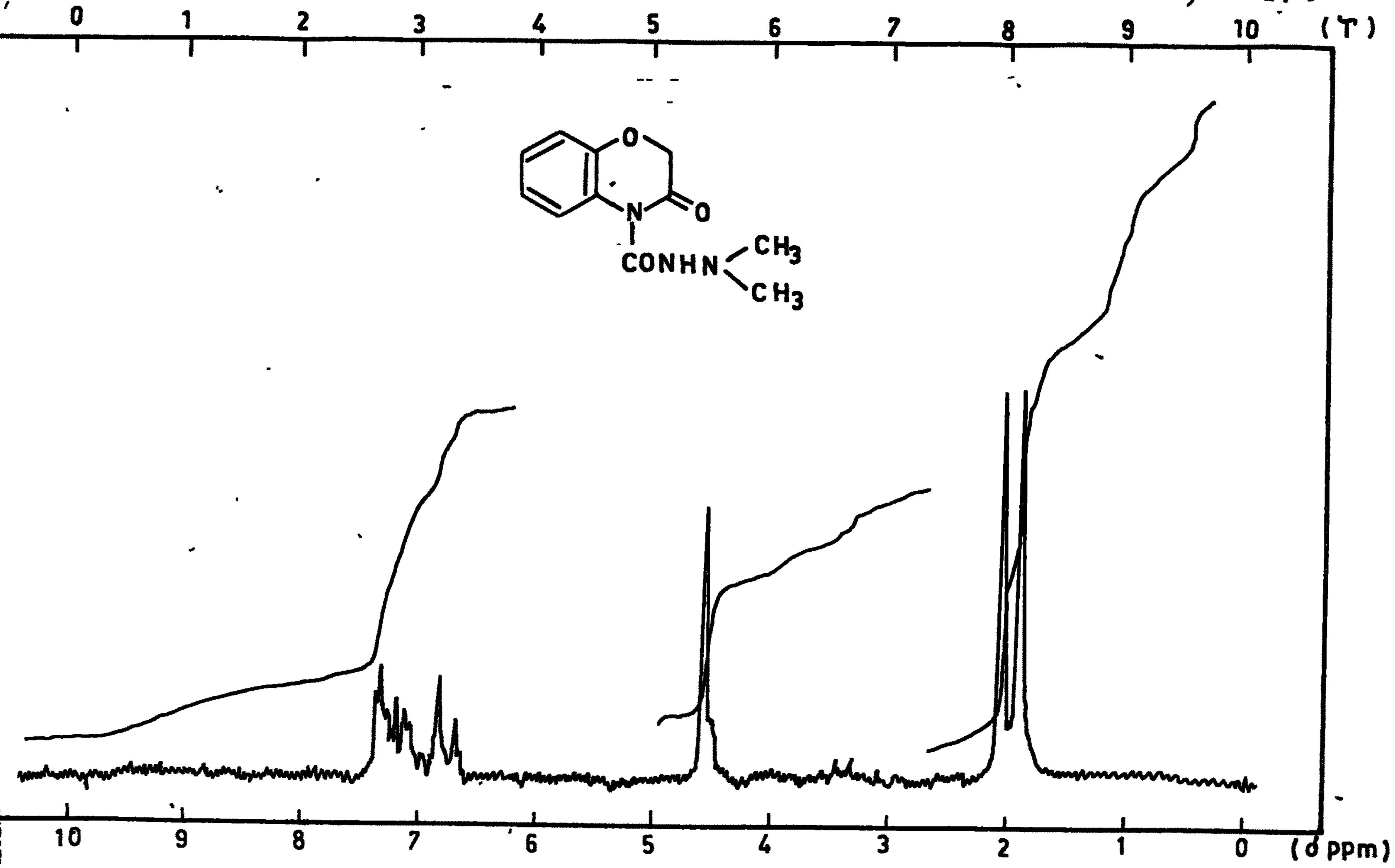


Fig. 13

IR Spectrum of 6-Methyl-4H-(1,2,4)-triazolo-3-oxo-[3,4-c]-benzoxazine,(VIII$_b$).

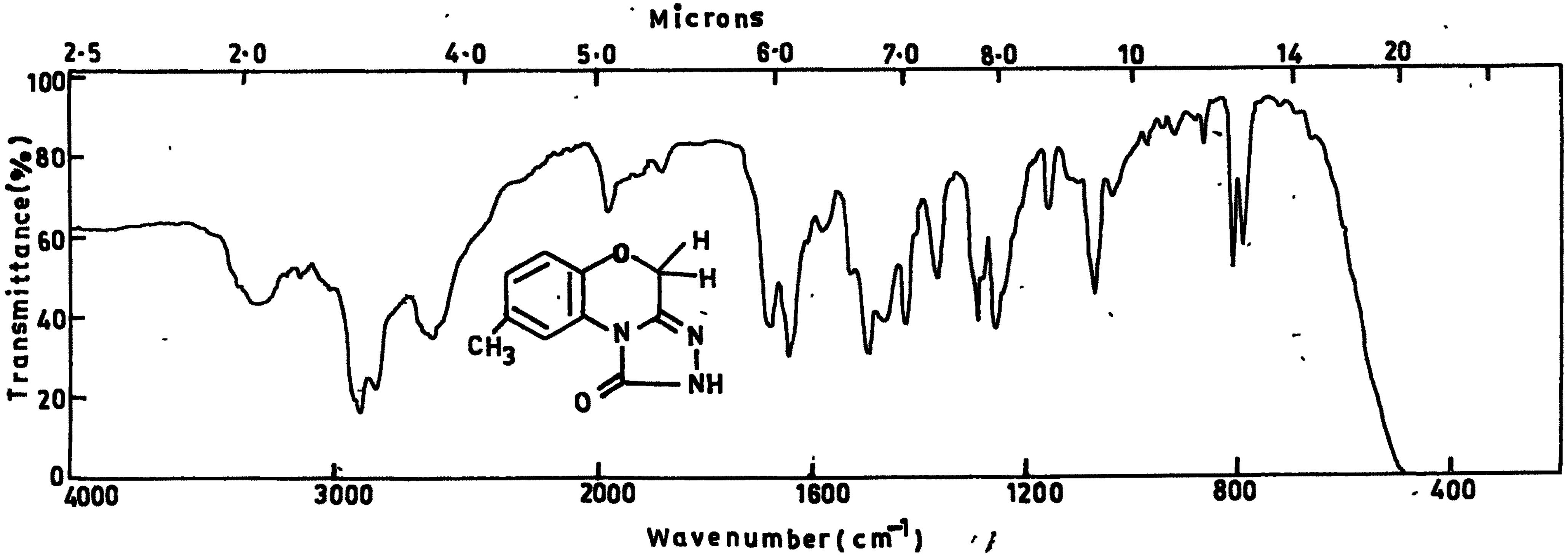


Fig. 14