CHAPTER-II

EXPERIMENTAL

EXPERIMENTAL WORK

Experimental work has been divided into three parts :

Part I : consists of synthesis of some new derivatives of N^1-Hydrazido-quinolin-2(1H) one.

Part II : consists of some new derivatives of N^1- Methyl-hydrazido-quinolin-2(1H)-ones.

Part III : consists of Antimicrobial screening of the synthesized compound.

i) GENERAL REMARKS :

i) Percentage yield, physical constants (M.P./B.P.), elemental analysis (found and calculated) and spectral characteristics of the synthesised compounds have been reported.

ii) M.P./B.P. were determined by open capillary method and are uncorrected.

iii) UV spectra were recorded in 95% ethanol on a "Beckmann DK-1" Spectrophotometer.

iv) IR spectra were recorded in KBr pellets/nujol on a "Perkin-Elmer-237" Spectrophotometer.

v) ^{1}HNMR spectra were recorded on "Perkin-Elmer R-32 Spectrometer" using TMS as an internal reference and $CCl_4/CDCl_3$/TFA as solvent The chemical shifts (δ values) were reported in ppm.

vi) MASS spectra were recorded on "El-MS computer" system.

vii) The purity of the compounds was checked by TLC using silica gel as adsorbent.

EXPERIMENTAL PROCEDURE

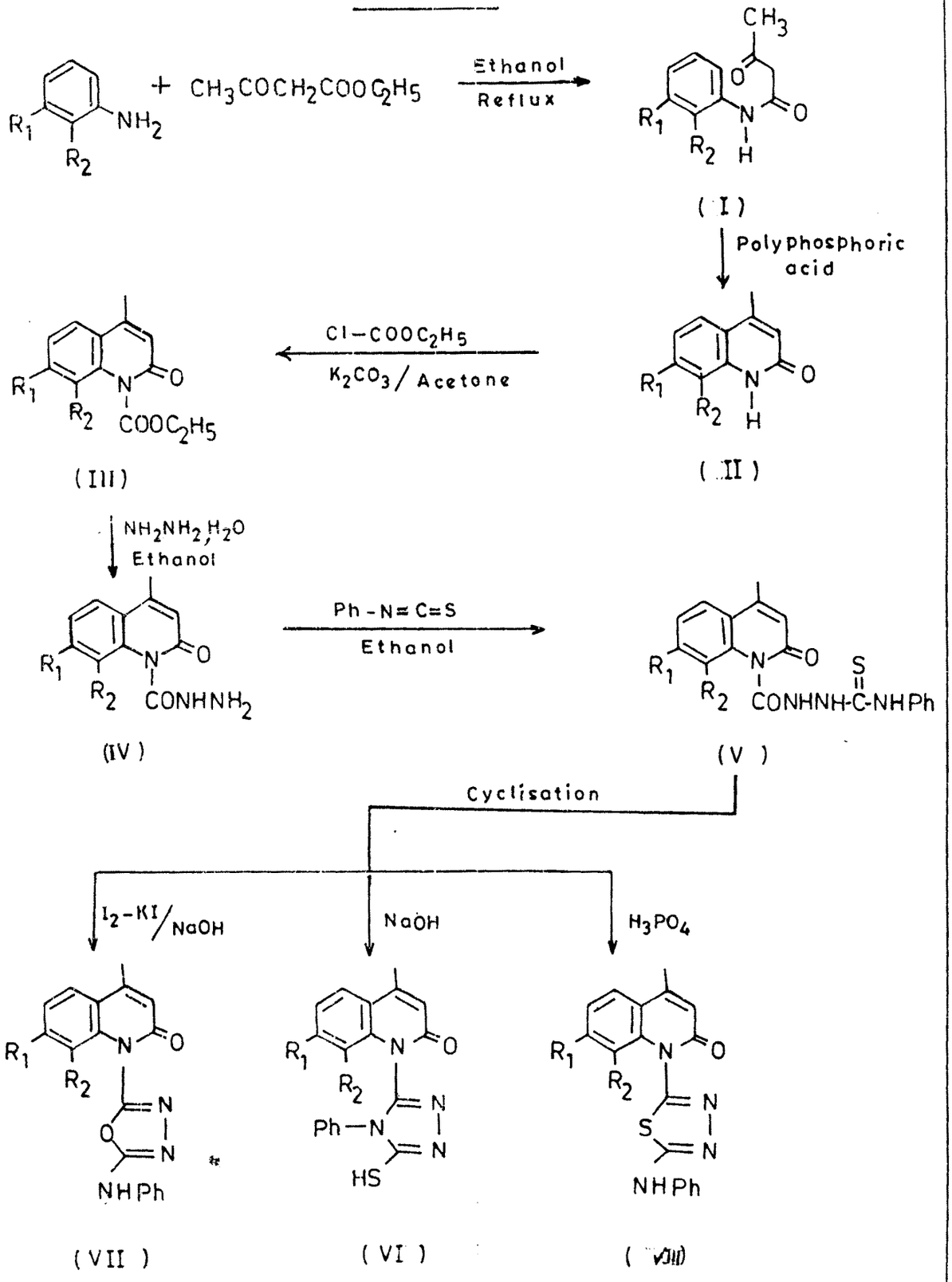
Part - I : Synthesis of some new derivatives of N^1-Hydrazido-quinolin-2(1H) one :

The strategy employed for the synthesis of N^1-substituted heterocyclic quinolin-2(1H)-one derivatives has been reported. First step is the preparation of substituted acctoacetanilides (I.) followed by PPA cyclisation to yield (II). N-Carbethoxylation of 4-methyl quinolin-2(1H)-ones(II) with ethyl chloroformate gave N^1-carbethoxy, 4-methyl quinoline-2(1H)-ones (III) which when reacted with hydrazine hydrate in ethanol formed N^1-hydrazido-4-methyl quinolin-2(1H)-ones(IV). The reaction of IV with phenylisothiocyanate yielded N^1-substituted quinolin-2(1H)-only thiosemicarbazides as a key intermediates (V).These when cyclised in presence of sodium hydroxide, I_2 inKI and phosphoric acid furnished targetted 5-aryl-2-(4'-methyl, quinolin--2'-one-1'-yl)-5-Mercapto-1,3,4-triazoles (VI), 5-phenyl amino-2(4'-methyl , quinolin-2'-one-1'-yl)-1,3,4-oxadiazoles (VII) and 5-aryl-amino-2-(4'-methyl, quinolin-2'-one-1'-yl)-1,3,4-thiadiazoles(VIII) respectively as shown in Scheme-I. The structures of these compound have been confirmed by IR, PMR, UV spectral and elemental analysis.

ii) Preparation of Acetoacetanilide (Ia) :

In a round bottom flask carrying a reflux condenser a mixture of aniline (9.4 gm, 0.001 mol) and acetoacetic ester (12.6 ml, 0.001 mole) in methanol (20 ml) was heated for 3-4 hours on heating mentle cooled

SCHEME-I


+ CH3COCH2COOC2H5
Ethanol
Reflux
(I)
Polyphosphoric acid
(II)
Cl–COOC2H5
K2CO3 / Acetone
(III)
NH2NH2,H2O
Ethanol
(IV)
Ph–N=C=S
Ethanol
(V)
Cyclisation
I2–KI/NaOH
NaOH
H3PO4
(VII)
(VI)
(VIII)

and neutralised with Na_2CO_3. Heavy liquid separated out was extracted in chloroform and the solvent was removed. The heavy liquid obtained was distilled under reduced pressure to give acetoacetanilide : 35 gm (84.75%), B.P. 139°C at 15 mm .

IR (Nujol) : ν, 3450-3200 (NH), 1700 (Ketone >C=0) 1670-1660 (amido >C=0) 1600 (>C=C<) cm^{-1}.

PMR ($CDCl_3$) : δ , 2.15 (3H,s, $-COCH_3$), 3.3 (2H,s, $-CH_2$), 4.55 (1H,s, NH exchangable with D_2O), 6.9-7.35 (5H,m, Aromatic Protons) ppm. Fig. 1

Other substituted acetoacetanilides have been prepared by similar method and their m.p.,yield & molecular formulla have been incorporated in the Table-Ia and IR, ^1HNMR spectral data in Table - Ib

Table - Ia

Physical and Analytical data of the Acetoacetanilide (1b-c) :

Sr.No.	R_1	R_2	B.P. °C at 15 mm	Yield %	Molecular formulla
Ib	H	CH_3	123	84.20	$C_{11}H_{13}O_2N$
Ic	Cl	H	130	88.90	$C_{10}H_9O_2NCl$

Table - Ib

^{1}H NMR and IR spectral data of the compounds (Ib-c) :

Compd.	Spectral Characteristics	Fig.No.
Ib	^{1}H NMR (CCl_4) : δ , 2.1 (3H, s, $-COCH_3$), 3.4 (2H, s, $-CH_2-$), 4.6 (1H, s, -NH exchangable with D_2O), 6.9 - 7.4 (3H, m- Aromatic protons) ppm.	2
Ib	IR (nujol) : ν, 3300-3200 (NH), 1700-1690 (ketone, >C=0), 1665-1555 (amido, >C=0), 1600-1580 (>C=C<) cm^{-1}.	-
Ic	^{1}H NMR (CCl_4) : δ , 2.12 (3H, s, $-COCH_3$), 2.2 (3H, s, Ar-CH_3), 3.4 (2H, s, $-CH_2-$), 6.8-7.3 (4H,m, Aromatic protons) ppm.	3
Ic	IR (Nujol) : ν, 3350-3200 (NH), 1700-1695 (ketone, >C=0), 1665-1655 (amido, >C=0), 1600 (>C=C<) 760 (C-Cl) cm^{-1}.	-

iii) Preparation of 4-Methyl, quinolin-2(1H)-One :

In a round bottom flask a mixture of acetoacetanilide 1a (17.7 gm, 0.1 mole) and conc. H_2SO_4 (40 ml) was heated on water bath at 70-80°C for 0.5 hr. initially and for 1.0 hr. at 100°C, cooled and poured in 500 ml ice-cold water with constant stirring. The separated product was filtered, dried and recrystallised from ethanol to give IIa, 13 gm, (81.76%); M.P. 227°C;(Found : C, 75.4; H, 5.16; N, 8.75. requires : C, 75.47; H, 5.66; N, 8.81%); IR (KBr): 3200-3100 broad (-NH), 1665 (cyclic amido, C=O), 1600 (C=C) cm^{-1}; ^1H NMR (TFA); δ, 2.45 (3H,s,4-CH_3), 6.6 (1H,s, =CH-), Fig.4. 7.8 - 7.0 (1H, dd, J_{ortho} = 8.0 Hz, J_{meta} = 2.5 Hz, C_6-H), 7.5-7.15 (1H,d, J_{ortho} = 8.0 Hz, C_5 - H), 7.15 - 7.35 (1H, dd, J_{ortho} = 8.0 Hz, J_{meta} = 2.5 Hz, C_8 - H), ppm.. Fig.5.

Other substituted quinolones have been prepared by similar method and their m.p., yield, molecular formula and elemental analysis data have been incorporated in the Table - IIa and IR, ^1H NMR spectral data in Table-IIb.

Table - IIa

Physical and Analytical data of the substituted quinolones (IIb-c) :

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
IIb	H	CH_3	258	80.92	$C_{11}H_{11}ON$	76.10 (76.30)	6.30 (6.36)	8.00 (8.09)
IIc	Cl	H	213	68.39	$C_{10}H_8ONCl$	62.00 (62.18)	4.05 (4.15)	7.05 (7.25)

Table - IIb

IR and ^{1}HNMR spectral data of the compounds (IIb-c)

Compound No.	Spectral characteristics	Fig.No.
IIb	^{1}H NMR($CDCl_3$) : δ, 2.35 (3H,s,Ar-CH_3), 2.45 (3H, s, =C-CH_3), 6.5 (1H, s, = CH-), 7.1-7.7 (3H, m, aromatic protons) ppm.	6
IIc	IR (KBr) : ν 3400-3250 broad (NH), 1660-1650 (cyclic amido, >C=O), 1600-1580 (>C=C<) cm^{-1}	7
IIc	^{1}H NMR (TFA) : δ 2.4 (3H,s, -C=C-CH_3), 6.75 (1H, s, >C=CH-); 6.8 - 7.5 (3H, m, Aromatic protons), PPm.	8
IIc	IR (KBr) : ν 3350-3200 (NH), 1665-1655 (cyclic amido, >C=O), 1600 (>C=C<), 760 (-C-Cl) cm^{-1}	9

iv) Synthesis of N^1- carbethoxy -4-methyl-2-quinolin-2(1H)-ones (IIIa) :

In a round bottom flask carrying reflux condenser and a guard tube, a mixture of 4-methyl-2-quinolon-2(1H)-one(IIa) (6 gm, 0.03 mole) and ethyl chloroformate (4.1 ml, 0.03 mole) in dry acetone containing anhydrous

potassium carbonate (2 gm) was refluxed for 24 hr., cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water filtered and recrystallised from ethanol to give IIIa • 7 gm, (77.01%), M.P. 87°C;(Found : C, 68.6; H, 5.25; N, 5.75. $C_{10}H_9NO$ requires: C, 68.88; H, 5.39; N, 5.81%);IR (KBr) : 1770 (ester >C=0), 1665 (amido, >C=0), 1600 cm^{-1} (>C=C<); ^1H NMR (TFA) : δ , 1.3 (3H,t, J = 8 Hz, ester - CH_3), 2.45 (3H,s, =C-CH_3), 4.15 (2H, q, -OCH_2), , 7 - 7.8 (3H, m, Ar-H) ppm. Fig. 10

Other substituted N^1-carb ethoxy-4-methyl-2-quinolin-2(1H)-ones have been prepared by similar method and their m.p., yield, molecular formula and elemental analysis data have been depicted in the Table - IIIa and IR, ^1HNMR spectral data in Table - IIIb.

Table - IIIa

Physical and Analytical data of the compounds (IIIb-c) :

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
IIIb	H	CH_3	48	75.00	$C_{13}H_{15}O_3N$	66.90 (66.95)	6.40 (6.44)	5.95 (6.01)
IIIc	Cl	H	55	86.21	$C_{13}H_{12}O_3HCl$	58.80 (58.87)	4.50 (4.53)	5.15 (5.28)

Table - IIIb

IR and ^{1}HNMR Spectral data of the compounds (IIIb-c) :

Compound No.	Spectral characteristics	Fig.No.
IIIb	^{1}H NMR (TFA) :δ,1.1-1.3 (3H,s, ester-CH_3), 2.35 (3H,s, Ar-CH_3), 2.4 (3H,s, =C-CH_3), 4.15 (2H,q, -OCH_2), 6.2 (1H,s, >C=C<u>H</u>-), 6.8-7.5 (3H,m, Aromatic protons) ppm.	-
IIIb	IR (KBr) :$\bar{\nu}$,1760-1750 (ester >C=0), 1665-1655 (cyclic amido >C=0), 1600 (>C=C<). cm^{-1}	11
IIIc	^{1}H NMR (TFA) :δ,1.1-1.3 (3H,s, ester-CH_3), 2.45 (3H,s =C^{CH_3}), 4.18 (2H,s, -OCH_2-), 6.15 (1H, s, >C=C<u>H</u>-), 6.9-7.7 (3H, m, Aromatic protons) ppm.	-
IIIc	IR (KBr) :$\bar{\nu}$,1760-1765 (ester >C=0), 1665-1650 broad (cyclic amido, >C=0), 1600 - 1580 (>C=C<), 760-755 (C-Cl) cm^{-1}	-

v) Synthesis of N^1- Hydrazido-4-methyl-quinolin-2(1H)-Ones (IVa) :

To a solution of compound IIIa in a flat bottom flask (6 gm, 0.01 mole) in ethanol (40 ml), hydrazine hydrate (0.8 ml, 0.01 mole) was added and the same reaction mixture was refluxed on a water bath using reflux condenser for 2 hr., cooled. The resulting solid was filtered and recrystallised from ethanol to furnish IVa, 4 gm (74.07%), M.P. 220°C (Found : C, 60.7; H, 5.0; N, 19.20. $C_{11}H_{11}O_2N_3$ requires : C, 60.83; H, 5.07; N, 19.35%); IR (KBr) : 3350 ($-NHNH_2$), 1670-1660 cm^{-1} (amido, C=O); ^{1}HNMR (Fig.No.12 $CDCl_3$); δ, 2.4 (3H,s, $=C-CH_3$), 2.5 (2H,s, $-NH_2$), 7 - 7.5 (4H,m, Ar-H)ppm. UV (ethanol) : λ_{max} 328 and 321 nm.

Other compounds have been prepared by similar method and their m.p., yield, molecular formula and elemental analysis data have been incorporated in the Table-IVa and IR, ^{1}H NMR spectral data in Table-IVb.

Table - IVa

Physical and Analytical data of other compounds (IVb-c) :

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
IVb	H	CH_3	265	73.39	$C_{12}H_{13}O_2N_3$	62.20 (62.34)	5.60 (5.63)	18.00 (18.18)
IVc	Cl	H	273	83.31	$C_{11}H_{10}O_2N_3Cl$	52.50 (52.59)	3.95 (3.98)	16.60 (16.73)

Table - IVb

IR and ^1H NMR spectral data of the compounds (IVb-c) :

Compound No.	Spectral characteristics	Fig.No.
IVb	^1H NMR ($CDCl_3$) : δ, 2.35 (3H,s, Ar-CH_3), 2.5 (3H,s,=C-CH_3), 6.65 (1H,s, >C=CH), 7.3 - 7.9 (3H,s, Aromatic protons) ppm.	13
IVb	IR (KBr) : ν, 3350-3200 ($NHNH_2$), 1670 - 1660 (cyclic & acyclic amido, >C=O), 1600 (>C = C<) cm^{-1}.	-
IVc	^1H NMR ($CDCl_3$) : δ, 2.40 (3H,s, =C-CH_3), 6.2 (1H, s, >C = C<u>H</u>-), 6.8 - 7.6 (3H,m, Aromatic protons), 4.5 (1H,s,-N<u>H</u>CO)ppm.	-
IVc	IR (KBr) : ν, 3350-3200 ($NHNH_2$), 1670-1660 broad (cyclic and acyclic amido, >C=O), 1600 (>C=C<), 760(-C-Cl) cm^{-1}.	14

vi) Synthesis of 4-Aryl-1-(N^1-quinolinoyl) thiosemicarbazide (Va) :

A mixture of N^1-Hydrazido-4-methyl-quinolin-2(1H)-ones (2.4 gm, 0.001 mole) and phenyl-isocyanate (1.4 gm, 0.001 mole) in ethanol (25 ml) was refluxed for 3-4 hr. then cooled and the solvent was removed under reduced pressure. The resulting residue was triturated with water and the solid obtained was recrystallised from ethanol to form Va, 3 gm (75.87%), M.P. 84°C (Found : C, 61.30; H, 4.50; N, 15.80. $C_{18}H_{16}O_2N_4S$ requires : C, 61.36; H, 4.55; N, 15.91%); IR (KBr) : ν, 3350-3450 (-NH), 1670 broad (-CONH) and 1345-1355 ($\rangle C{=}S$) cm^{-1}; NMR (TFA) δ, 2.4 (3H,s, $=C^{CH_3}$), 6.2 (1H,s, = CH-), 6.5 - 7.6 (9H, m, Ar-H) ppm. Fig. 15.

UV (ethanol) : ν_{max}, 355 nm.

Other compounds were prepared by similar method and their m.p. yield, molecular formula and elemental analysis have been incorporated in the Table-Va and IR, ^{1}HNMR spectral data in Table - Vb.

Table - Va

Physical and Analytical data of the compounds (Vb-c) :

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
Vb	H	CH_3	113	84.80	$C_{19}H_{18}N_4O_2S$	65.05 (65.14)	5.10 (5.14)	15.90 (16.00)
Vc	Cl	H	60	80.01	$C_{18}H_{15}O_2N_4SCl$	55.8 (55.96)	3.80 (3.89)	14.35 (14.51)

Table - Vb

IR and ^1H NMR spectral data of the compounds (Vb-c)

Compound No.	Spectral characteristics	Fig.No.
Vb	^1H NMR (TFA):δ,2.3 (3H,s,Ar-CH_3), 2.45 (3H,s,=C-CH_3), 3.9 (1H,s,-NH), 6.65 (1H,s, >C=CH-), 6.9-7.1 (9H,m, aromatic protons) ppm.	16
Vb	IR (KBr) :ν̄,3300-3200 (NH), 1670-1660 broad (amido >C=O), 1600 (>C=C<), 1355 - 1350 (>C=S), cm^{-1}	-
Vc	^1H NMR (TFA) : δ ,2.4 (3H,s, =C-CH_3), 4.55 1H, s,-NH), 6.15 (1H,s, -C=CH-), 6.8 - 7.6 (8H, m, Aromatic protons) ppm.	-
Vc	IR (KBr) :ν̄,3350 - 3200 broad (NH), 1670 - 1660 (amido, >C=O), 1600 -1580 (>C=C<), 1355 - 1350 (>C=S), 760(>C-Cl) cm^{-1}	-

vii) Synthesis of 5-Aryl-2-[N^1-(4'-methyl quinolin-2'-one-1'-yl)]-5-mercapto-1,3,4-triazole (VIa) :

Compound Va (0.923 gm, 0.001 mole) was refluxed with 2N NaOH (2 ml) for 3 hr. cooled, and filtered and the filtrate was acidified with glacial acetic acid to give a solid which when recrystallised from ethanol furnished VIa, 0.57 gm, (67.89%) M.P. 266°C (Found : C, 63.3; H, 4.3; N, 17.30. $C_{18}H_{14}ON_4S$ requires : C, 63.35; H, 4.35; N, 17.39%); IR(KBr): 2550 - (-SH)(SH), 1664 (amido cyclic >C=O), 1620 (>C=N) cm^{-1}; Fig.17 ^{1}H NMR (TFA) : δ , 2.4 (3H, s, = C-CH_3), 6.2 (1H,s, = CH-), 7-7.9 (9H,m, Ar-H), UV (ethanol) : λ_{max} , 286 and 344 nm.

Other compounds have been synthesised by similar method and their M.P., yield, molecular formula and elemental analysis data have been incorporated in the Table - VIa and IR, NMR spectral data in Table-IVb.

Table - VIa

Physical and Analytical data of the compounds (VIb-c)

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
VIb	H	CH_3	272	81.71	$C_{19}H_{16}ON_4S$	57.10 (57.30)	3.60 (3.65)	15.60 (15.73)
VIc	Cl	H	210	76.38	$C_{17}H_{13}N_4OSCl$	70.3 (70.37)	4.90 (4.93)	17.10 (17.28)

Table - VIb

IR and ^1H NMR spectral data of the compounds (VIb-c):

Compound No.	Spectral characteristics	Fig.No.
VIb	^1H NMR (TFA) : δ,2.3 (3H,s, Ar-CH_3), 2.42 (3H,s, =C-CH_3), 6.15 (1H,s, >C=C<u>H</u>-), 6.9 - 7.6 (8H, m, Aromatic protons), 11.5-12 (1H,s, S<u>H</u> exchangable with D_2O) ppm.	-
VIb	IR (KBr) : ν,2550 -2560 (SH), 1665-1655 (amido >C = 0), 1620 (>C=N-), 1600 - 1580 (>C=C<) cm^{-1}.	-
VIc	^1H NMR (TFA) : δ, 2.4 (3H,s, =C-CH_3), 4.5 (1H,s, -N<u>H</u>), 6.2 (1H,s, >C=C<u>H</u>-), 6.8 - 7.6 (8H, m. aromatic protons)ppm.	-
VIc	IR (KBr) : ν, 2550 - 2560 (SH), 1665 - 1660 (cyclic >C=0), 1620 (>C=N), 1580 (>C=C<), 760 (>C-Cl) cm^{-1}.	-

viii) Synthesis of 5-Aryl amino-2-(4'-methyl-1uinolin-2-one-1'-yl)-1,3,4-oxadiazole (VIIa) :

To a mixture of VIa (0.972 gm, 0.001 mole) in NaOH (4N, 4ml), I_2 inKI was added till the colour of I_2 persisted and the same reaction mixture was further concentrated for 4-5 hr., cooled and poured into ice-cold water. The resulting solid was filtered and recrystallised from ethanol to yield VIIa, 0.68 gm (77.5%), M.P. 283°C. (Found : C, 67.8; H, 4.3; N, 17.5. $C_{18}H_{14}O_2N_4$. requires : C, 67.92; H, 4.40; N, 17.6%); IR (KBr) : $\bar{\nu}$, 3150-3250 (-NH), 1665-1670 (-NHCO); 1620 (>C=N-) cm^{-1}. ^1H NMR (CDCl$_3$) δ, 2.45 (3H, s, =C-CH_3), 4.5 (1H,s, -NH), 6.2 (1H,s, = CH-), 7-7.5 (9H,m, Ar-H) ppm.

Other compounds have been prepared by similar method and their m.p., yield, molecular formula, and elemental analysis data have been given in the Table - VIIa and IR, NMR spectral data in Table - VIIb.

Table - VIIa

Physical and Analytical data of the compounds (VIIb-c) :

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
VIIb	H	CH_3	295	89.50	$C_{19}H_{16}O_2N_4$	68.60 (68.67)	4.80 (4.82)	16.80 (16.87)
VIIc	Cl	H	274	57.46	$C_{18}H_{13}O_2N_4Cl$	61.30 (61.36)	3.65 (3.69)	15.80 (15.91)

Table - VIIb

IR and ^1H NMR spectral data of the compounds (VIIb-c)

Compound No.	Spectral characteristics	Fig.No.
VIIb	^1H NMR (TFA) : δ , 2.35 (3H,s, Ar-CH_3), 2.45 (3H,s, =C-CH_3), 4.55 (1H,s, -NH), m, 6.18 (1H, s, -C=CH-), 7-7.8(8H, Aromatic protons) ppm.	-
VIIb	IR(KBr) : 3350-3200 (NH), 1665-1655 cyclic amido, C = 0), 1580 (C=C), 1050 (C-O-C) cm^{-1}.	-
VIIc	^1H NMR (TFA) : δ , 2.4 (3H,s, =C-CH_3), 4.55 (1H,s, -NH), 6.15 (1H,s, C=CH-), 6.9-7.7 (8H,m, Aromatic proton)ppm.	-
VIIc	IR (KBr) : 3350-3200 (NH), 1665-1660 (cyclic amido C=0), 1620 (C=N-),1580 (C=C), 1060 (C-O-C) cm^{-1}.	18

ix) Synthesis of 5-Aryl amino-2-(4'-methyl quinazolin-2'-one-1'-yl) 1,3,4-thiadiazole (VIIIa) :

Compound VIIa (1.134 gm, 0.001 mole) was dissolved in syrupy phosphoric acid (5 ml) and heated at 120°C for 50 min., kept over night and then poured into ice-cold water. The resulting solid was filtered and recrystallised from ethanol to form VIIIa, 0.826 gm (76.48%); M.P. 298°C; (Found : C, 64.6; H, 4.10; N, 16.7. $C_{18}H_{14}ON_4S$ requires : C, 64.67; H, 4.19; N, 16.77); IR (KBr) : 3200-3300 (NH), 1665 (amido >C=O), 1610-1620 (>C=N), 700-720 (C-S-C) cm^{-1}; ^1H NMR (TFA) 2.3 (3H, s, $=C-CH_3$), 3.8 (1H,s,-NH); 6.15 (1H,s, = CH), 7-7.8 (9H,m, Ar-H) ppm.

Other compounds have been prepared by similar method and their m.p.,yield, Molecular formula and elemental analysis data have been incorporated in the Table-VIIIa and IR, NMR spectral data in Table-VIIIb.

Table - VIIIa

Physical and Analytical data of the compounds (VIIIb-c)

Sr. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
VIIIb	H	CH_3	> 300	79.63	$C_{19}H_{16}ON_4S$	65.45 (65.52)	4.50 (4.60)	16.00 (16.09)
VIIIc	Cl	H	> 300	70.34	$C_{18}H_{13}ON_4SCl$	58.55 (58.70)	3.50 (3.53)	15.10 (15.22)

Table - VIIIb

IR and ^1H NMR spectral data of the compounds (VIIIb-c)

Compound No.	Spectral characteristics	Fig.No.
VIIIb	^1H NMR (TFA) : δ 2.35 (3H,s,Ar-CH_3) 2.4 (3H,s,=C-CH_3), 4.5 (1H,s,-NH), 6.2 (1H, s, >C=CH-), 7-7.6 (8H,m, Aromatic protons) ppm.	-
VIIIb	IR(KBr): ν 3350-3200 (NH), 1665 (cyclic amido >C=O), 1620 (>C=N), 1580 (>C=C<), cm^{-1}.	-
VIIIc	^1H NMR (TFA) : δ 2.45 (3H,s,=C-CH_3), 4.55 (1H, s,-NH), 6.18 (1H,s, >C=CH-), 7-7.8 (8H, m, Aromatic protons)ppm.	-
VIIIc	IR (KBr) : ν 3350-3200 (NH), 1665 (cyclic amido, >C=O), 1620 (>C=N), 1600 (>C=C<) 750(>C-Cl) cm^{-1}.	-

IR, ^{1}H NMR SPECTRA

^1H NMR SPECTRUM OF ACETOACETANILIDE (Ia) .

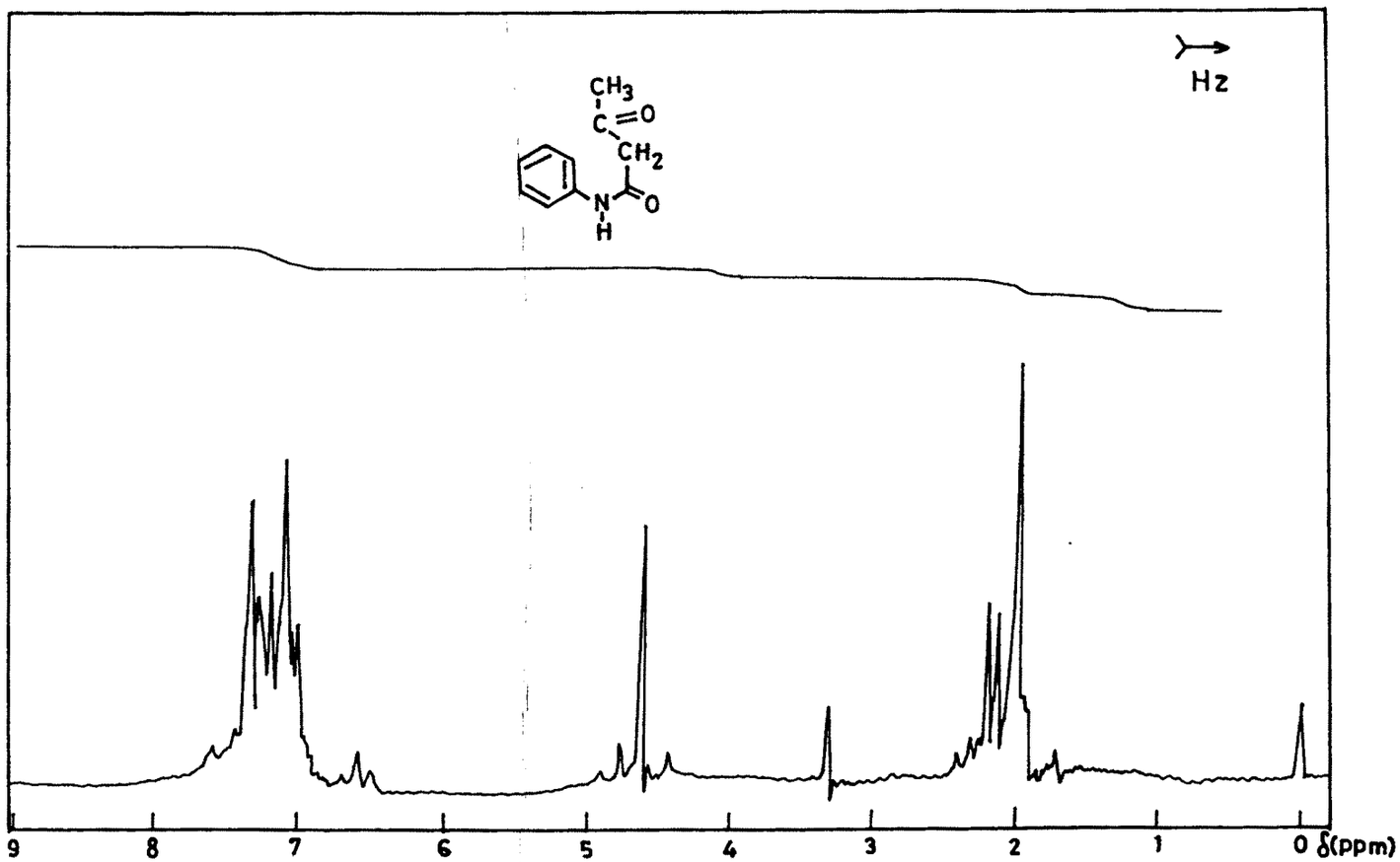


FIG. NO. 1

^1H NMR SPECTRUM OF o-METHYL ACETOACETANILIDE (I_b) .

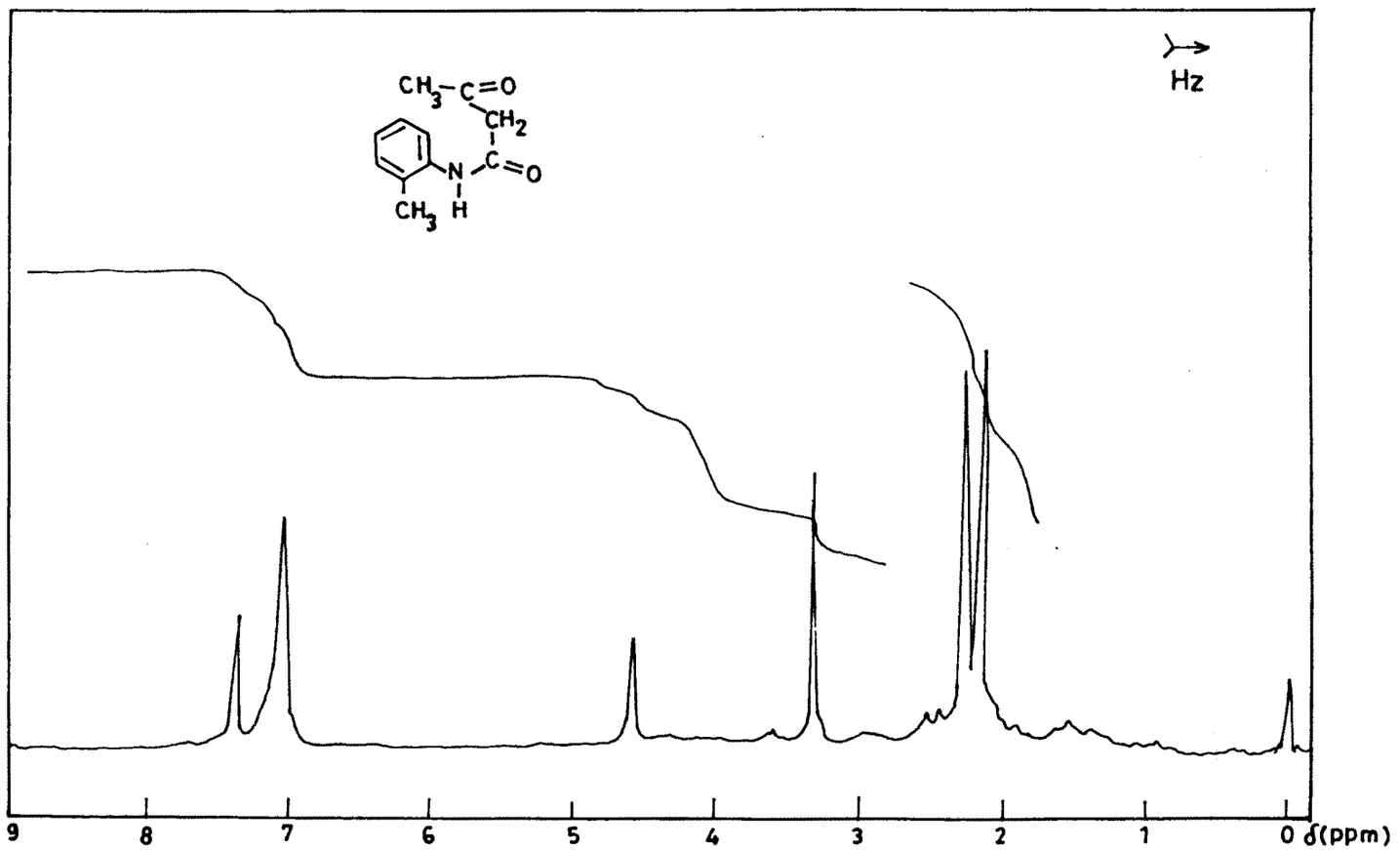


FIG. NO. 2

1H NMR SPECTRUM OF m-CHLORO ACETOACETANILIDE (I_C).

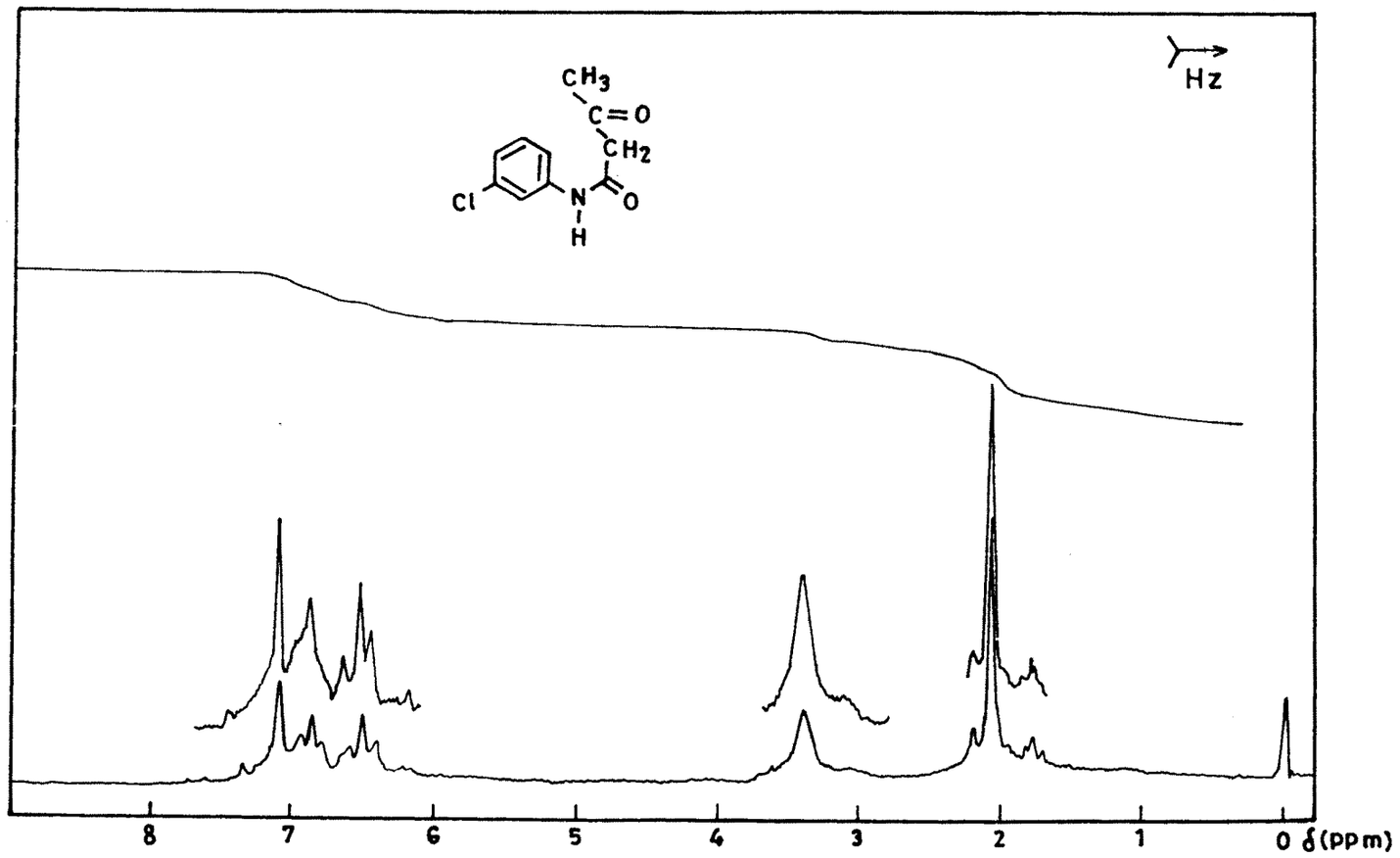


FIG. NO.3

IR SPECTRUM OF 4-METHYL QUINOLIN-2(1H)ONE (II_a).

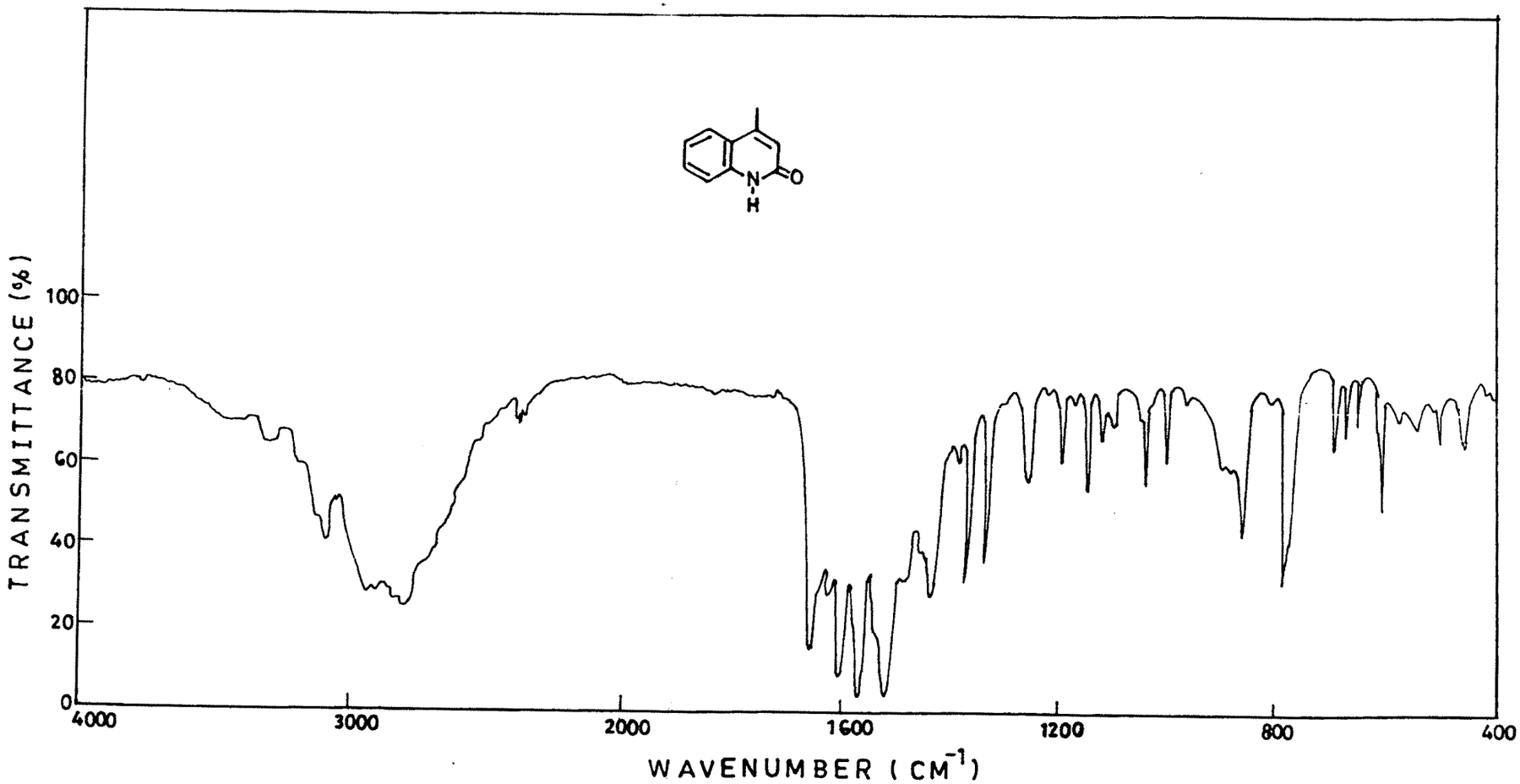


FIG. NO. 4

^{1}H NMR SPECTRUM OF 4-METHYL QUINOLIN-2(1H) ONE (II_a) .

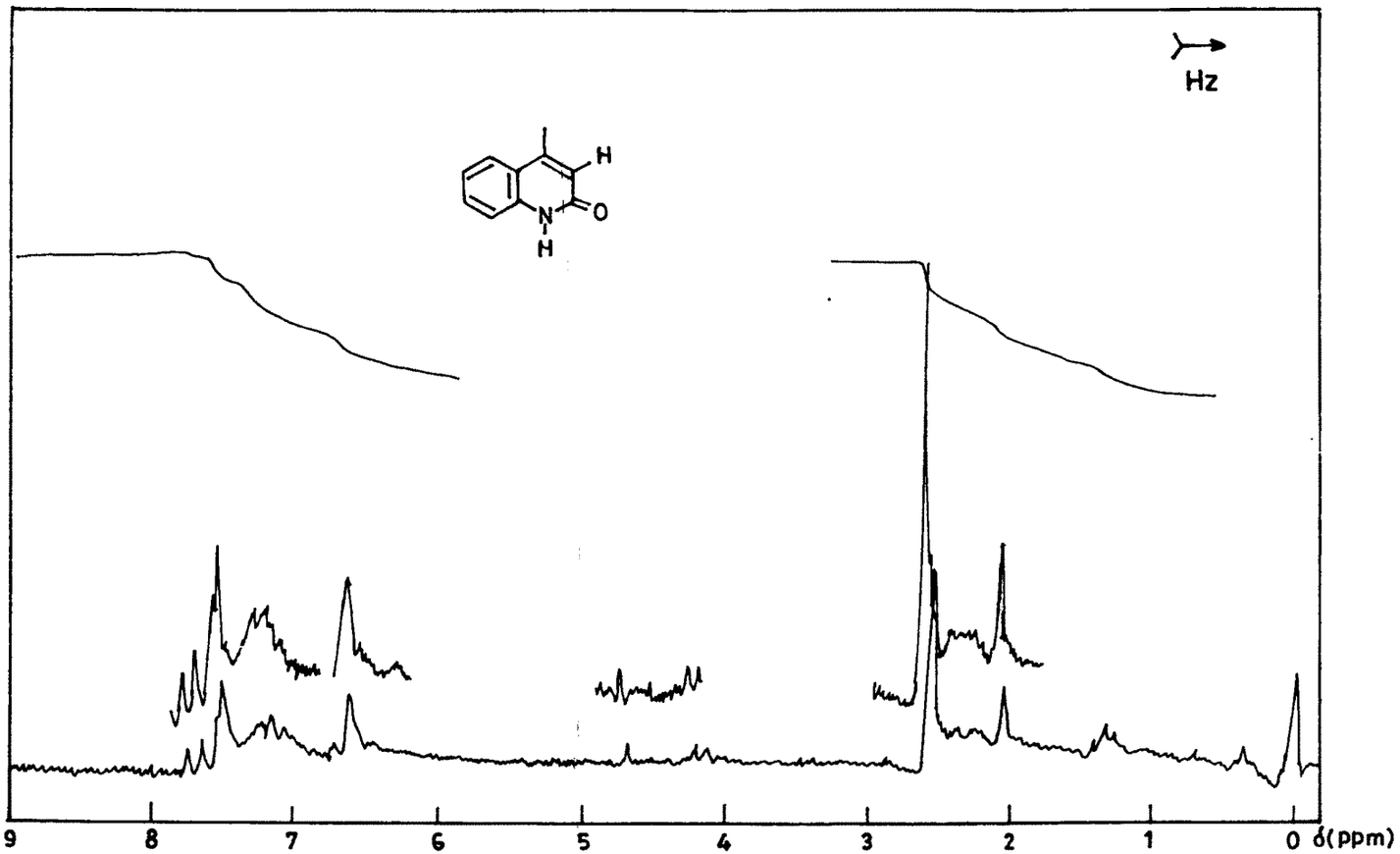


FIG. NO. 5

^1H NMR SPECTRUM OF 4,8-DIMETHYL QUINOLIN-2-(1H) ONE (II_b) .

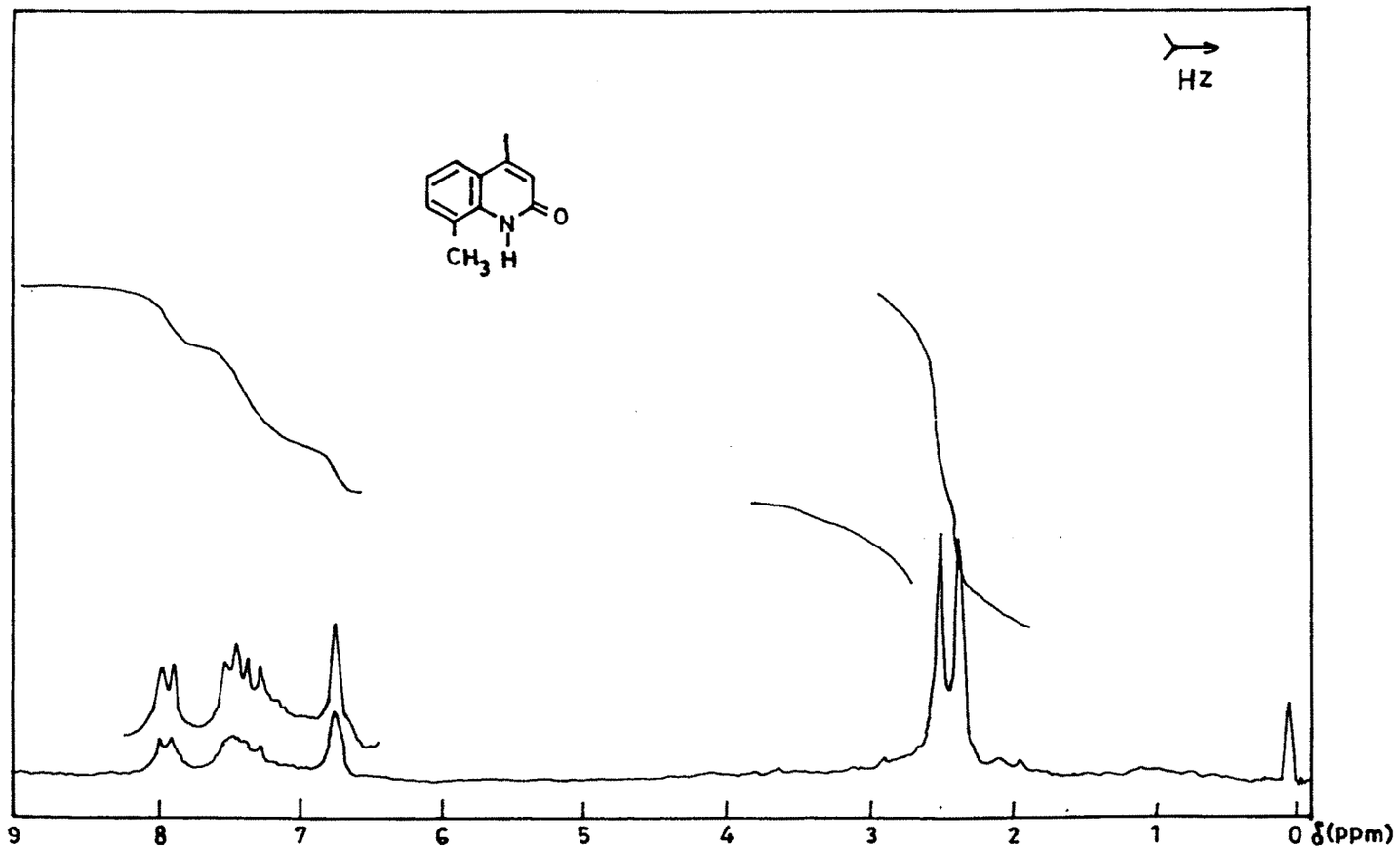


FIG. NO. 6

IR SPECTRUM OF 4,8-DIMETHYL QUINOLIN-2(1H)ONE (II_b)

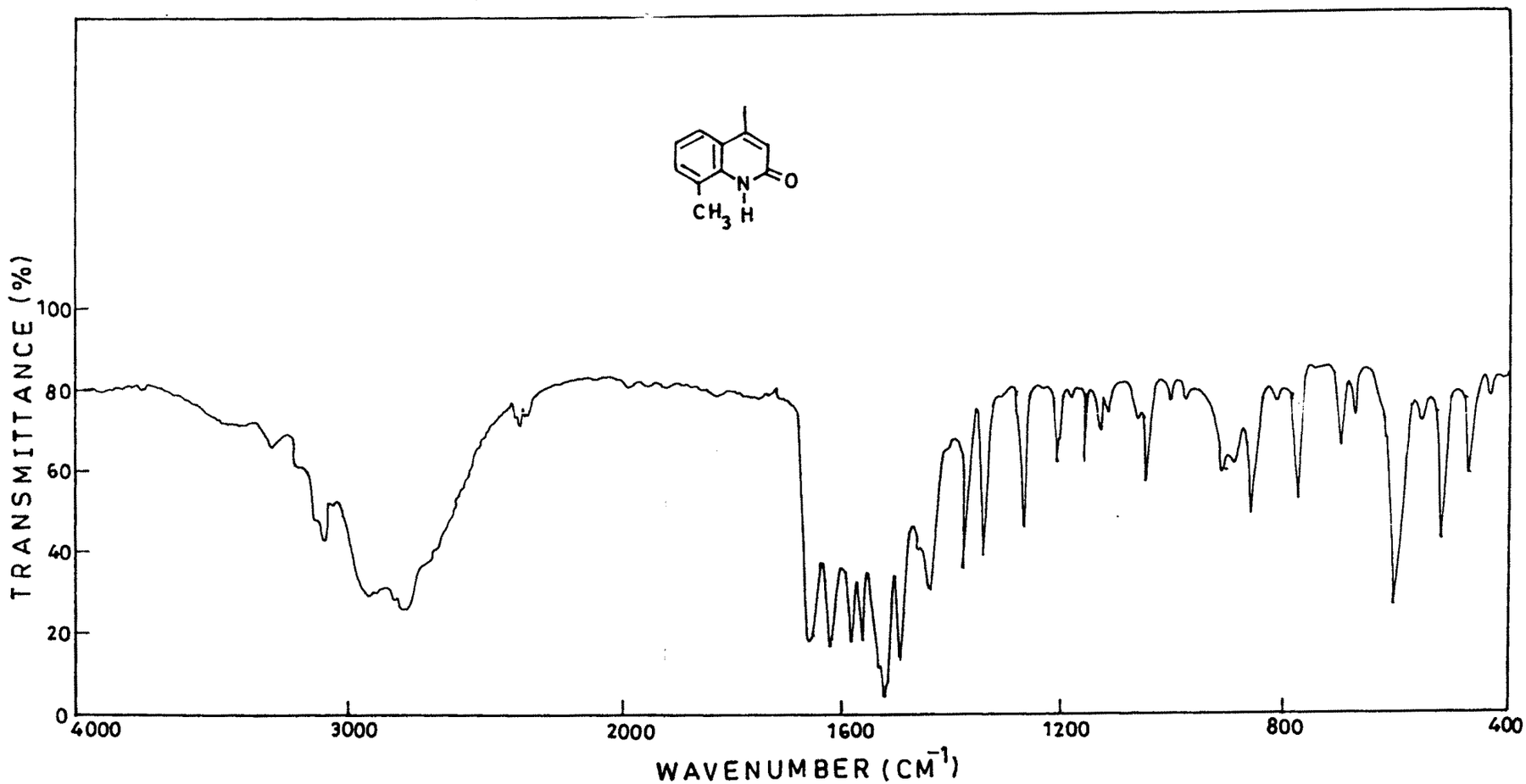


FIG. NO. 7

^{1}H NMR SPECTRUM OF 4-METHYL, 7-CHLORO QUINOLIN-2 (1H) ONE (IIc).

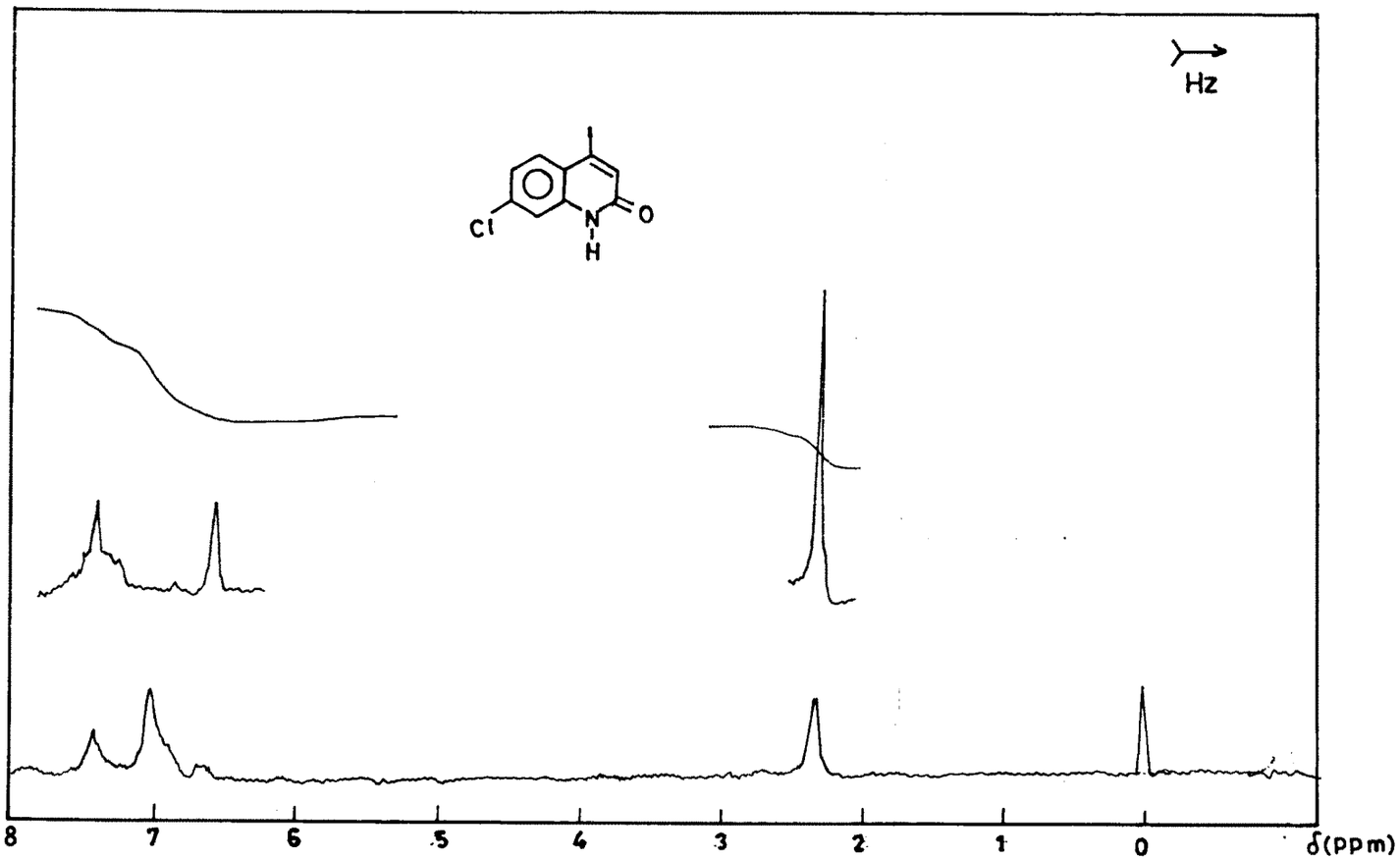


FIG. NO. 8

IR SPECTRUM OF 7-CHLORO-4-METHYL QUINOLIN-2(1H) ONE (IIc).

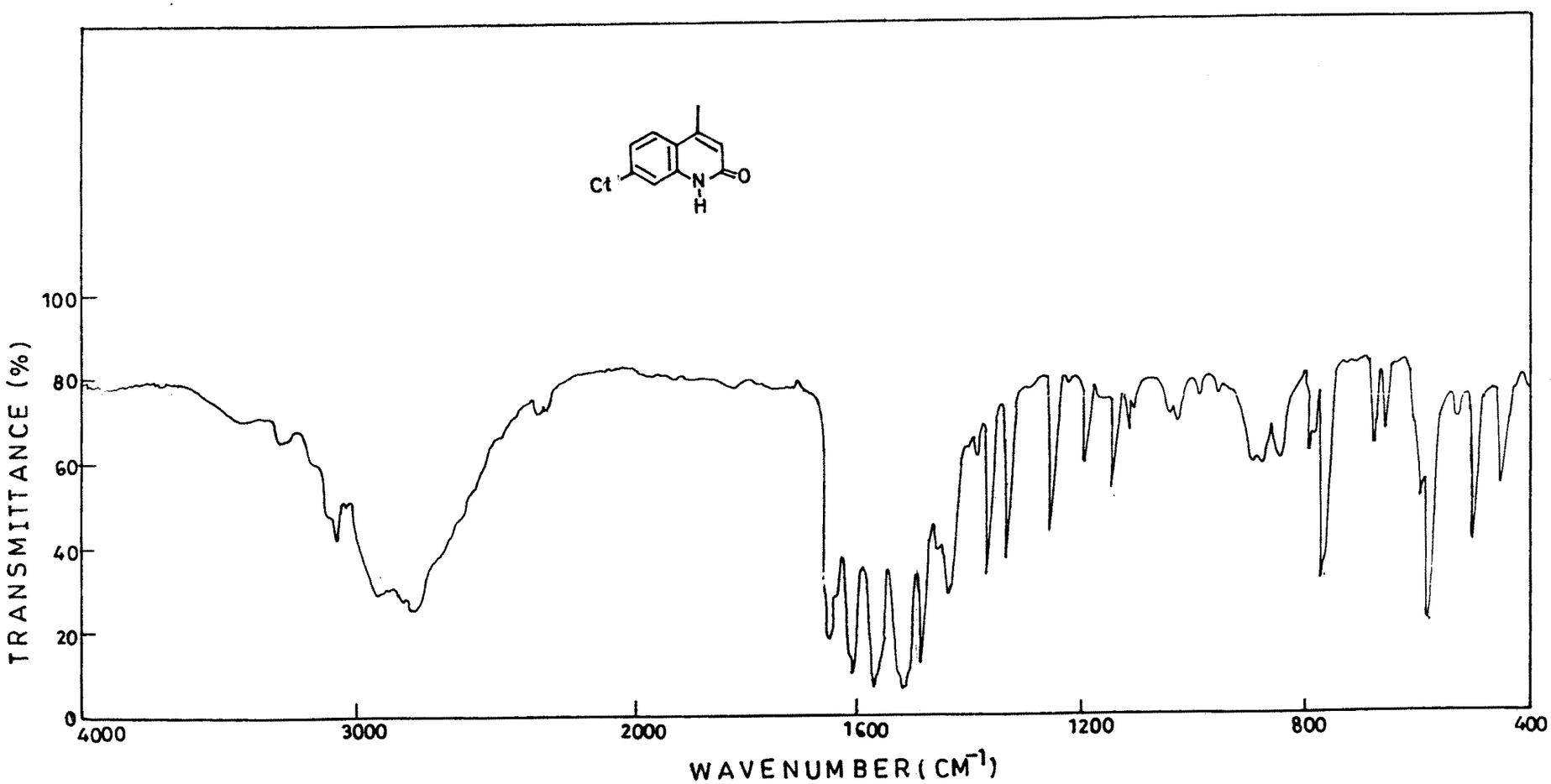


FIG. NO. 9

^{1}H NMR SPECTRUM OF 4-METHYL , N^1-CARBETHOXY QUINOLIN-2 (1H) ONE (IIIa).

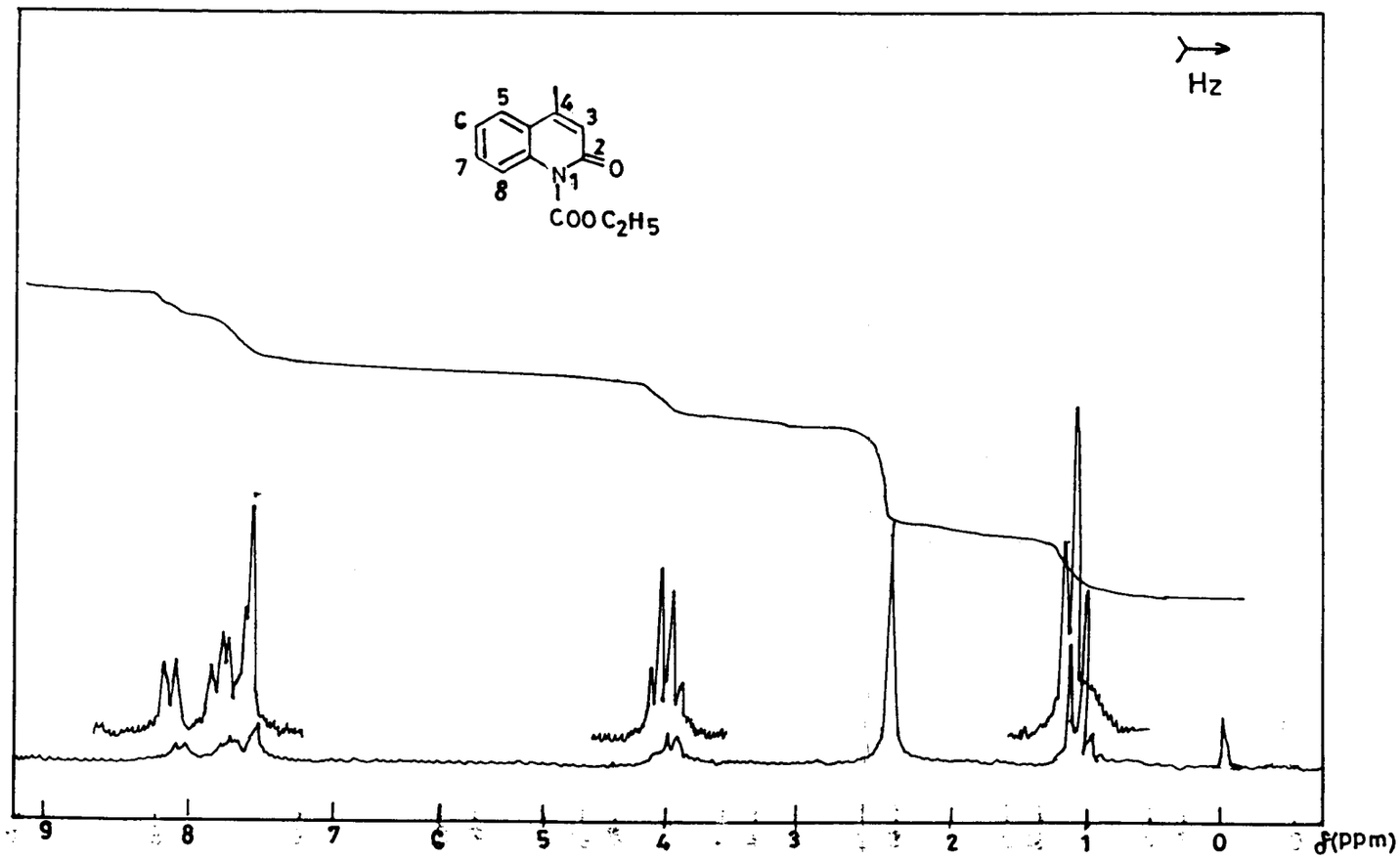


FIG. NO. 10

IR SPECTRUM OF 4,8-DIMETHYL N^1-CARBETHOXY QUINOLIN-2(1H) ONE (III_b).

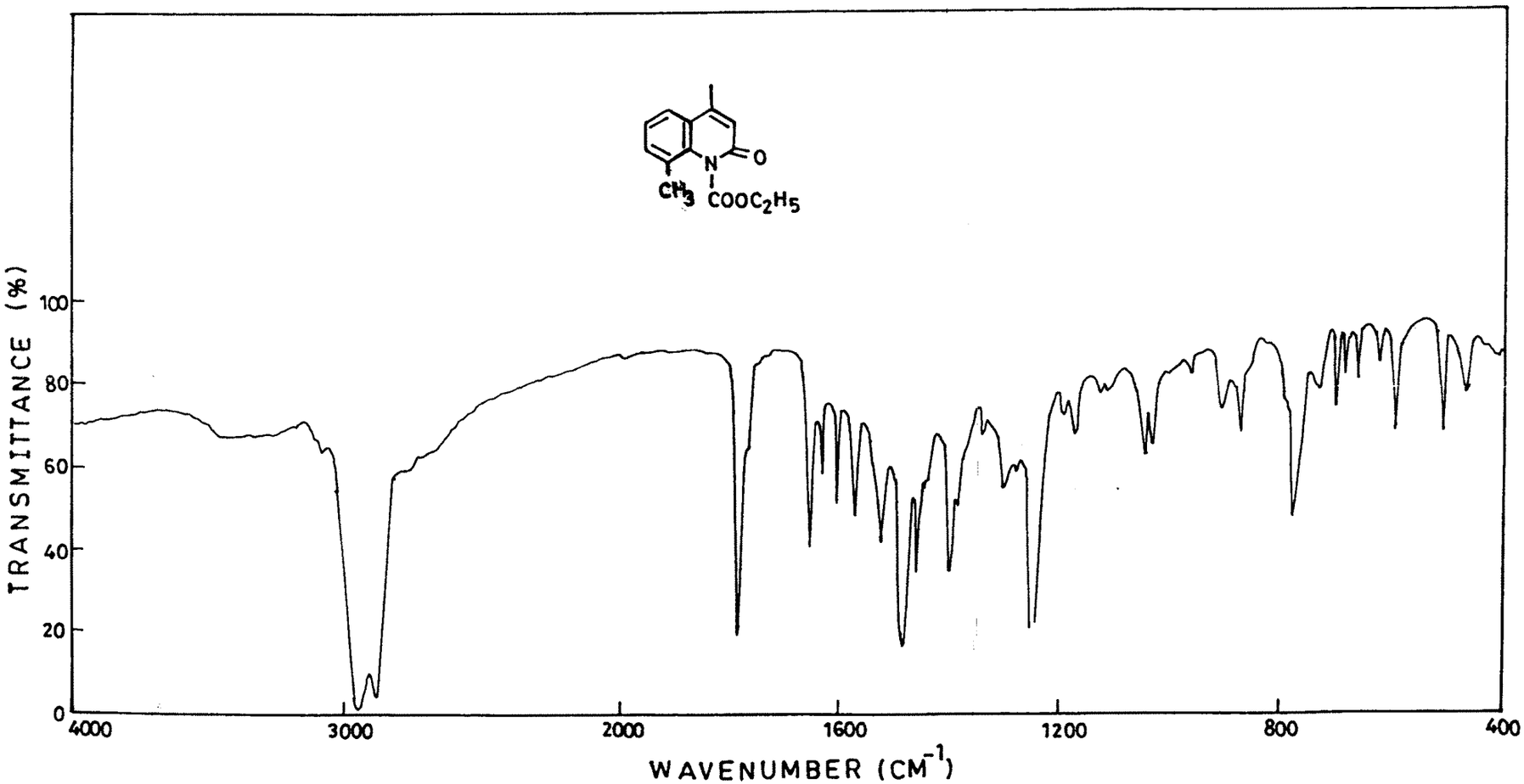


FIG. NO. 11

IR SPECTRUM OF 4-METHYL, N^1-HYDRAZIDO-QUINOLIN-2(1H) ONE (IV_a).

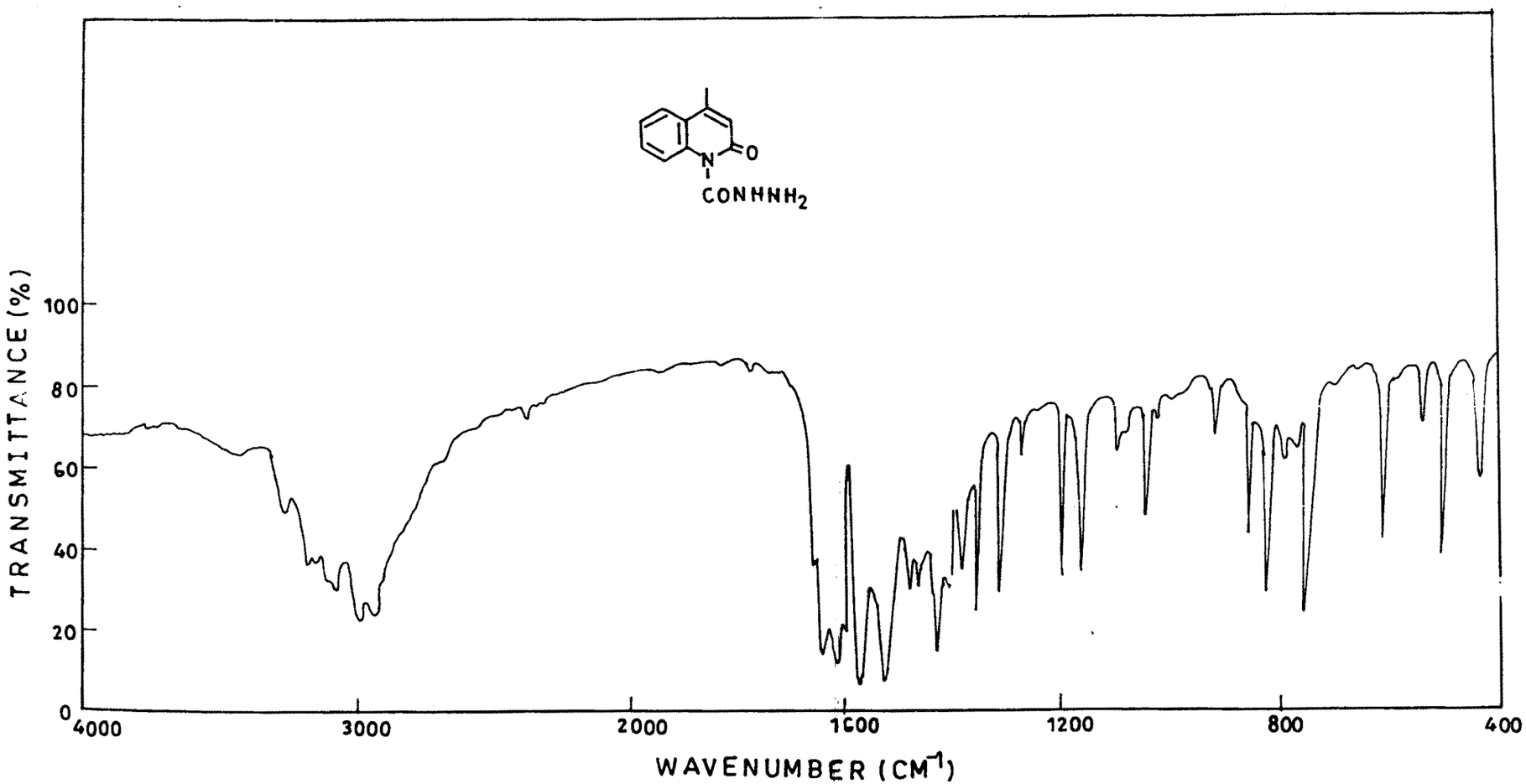


FIG. NO. 12

^{1}H NMR SPECTRUM OF 4,8-DIMETHYL N^1-[illegible]DRAZIDO-2 (1H) ONE (IV_D) .

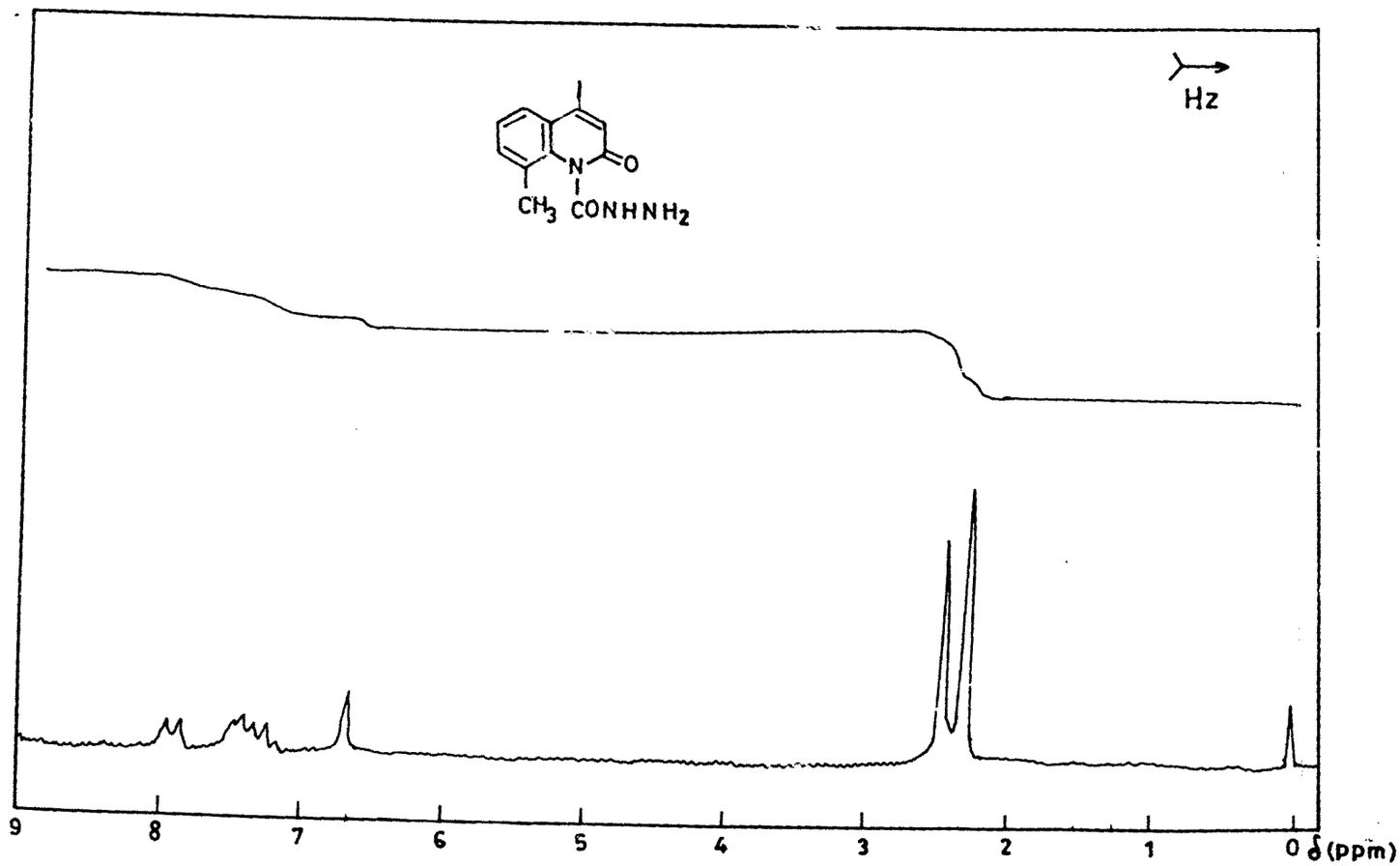


FIG. NO. 13

7-CHLORO

IR SPECTRUM OF 4-METHYL,N^1-HYDRAZIDO-QUINOLIN-2 (1H) ONE (IV_c).

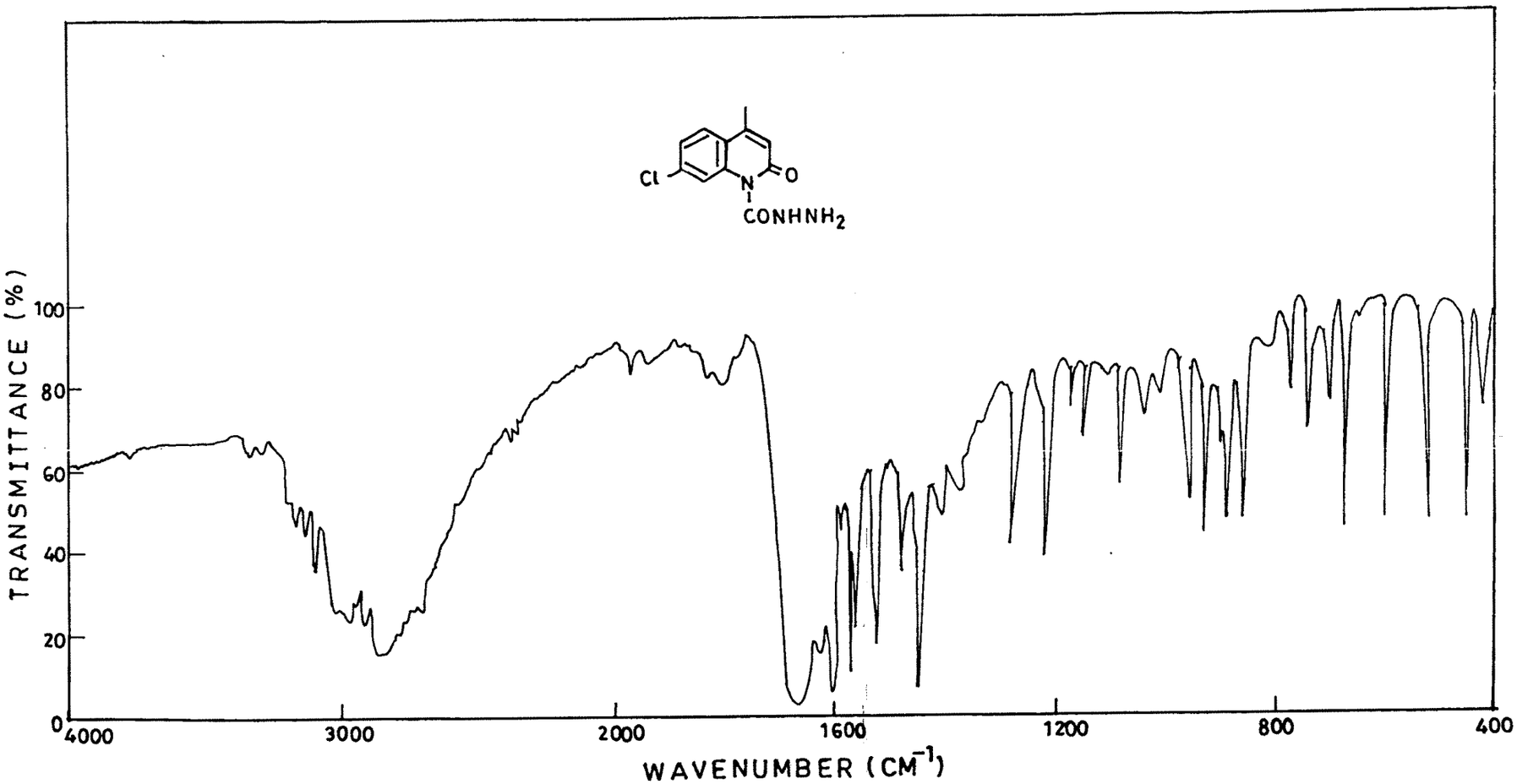


FIG. NO. 14

^{1}H NMR SPECTRUM OF 4-PHENYL,1-(4'-METHYL -QUINOLIN-2'-ONE-1'-YL)-OXO-THIO SEMICARBAZIDE (V a) .

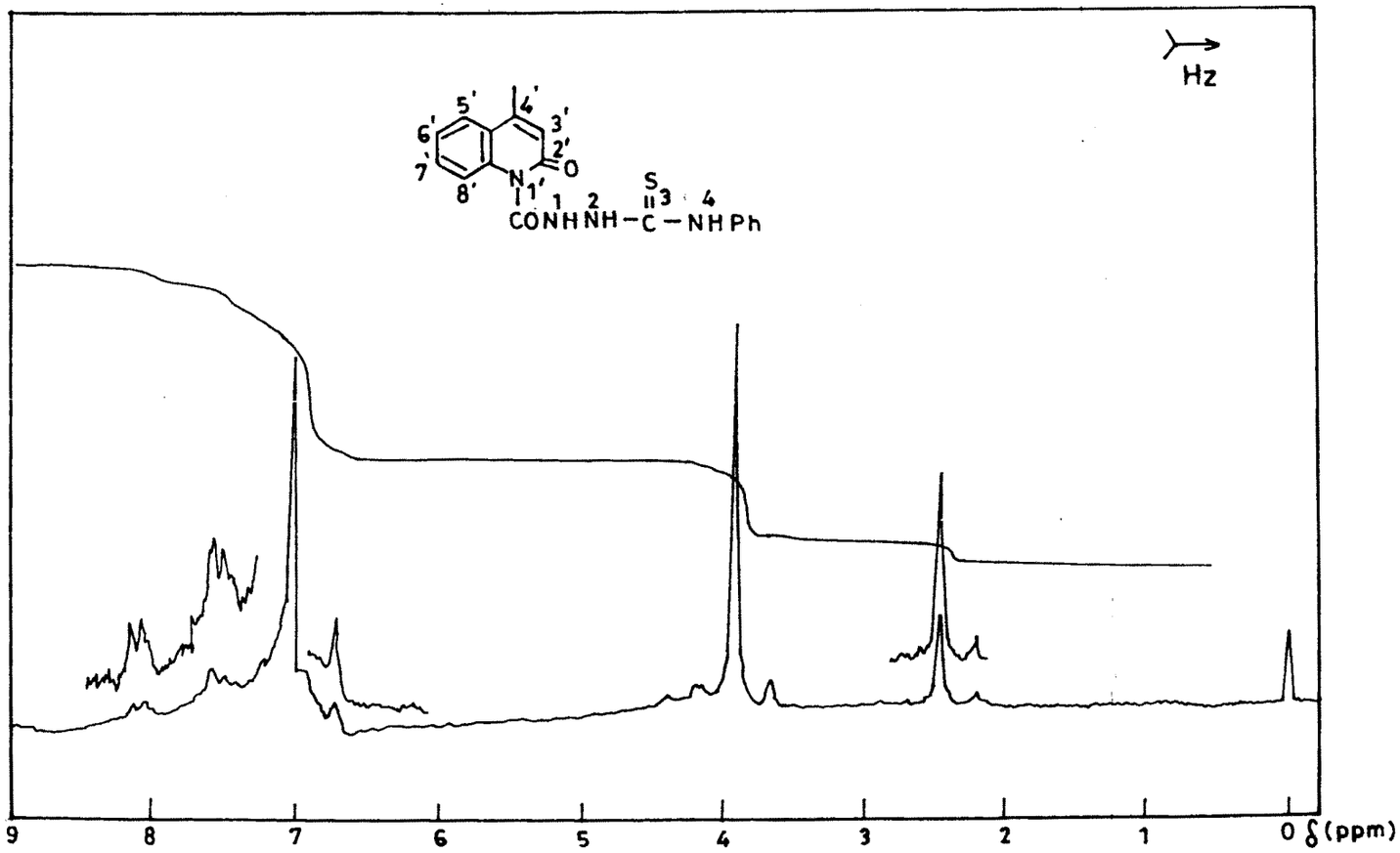


FIG. NO. 15

^1H NMR SPECTRA OF 4-PHENYL, 1— (4', 8'—DIMETHYL QUINOLIN-2 (1H)-ONE-YL) — OXO-THIOSEMICARBAZIDE (V $_b$).

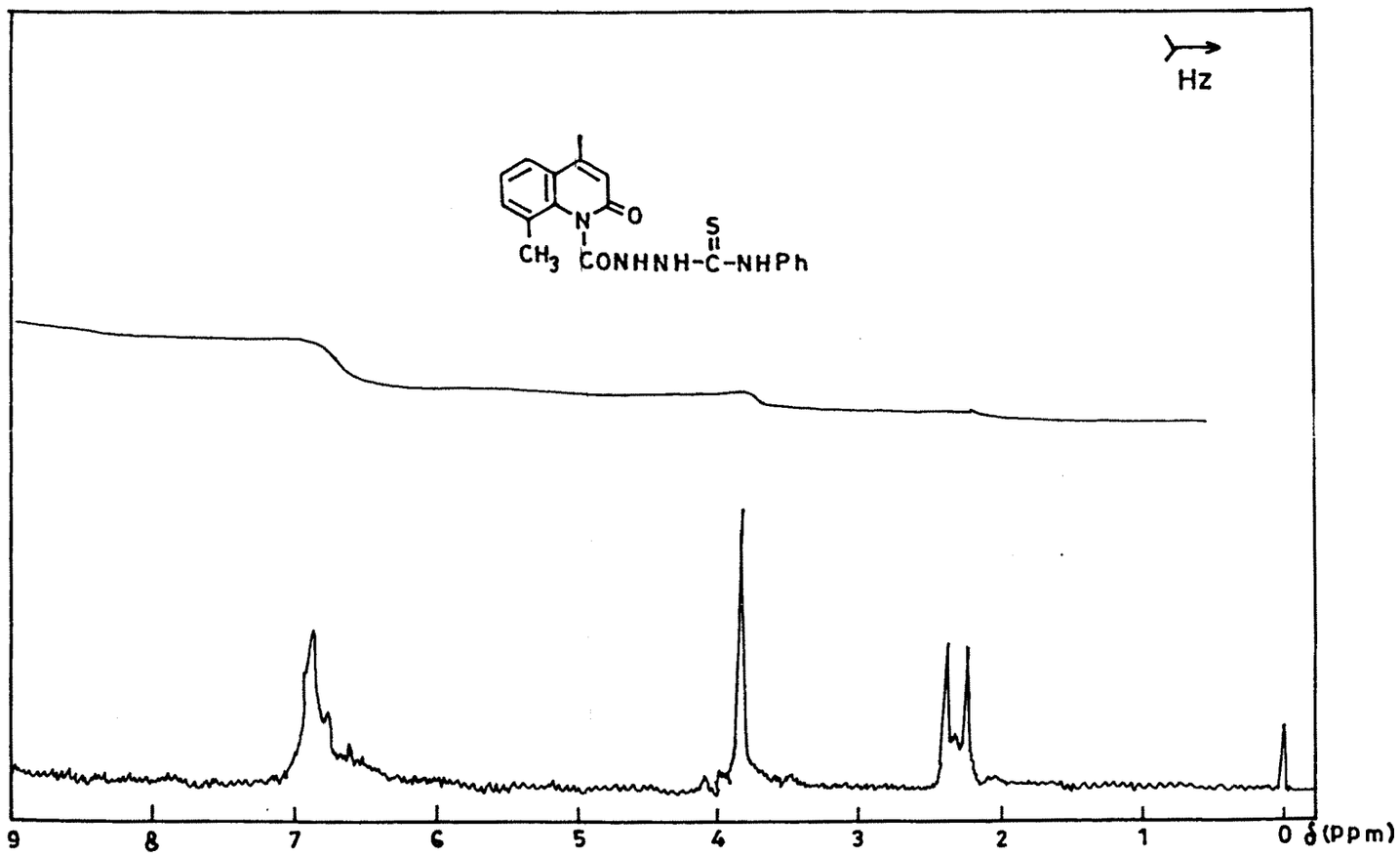


FIG. NO. 16

IR SPECTRUM OF 4-METHYL , N^1-(5'-MERCAPTO-1',3',4'-TRIAZOL-2'-YL) QUINOLIN-2(1H) ONE (VI$_a$) .

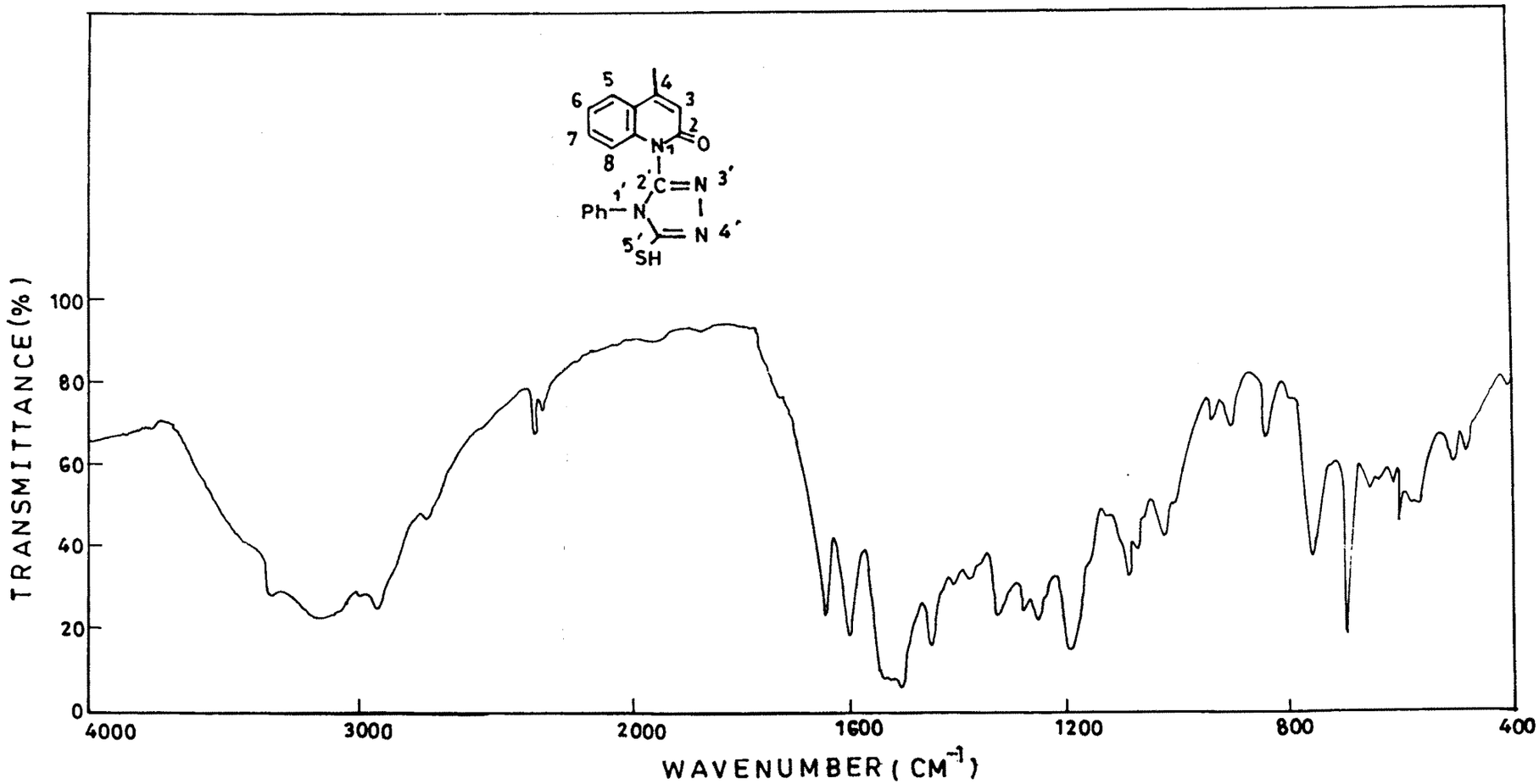


FIG. NO. 17

IR SPECTRUM OF 5-PHENYLAMINO-2-(4' METHYL-7'-CHLORO QUINOLIN-2-ONE-1'-YL)-1, 3, 4-OXADIAZOLE ($VIII_c$) .

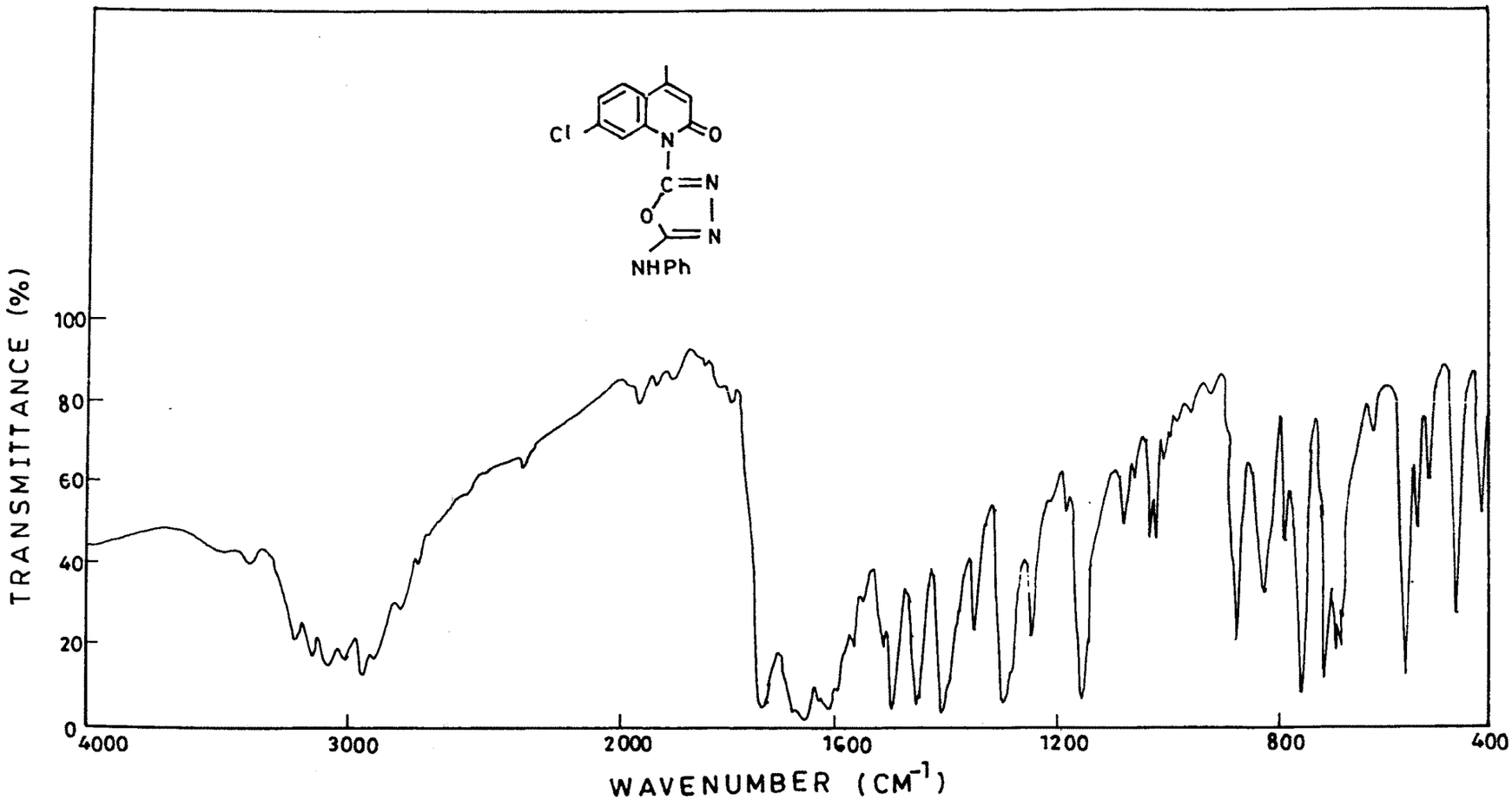


FIG. NO. 18

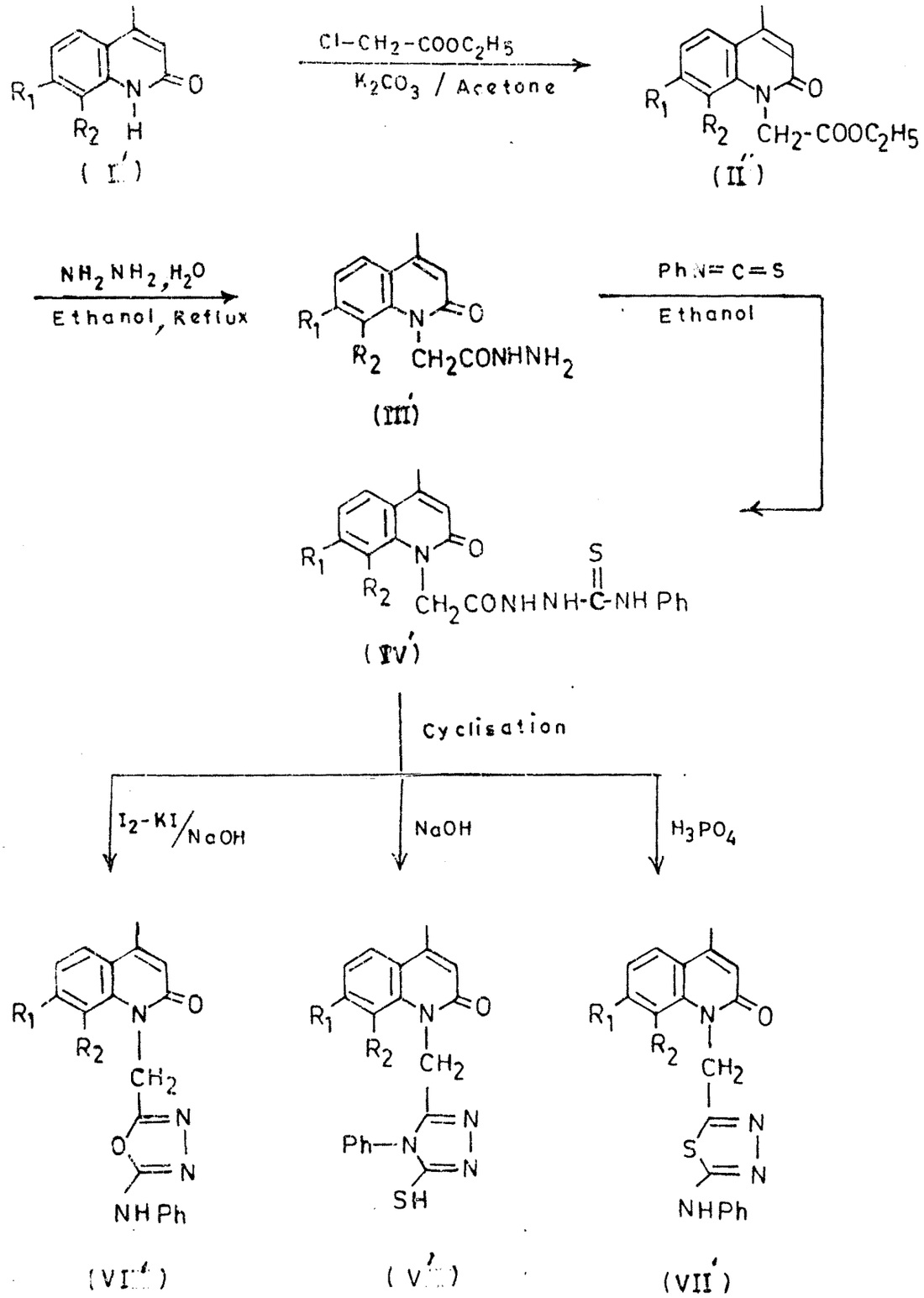
PART - II

Synthesis of Some New Derivatives of N^1-Methyl hydrazido-quinoline-2 (1H)-Ones :

The key intermediate involved in the synthesis of N^1-substituted heterocycle were N^1-substituted quinolin-2-one-1-yl, thiosemicarbazides(IV'). The strategy employed in the synthesis of desired compounds involved N-Methyl carbmethoxylation of 4-Methyl quinolin-2(1H) ones (I') to form N^1-carbmethoxymethyl quinolin-2(1H)-ones (II') which when reacted with hydrazine hydrate in ethanol gave N^1-Methyl hydrazido-4-methyl, quinolin-2 (1H) ones (III'). The reaction of (III') with phenylisocyanate yielded quinolin-2(1H)-one-1-yl, methyl thiosemicarbazides (IV') as key intermediates These when cyclised in presence of sodium hydroxide, I_2 in KI and phosphoric acid furnished targetted 1-Phenyl-2-(4'-Methyl, quinolin-2'-one-meth-1-yl)-1,3,4-triazole (V'), 5-Anilino-2-(4'-Methyl, quinolin-2'-one-meth-1-yl)-1,3,4-oxadiazole (VI') and 5-Anilino-2-(4'-Methyl, quinolin-2'-one-meth-1'-yl)-1,3,4-thiadiazole (VII') respectively (Scheme - II). The structures of these compounds have been confirmed by IR, PMR and elemental analysis.

Preparation of Acetoacetanilide and 4-Methyl-2-quinolin-2(1H)-ones are reported in Part-I of this dissertation.

SCHEME-II


Cl-CH2-COOC2H5
K2CO3 / Acetone
NH2NH2,H2O
Ethanol, Reflux
PhN=C=S
Ethanol
Cyclisation
I2-KI/NaOH
NaOH
H3PO4
(I')
(II')
(III')
(IV')
(VI')
(V')
(VII')

i) Synthesis of N^1-carbmethoxy methyl-4-methyl quinolin-2(1H)-ones (II') :

In a round bottom flask carrying reflux condenser and a guard tube, a mixture of 4-Methyl, quinolin-2(1H)-one (Ia) (13 gm, 0.03 mole) and methylchloroacetate (8 gm, 0.03 mole) in dry acetone containing anhydrous potassium carbonate (2 gm) was refluxed for 24 hrs., cooled and the solvent was removed under reduced pressure. The resulting white solid was washed with water, filtered and recrystallised from ethanol to give II'a, 7.5 gm (86%), M.P. 68°C; (Found : C, 67.4; H, 5.70; N, 6.00. $C_{13}H_{13}ON$ requires : C, 67.53; H, 5.63; N, 6.06%); IR (KBr) : 1780 (ester, $\rangle C=O$), 1665 (cyclic amido, $\rangle C=O$), 1600 cm^{-1} ($\rangle C=C\langle$) cm^{-1}; ^1H NMR (TFA) : δ, 2.45 (3H, s $=C-CH_3$), 3.8 (3H, s, $-OCH_3$), 3.95 (3H, s, $-NCH_2$), 6.15 (1H, s, = CH-), 7 - 7.6 (3H, m, Ar-H) ppm. Fig-19 For other compounds physical and analytical and spectral data have been reported in Table-IXa and Table - IXb respectively.

Table - IXa

Physical and Analytical data of the Compounds (II'b-c)

Comp. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
IIb	H	CH_3	165	85.88	$C_{15}H_{17}NO_3$	69.35 (69.49)	6.50 (6.56)	5.35 (5.41)
IIc	Cl	H	243	87.84	$C_{13}H_{12}O_3NCl$	58.80 (58.87)	4.50 (4.53)	5.20 (5.28)

Table - IXb

IR and ^1H NMR spectral data of the compounds (II'b-c)

Compound No.	Spectral characteristic	Fig.No.
II'b	^1H NMR (TFA) : δ,1.25 (3H,s,Ar-CH_3), 2.45 (3H,s, =C-CH_3), 3.8 (3H,s, - OCH_3), 3.95 (2H,s, -NCH_2-), 6.25 (1H, s, = C<u>H</u>-), 7.15 - 7.5 (3H,m, Aromatic protons) ppm.	20
II'b	IR(KBr) : ν, 1770-1760 (ester, >C=0), 1660 - 1650 (cyclic amido, >C=0), 1600 - 1580 (>C=C<) cm^{-1}.	-
II'c	^1H NMR (TFA) : δ , 2.4 (3H,s, =C-CH_3), 3.75 (3H,s, -OCH_3), 3.95 (2H,s, -NCH_2-), 6.15 (1H, s, = <u>CH</u>-), 7-7.6 (3H,m, Aromatic protons) ppm.	-
II'c	IR (KBr) : ν, 1770 (ester, >C=0), 1650 (cyclic amido (Lactam), >C=0), 1600 (>C=C<), 770-760(>C-Cl) cm^{-1}.	21

ii) Synthesis of N^1-Methyl hydrazido-4-methylquinolin-2 (1H)-Ones (III'a) :

To a solution of compound II'a (7 gm, 0.01 mole) in ethanol (40 ml), hydrazine hydrate (5 ml, 0.01 mole) was added and the reaction mixture was refluxed on water bath for 2hr., cooled and resulting solid was filtered and recrystalised from ethanol to give III'a, 6.3 gm (89%); M.P. 284°C, (Found : C, 62.45; H, 5.58; N, 18.00; $C_{12}H_{13}O_2N_3$ requires : C, 62.54; H, 5.63; N, 18.18%); IR (KBr) : 3350-3200 (-NH-NH_2), 1665 cm^{-1} (cyclic amido, >C=0) cm^{-1}; Fig. 22 ^1H NMR ($CDCl_3$) : δ , 2.4 (3H,s, =C-CH_3), 2.5 (2H,s, -NH_2), 3.92 (2H,s, -N-CH_2), 7 - 7.5 (4H, m, Ar-H) ppm. UV (ethanol) : λ_{max}, 328 and 321 nm. For other compounds physical and analytical and spectral data have been depicted in the Table - Xa and Table - Xb respectively.

Table - Xa

Physical and Analytical data of the compounds (III'b-c)

Comp. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
III'b	H	CH_3	298	91.79	$C_{13}H_{15}O_2N_3$	63.60 (63.67)	7.30 (7.35)	17.15 (17.34)
III'c	Cl	H	317	78.37	$C_{12}H_{12}O_2N_3Cl$	54.30 (54.34)	4.50 (4.53)	15.8 (15.85)

Table - Xb

IR, ^1H NMR, UV and Mass Spectral data of the Compounds (III'b-c)

Compd.No.	Spectral characteristics	Fig.No.
III'b	^1H NMR($CDCl_3$) : δ, 2.35 (3H,s,Ar-CH_3), 2.45 (3H,s,=C-CH_3), 4.0 (2H,s, -N-CH_2), 6.25 (1H,s, = CH-), 7.15 - 7.5 (3H,m, Aromatic protons) ppm.	-
III'b	IR(KBr) : ν 3400-3180 (-$NHNH_2$), 1670 - 1660 (-lactum, >C=0), 1650 - 1640 (acyclic amido, >C=0), 1600 (>C=C<) cm^{-1}	23
III'b	Mass (70 EV) : M/E, 245 (1%), 187 (98%), 172 (100%), 156(11%), 144(35%), 128(7%), 115 (17%), 103 (10%), 89 (11%), 77(11%).	24
	Mass spectral fragmentation :	SCHEME- III
III'b	UV (ethanol) : λ_{max}, 373 nm.	
III'c	^1H NMR ($CDCl_3$) : δ, 2.4 (3H,s,=C-CH_3), 2.5 (2H,s, -NH_2), 3.95 (2H,s,-NCH_2), 6.2 (1H,s, = CH-), 7-7.6 (3H,m, Aromatic protons) ppm.	-
III'c	IR (KBr) : ν 3500-3100 (-NH-NH_2), 1665-1645 broad (cyclic and acyclic amido), 1605 (>C=C<) 770(>C-Cl) cm^{-1}.	-
III'c	Mass (70 Ev) : M/E, 266 (10.5%), 207(100%), 192 (12%), 177 (13%), 172 (26%), 164(42%), 155 (12%), 143 (12%), 128 (13%), 123(11%), 99 (21%), 86 (6%), 75 (15%), 63(8%).	25
	Mass spectral fragmentation :	SCHEME- IV

iii) Synthesis of 4-Phenyl-1-(4'-Methyl, quinolino-methyl-oxo-) thiosemicarbazide (IV'a) :

A mixture of III'a (5 gm, 0.01 mole) and phenyl isothiocyanate (2.5 gm, 0.001 mole) in ethanol (25 ml) was refluxed for 3-4 hr., cooled and the solvent was removed under reduced pressure. The resulting residue was triturated with water and the solid obtained was recrystallised from ethanol to yield IV'a, 5 gm (63%); M.P. 187°C, (Found : C, 62.00; H, 4.85; N, 15.1. $C_{19}H_{18}O_2N_4S$ requires : C, 62.30; H, 4.92; N, 15.30%); IR (KBr) : 3350 - 3400 (-NH), 1670 broad (amido-CONH) and 1325 - 1355 (>C=S)cm^{-1} ^1H NMR (TFA) : δ , 2.4 (2H, s, =C-CH_3), 3.90 (2H,s, -N-CH_2), 6.18 (1H, s, = CH-), 6.9 - 7.1 (9H, m, Ar-H) PPm.

Fig. 26

. For other compounds the physical and analytical and spectral data have been reported in the Table - XIa and Table - XIb respectively.

Table - XIa

Physical and Analytical data of the compounds (IV'b-c)

Comp. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
IV'b	H	CH_3	105	65.31	$C_{20}H_{20}O_2N_4S$	63.00 (63.16)	5.20 (5.26)	14.70 (14.74)
IV'c	Cl	H	73	79.56	$C_{19}H_{17}O_2N_4I$	56.75 (57.00)	4.20 (4.25)	13.80 (14.00)

Table - XIb

IR and ^1H NMR spectral data of the compounds (IV'b-c)

Compound No.	Spectral Characteristics	Fig.No.
IV'b	^1H NMR (TFA) : δ, 2.30 (3H,s, Ar-CH_3), 2.47 (3H,s, =C-CH_3), 4.6 (1H,s, -NH), 7.4-7.7 (3H,m, Aromatic protons)ppm.	-
IV'b	IR (KBr) : ν, 3350-3200 (-NH), 1670-1660 broad (cyclic and acyclic amido), 1600-1580 (>C=C<); 1355-1350 (>C=S)cm^{-1}.	27
IV'c	^1H NMR (TFA) : δ, 2.45 (3H,s, =C-CH_3), 3.9 (2H,s, -NCH_2-), 4.55 (1H,s, -NH), 6.15 (1H,s, >C=C<u>H</u>), 7 - 7.5 (8H, m, Aromatic protons) ppm.	-
IV'c	IR (KBr) : ν, 3350 - 3200 (-NH), 1670 - 1660 broad (cyclic and acyclic amido >C=0), 1355 (>C=S), 760 (C-Cl) cm^{-1}.	-

iv) Synthesis of 1-Phenyl-2-(4'-methyl quinolin-2'-one-meth-1-yl)-5-mercapto-1,3,4-triazole (V'a) :

Compound IV'a (3.246 gm, 0.001 mole) was refluxed with 2N NaOH (2 ml) for 3 hr. cooled and filtered and filtrate was acidified with glacial acetic acid to give a solid which when recrystallised from ethanol to furnish V'a, 1.92 gm (62.14%); M.P. 296°C; (Found : C, 65.50; H, 4.55; N, 16.0. $C_{19}H_{16}N_4OS$. requires : C, 65.52; H, 4.60; N, 16.09%); IR (KBr) : ν, 2550-2560(SH), 1665 (amido cyclic $\rangle C{=}O$), 1620 ($\rangle C{=}N$) cm^{-1}; ^1H NMR (TFA) : δ, 2.4 (3H, s, $=C-CH_3$), 3.95 (2H, s, $-N-CH_2-$), 6.15 (1H, s, $=CH-$), 7 - 7.9 (9H,m, Ar-H), ppm.

UV (ethanol) : λ_{max}, 286 and 344 nm. For other compounds physical and analytical and spectral data have been included in Table-XIIa and table-XIIb respectively.

Table - XIIa

Physical and Analytical data of the compounds (V'b-c) :

Comp. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
V'b	H	CH_3	260	67.14	$C_{20}H_{18}ON_4S$	66.20 (66.30)	4.90 (4.90)	15.4 (15.47)
V'c	Cl	H	273	61.38	$C_{19}H_{15}ON_4SCl$	65.6 (65.71)	4.30 (4.32)	6.10 (16.14)

Table - XIIb

IR and ^1H NMR spectral data of the compounds (V'b-c)

Compound No.	Spectral Characteristics	Fig.No.
V'a	^1H NMR (TFA) : δ, 2.3 (3H, s, Ar-CH_3), 2.45 (3H, s, =C(-CH_3)), 3.95 (2H,s, -NCH_2), 6.18 (1H, s, = CH-), 6.9-7.6 (8H, m, Aromatic protons), ppm.	
V'b	IR (KBr) : ν, 2550 - 2560 (-SH), 1665-1660 (cyclic amido, >C=0), 1620 (>C=N-), 1600 - 1580 (>C=C<) cm^{-1}.	
V'c	^1H NMR (TFA) : δ, 3.42 (3H, s, =C(-CH_3)), 3.98 (2H,s, -N-CH_2-), 6.25 (1H,s, = CH-), 6.9 - 7.6 (8H,m, Aromatic protons), ppm.	
V'c	IR (KBr) : ν, 3450 - 3350 (-SH), 1665-1655 (Cyclic amido, >C=0), 1620 (>C=N), 1600 (>C=C<), 755(>C-Cl) cm^{-1}.	

v) Synthesis of 5-Anilino-2-(4'-methyl-quinolin-2'-one,meth-1'-yl) 1,3,4-Oxadiazole (VI'a) :

To a mixture of IV'a (1.836 gm, 0.001 mole) in NaOH (4N, 4 ml), I_2 in KI was added till the colour of I_2 persisted and the reaction mixture was further concentrated for 4-5 hr. cooled and poured into ice-cold water. The resulting solid was filtered and recrystallised from ethanol to furnish VI'a, 1.1 gm (66%), M.P. 278°C; (Found : C, 68.6; H, 4.75; N, 16.8. $C_{19}H_{16}O_2N_4$ requires : C, 68.67; H, 4.82; N, 16.85%); IR (KBr): ν 3350-3250 (-NH), 1665-1655 (-NHCO), 1620 (>C=N), ^{1}H NMR (TFA) : δ, 2.45 (3H, s, =C-CH_3), 4.0 (2H, s, - N-CH_2), 4.5 (1H, s, -NH), 6.12 (1H, s, = CH-), 7 - 7.5 (9H, m, Ar-H) ppm. For other compounds physical and analytical and spectral data have been incorporated in Table - XIIIa and Table - XIIIb respectively.

Table - XIIIa

Physical and Analytical data of the compounds (VI'b-c):

Comp. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
VI'b	H	CH_3	245	74.25	$C_{20}H_{18}O_2N_4$	69.30 (69.36)	5.10 (5.20)	16.05 (16.18)
VI'c	Cl	H	284	63.80	$C_{19}H_{15}O_2N_4Cl$	62.2 (62.30)	4.00 (4.10)	15.20 (15.30)

Table - XIIIb

IR and ^1H NMR spectral data of the compounds (VIb-c) :

Compound No.	Spectral characteristics	Fig.No.
VI'b	^1H NMR (TFA) : δ, 2.35 (3H,s,Ar-CH_3), 2.42 (3H,s,=C(-CH_3)), 4.05 (2H,s,-N-CH_2), 4.55 (1H,s, -NH), 6.2 (1H,s, =CH-), 7-7.8 (8H,m, Aromatic proton) ppm.	-
VI'b	IR (KBr) : ν, 3350-3200 (-NH), 1665 (cyclic amido, >C=O), 1620 (>C=N-), 1600 (>C=C<) cm^{-1}.	-
VI'c	^1H NMR (TFA) : δ, 2.42 (3H,s,=C(-CH_3)), 3.95 (2H,s, -N-CH_2), 4.6(1H,s,- NH), 6.15 (1H,s, >C=CH-), 6.8-7.6 (8H,m, Aromatic proton) ppm.	-
VI'c	IR (KBr) : ν, 3350 - 3200 (-NH), 1665-1600 (cyclic amido, >C=O), 1615 (>C=N-), 1580 (>C=C<), 760(>C-Cl) cm^{-1}.	-

vi) Synthesis of 5-Anilino-2-(4'-Methyl-quinolin-2'-one-meth-1'-yl) 1,3,4-thiadiazole (VII'a) :

Compound IV'a (1.32 gm, 0.001 mole) was dissolved in syrupy phospho ric acid (5 ml) and heated at 120°C for 50 min., kept over night and then poured into ice cold water. The resulting solid wasfiltered and recrystallised from ethanol to give VII'a, 0.875 gm (73%); M.P. 55°C; (Found : C, 68.60; H, 4.75; N, 16.80. $C_{19}H_{16}ON_4S$ requires : C, 68.67; H, 4.82; N, 16.85%); IR (KBr) : 3300 - 3200 (-NH), 1665 (amido >C=0), 1610 - 1620 (>C=N), 700-720 (C-S-C) cm^{-1}; ^1H NMR (TFA) : δ , 2.4 (3H, s, =C(—CH_3)), 4.0 (2H,s, -N-CH_2-), 4.7 (1H,s, -NH), 6.15 (1H,s, =CH-), 7 - 7.8 (9H, m, Ar-H) ppm. For other compounds physical and analytical and spectral data have been incorporated in Table - XIVa and Table-XIVb respectively.

Table - XIVa

Physical and Analytical data of the Compounds (VII'b-c)

Comp. No.	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
VII'b	H	CH_3	318	60.00	$C_{20}H_{18}ON_4S$	66.20 (66.30)	4.90 (4.97)	15.40 (15.47)
VII'c	Cl	H	312	67.39	$C_{19}H_{15}ON_4Cl$	65.10 (65.14)	4.20 (4.29)	15.75 (16.0)

Table - XIVb

IR and NMR spectral data of the compounds (VII'b-c)

Compound No.	Spectral characteristics	Fig.No.
VIII'b	^{1}H NMR (TFA) : δ, 2.3 (3H,s, Ar-CH_3), 2.4 (3H,s, =C-CH_3), 4.6 (1H,s, -NH), 6.25 (1H,s, = CH-), 6.75 - 7.6 (8H, m, Aromatic Protons) ppm.	-
VIII'b	IR (KBr) : ν, 3470 - 3100 broad (-NH), 1670 broad (- lactam, >C=0), 1605 (>C=N- and >C=C<) cm^{-1}.	28
VII'c	^{1}H NMR (TFA) : δ, 2.43 (3H,s, =C-CH_3), 4.62 (1H,s, -NH-), 6.18 (1H,s, = CH-), 6.8 - 7.6 (8H,M, Aromatic protons) ppm.	-
VII'c	IR (KBr) : ν, 3400 - 3200 (-NH), 1670-1660 broad (cyclic amido, >C=0), 1610 (>C=N-), 1580 (>C=C<) cm^{-1}.	-

IR, ^{1}H NMR AND MASS SPECTRA

^{1}H NMR SPECTRUM OF 4-METHYL ,N^1–CARBMETHOXYMETHYL QUINOLIN-2(1H)ONE(II$'_a$)

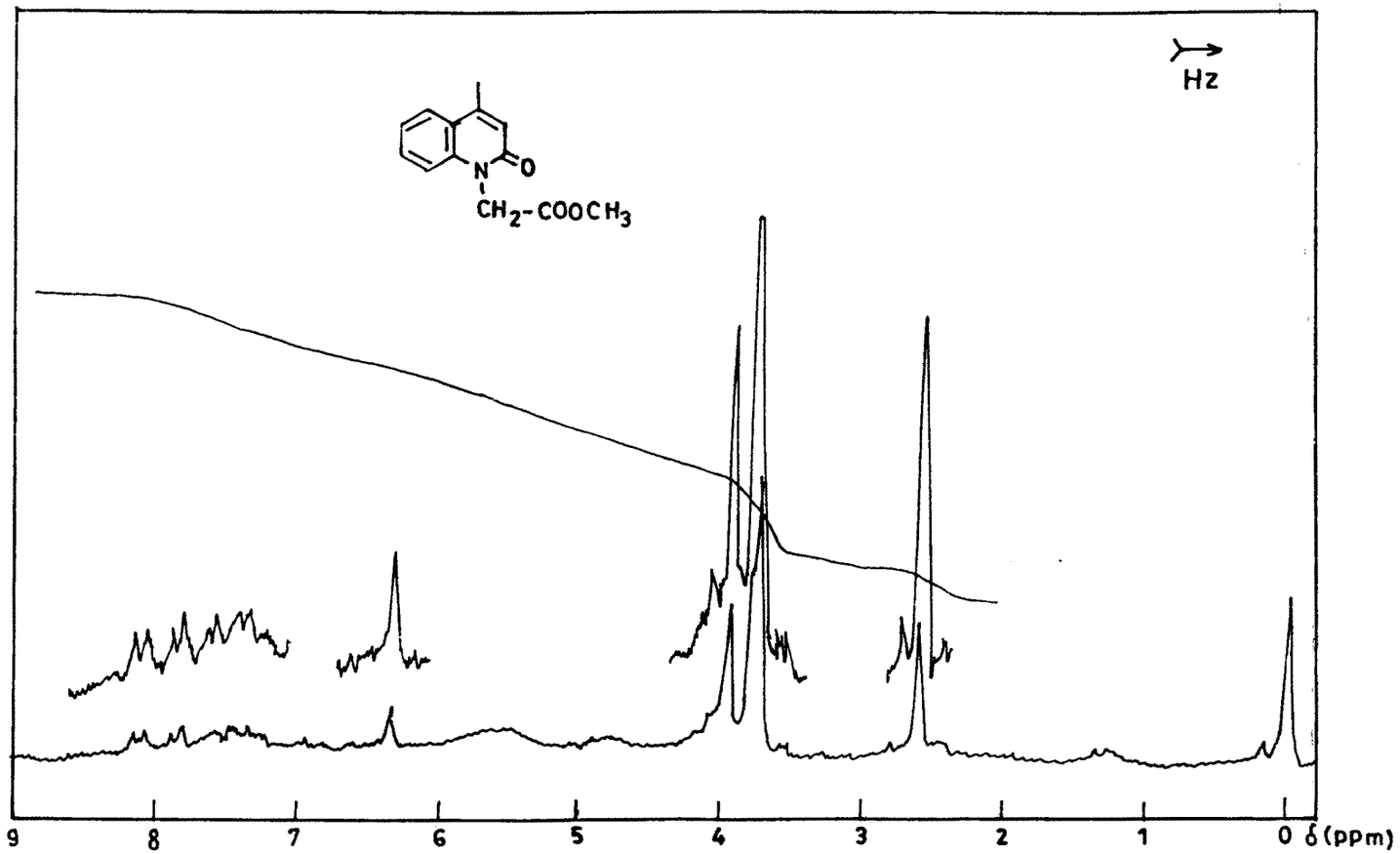


FIG. NO. 19

^1H NMR SPECTRUM OF 4,8-DIMETHYL N^1-CARBOETHOXY METHYL QUINOLIN-2(1H) ONE (II'_b) .

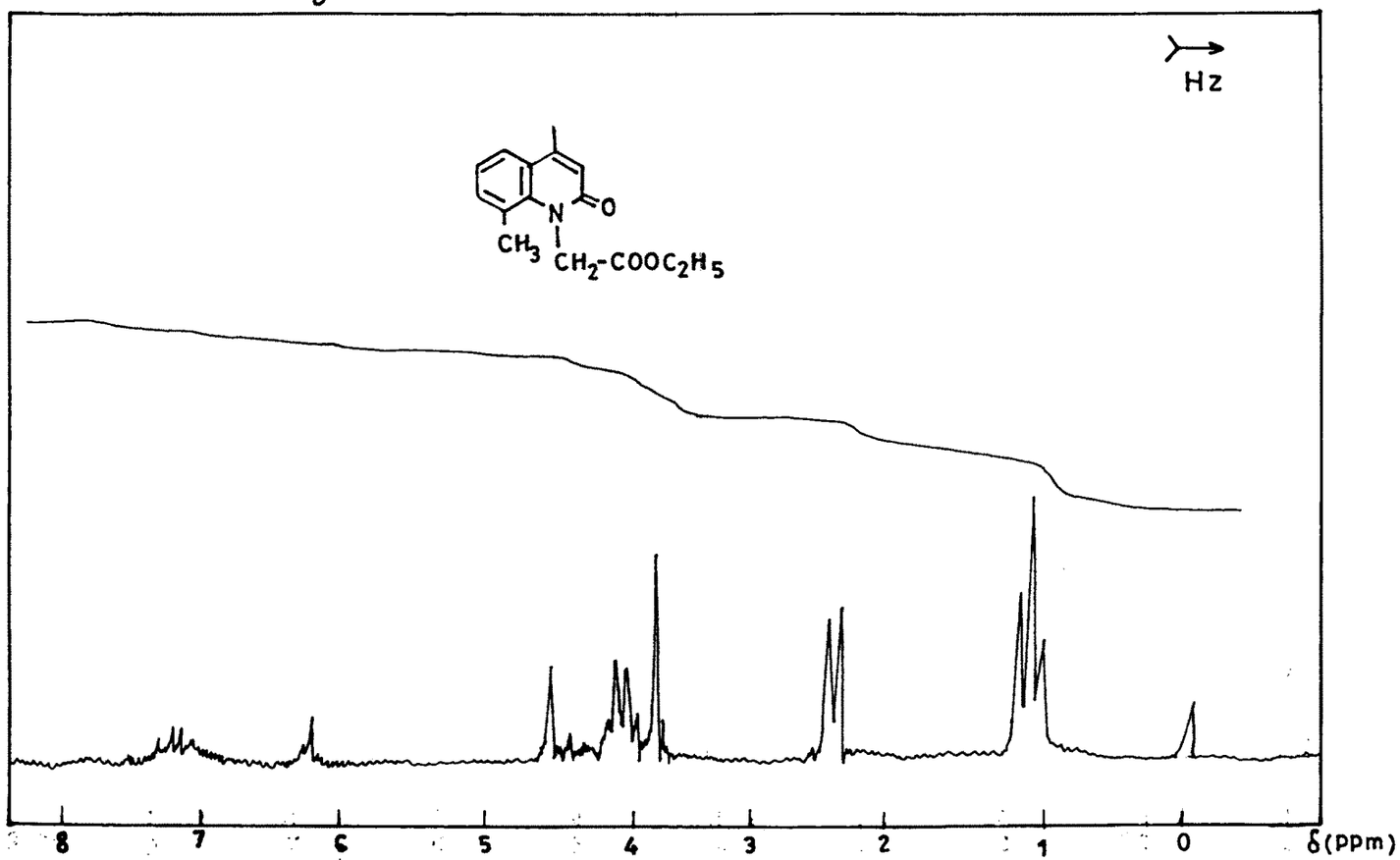


FIG. NO. 20

IR SPECTRUM OF 4-METHYL, 7-CHLORO, N^1-CARBETHOXY METHYL, QUINOLIN-2(1H) ONE (II_C').

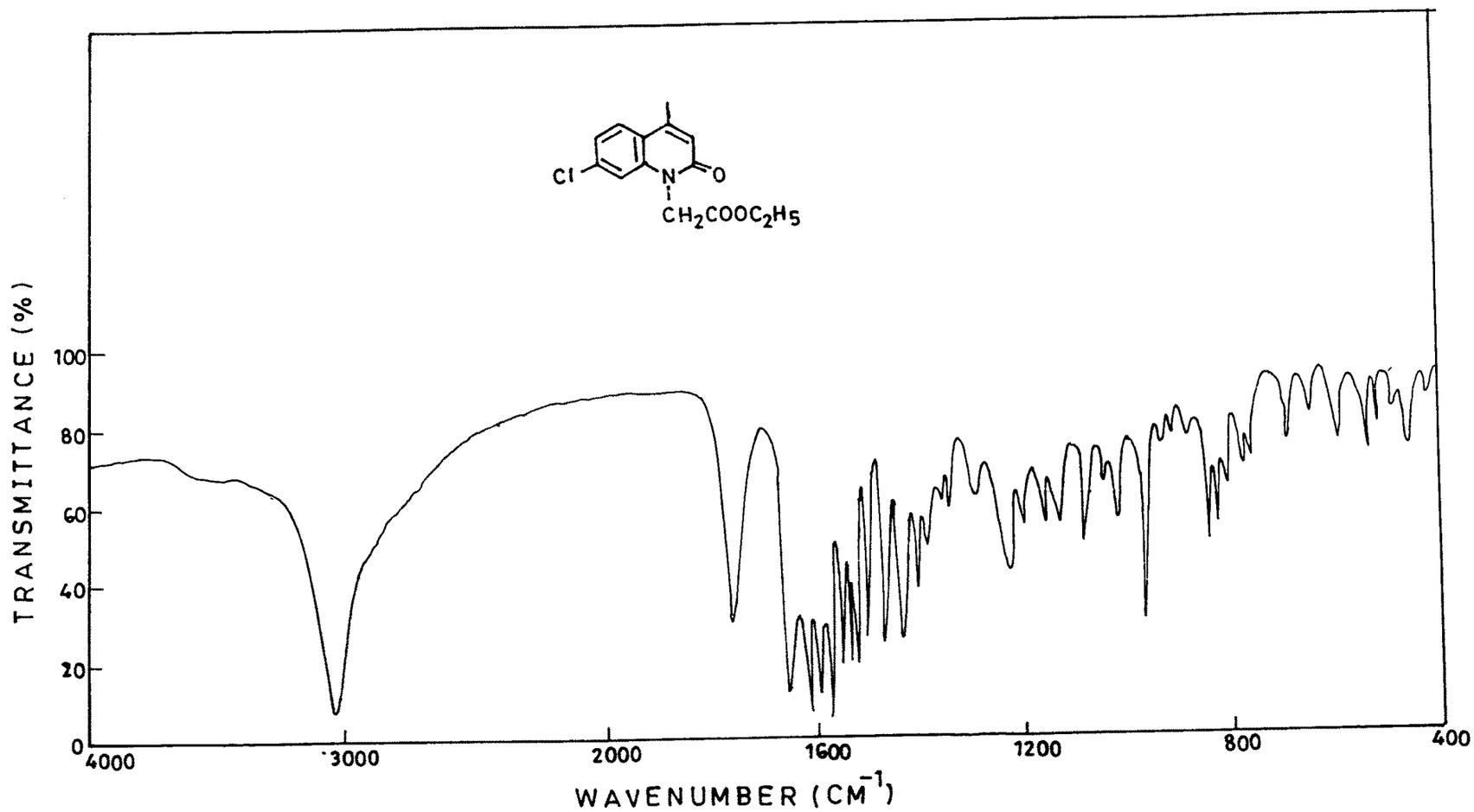


FIG. NO. 21

IR SPECTRUM OF 4-METHYL, N^1 HYDRAZIDOMETHYL QUINOLIN-2(1H) ONE (III'_a).

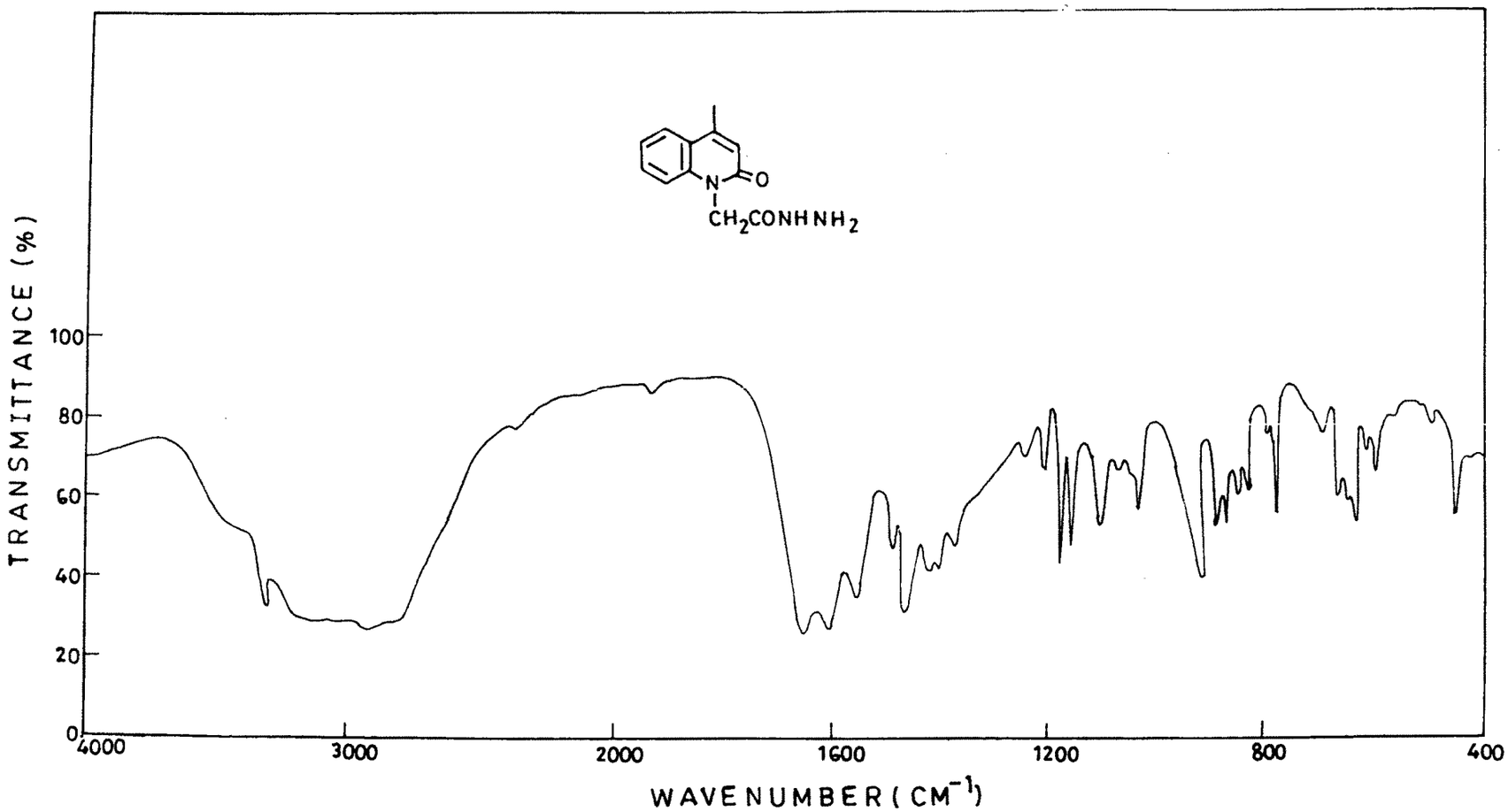


FIG. NO. 22

IR SPECTRUM OF 4,8-DIMETHYL, N^1-HYDRAZIDOMETHYL QUINOLIN-2(1H) ONE (III'_b).

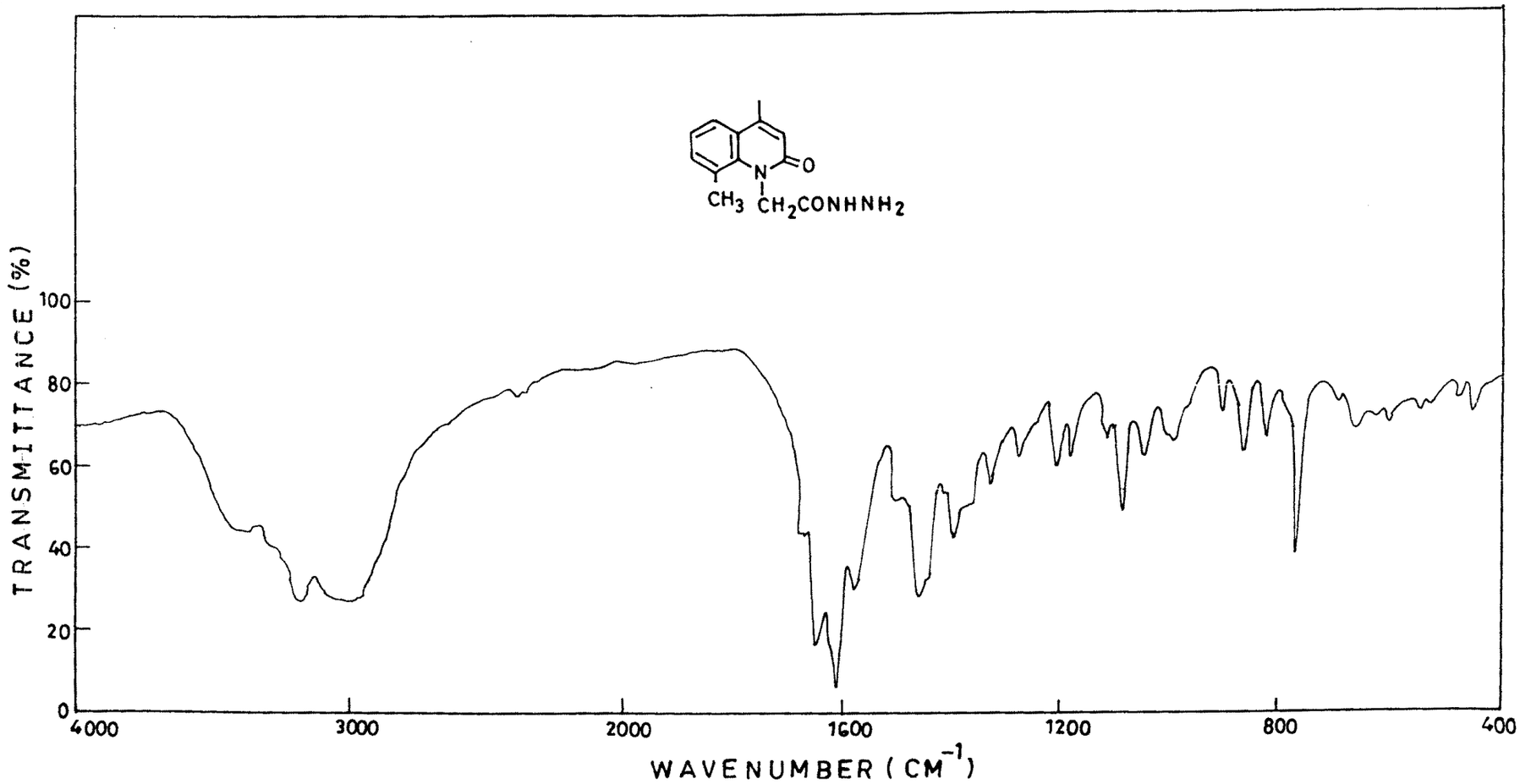


FIG. NO. 23

MASS SPECTRUM OF N^1–METHYLHYDRAZIDO - 8 METHYL-QUINOLIN– 2 (1H) – ONE .

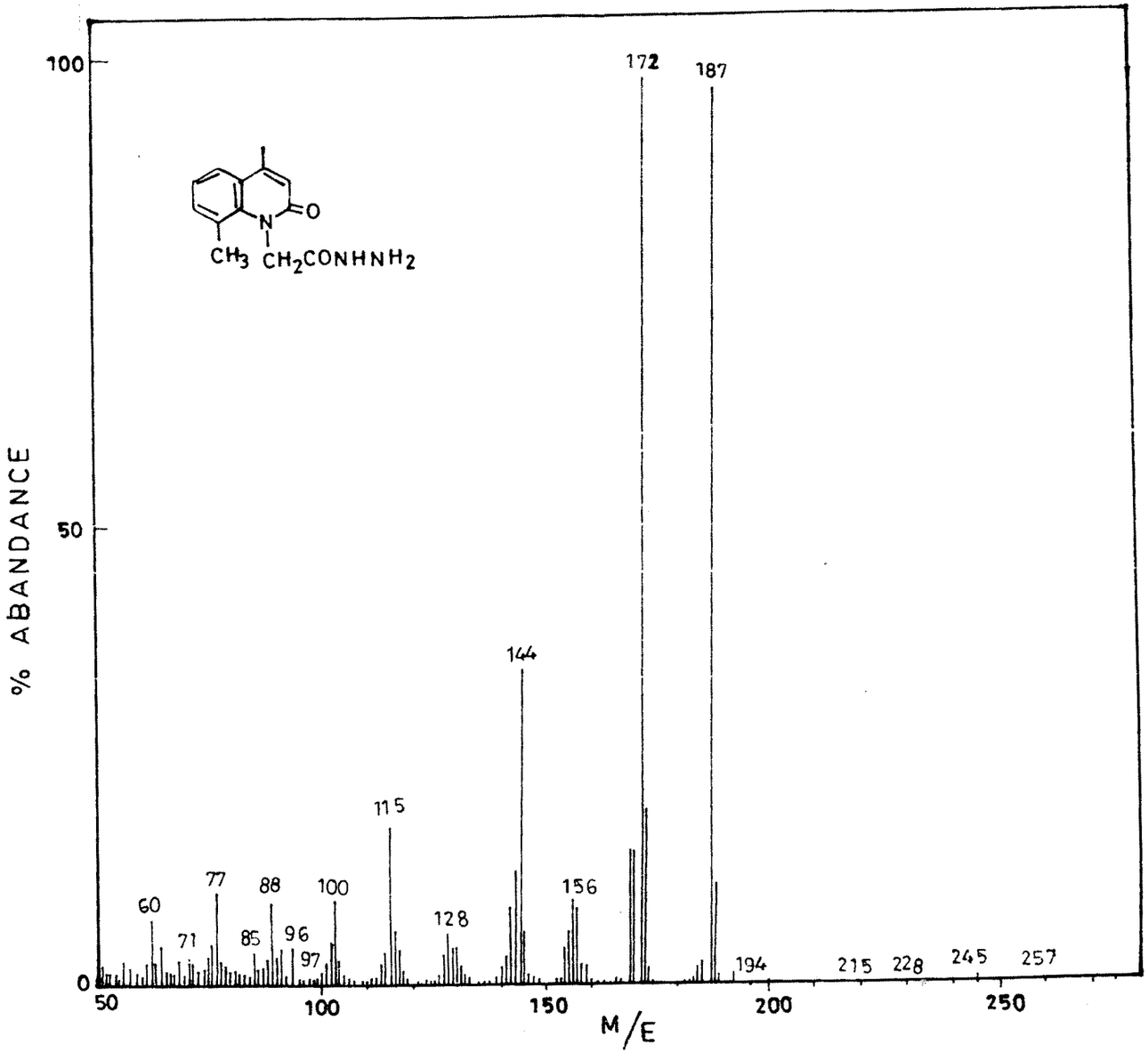
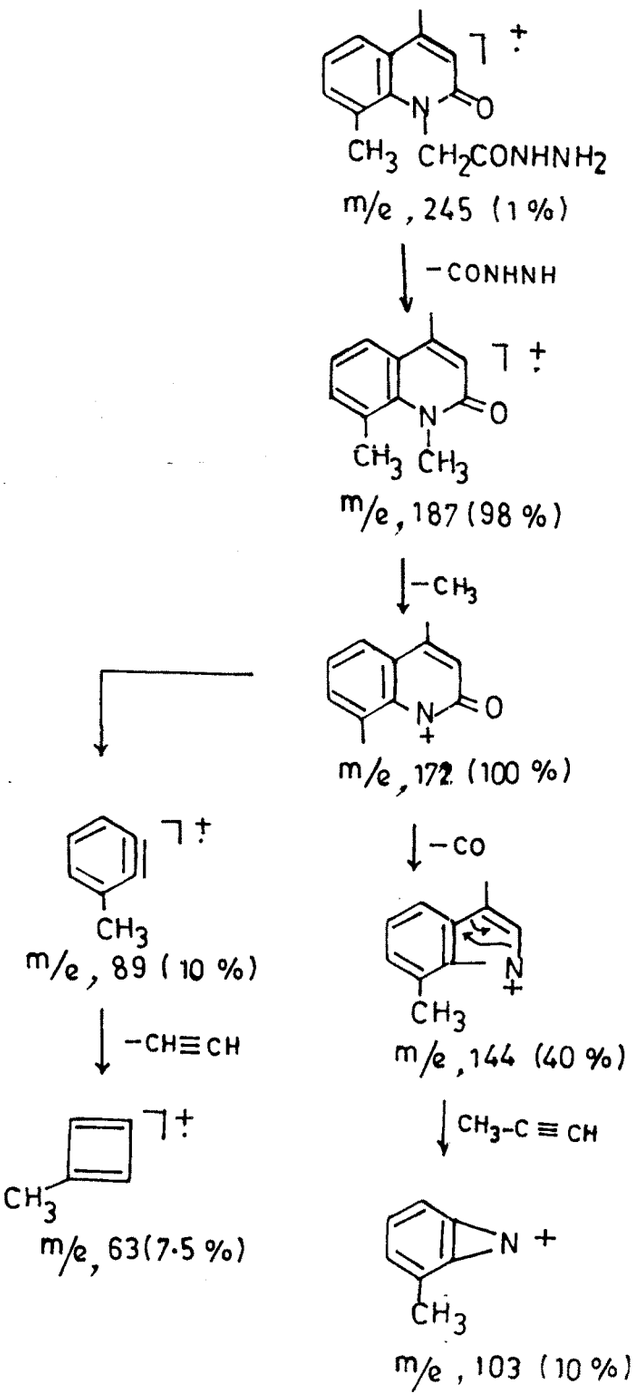


FIG. NO. 24

SCHEME-III

PROBABLE MASS SPECTRAL FRAGMENTATION OF N^1- METHYLHYDRAZIDO-8-METHYL QUINOLIN-2(1H) ONE.



MASS SPECTRUM OF N^1-METHYLHYDRAZIDO-7-CHLORO QUINOLIN-2(1H) ONE.

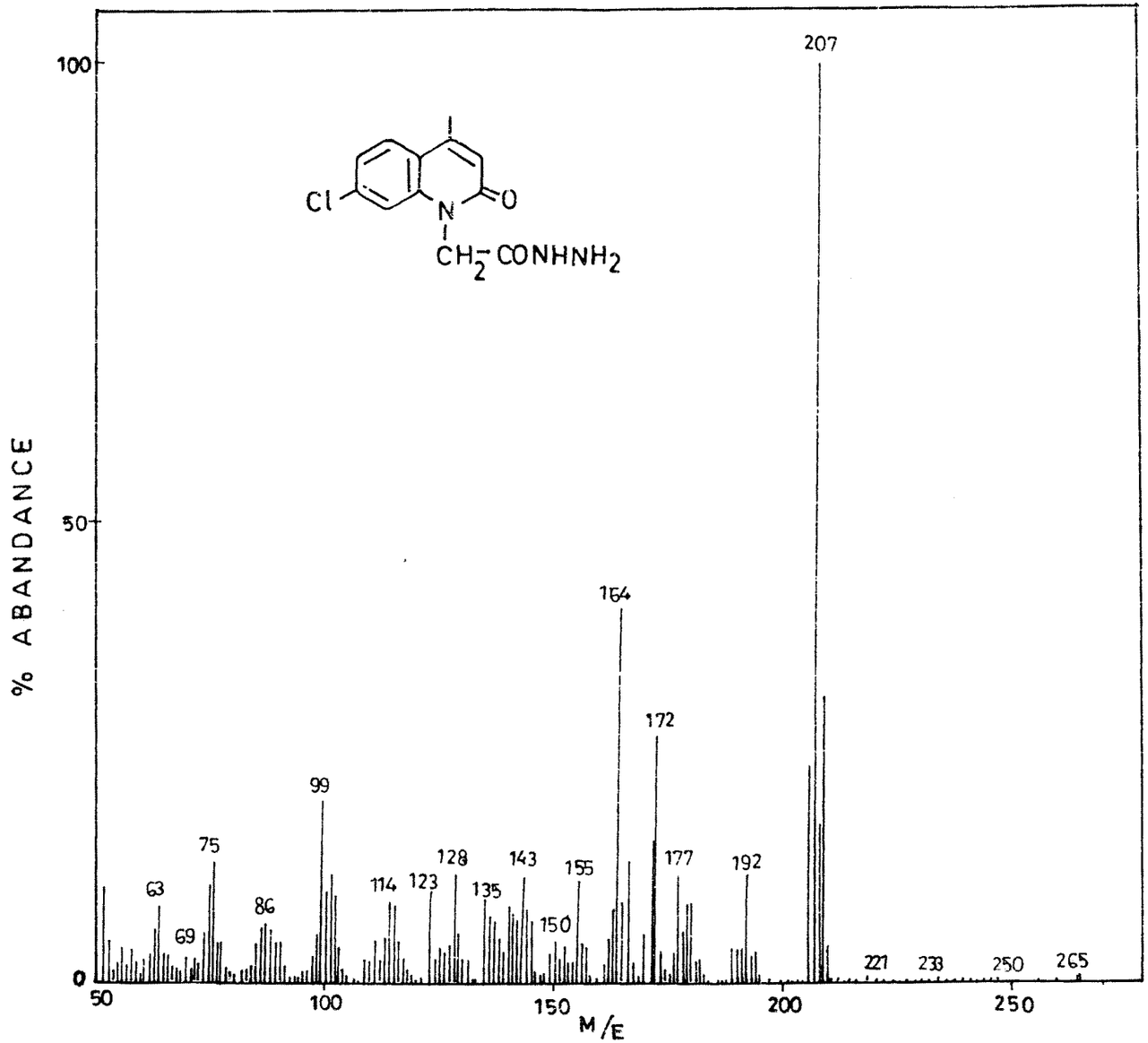
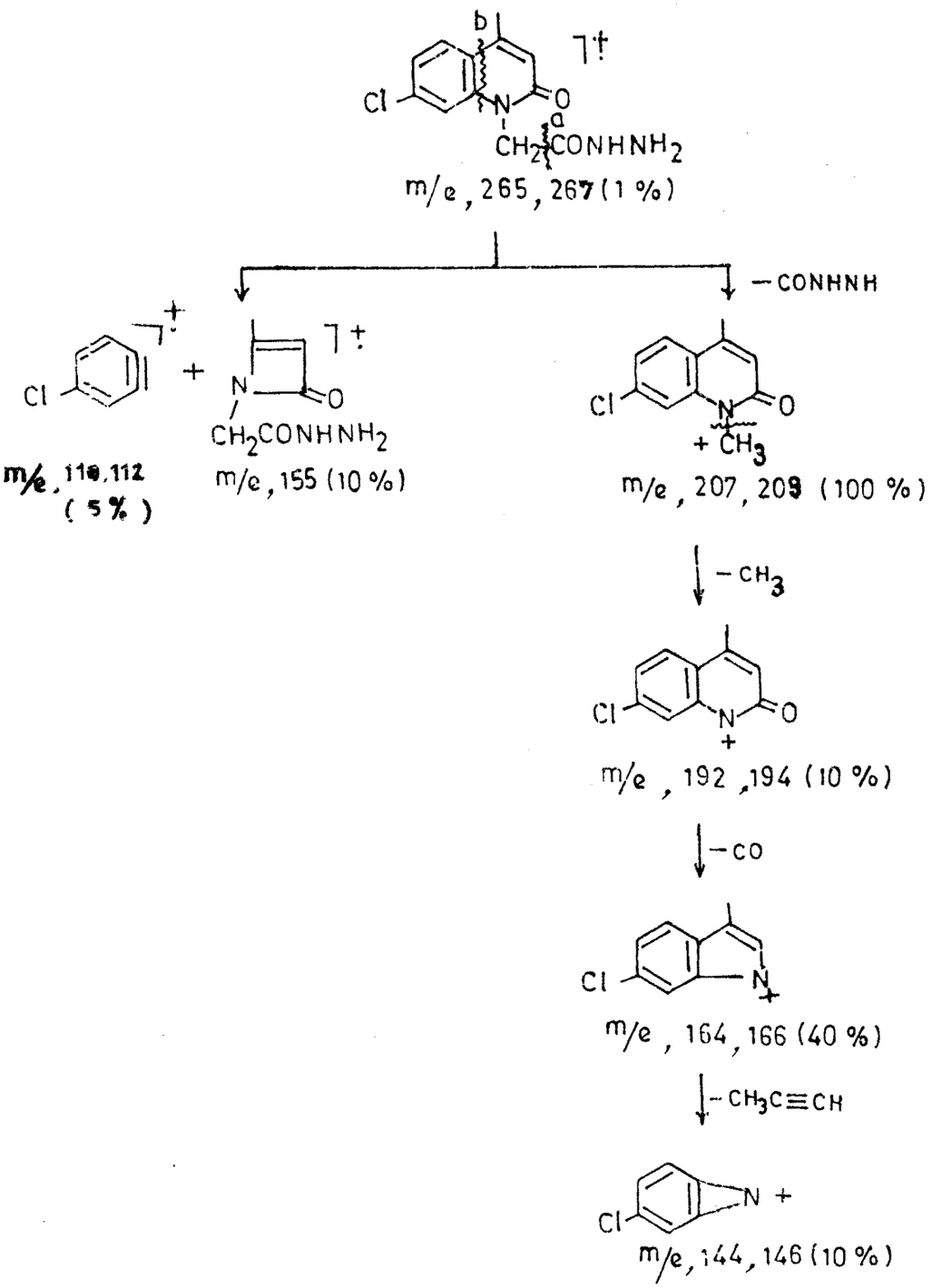


FIG. NO. 25

SCHEME-IV

MASS SPECTRAL FRAGMENTATION OF

N^1-METHYLHYDRAZIDO-7-CHLORO-QUINOLIN-2(1H) ONE.



^1H NMR SPECTRUM OF 4-PHENYL,1-(4'-METHYL QUINOLINE-2'-ONE-1'-YL)-METHYL-OXO-THIOSEMICARBAZIDE (IV'_a).

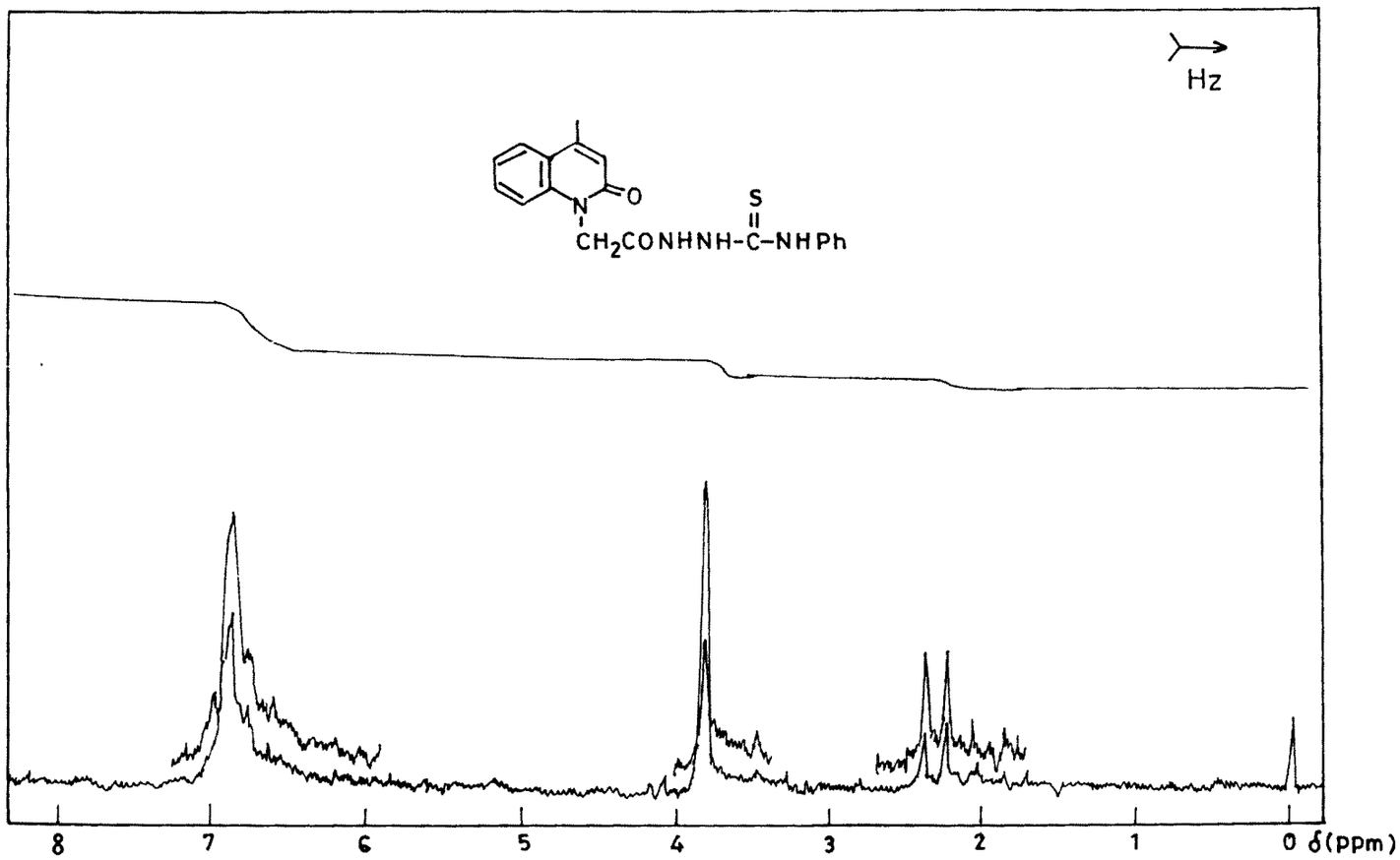


FIG. NO. 26

IR SPECTRUM OF 1-PHENYL-2-(4′,8′ DIMETHYL QUINOLIN-2′-ONE-METH-1′-YL)-5-MERCAPTO-1,3,4-TRIAZOLE (Va′).

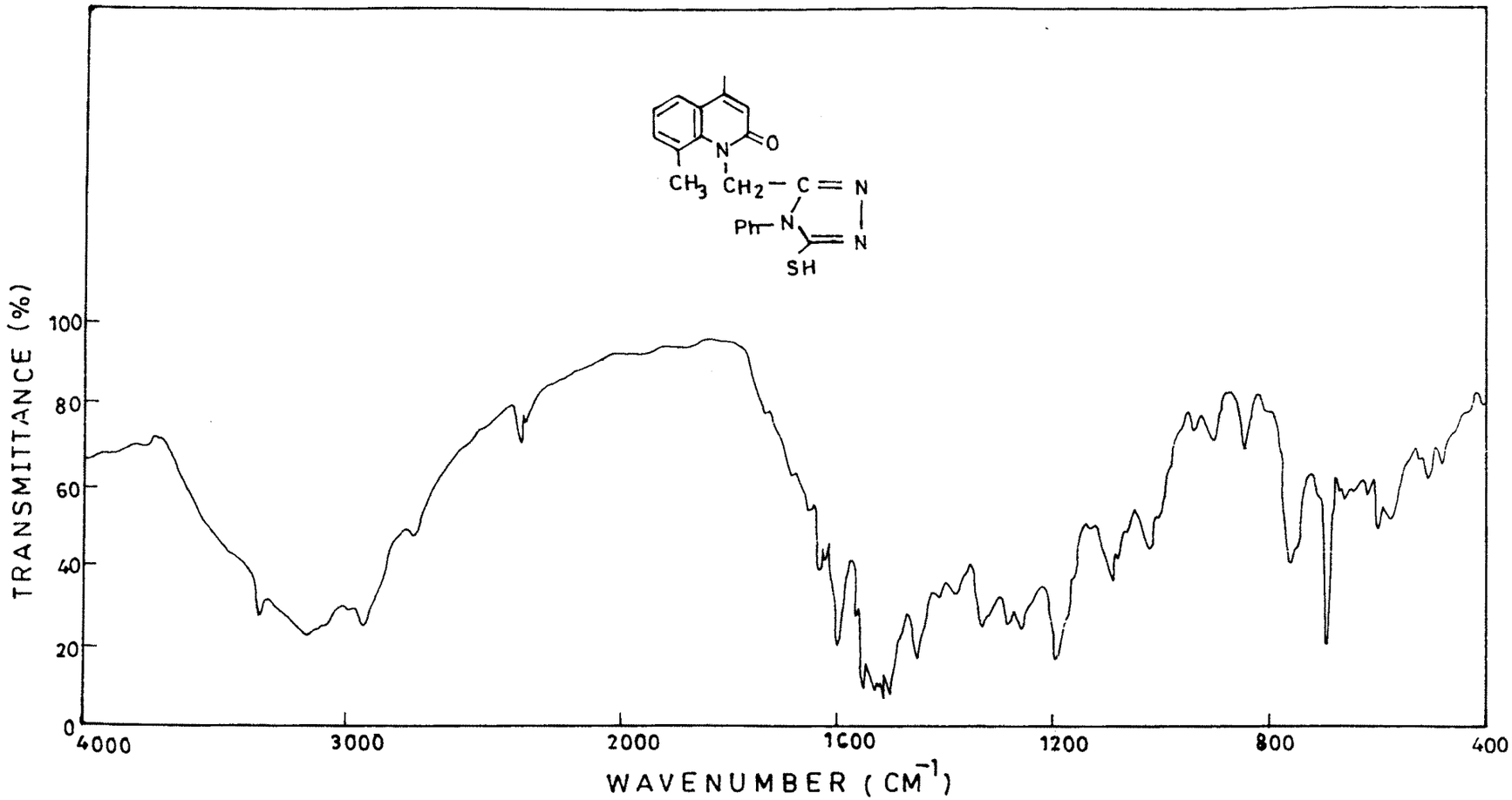


FIG. NO. 27

IR SPECTRUM OF-5-PHENYL AMINO -2 -(4',8'- DIMETHYL QUINOLIN-2'-ONE-1'- YL) 1,3,4 -THIADIAZOLE (VII')

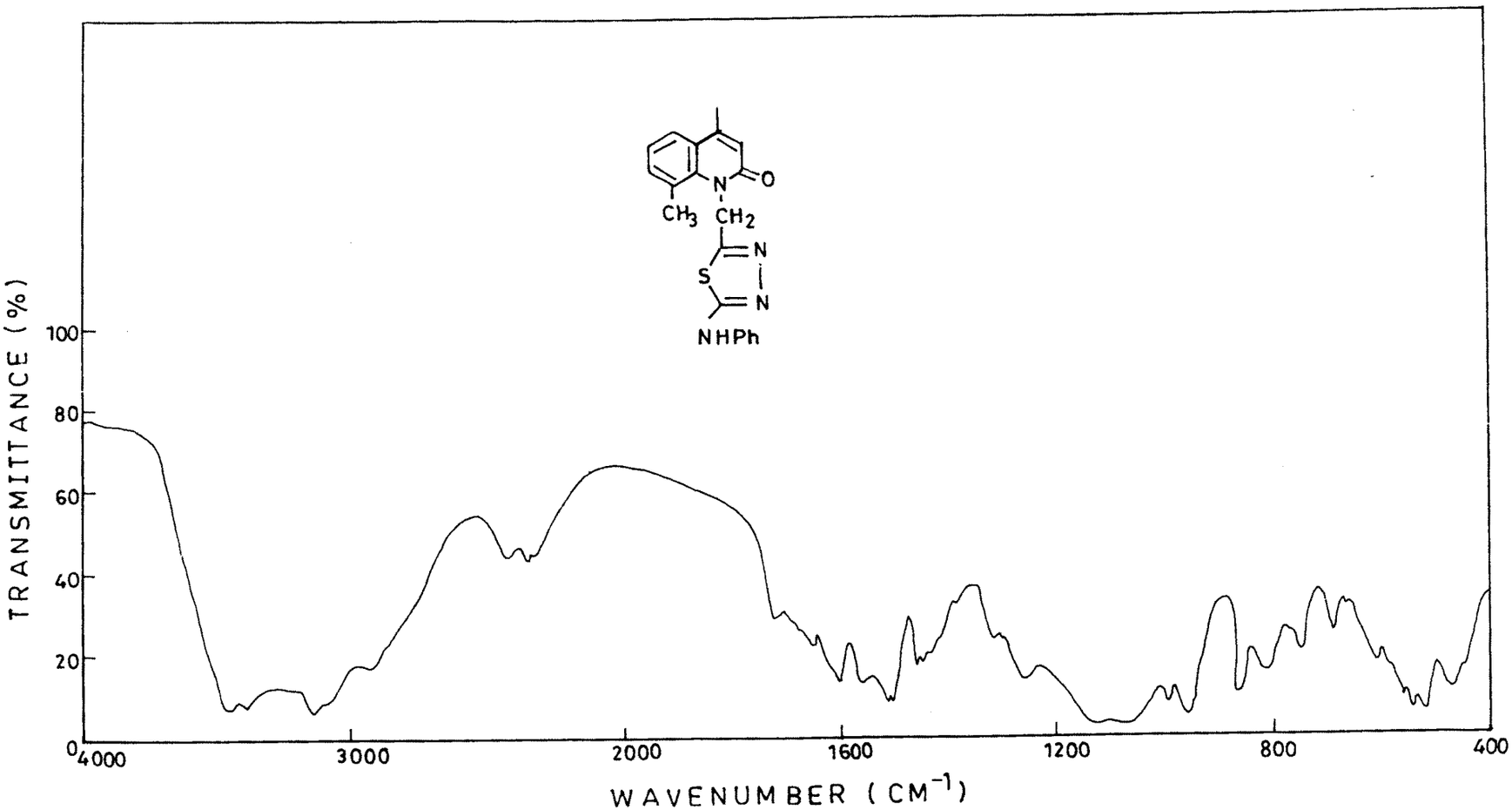


FIG. NO. 28

PART - III

Preparations of Acetoacetanilides, 4-Methyl-2-quinolon-2(1H)-ones and synthesis of N^1-hydrazido/methyl hydrazido-quinolin-2(1H)-ones are reported in Part-I and Part-II of this dissertation.

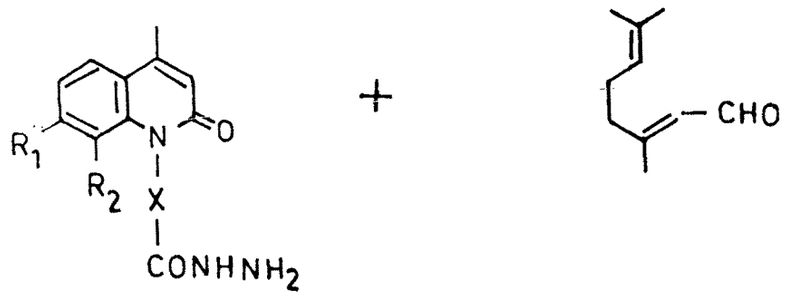
Synthesis of N^1-citralidene hydrazido-4-methyl quinolin-2(1H)-one : (Scheme-V)

A mixture of N^1-hydrazido-quinolin-2(1H)-one (2 gm, 00.1 mole) and citral (4 ml, 0.001 mole) in ethanol (20 ml) was refluxed for 3 hr.& solvent was removed. The resulting residue was triturated with water and the solid obtained was recrystallised from ethanol to yield 1"a (1.9 gm, 66.66%); M.P. 186°C; (Found : C, 70.58; H, 7.64; N, 12.35. $C_{20}H_{26}O_2N_3$ requires : C, 70.50; H, 7.60; N, 12.30%); IR (KBr) : 3350 - 3150 (NH), 1670 - 1660 (amido >C=O), 1620 (>C=N-), 1600 (C=C) Cm^{-1}.

^{1}H NMR($CDCl_3$) : δ, 2.0 - 2.35 (13H, m, 3x-CH_3 and 2xCH_2), 2.45 (3H,s, =C-CH_3), 5.8 - 6.3 (3H,m, =CH), 6.9 - 7.6 (4H,m, aromatic protons) ppm.

For other compounds the physical, Analytical and spectral data have been reported in the Table-XVa and Table-XVb respectively.

SCHEME-V



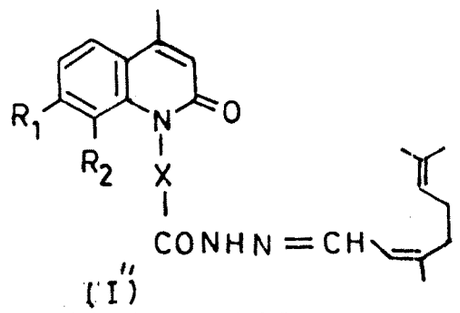
X = O

X = CH_2

Reflux

Ethanol,

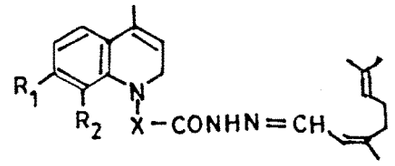
AcOH



(I'')

Table - XVa

Physical and Analytical data of the compounds (I"b-c)



for I''_b, X = O

I''_c, X = $-CH_2$

Comp. No.:	R_1	R_2	M.P. °C	Yield %	Molecular formula	Elemental analysis found (%) / (calcd.) C	H	N
I"b	H	CH_3	160	65.35	$C_{21}H_{27}O_2N_3$	71.10 (71.18)	7.80 (7.90)	2.00 (2.03)
I"c	Cl	H	155	65.38	$C_{21}H_{25}O_2N_3Cl$	72.10 (72.11)	7.00 (7.04)	11.80 (11.83)

Table - XVb

IR and ^1H NMR spectral data of the compounds (I"b-c)

Compound No.	Spectral characteristics	Fig.No.
I"b	^1H NMR (TFA) : δ, 2.0-2.35 (16H, m, 4x-CH_3 and 2xCH_2- 2.45 (3H, m, =C-CH_3), 5.9-6.15 (3H, m, = CH-), 7-7.6 (3H, m, Aromatic protons) ppm.	-
I"b	IR(KBr) : ν 3400-3150 (-NH-), 1680(acyclic amido, >C=O), 1655 (cyclic amido >C=O), 1620 (>C=N-), 1600 (>C=C<) cm^{-1}.	-
I"c	^1H NMR (TFA) : δ, 2-3.35 (13H, m, 3x-CH_3 & 2x-CH_2) 2.45 (3H, s, =C-CH_3), 5.9-6.1 (3H, m, 3x = CH), 7.3-7.6 (3H, m, aromatic protons).	-
I"c	IR (KBr) : ν 3400-3150 (NH), 1680 (acyclic amido). 1660 (cyclic amido >C=O), 1620 (>C=N-) 1600(>C=C<), 760 (C-Cl) cm^{-1}.	-