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Statement under O.Ph.D. 7 of Saurashtra University

The work included in the thesis is my own work under the supervision of ***Dr. Shipra Baluja*** and leads to some contribution in chemistry subsidised by a number of references.

Dt. : 02 -03 -2006

(NIRMAL D. PANDYA)

Place : Rajkot.

This is to certify that the present work submitted for the Ph. D. Degree of Saurashtra University by ***Nirmal D. Pandya*** is his own work and leads to advancement in the knowledge of chemistry.
The thesis has been prepared under my supervision.

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CONTENTS

INTRODUCTION

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. The resultant compound containing functional group -CH=N- is called an imine, anil, azomethine or Schiff base to honor Schiff(1), who synthesized such compounds. Imines can also be prepared from ketones but the reaction tends to occur less readily than that with aldehyde.

Schiff base are important due to their vivid applications owing to their characteristic properties such as high synthesis flexibility, varied coordinating ability, thermal stability, novel structures, biological activities and medicinal utility. So, different types of Schiff bases (2-16) have been synthesized by various workers. Dayagi and Degani (17) have reported some methods for the synthesis of Schiff bases. Mehta et al (18) have synthesized some Schiff bases from 2-hydroxy-naphthaldehyde and amino acids and studied their physicochemical properties. Synthesis of some other Schiff bases has also been carried out by Sondhi et al (19). Krylov and Stolyarov(20) synthesized Schiff bases from N,N-dialkyl hydroxylamine. Some Schiff bases derived from thiazoles and benzothiazoles have also been synthesized by Dash et al(21). Hori and Takahashi(22) have also synthesized these bases from salicyldehyde and (bis)[2-amino ethyl] sulphide. Sheevens and Pandit(23) have synthesized some Schiff bases from substituted benzaldehyde and cyclohexylamine. Synthesis and characterization of new Schiff base have also been reported by Siddiqui and Nishat(24). Benzo-12-crown-4 Schiff bases(25) and crowned Schiff bases(26) were also synthesized by some workers. Some new (N-indolidene-DL-glycine, N-indolidene-DL-alanine and N-indolidene DL-valine amino acid Schiff bases were prepared by the condensation of indole-3-carboxaldehyde and DL-glycine, DL-alanine and DL valine(27). Synthesis of N- (5-Pyrazolayl) Schiff bases from aryl tri fluro methyl ketones was reported by Vovk and coworkers(28). Recently, some lateral macro bicycle Schiff base synthesis has been reported(29).

The characterization of Schiff bases have been done by spectroscopic study. Various workers studied UV spectra of many Schiff bases and their complexes(30-35). Suzuki and Kito studied the absorption spectra of a Schiff base compound of retinal(36). Schaffer and co-workers have also studied experimental and theoretical investigation of the absorption spectra of some Schiff bases(37). Lin and Mathines(38) also studied absorption spectra of some Schiff bases. Issa and coworkers investigated spectroscopic nature in some thio Schiff bases(39). Temperature dependent absorption spectroscopy of some tautomeric azo dyes and Schiff bases was given by Joshi and co-workers(40). Raman et al also reported UV spectra of Schiff bases derived from acetyl acetone and p-anisidine(41). Ruan and coworkers(42) studied UV spectra of some Schiff bases and oxo diiron Schiff base complexes.

Infrared spectra of various Schiff bases have also been studied(43-49). Ueno and Martell(50) have studied the IR spectra of some Schiff bases of N-N'-ethyl enebis and similar ligands. Rao(51) and Kovacic(52) showed absorption band of =C=N- group at 1640 cm^{-1} and 1620 cm^{-1} respectively. IR spectra of some Schiff bases derived from various hydroxyl aromatic aldehyde and anilines have also been reported by Minkin et al(53). Abdel and co-workers(54) studied IR spectra of Schiff bases of 3-Cinnamoyl naphtha pyrimidens and reported the band at 1620 cm^{-1} for =C=N-. Agrawal and co-workers(55) have also studied the IR spectra of some Schiff bases and their aluminium(III) complexes. Shah et al(56) reported the IR spectra of Schiff bases derived from 8-hydroxy, 8-methoxy and 7-hydroxy coumarins. IR spectral study of some Schiff bases of amino acid was reported by Nath and Yadav(57). IR spectral data of Quinoline Schiff base complexes was also reported(58). Mohan and Saravanan(59) have studied IR spectra of 2-amino-3-(N-Tolyl carboxamido)-4,5-trimethelene thiophenes) Schiff bases. Parra et al(60) reported IR spectra of some heterocyclic Schiff bases. Craenenbroeck and coworkers(61) have studied the IR spectra of some bidentate Schiff bases.

NMR study for Schiff base compounds are important to know behavior or attachment of hydrogen atom and so many workers studied NMR spectra of various Schiff bases(62-67). Iskander et al(68) studied the NMR spectra of some bidentate Schiff bases derived from hydrazine S-methyl dithiocarboxylate and thiosemicarbazide and their complexes. Iriepe et al(69) reported NMR spectra of Schiff bases of salicyloyl hydrazide-salicylaldehyde and anthranilic acid- salicylaldehyde and their Lanthanide complexes. Tietze et al(70) studied NMR (both ^{1}H and ^{13}C) of some Schiff bases derived from 3-acetaltetramic acids with ethylene diamine. Tautomerism in Schiff bases derived from salicyaldehyde have also been studied by NMR spectra(71). NMR study of proton transfer equilibrium in Schiff bases derived from 2-hydroxy-1-naphthaldehyde and 1-hydroxy-2-aceto-naphthone was carried out by Dziembewska et al(72). Schiff et al(73) investigated intermolecular hydrogen bond in Schiff bases of 2-hydroxy-1-naphthaldehydes by NMR study. Kraichova and co-worker(74) also reported NMR spectral data of 5-methyl furyl Schiff bases. The NMR studies of Schiff bases of 4-amino antipyrine have been studied recently by Isaa et al(75).

Mass spectra of some Schiff bases have also been studied by some workers(76-78). Dash and coworkers(79) have studied mass spectral fragmentation pattern of some p-hydroxy benzaldehyde Schiff bases. Salman et al(80,81) have reported the mass spectra of tautomerism in some Schiff bases. Holla et al studied the mass spectra of some 1,2,4-triazoles Schiff bases(82). Piotr et al also reported the mass spectra of some Schiff base complexes of gossypol with 5-hydroxy-3-oxopentylamine and some monovalent cation(83).

Schiff base have various applications in different fields (84-94). Some Schiff bases are known to be used in fluorometry (95), as NMR contrast agent (96), as catalyst(97,98), as corrosion inhibitor(99), as dyes(100), as potential ligands in comparative study of allylic alkylation(101) etc. Some Schiff bases are also known to be used as parameters of lipid per oxidation in the pregnant woman and the fetus(102). Some are known to be used as substrates in the preparation of a large number of bioactive and industrial important compounds(103, 104).

Further, Schiff bases are known to have biological activities (105-112) such as antibacterial, antifungal, antitubercular, antitumor activities etc. Jones and McCleverty also studied some pharmaceutically applicable Schiff bases (113). Antibacterial, antifungal, antiamoebic and antihelmintic properties of some Schiff bases of coumarin derivatives have also been reported by Shridhar et al(114). The antibacterial activity of some other Schiff base have been studied(115). The anti microbial activity of some bis (imido) Schiff bases derived from thiosemicarbazide with 2-hydroxy aldehydes have also been studied(116) along with their metal complexes. However, it was found that metal complexes showed more activity than Schiff bases. The antimicrobial activities of N-(2-hydroxy-3-methoxy benzilidene)-1-amino naphthalene Schiff base was reported by Yildiz and co-workers(117).

The dissociation constant of some Schiff bases have also been reported(118-120). Pardeshi et al(121) studied dissociation constant of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and 2-substituted anilines. McClelland et al(122) reported the acidity constant of benzidine and N,N-dimethylbenzidine.

Literature survey shows that very little work has been done for the study of physico chemical studies such as thermal properties(123-125), refractive index(126), conductance(127,128) and ultrasonic(129-131) of the Schiff bases. More and Bhalvankar(132) studied thermal properties of some Schiff bases derived from 2-amino-5-(o-methoxyphenyl-1,3,4-thiadiazole). Nath and Yadav(57) have studied thermal properties of some Schiff bases derived from amino acid. Thomas and Parameswaran(133) also studied the thermal properties of some Schiff bases and their complexes. In our laboratory, physico chemical properties of some Schiff bases have been studied in different solvents(134,135).

Thus, in the present work, an attempt has been made to study the physicochemical properties of some Schiff bases. The Schiff bases have been synthesized from benzidine and α-naphthalamine. Benzidine has been reported to have genotoxic activity, mutagenic and carcinogenic activities (136-138). Benzidine and its some derivatives are also known to have biological and therapeutic application (139) and is also useful in textile industry(140). α-naphthalamine and its derivatives are known to have hemostatic, carcinogenic and neuro protective effect(141-144). So, due to these properties of benzidine and α-naphthalamine, Schiff bases of these compounds have been synthesized and characterized by TLC, ^{1}H NMR, IR and mass spectral data.

Various physicochemical properties such as refractive index, heat of solution, dissociation constant, conductance and acoustical properties for

Schiff bases were determined in different solvents. Further, thermal properties and biological activity of some Schiff bases have also been studied.

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The following Schiff bases have been synthesized from α-naphthyl amine.

(1) N- [(1E) - phenyl methylene] naphthalene-1-amine (NDP-1)

(2) 2-(E)-(1-naphthylimino) methyl] phenol (NDP-2)

(3) N-[(1E)-(4-methoxy phenyl) methylene]-N-1-naphthylamine(NDP-3)

(4) N-[(1E)-(3-nitro phenyl) methylene] naphthalene-1-amine(NDP-4)

(5) N-{ [(1E)-[4-(dimethyl amino) phenyl] methylene }-N-1-naphthyl-amine (NDP-5)

(6) 4-[(1E)-(1-naphthylimino) methyl] phenol(NDP-6)

(7) N-[(1E)-(4-chlorophenyl) methylene]-N-naphthyl amine(NDP-7)

(8) N-[(1Z)-2-furyl methylene]-N-1-naphthyl amine(NDP-8)

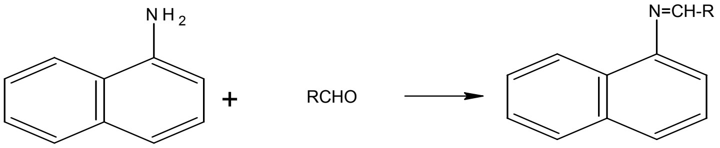
(9) [(1E)-(4-Florophenyl) methylene]-N-1-naphthyl amine(NDP-9)

(10) N-[(1E)-(2-nitro phenyl) methylene]naphthalene-1-amine(NDP-10)

Synthesis

1.43 gm of α-napthylamine was dissolved in 25-30 ml of methanol. 0.01 mole of aldehyde derivative was added in this solution along with few drops of glacial acetic acid. The mixture was refluxed for 15 hours in a waterbath at 60-70 ^{0}C. Then it is poured on crushed ice, filtered and dried.

Reaction scheme



The products were recrystalized. The melting points, % yield and R_f values of these Schiff bases are given in Table 2.1

Table-2.1 : The melting point, % yield and R_f values of these Schiff bases derived from α-napthylamine.

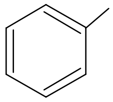
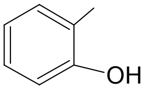
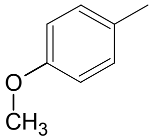
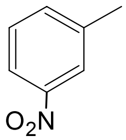
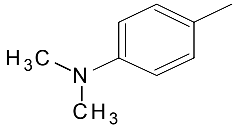
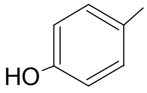
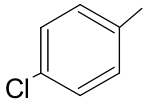
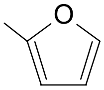
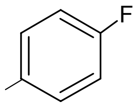
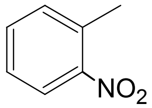
CODE	R	Molecular Formula	Molecular Weight (g)	M.P. ^{0}C	Yield %	R_{f^*}
NDP-1		$C_{17}H_{13}N$	231	85	93.07	0.739
NDP-2		$C_{17}H_{13}NO$	247	89	80.57	0.761
NDP-3		$C_{18}H_{15}NO$	261	104	94.25	0.479
NDP-4		$C_{17}H_{12}N_2O_2$	276	80	70.29	0.547
NDP-5		$C_{19}H_{18}N_2$	274	130	59.85	0.386

Table-2.1 (cont….)

CODE	R	Molecular Formula	Molecular Weight (g)	M.P. ^0C	Yield %	R_{f*}
NDP-6		$C_{17}H_{13}NO$	247	204	60.73	0.477
NDP-7		$C_{17}H_{12}NCl$	265.5	122	77.59	0.710
NDP-8		$C_{15}H_{11}NO$	221	193	50.23	0.788
NDP-9		$C_{12}H_{12}NF$	248	85	55.09	0.670
NDP-10		$C_{17}H_{12}N_2O_2$	276	104	76.09	0.523

* Ethyl acetate : Hexane (2:8) for 1,2,3,4,7,9 and 4:6 for 5,6
* Benzene: Acetone (7:3) for 8

Synthesis of Schiff bases from benzidine.

The following Schiff base have been synthesized.

(1) N-[(1E)-phenylmethylene]-N'-[(1Z)-phenylmethylene] biphenyl -4,4'-diamine(DVA-1)

(2) N-[(1E)-(2-nitrophenyl)methylene]-N'-[(1Z)-(2-nitrophenyl)methylene] biphenyl-4,4'-diamine(DVA-2)

(3) N-[(1E)-(4-hydroxyphenyl)methylene]-N'-[(1Z)-(2-hydroxyphenyl) methylene] biphenyl-4,4'-diamine(DVA-3)

(4) N-[(1E)-(2-chlorophenyl)methylene]-N'-[(1Z)-(2-chlorophenyl)methylene] biphenyl-4,4'-diamine(DVA-4)

(5) N-[(1E)-(2-phenylvinyl)]-N'-[(1Z)-(2-phenylvinyl)]biphenyl-4,4'-diamine(DVA-5)

(6) N-[(1E)-(2-hydroxyphenyl)methylene]-N'-[(1Z)-(2-hydroxyphenyl) methylene] biphenyl-4,4'-diamine(DVA-6)

(7) N-[(1E)-anthrylmethylene]-N'-[(1Z)-anthrylmethylene]biphenyl-4,4'-diamine(DVA-7)

(8) N-[(1E)-(3-methoxy,4-hydroxyphenyl)methylene]-N'-[(1Z)-(3-Methoxy, 4-hydroxy phenyl)methylene] biphenyl-4,4'-diamine(DVA-8)

(9) N-[(1E)-2-furylmethylene]-N'-[(1Z)-2-furylmethylene]biphenyl-4,4'-diamine(DVA-9)

(10) N-[(1E)-(N-N-dimethy)methylene]-N'-[(1Z)-(N-N-dimethy)methylene] biphenyl -4,4'-diamine(DVA-10)

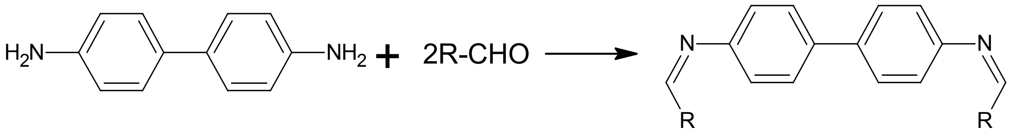
(11) N-[(1E)-(4-chlorophenyl)methylene]-N'-[(1Z)-(4-chlorophenyl) methylene] biphenyl-4,4'-diamine(DVA-11)

(12) N-[(1E)-(4-florophenyl)methylene]-N'-[(1Z)-(4-florophenyl)methylene] biphenyl-4,4'-diamine(DVA-12)

Synthesis

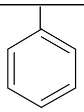
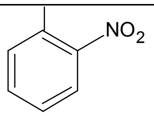
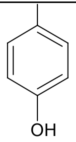
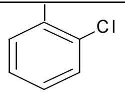
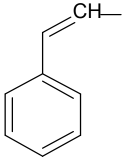
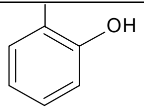
Methanolic solution of benzidine(0.01mole) is mixed with few drops of glacial acetic acid and different aldehydes(0.02mole). The mixture was refluxed for 15 hours in water bath, then poured on crushed ice, filtered and dried.

Reaction



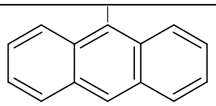
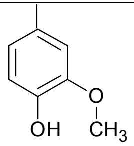
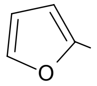
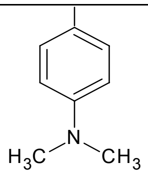
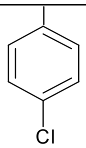
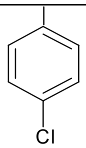
The melting points, % yield and R_f values of these synthesized Schiff bases is given in Table 2.2

Table-2.2: The melting point, % yield and R_f values of these Schiff bases derived from benzidine.

CODE	**R**	**Molecular Formula**	**Molecular Weight (g)**	**M.P. ^0C**	**Yield %**	**R_f**
DVA-1		$C_{26}H_{20}N_2$	360	220	84	$0.64^{@}$
DVA -2		$C_{26}H_{18}O_4N_4$	450	208	86	$0.47^{\#}$
DVA -3		$C_{26}H_{20}O_2N_2$	392	260	87	$0.44^{\$}$
DVA -4		$C_{26}H_{18}N_2Cl_2$	429	175	88	0.94^{*}
DVA -5		$C_{30}H_{24}N_2$	412	162	87	$0.63^{@}$
DVA -6		$C_{28}H_{20}O_4N_2$	392	138	89	$0.61^{@}$

$^{@}$Ethyl Acetate : Hexane (6:4) for 1, 5, 6,
$^{\#}$Ethyl Acetate : Hexane (4:6) for 2
$^{\$}$Ethyl Acetate : Hexane (3:7) for 3
*Acetone : Hexane (3:7) for 4

Table-2.2 (conti….)

CODE	R	Mole. Formula	Mole. Weight (g)	M.P. ^{0}C	Yield %	R_f
DVA -7		$C_{42}H_{28}N_2$	560	179	70	0.87$^{@}$
DVA -8		$C_{28}H_{24}N_2O_4$	452	169	75	0.55$^{\$}$
DVA -9		$C_{22}H_{16}N_2$	340	265	71	0.73$^{\$}$
DVA 10		$C_{30}H_{30}N_4$	446	285	80	0.29$^{\$}$
DVA-11		$C_{26}H_{18}N_2Cl_2$	429	234	80	0.46$^{\#}$
DVA-12		$C_{26}H_{18}N_2F_2$	394	216	80	0.71$^{\#}$

$^{@}$Ethyl Acetate : Hexane (6:4) for 7
$^{\#}$Ethyl Acetate : Hexane (4:6) for 11, 12
$^{\$}$Ethyl Acetate : Hexane (3:7) for 8, 9, 10

Spectral study of Schiff bases

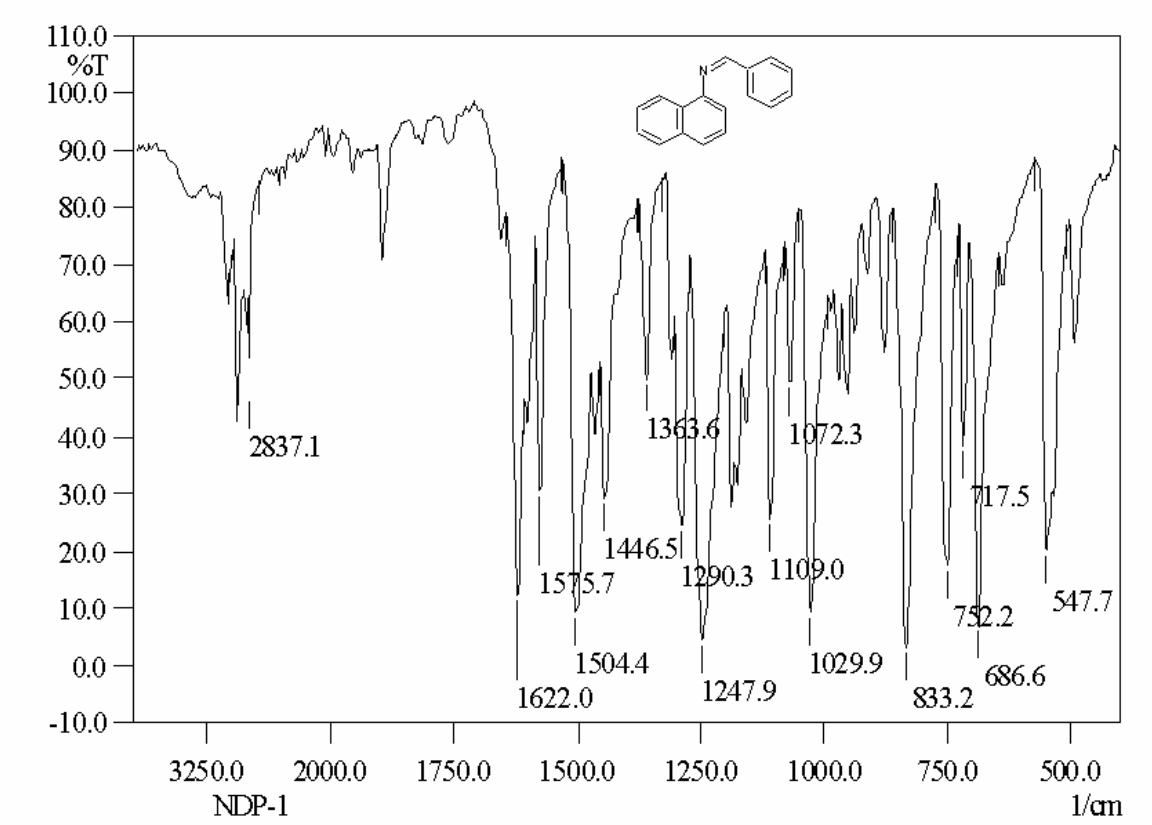
The Schiff bases were characterized by infrared, nuclear magnetic spectroscopy and mass spectrometry.

Infrared Spectroscopy

Infrared spectroscopy is an excellent method for the qualitative analysis. It is used to determine the force constant, bond strength, identification of compounds, presence of certain groups in the molecules, identification of hydrogen bonding, study of co-ordination compounds, polymers and detection of impurity etc. This technique is often faster than any other analytical method.

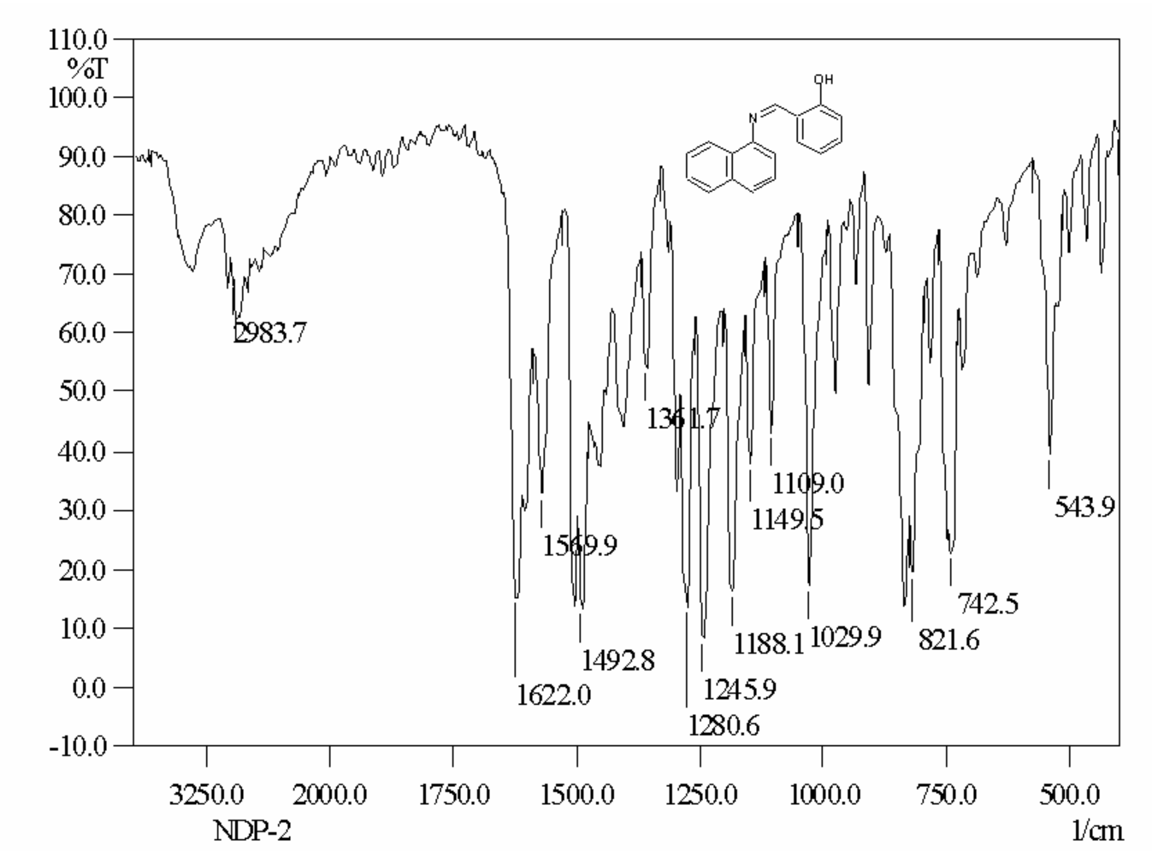
The IR spectra (KBr pellets) of Schiff bases scanned on "SHIMDZU FTIR - 8400" over the frequency range from 4000 cm^{-1} to 400 cm^{-1}. The characteristic absorption frequencies(cm^{-1}) are given in Tables 2.3 to 2.24.

Table-2.3: IR SPECTRAL STUDY OF N-(1Z)-PHENYL METHYLENE] NAPHTHALEN-1-AMINE [NDP-1]



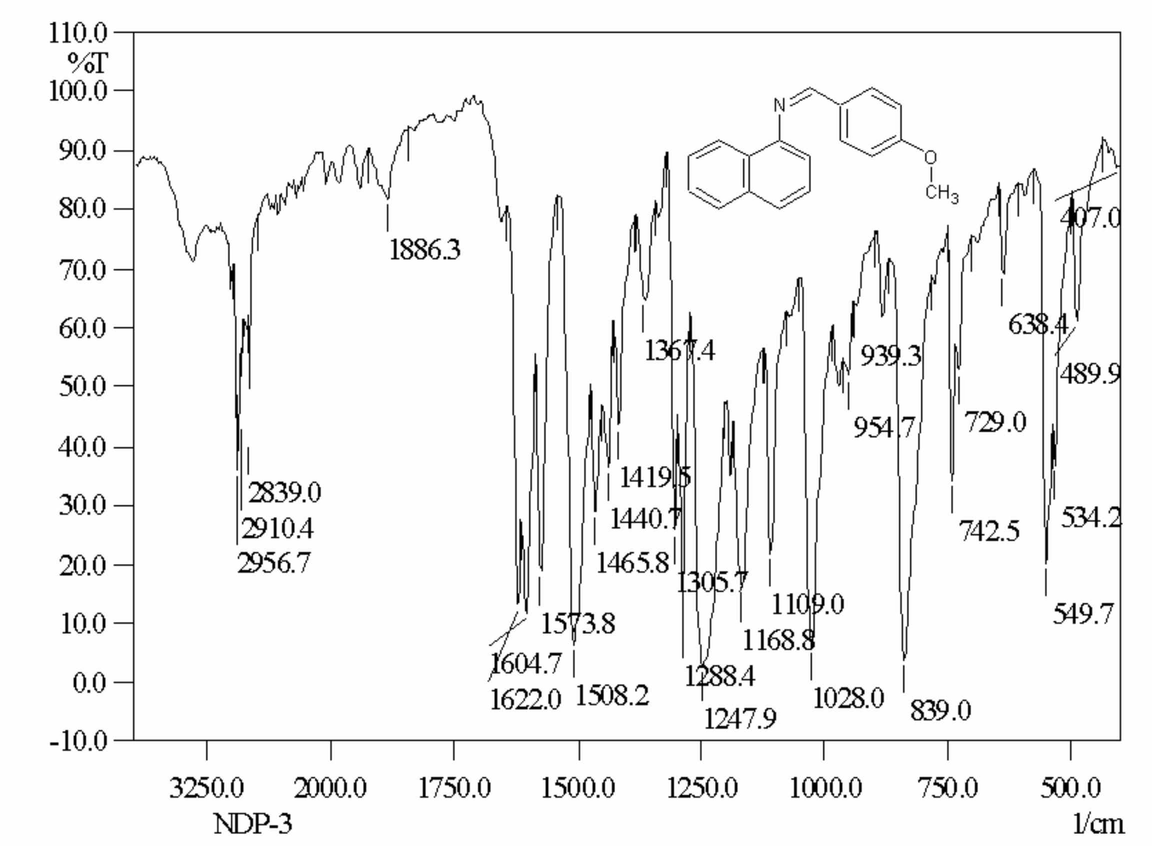
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1576	1600-1450
	C-C	687,718	710-675
	C-H (i.p.d.)	1248,	1300-1000
Ar-N=C-Ar	N=C	1622	1640-1585

Table-2.4 : IR SPECTRAL STUDY OF [(Z)-(1-NAPHTHYL IMINO) METHYL] PHENOL [NDP-2]



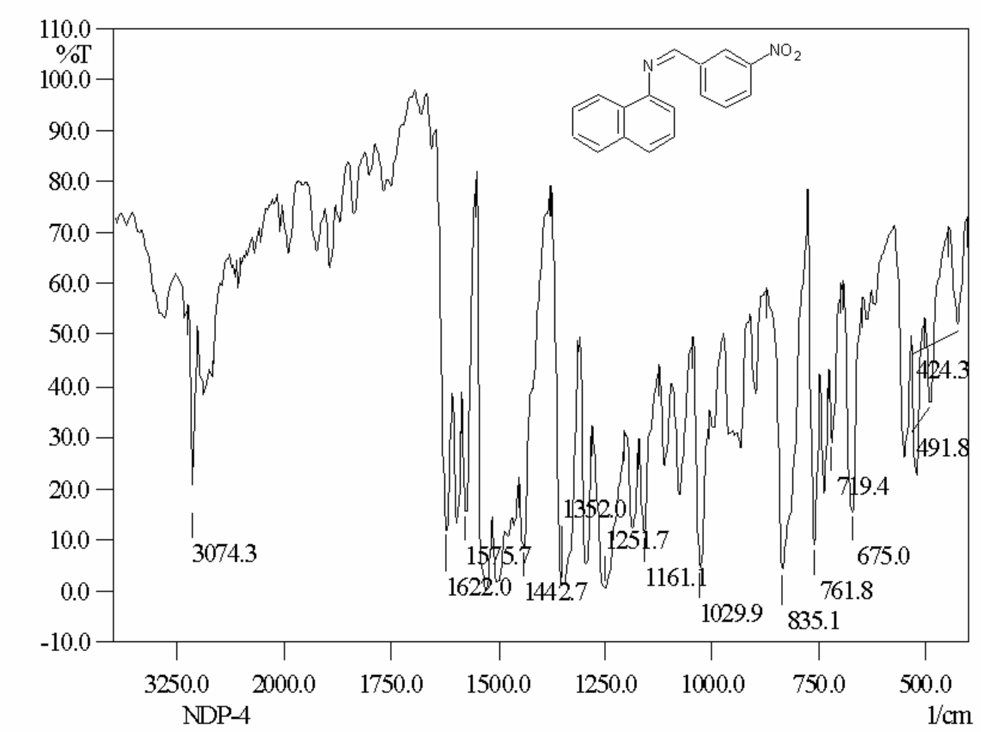
Type	**Vibration mode**	**Frequency in cm^{-1}**	**Expected frequency in cm$^{-1[1-3]}$**
Aromatic	C=C	1570	1600-1450
	C-C	742	710-675
	C-H	1246	1300-1000
Ar-N=C-Ar	N=C	1622	1640-1580
Phenolic(-OH)	O-H(str.)	3436	3580-3420
	O-H(bend.)	1362	1410-1310

Table-2.5 : IR SPECTRAL STUDY OF N-[(1Z)-(4-METHOXY PHENYL) METHYLENE] NAPHTHALEN-1-AMINE[NDP-3]



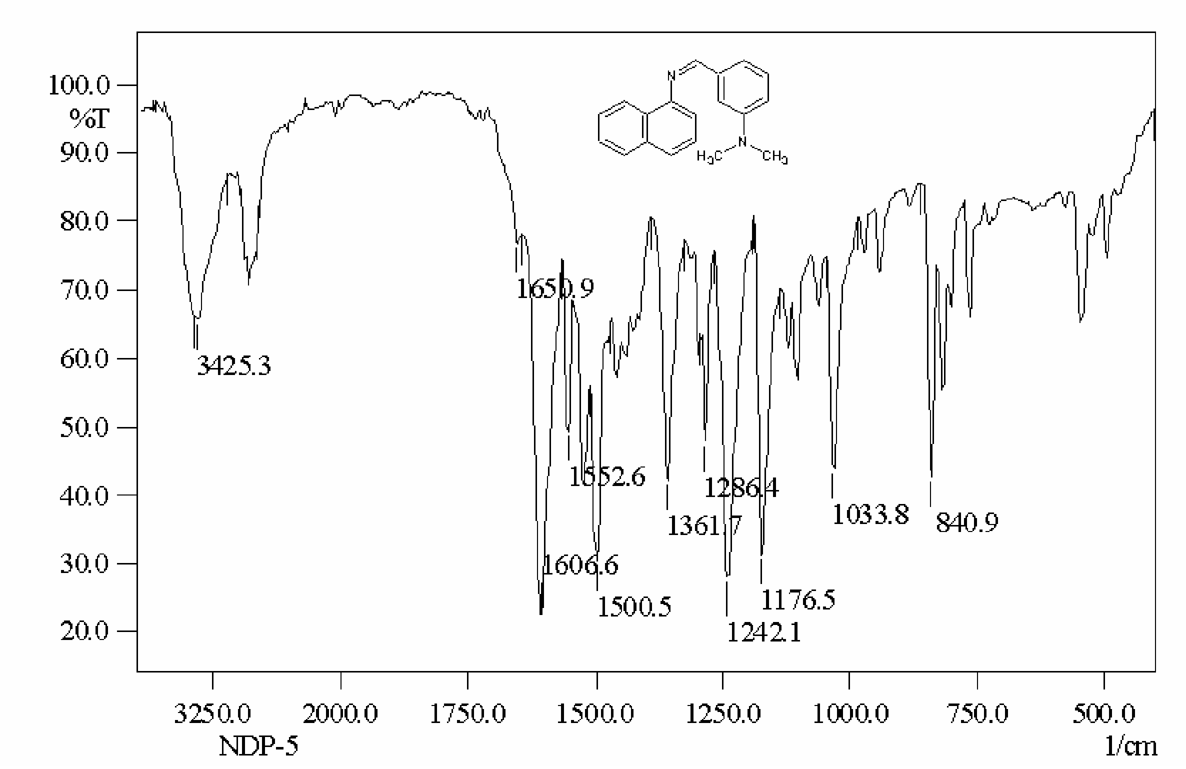
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1465	1600-1450
Aromatic	C-H	839,729,742	900-675
	C-H	1248	1300-1000
Ar-N=C-Ar	N=C	1622	1640-1580
Ar-O-CH_3	-O-CH_3	2852	2880-2915

Table-2.6 : IR SPECTRAL STUDY OF N-[(1Z)-(3-NITROPHENYL) METHYLENE] NAPHTHALEN-1-AMINE[NDP-4]



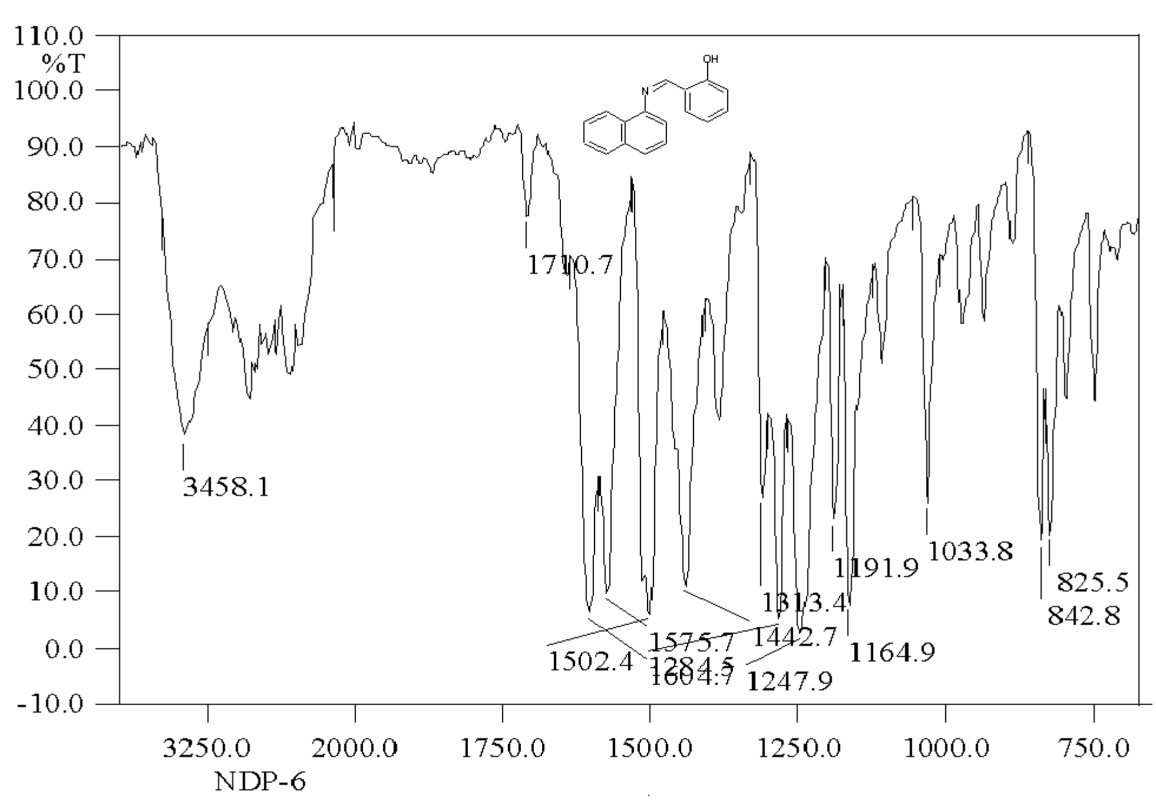
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1575	1600-1450
	C-H	251	1300-1000
	C-H	835	900-675
Ar-N=C-Ar	N=CH	1622	1640-1580

Table-2.7 : IR SPECTRAL STUDY OF N-{(1Z)-[3-(DIMETHYLAMINO) PHENYL] METHYLENE}NAPHTHALEN-1-AMINE [NDP-5]



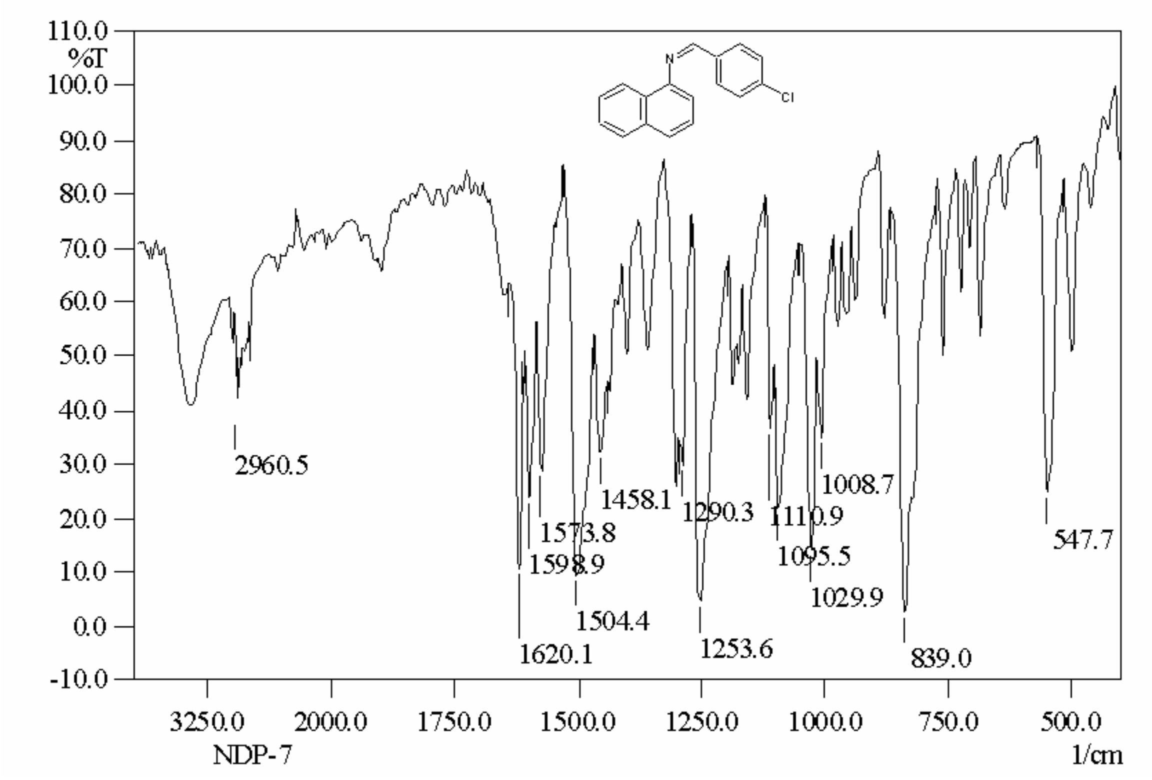
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1500	1600-1450
	C-H(i.p.d.)	1242	1300-1000
Ar-N=C-Ar	-C-H(o.o.p.d.)	841	900-675
	N=C (str.)	1607	1640-1580
Ar-N-$(CH_3)_2$	C-N	3425	3550-3420

Table-2.8 : IR SPECTRAL STUDY OF 3-[(Z)-(1-NAPHTHYLIMINO) METHYL] PHENOL[NDP-6]



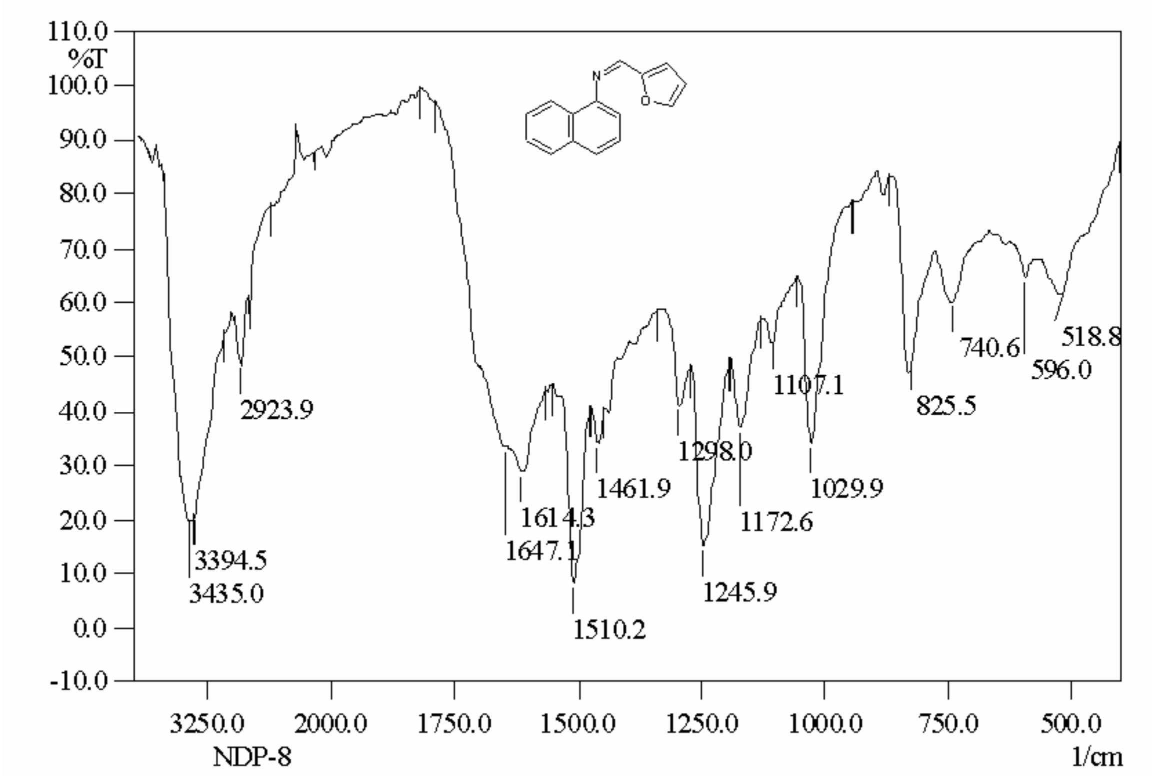
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1575	1600-1450
	C-H (i.p.d.)	1248	1300-1000
	C-H (o.o.p.d.)-	843,825	900-675
Ar-N=C-Ar	-N=C (str.)	1605	1640-1580
Phenolic (OH)	O-H (str.)	3458	3580-3420
	-O-H (bend.)	1381	1410-1310

Table-2.9 : IR SPECTRAL STUDY OF N-[(1Z)-(4-CHLOROPHENYL) METHYLENE] NAPHTHALEN-1- AMINE[NDP-7]



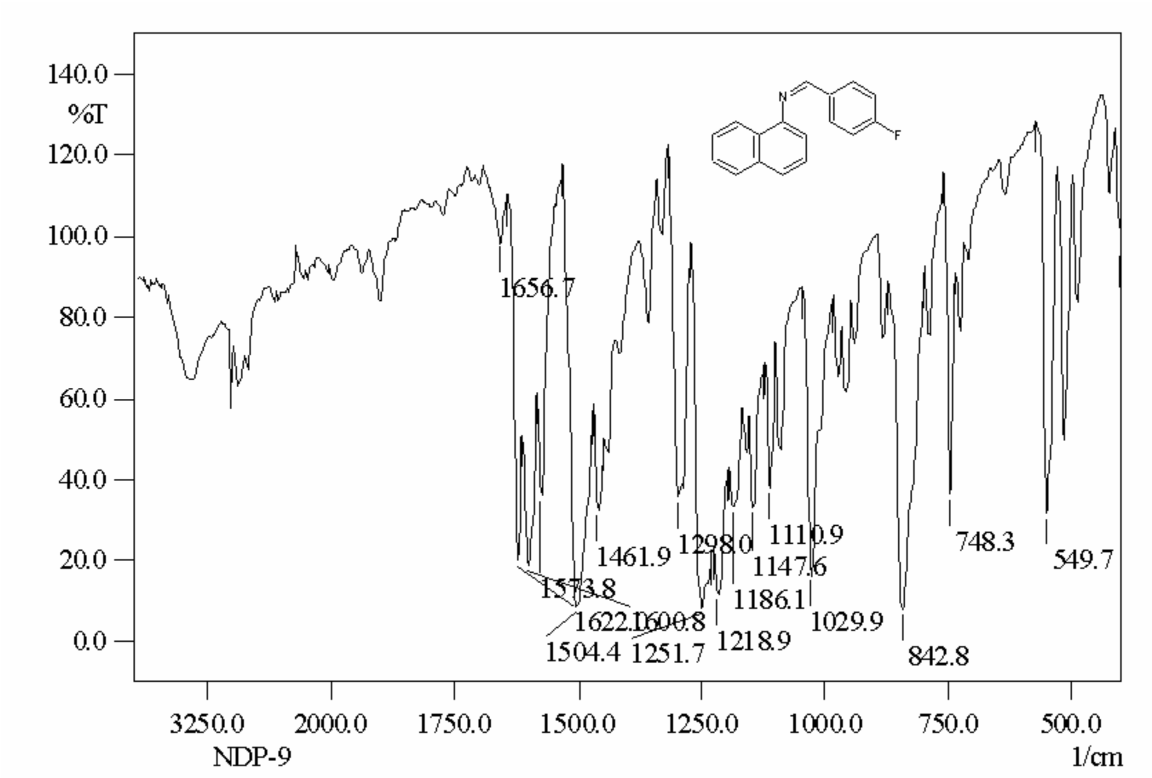
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1598	1600-1450
	C-H (i.p.d.)	1254	1300-1000
	C-H (o.o.p.d.)	839	900-675
Ar-N=C-Ar	-N=C (str.)	1620	1640-1580
C-Cl	C-Cl (str.)	723	700-800

Table-2.10 : IR SPECTRAL STUDY OF N-[(1Z)-2-FURYLMETHYLENE] NAPHTHALEN-1-AMINE [NDP-8]



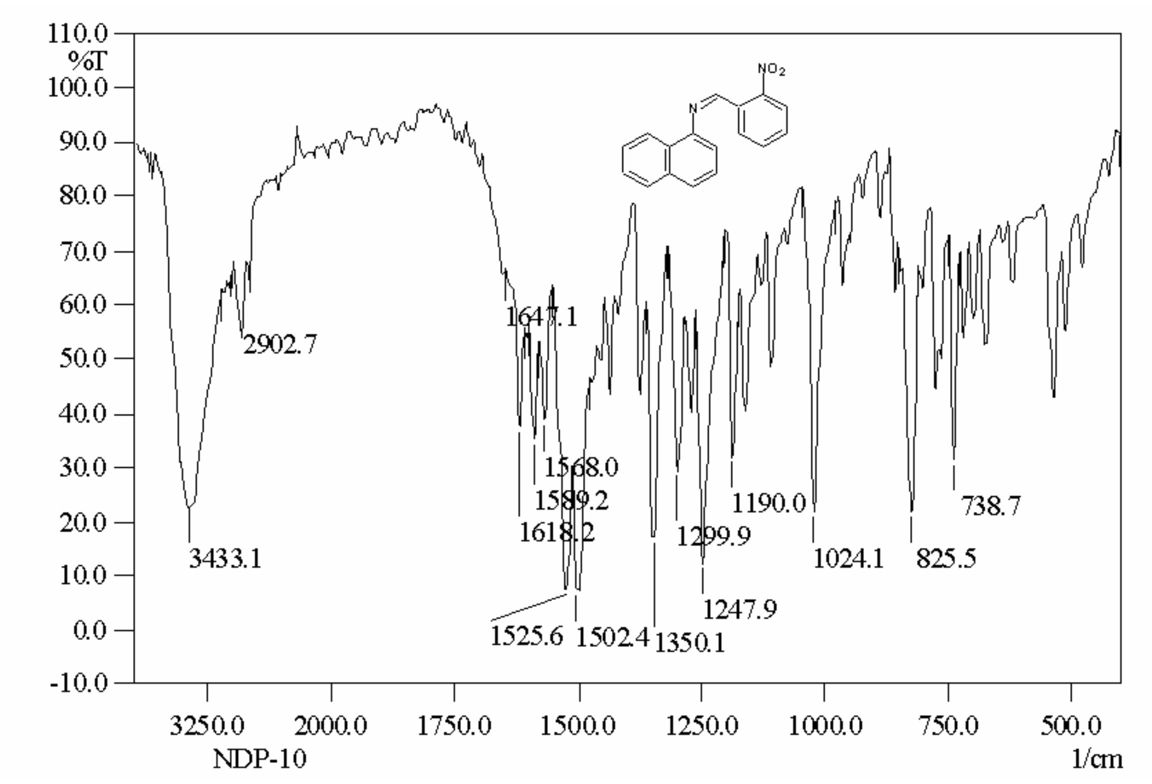
Type	**Vibration mode**	**Frequency in cm^{-1}**	**Expected frequency in cm$^{-1[1-3]}$**
Aromatic	C=C	1461	1600-1450
	C-H (i.p.d.)	1298	1300-1000
	C-H (o.o.p.d.)	825,741	900-675
Ar-N=C-Ar	N=C	1614	1640-1580
-C-O-C-	-C-O-C-	1462	1350-1450

Table-2.11 : IR SPECTRAL STUDY OF N-[(1Z)-(4-LUOROPHENYL)
METHYLENE] NAPHTHALEN-1-AMINE [NDP-9]



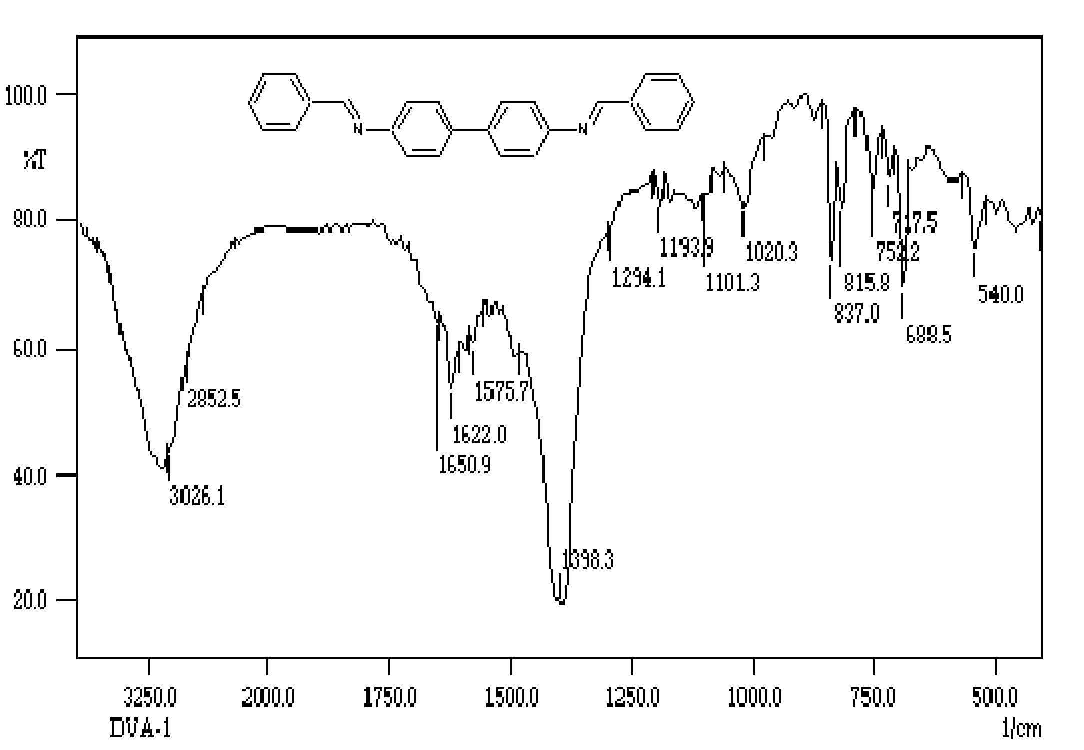
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1461	1600-1450
	C-H (o.o.p.d.)	843	900-675
	-C-H (i.p.d.)	1298,1029	1300-1000
Ar-N=C-Ar	-N=C	1622	1640-1580
C-F	C-F	748	750-700

Table - 2.12 : IR SPECTRAL STUDY OF N-[(1Z)-(2-NITROPHENYL) METHYLENE] NAPHTHLEN-1-AMINE[NDP-10]



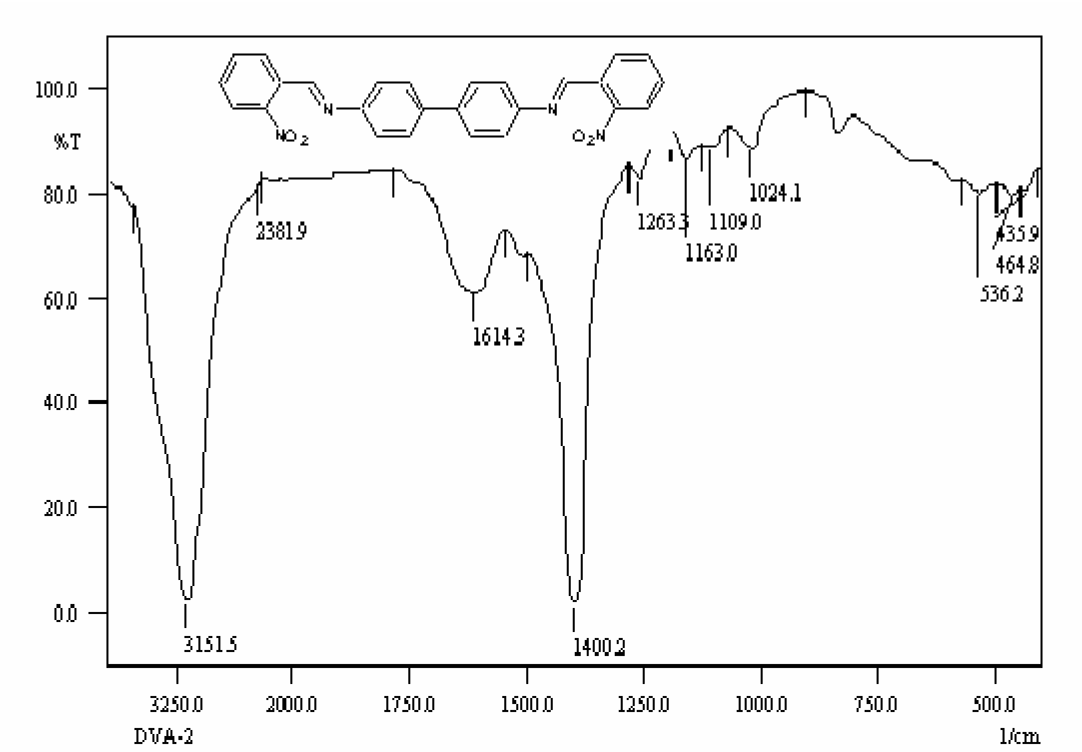
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1502	1600-1450
	C-H (i.p.d.)	1350,1024	1300-1000
	C-H (o.o.p.d.)	825	900-675
Ar-N=C-Ar	-N=C (str.)	1618	1640-1580
Ar-NO_2	-N-C (str.)	1589	1625-1610

Table-2.13: IR SPECTRAL STUDY OF N-[(1E)–PHENYLMETHYLENE]-N’-[(1Z)– PHENYLMETHYLENE] BIPHENYL-4,4’-DIAMINE(DVA-1)



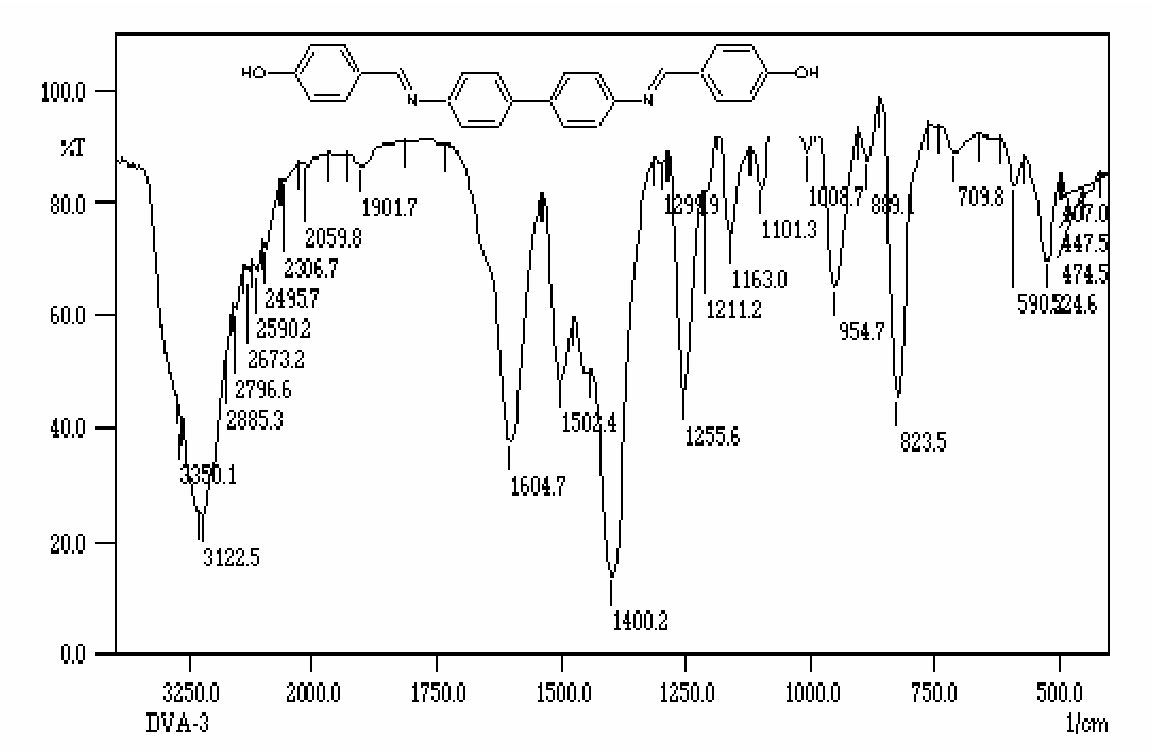
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1575	1600-1450
	C-H (o.o.p.d.)	827,815	900-675
Ar-N=C-Ar	-N=CH-str.	1622	1640-1580

Table-2.14 : IR SPECTRAL STUDY OF N-[(1E)-(2-NITROPHENYL) METHYLENE]- N’-[(1Z)-(2-NITROPHENYL) METHYLENE BIPHENYL-4,4’-DIAMINE(DVA-2)



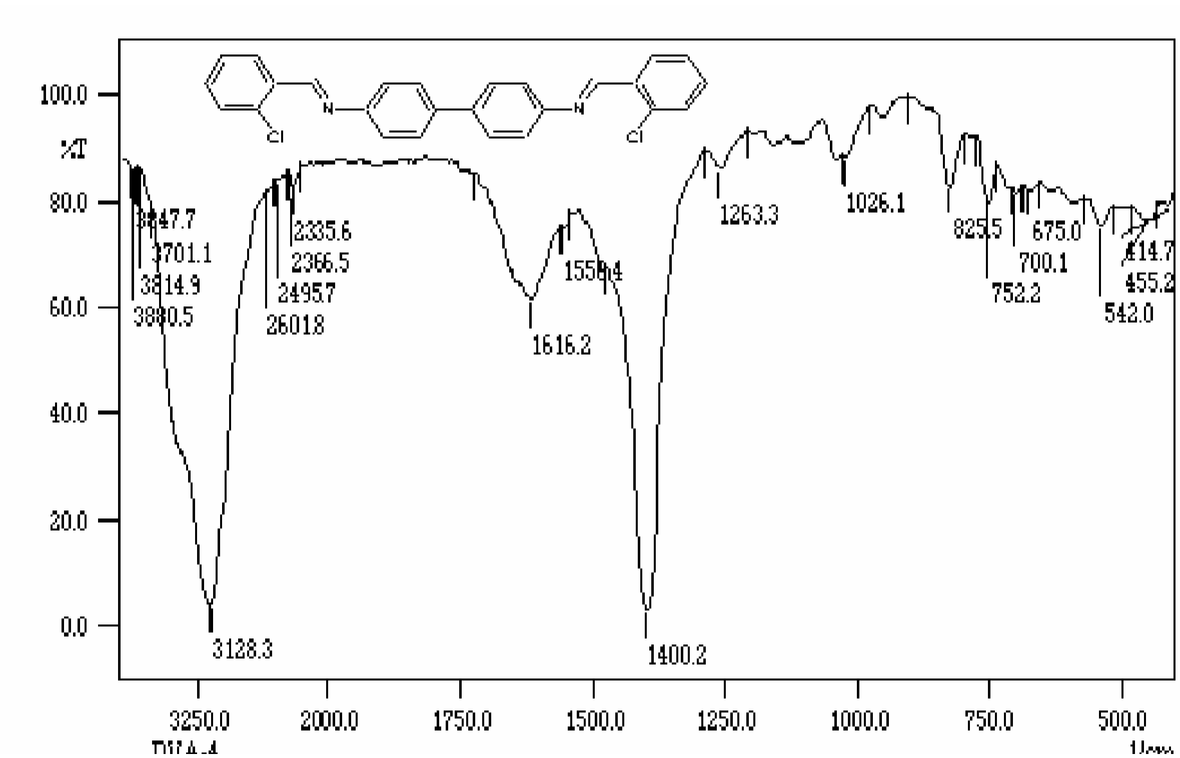
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1400	1600-1450
	C-H(i.p.d.)	1163, 1109	1300-1000
Ar-N=C-Ar	N=C	1614	1640-1580
Ar-NO_2	C-NO_2	1263	1370-1300

Table – 2.15 : IR SPECTRAL STUDY OF N-[(1E)-(4-HYDROXY PHENYL) METHYLENE]-N’-[(1Z-(4-HYDROXYPHENYL)METHYLENE BIPHENYL-4,4’-DIAMINE(DVA-3)



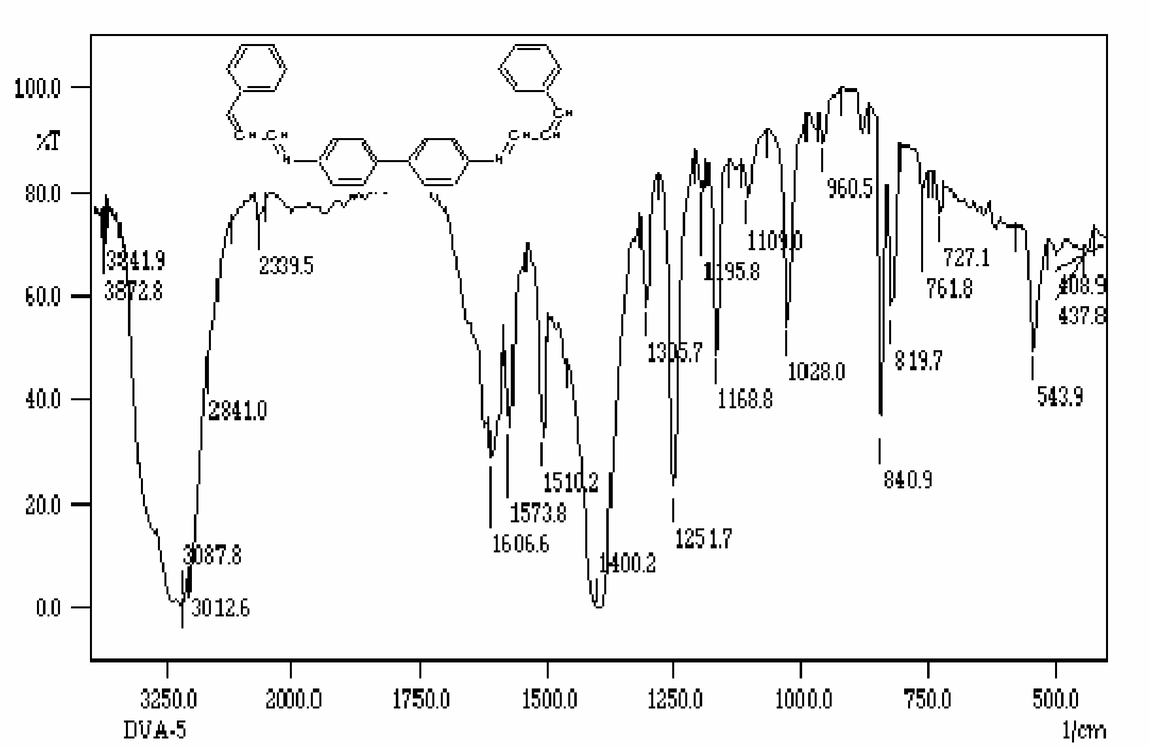
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1502	1600-1450
	C-H	1255	1300-1000
Phenolic(OH)	O-H	3350	3580-3420
Ar-N=C-Ar	N=C	1605	1640-1580

Table-2.16: IR SPECTRAL STUDY OF N-[(1E)-(2-CHLOROPHENYL) METHYLENE]-N’1Z) -(2-CHLORO PHENYL) METHYLENE] BIPHENYL-4,4’-DI AMINE (DVA-4)



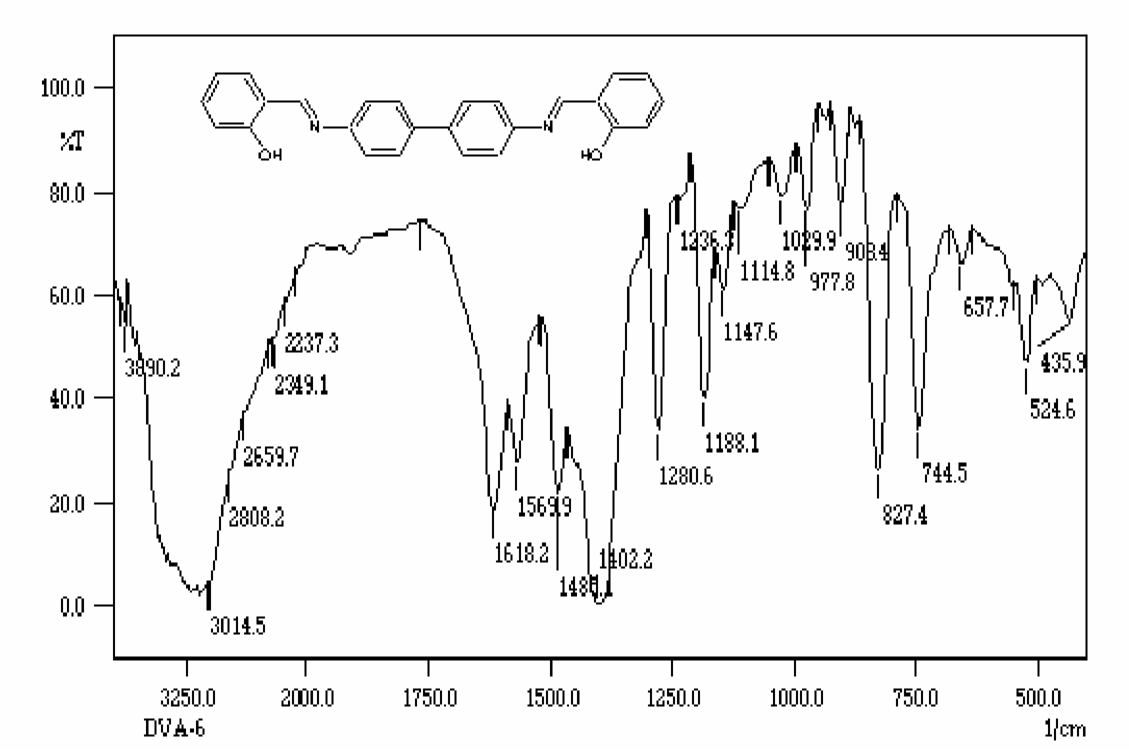
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1400	1600-1450
	C-H(o.o.p.d.)	822	900-675
Ar-N=C-Ar	C-N	1263	1340-1250
	N=C	1616	1640-1580
C-Cl	C-Cl	752	800-600

Table-2.17 : IR SPECTRAL STUDY OF N-[(1E)-(2-HYDROXYPHENYL) METHYLENE]-N'-[(1Z)-(2-HYDROXY PHENYL) METHYLENE BIPHENYL-4,4'-DI AMINE (DVA-5)



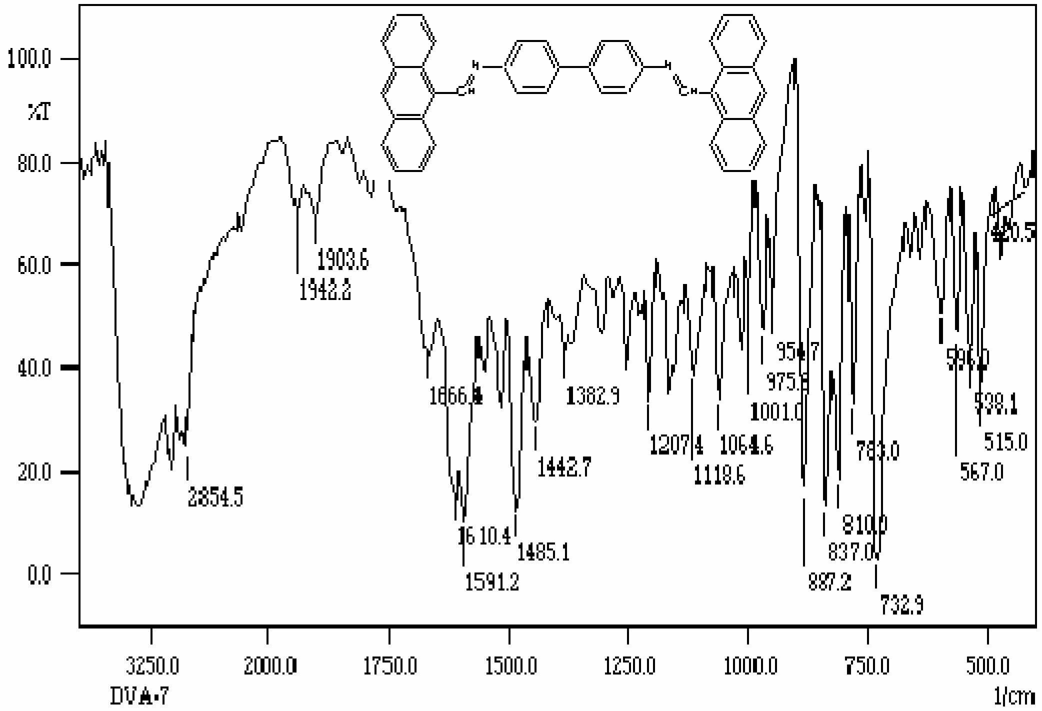
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1493	1600-1450
Ar-N=C-Ar	N=C	1607	1640-1580
Alkenes	-CH=CH-CH=	988	995-985
	-C-H (bend)	1383	1470-1340

Table-2.18: IR SPECTRALSTUDYOF N-[(1E)-(2-HYDROXYPHENYL) METHYLENE]-N'- [(1Z)-(HYDROXYROPHENYL)METHYLENE] BIPHENYL- 4, 4'-DIAMINE(DVA-6)



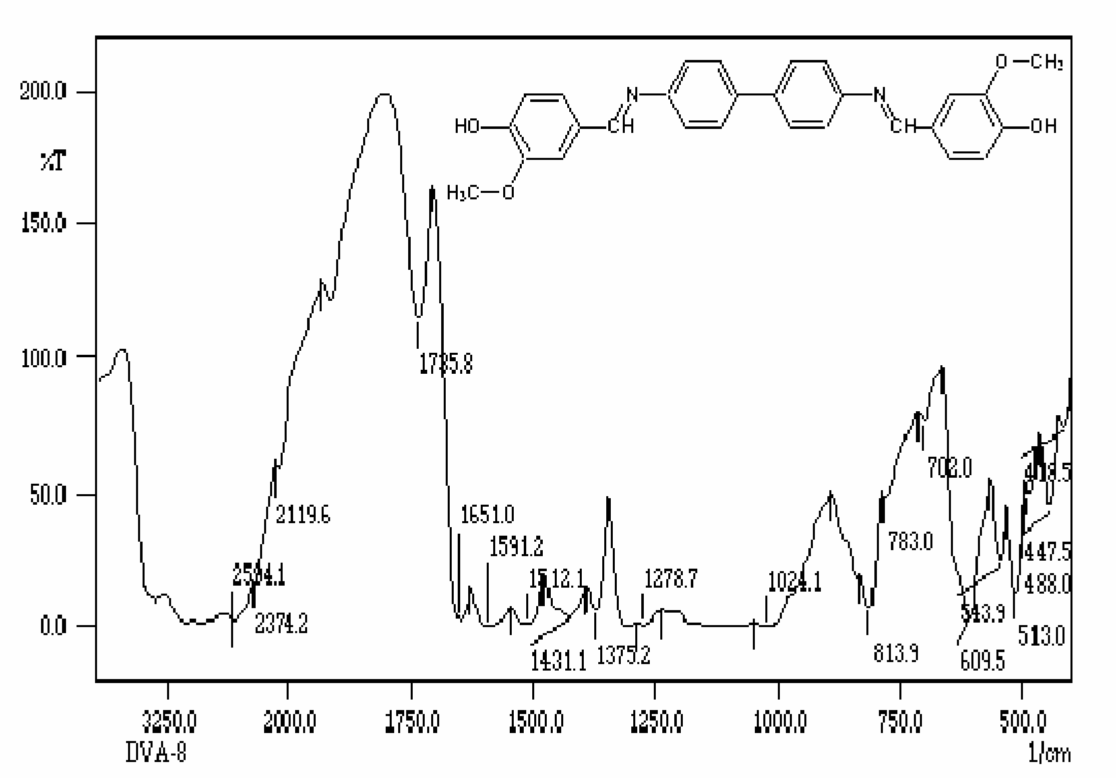
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1570	1600-1450
Ar-N=C-Ar	-N=C (str.)	1618	1640-1580
Phenolic (OH)	-O-H (bend.)	1148	1410-1050
	-O-H (str.)	2660, 2227	2700-2500

Table-2.19: IR SPECTRAL STUDY OF N-[(1E)-ANTHRYLMETHYLENE]-N'-[(1Z)-ANTHRYL METHYLENE] BIPHENYL-4,4'-DIAMINE (DVA-7)



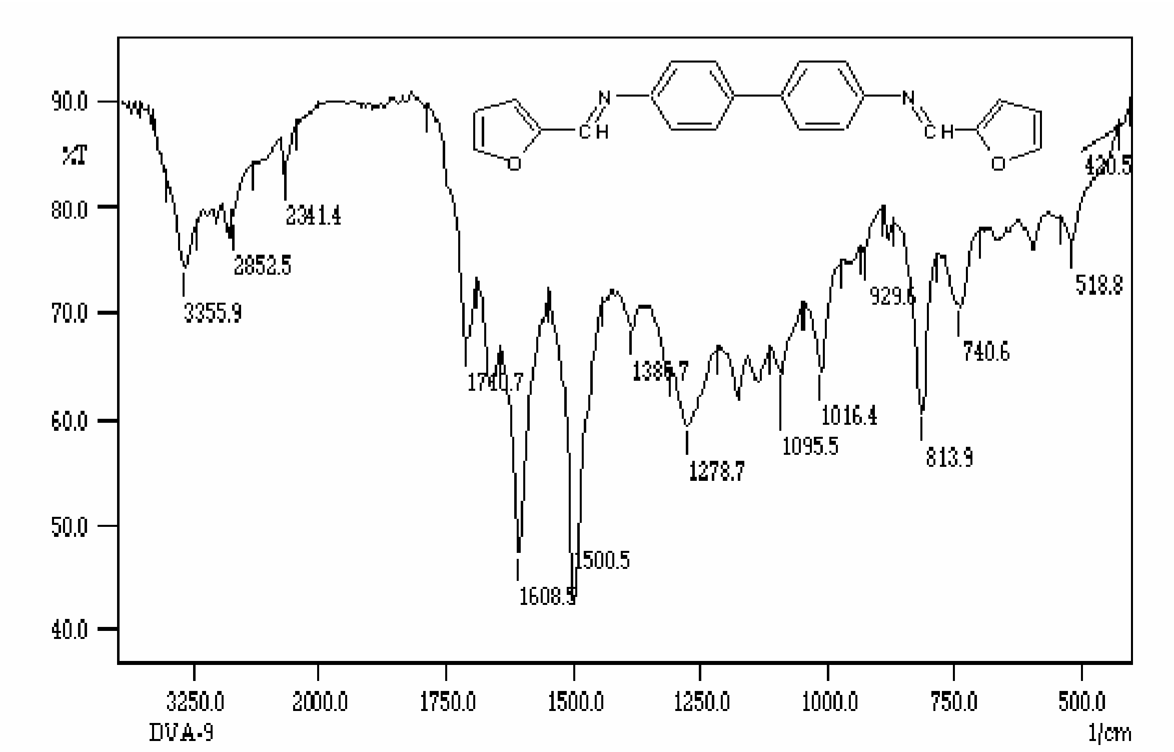
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1485	1600-1450
Aromatic	C-H(o.o.p.d.)	733	900-675
Ar-CH=N-Ar	-CH=N- str	1610	1640-1580
Alkene	-CH=CH-	976,955	995-985

Table-2.20 : IR SPECTRAL STUDY OF N-[(1E)-(3-METHOXY,4-HYDROXY PHENYL)METHYLENE]-N'-[(1Z)-(3-METHOXY,4-HYDROXY PHENYL)METHYLENE]BIPHENYL-4,4'-DIAMINE (DVA-8)



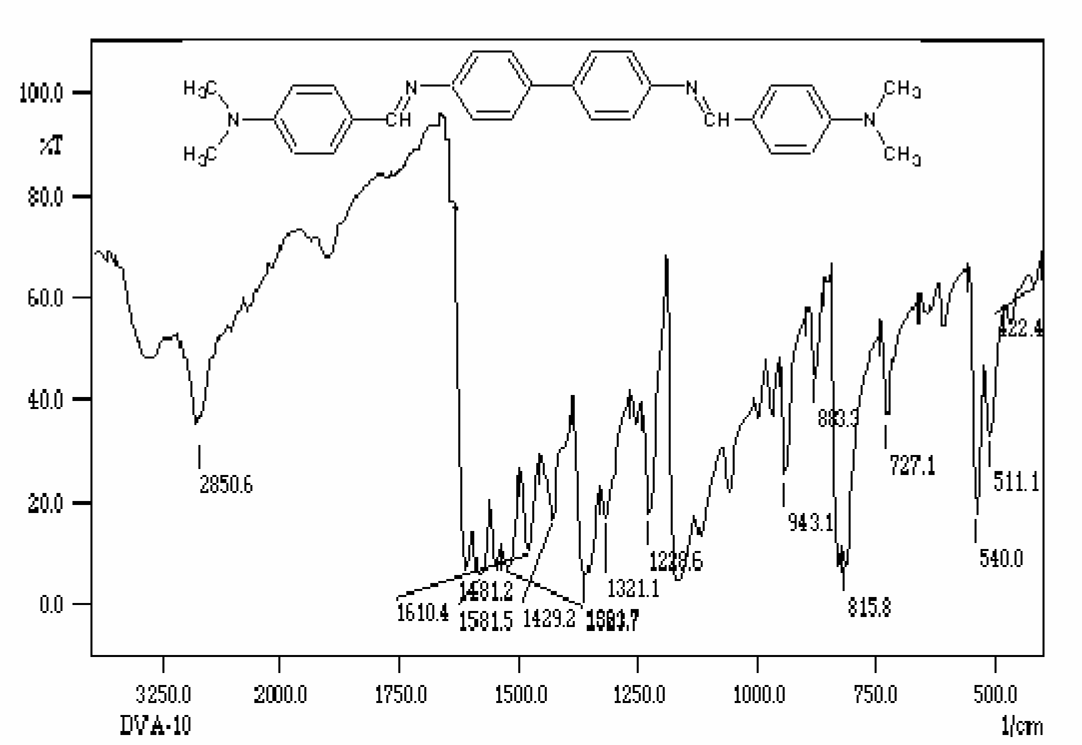
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1512	1600-1450
	C-O	1065,1022	1350-1450
Ar-N=C-Ar	N=C	1591	1640-1580
-C-O-C-	-C-O-C-	1065,1022	1350-1450
Phenolic (OH)	-O-H	3632, 3231	3650-3590

Table-2.21: IR SPECTRAL STUDY OF N-[(1E)-2-FURYLMETHYLENE]-N'-[(1Z)-2- FURYLMETHYLENE]BIPHENYL-4,4'-DIAMINE (DVA-9)



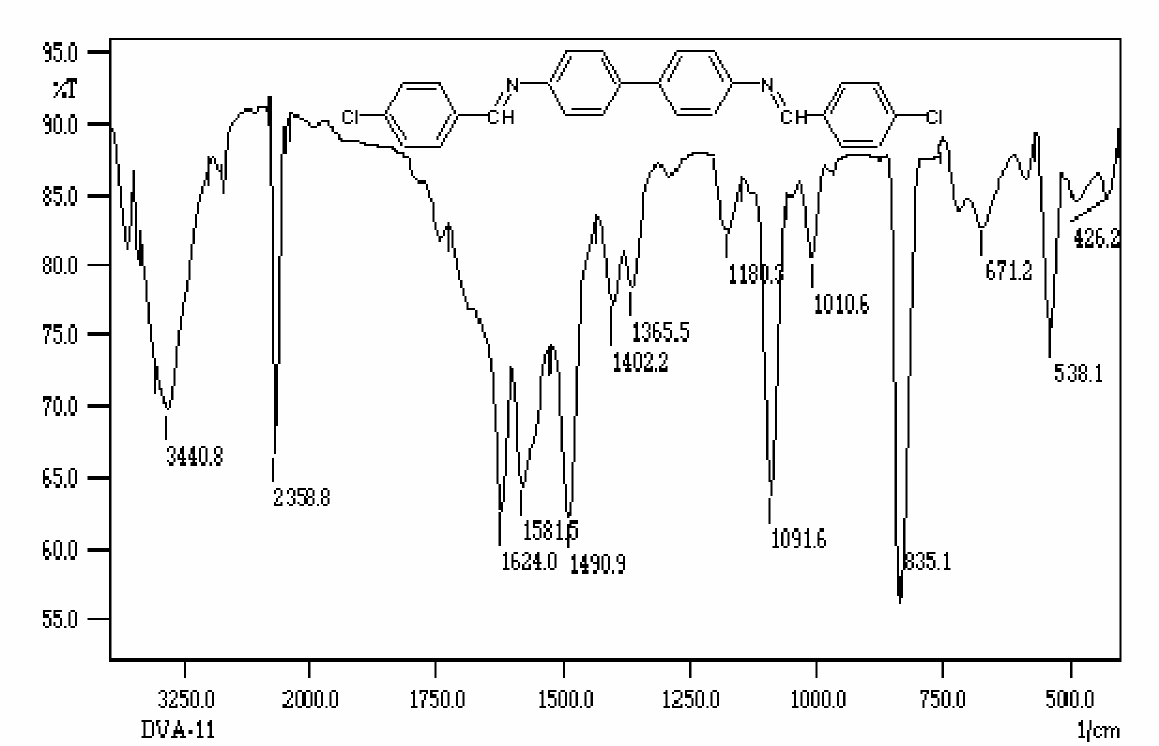
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1500	1600-1450
	C-O(str.)	1711	1725-1705
Ar-N=CH-Ar	C-N(str.)	1279	1350-1280
	C=N	1609	1640-1580

Table-2.22 : IR SPECTRAL STUDY OF N-[(1E)-(N-N-IMETHYL)METHYLENE]-N'-[(1Z)-(N-N-DIMETHYL)METHYLENE] BIPHENYL-4,4'-DI AMINE (DVA-10)



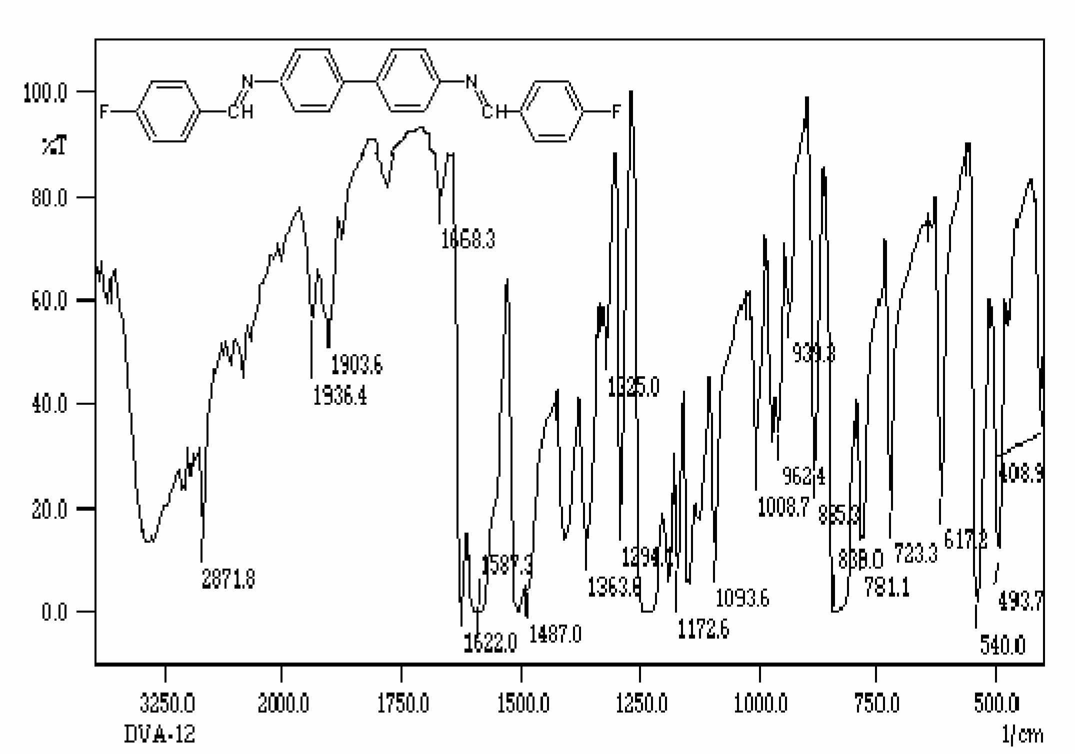
Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}[1-3]
Aromatic	C=C	1481	1600-1450
Aromatic	-CH=CH-(str.)	943	995-905
Ar-N=C-Ar	-N=C (str.)	1611	1640-1580
Ar-N-$(CH_3)_2$	C-N	3425	3550-3420

Table-2.23 : IRSPECTRAL STUDY OF N-[(1E)-(4-CHLOROPHENYL) METHYLENE]-N’-[(1Z)-(4-CHLOROPHENYL) METHYLENE]BIPHENYL -4,4’-DIAMINE(DVA-11)



Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm^{-1}
Aromatic	C=C	1491	1600-1450
	C-N	1402,1092	1340-1410
	-CH=CH-	1011	995-985
Ar-N=C-Ar	-N=C	1624	1640-1580
C-Cl	C-Cl	671	800-600

Table-2.24 : IR SPECTRAL STUDY OF N-[(1E)-(4-FLOROPHENYL) METHYLENE]-N’[(1Z)-(4-LOROPHENYL)METHYLENE]BIPHENYL -4,4’-DIAMINE (DVA-12)



Type	Vibration mode	Frequency in cm^{-1}	Expected frequency in cm$^{-1[1-3]}$
Aromatic	C=C	1487	1600-1450
	C-H(str.)	781,723	750-700
.Ar-N=C-Ar	-N=C (str.)	1622	1640-1580
C-F	-C-F (str.)	1325	1400-1000

Nuclear Magnetic Resonance Spectroscopy

In 1946 , E. M. Purchell and F. Bloch first developed this method which is based on the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 900 MHz. It is one of the most powerful tools available to the chemists and biochemists for elucidating the structure of chemical species. Nuclear magnetic resonance involves the interaction between an oscillating magnetic field of electro-magnetic radiation and the magnetic energy of the hydrogen nucleus or some other type of nuclei when these are placed in an external static magnetic field. The sample absorbs electro-magnetic radiations in radio-wave region at different frequencies since absorption depends upon the type of protons or certain nuclei contained in sample.

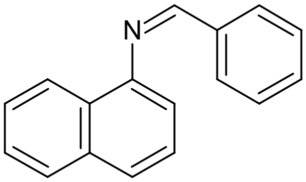
The NMR spectrum gives valuable data about the carbon chain, structural diagnosis, conformational analysis, determination of reaction velocities, keto-enol tautomerism. It also helps to study exchange effects, in determination of activation energy etc.

^{1}H NMR spectra were scanned on "BRUKER-Spectrometer-NMR 300MHz by using deuterated chloroform or dimenthyl sulfoxide as a solvent.

The chemical shift (δ ppm), and multiplicities of these Schiff bases are reported in Tables 2.25-2.21 and along with Figures 2.25 – 2.16.

Table-2.25 : NMR SPECTRAL STUDY OF N-[(1Z)-PHENYLMETHYLENE] NAPHTHALEN-1-AMINE [NDP-1]

Structure:



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	6.88-6.91	2H	Doublet	Ar-H
2	7.18-7.22	3H	Doublet	Ar-H
3	7.40-7.41	3H	Triplet	Ar-H
4	7.84-7.87	4H	Quartet	Ar-H
5	8.40	1H	Singlet	CH=N

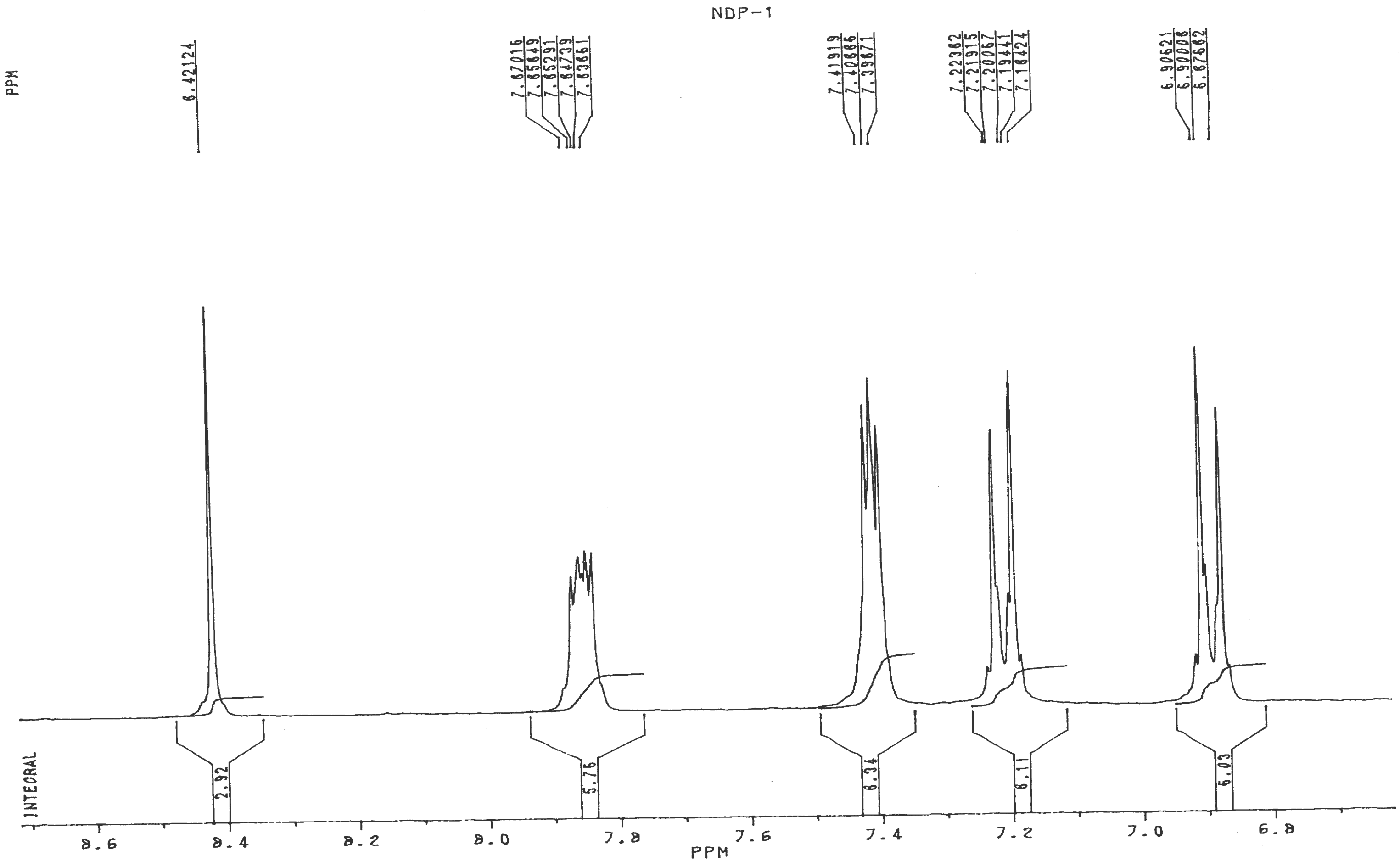
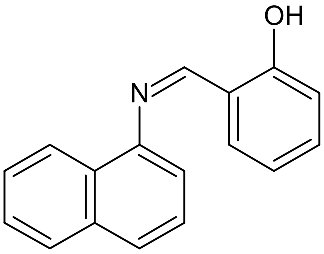


Figure 2.1: NMR SPECTRA OF N- [(1E) – PHENYL METHYLENE] NAPHTHALENE-1-AMINE (NDP-1)

Table-2.26 : NMR SPECTRAL STUDY OF [(Z)-(1-NAPHTHYLIMINO) METHYL] PHENOL [NDP-2]

Structure



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	6.83-6.89	4H	Triplet	Ar-H
2	6.94-6.97	2H	Doublet	Ar-H
3	7.19-7.31	5H	Multiplet	Ar-H
4	8.52	1H	Singlet	CH=N
5	13.37	1H	Singlet	Ar-OH

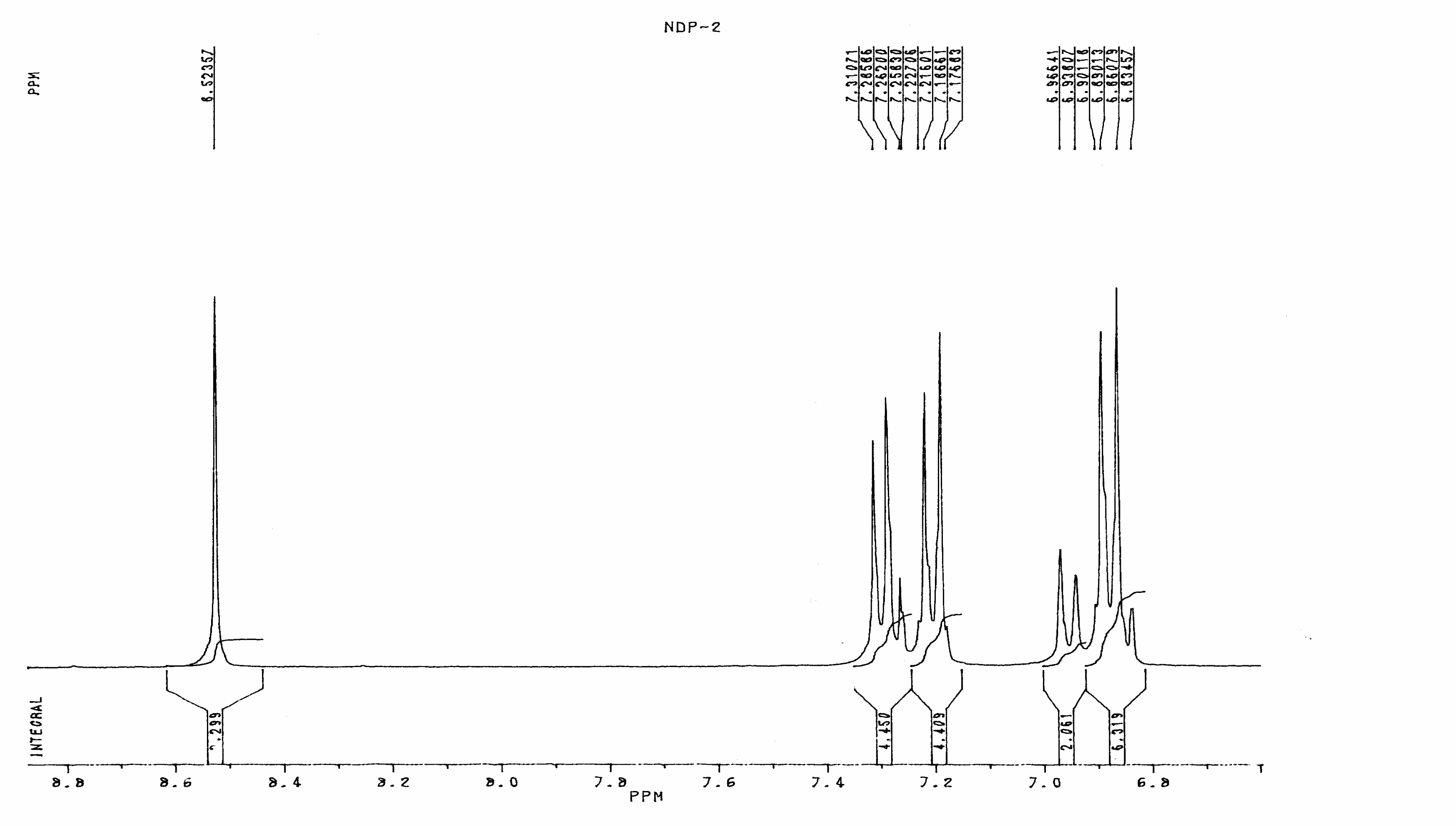
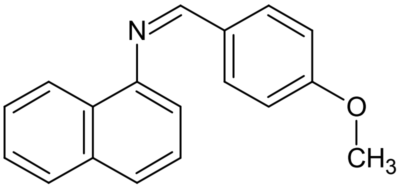


Figure 2.2 : NMR SPECTRA OF 2-(E)-(1-NAPHTHYLIMINO) METHYL] PHENOL (NDP-2)

Table-2.27 : NMR SPECTRAL STUDY OF N-[(1Z)-(4-METHOXYPHENYL) METHYLENE] NAPHTHALEN-1-AMINE [NDP-3]

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	3.80	3H	Singlet	Ar-O-C$\underline{H}_3$
2	6.89-6.97	2H	Quartet	Ar-$\underline{H}$
3	7.16-7.21	2H	Doublet	Ar-$\underline{H}$
4	7.79-7.84	2H	Doublet	Ar-$\underline{H}$
5	8.38	1H	Singlet	Ar-C$\underline{H}$=N

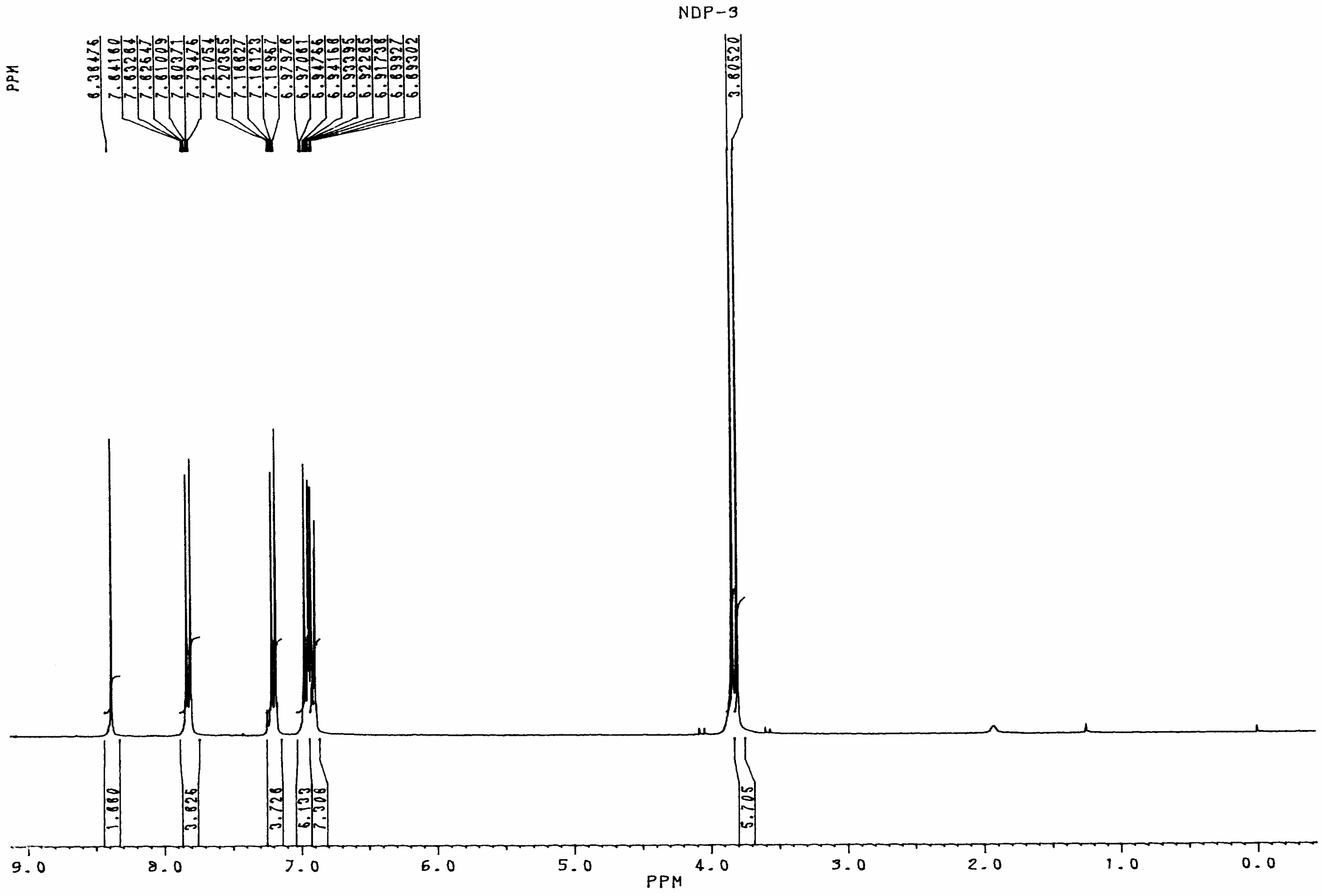
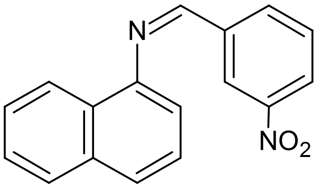


Figure 2.3: NMR SPECTRA OF N-[(1E)-(4-METHOXY PHENYL) METHYLENE]-N-1-NAPHTHYLAMINE(NDP-3)

Table-2.28 : NMR SPECTRAL STUDY OF N-[(1Z)-(3-NITROPHENYL) METHYLENE] NAPHTHALEN-1-AMINE [NDP-4]

Structure:



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	6.92-6.96	3H	Doublet	Ar-<u>H</u>
2	7.58-7.63	1H	Triplet	Ar-<u>H</u>
3	8.18-8.27	2H	Multiplet	Ar-<u>H</u>
4	8.53	1H	Singlet	Ar-<u>H</u>
5	8.58-8.59	1H	Singlet	C<u>H</u>=N

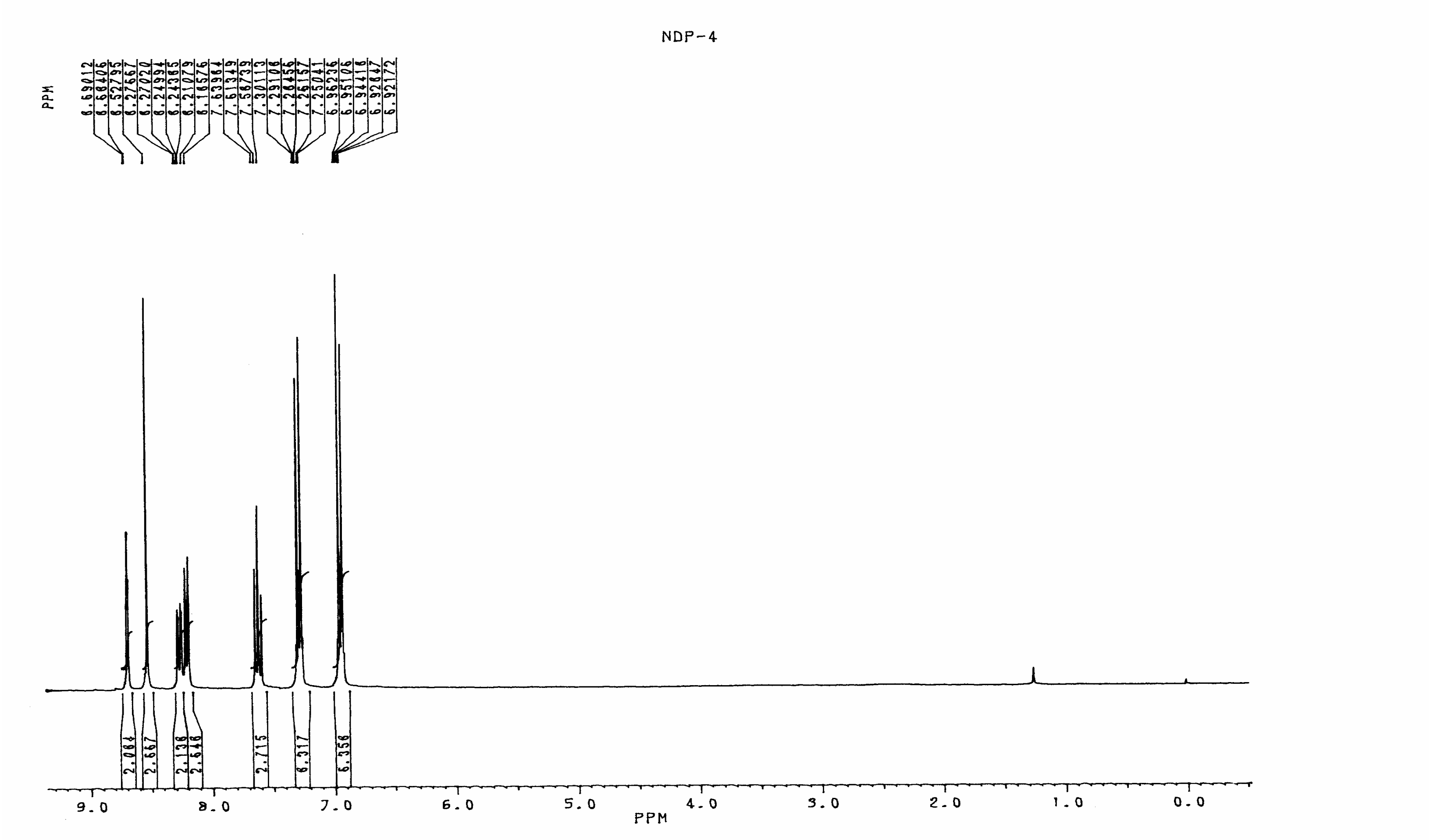
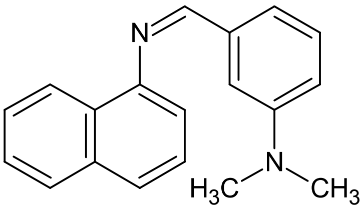


Figure 2.4: NMR SPECTRA OF N-[(1E)-(3-NITRO PHENYL) METHYLENE] NAPHTHALENE-1-AMINE(NDP-4)

Table-2.29 : NMR SPECTRAL STUDY OF N-{(1Z)-[3-(DIMETHYLAMINO) PHENYL]METHYLENE }NAPHTHALEN-1-AMINE [NDP-5]

Structure :



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	3.02	3H	Singlet	Ar-N-(C<u>H</u>$_3$)$_2$
2	6.69-6.72	4H	Doublet	Ar-<u>H</u>
3	6.88-6.91	2H	Doublet	Ar-<u>H</u>
4	7.16-7.24	2H	Doublet	Ar-<u>H</u>
5	7.72-7.75	1H	Doublet	Ar-<u>H</u>
6	8.32	1H	Singlet	C<u>H</u>=N

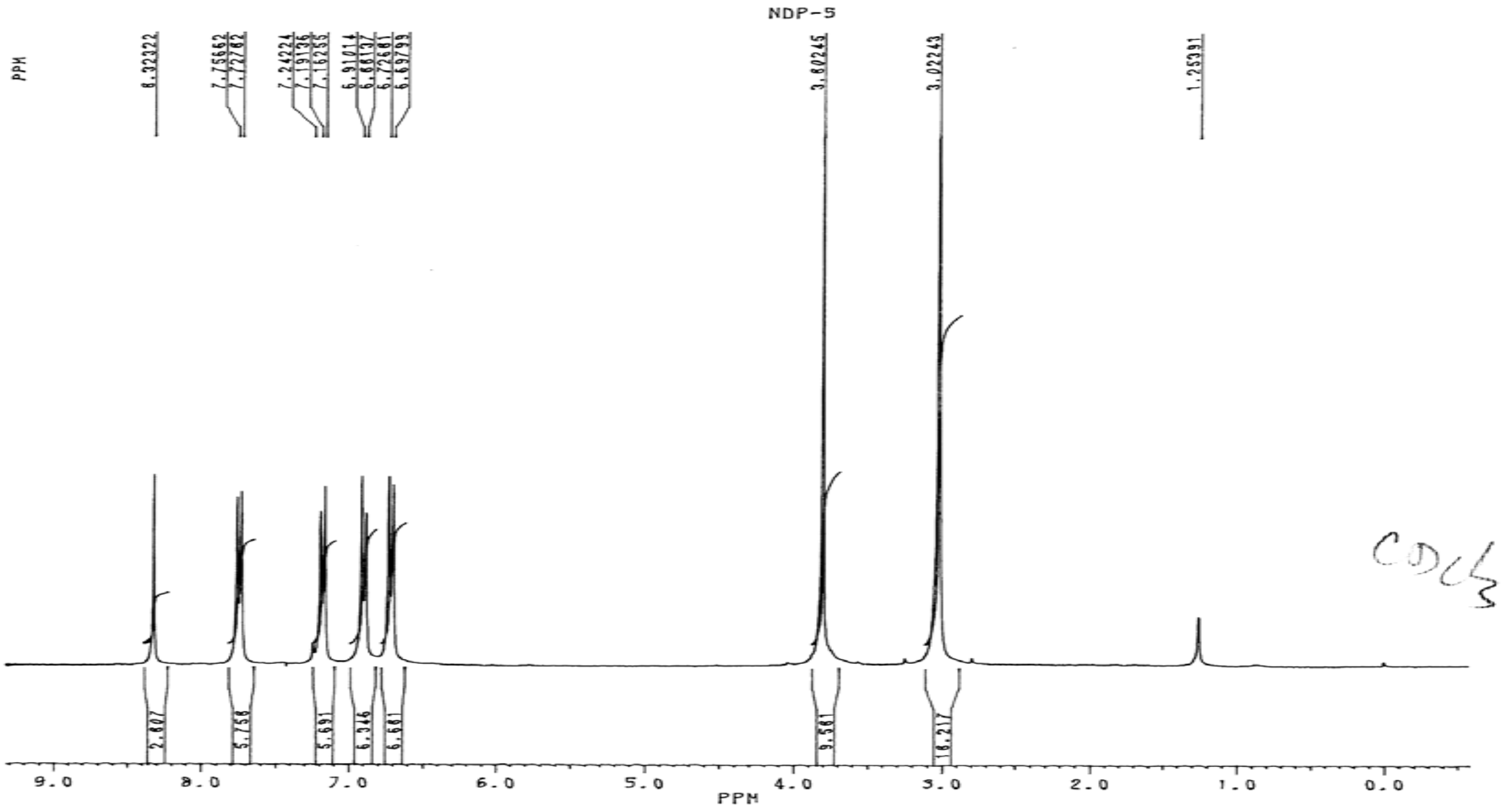
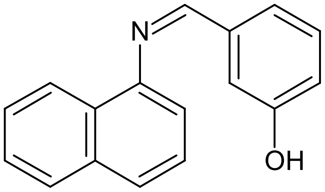


Figure 2.5: NMR SPECTRA OFN-{(1Z)-[3-(DIMETHYLAMINO)PHENYL]METHYLENE }NAPHTHALEN-1-AMINE[NDP-5]

Table-2.30 : NMR SPECTRAL STUDY OF [(Z)-(1-NAPHTHYL IMINO) METHYL] PHENOL (NDP-6)

Structure



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	6.88-6.92	7H	Multiplet	Ar-<u>H</u>
2	7.14-7.19	2H	Doublet	Ar-<u>H</u>
3	7.70-7.73	2H	Doublet	Ar-<u>H</u>
4	8.36	1H	Singlet	C<u>H</u>=N
5	8.45	1H	Singlet	Ar-O<u>H</u>

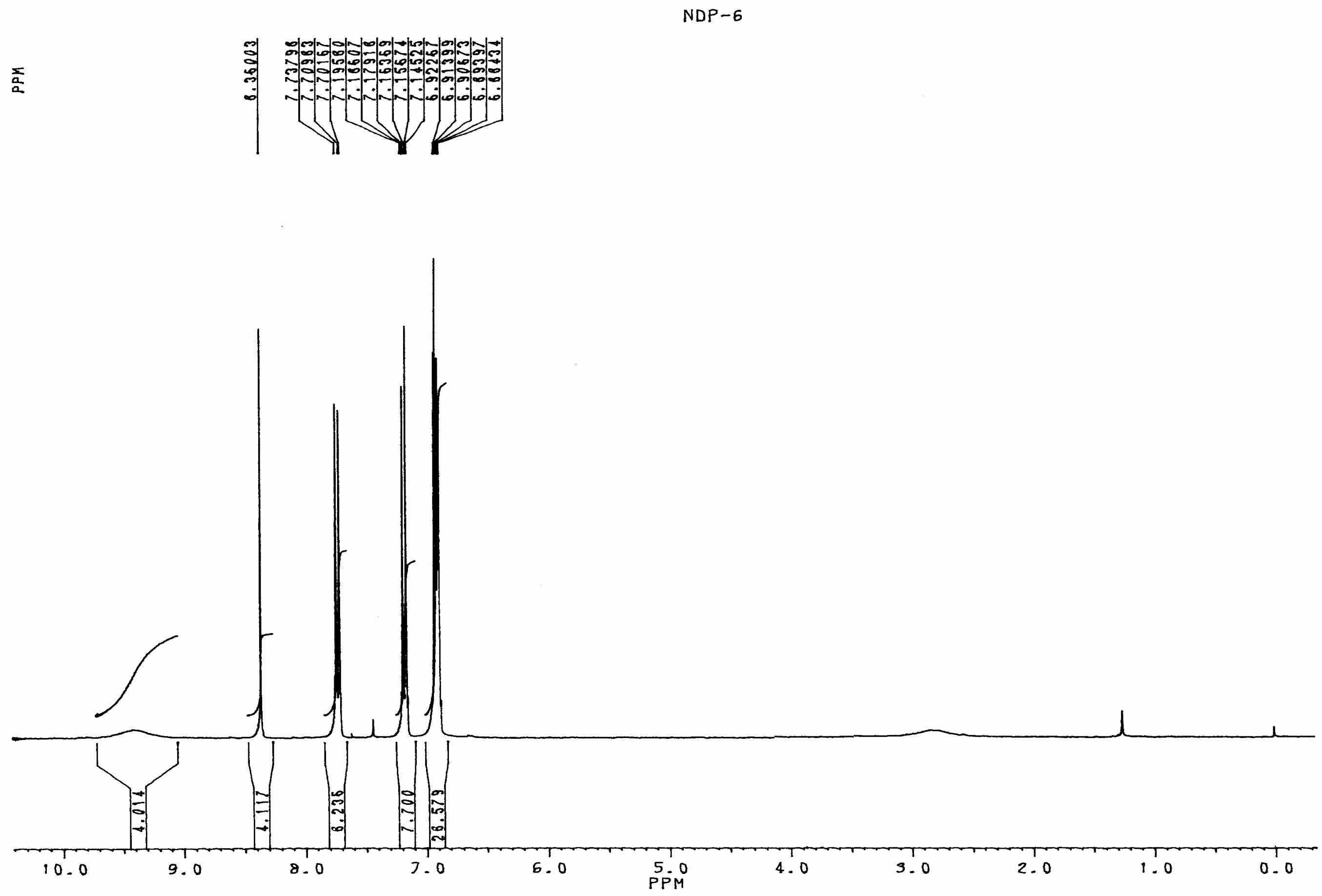
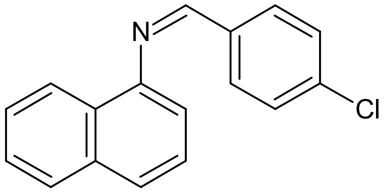


Figure 2.6: NMR SPECTRA OF 4-[(1E)-(1-NAPHTHYLIMINO) METHYL] PHEN OL (NDP-6)

Table-2.31 : NMR SPECTRAL STUDY OF N-[(1Z)-(4-CHLOROPHENYL) METHYLENE] NAPHTHALEN-1-AMINE [NDP-7]

Structure :



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	6.91-6.94	3H	Doublet	Ar-<u>H</u>
2	7.21-7.25	2H	Doublet	Ar-<u>H</u>
3	7.41-7.43	4H	Doublet	Ar-<u>H</u>
4	7.80-7.83	2H	Singlet	Ar-<u>H</u>
5	8.43	1H	Singlet	C<u>H</u>=N

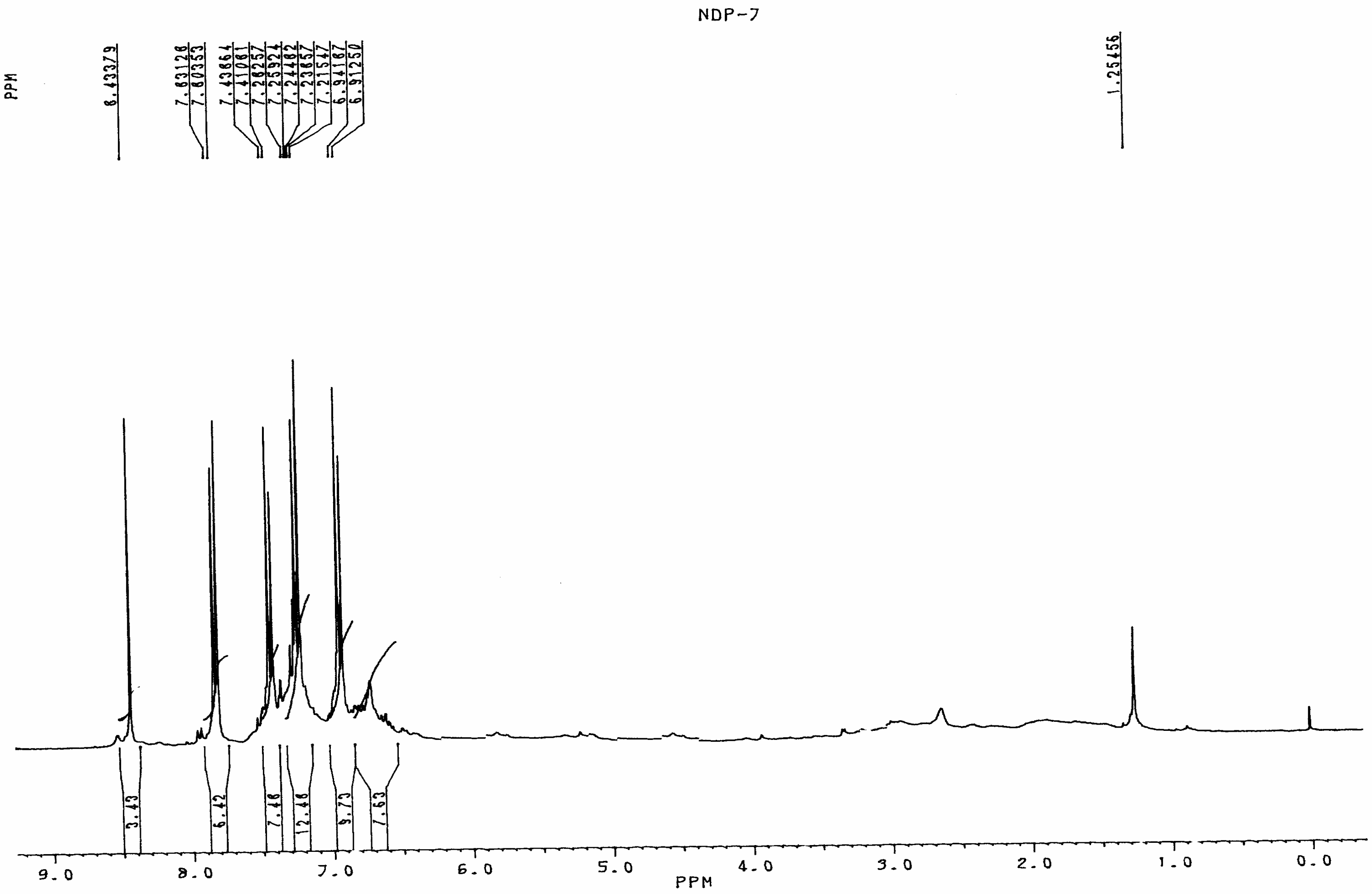
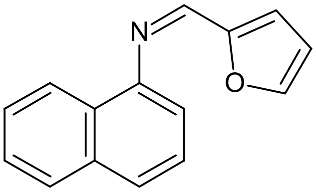


Figure 2.7: NMR SPECTRA OF N-[(1E)-(4-CHLORO PHENYL) METHYLENE]-N-NAPHTHYL AMINE (NDP-7)

Table-2.32 : NMR SPECTRAL STUDY OF N-[(1Z)-2- FURYLMETHYLENE] NAPHTHALEN-1-AMINE [NDP-8]

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	3.56-3.93	5H	Doublet	Ar-H
2	6.53-7.12	5H	Doublet	Ar-H
3	7.14-7.28	1H	Multiplet	CH=N

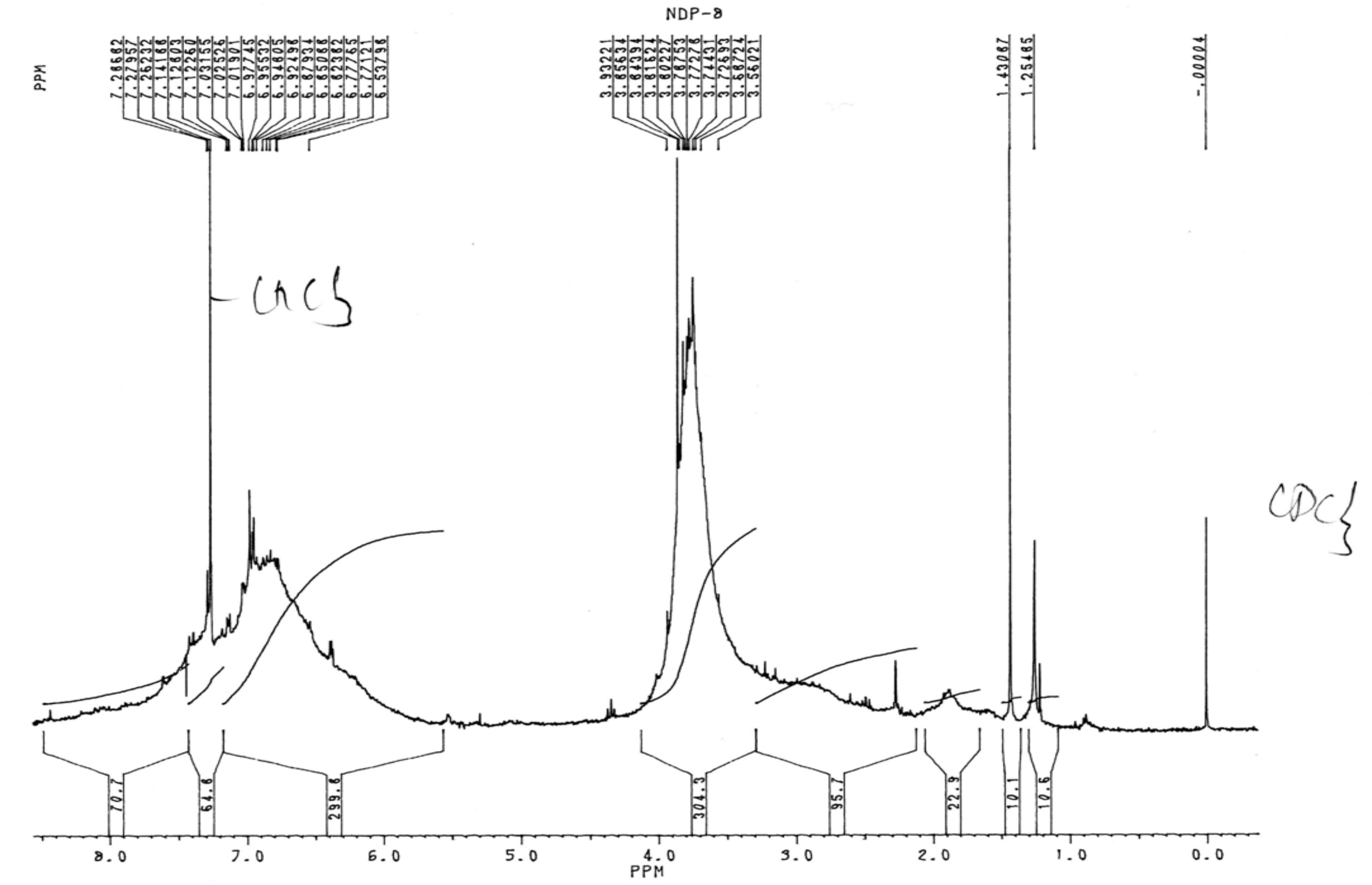
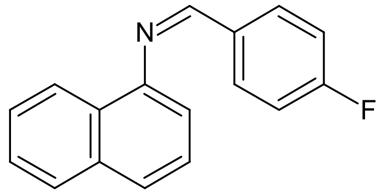


Figure 2.8: NMR SPECTRA OF N-[(1Z)-2- FURYLMETHYLENE] NAPHTHALEN-1-AMINE [NDP-8]

Table-2.33 : NMR SPECTRAL STUDY OF N-[(1Z)-(4-FLUOROPHENYL) METHYLENE] NAPHTHALEN-1-AMINE [NDP-9]

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	6.88-6.91	2H	Doublet	Ar-<u>H</u>
2	7.01-7.13	3H	Triplet	Ar-<u>H</u>
3	7.18-7.21	2H	Doublet	Ar-<u>H</u>
4	7.82-7.86	4H	Quartret	Ar-<u>H</u>
5	8.38	1H	Singlet	C<u>H</u>=N

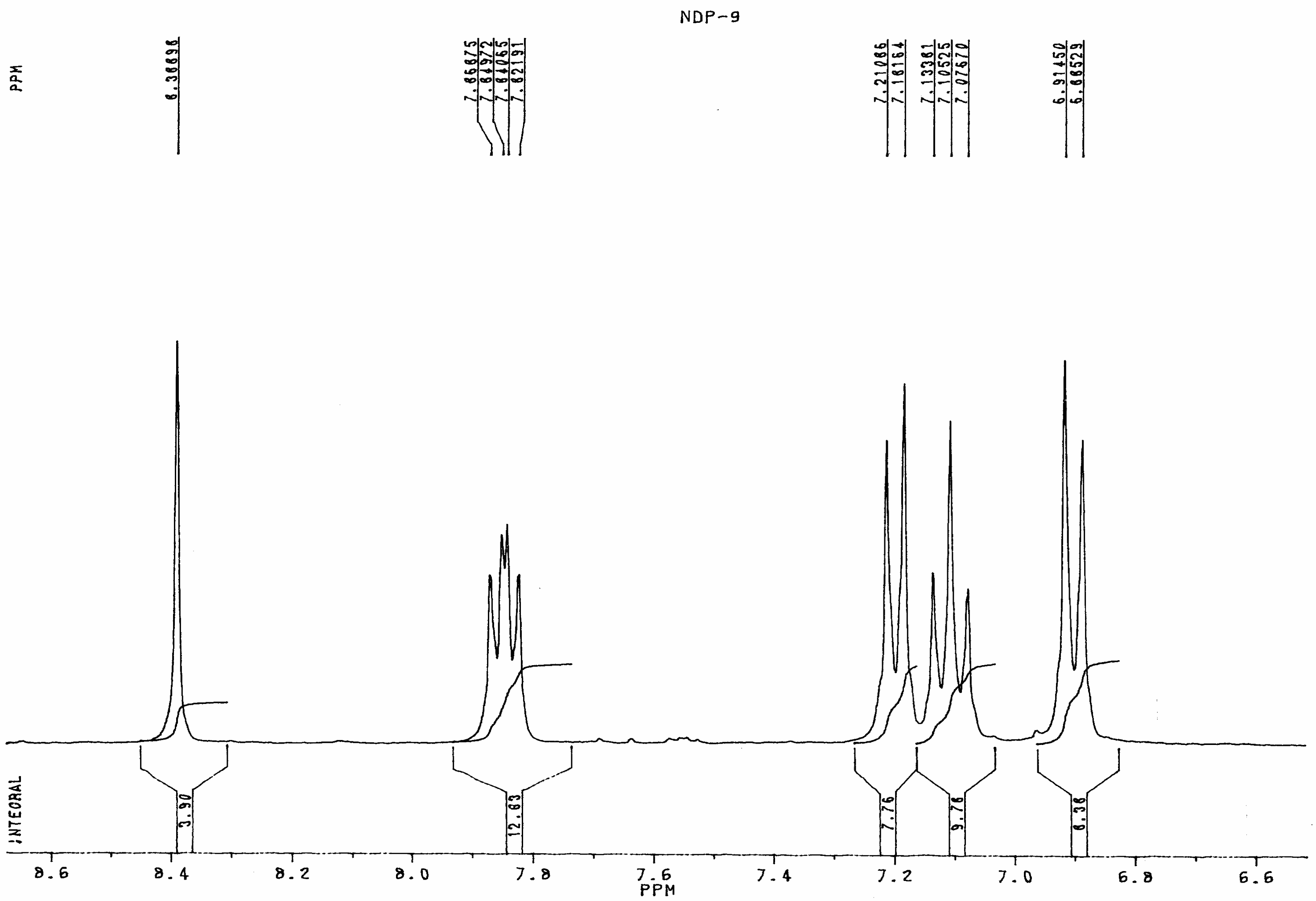
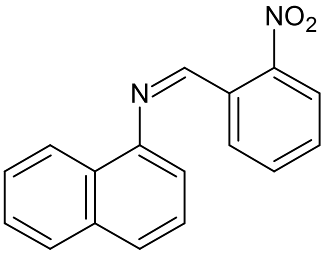


Figure 2.9: NMR SPECTRA OF [(1E)-(4-FLORO PHENYL) METHYLENE]-N-1-NAPHTHYL AMINE(NDP-9)

Table-2.34 : NMR SPECTRAL STUDY OF N-[(1Z)-(2-NITROPHENYL) METHYLENE] NAPHTHLEN-1-AMINE [NDP-10]

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	6.92-6.96	4H	Doublet	Ar-<u>H</u>
2	7.28-7.31	3H	Doublet	Ar-<u>H</u>
3	7.54-7.59	1H	Triplet	Ar-<u>H</u>
4	7.67-7.72	1H	Triplet	Ar-<u>H</u>
5	8.02-8.04	1H	Doublet	Ar-<u>H</u>
6	8.28-8.31	1H	Doublet	Ar-<u>H</u>
7	8.94	1H	Singlet	Ar-C<u>H</u>=N-

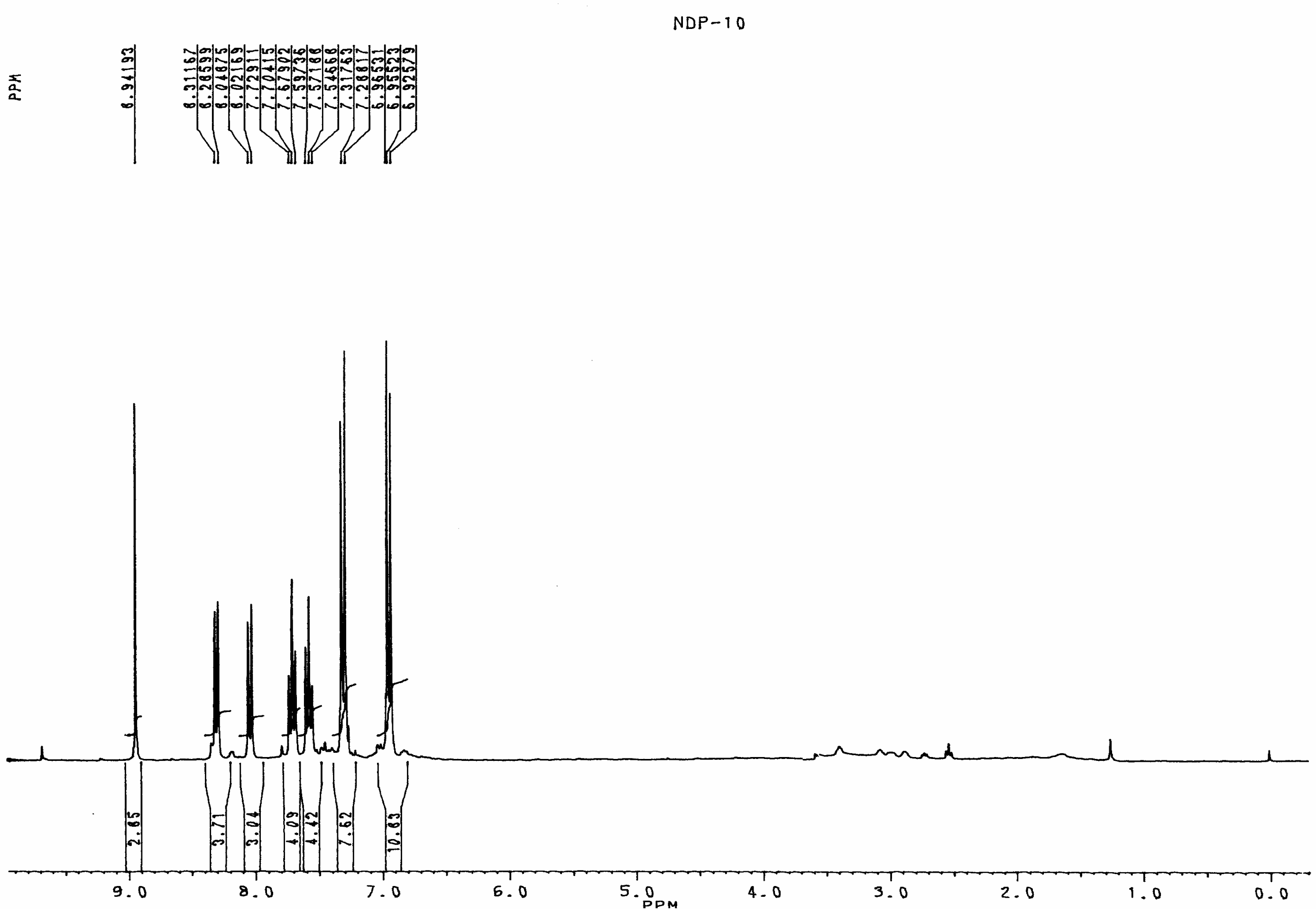
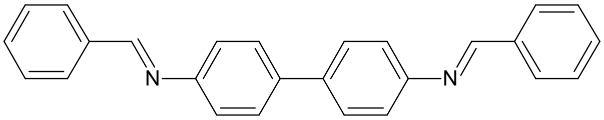


Figure 2.10: NMR SPECTRA OF N-[(1E)-(2-NITRO PHENYL) METHYLENE] NAPHTHALENE-1-AMINE (NDP-10)

Table-2.35 : NMR SPECTRAL STUDY OF N-[(1E)-PHENYLMETHYLENE]-N'-[(1Z)-PHENYLMETHYLENE] BIPHENYL-4,4'-DIAMINE (DVA-1)

Structure



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	7.51-7.87	14H	Multiplet	Ar-H
2	9.28-9.97	2H	Singlet-Singlet	-CH=N

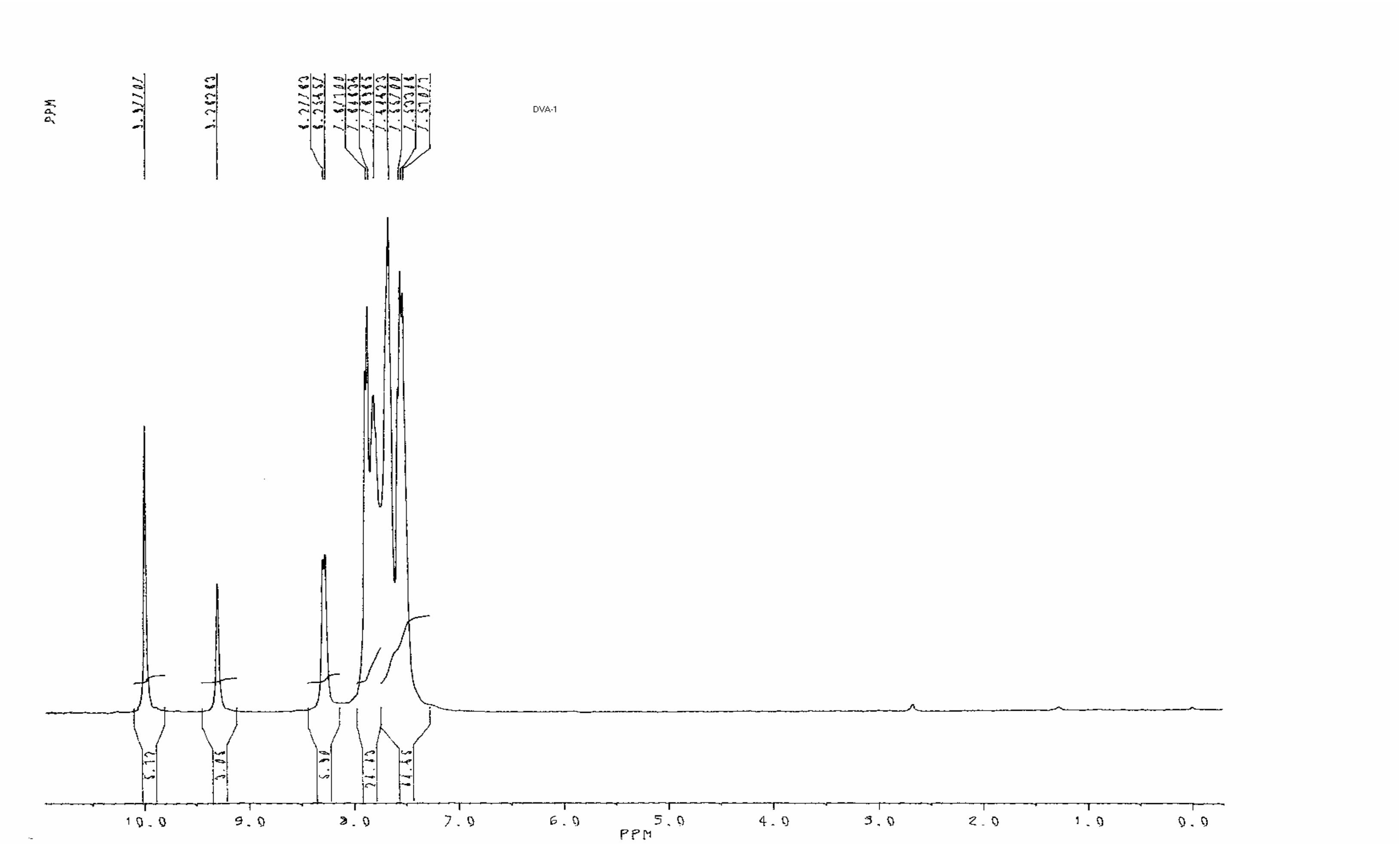
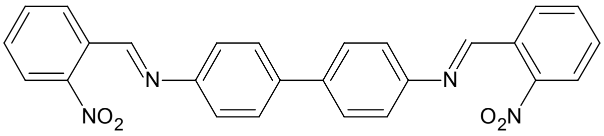


Figure 2.11: NMR SPECTRA OF N-[(1E)-PHENYLMETHYLENE]-N'-[(1Z)-PHENYLMETHYLENE]BIPHENYL-4,4'-DIAMINE(DVA-1)

Table-2.36: NMR SPECTRAL STUDY OF N- [(1E)-(2-NITRO PHENYL) METHYLENE]-N'-[(1Z)-(2-NITROPHENYL) METHYLENE BIPHENYL-4,4'-DIAMINE(DVA-2)

Structure



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	7.56-8.79	8H	Multiplet	Ar-H
2	8.40-9.65	8H	Doublet	Ar-H
3	8.86-9.21	2H	Singlet	-CH=N-

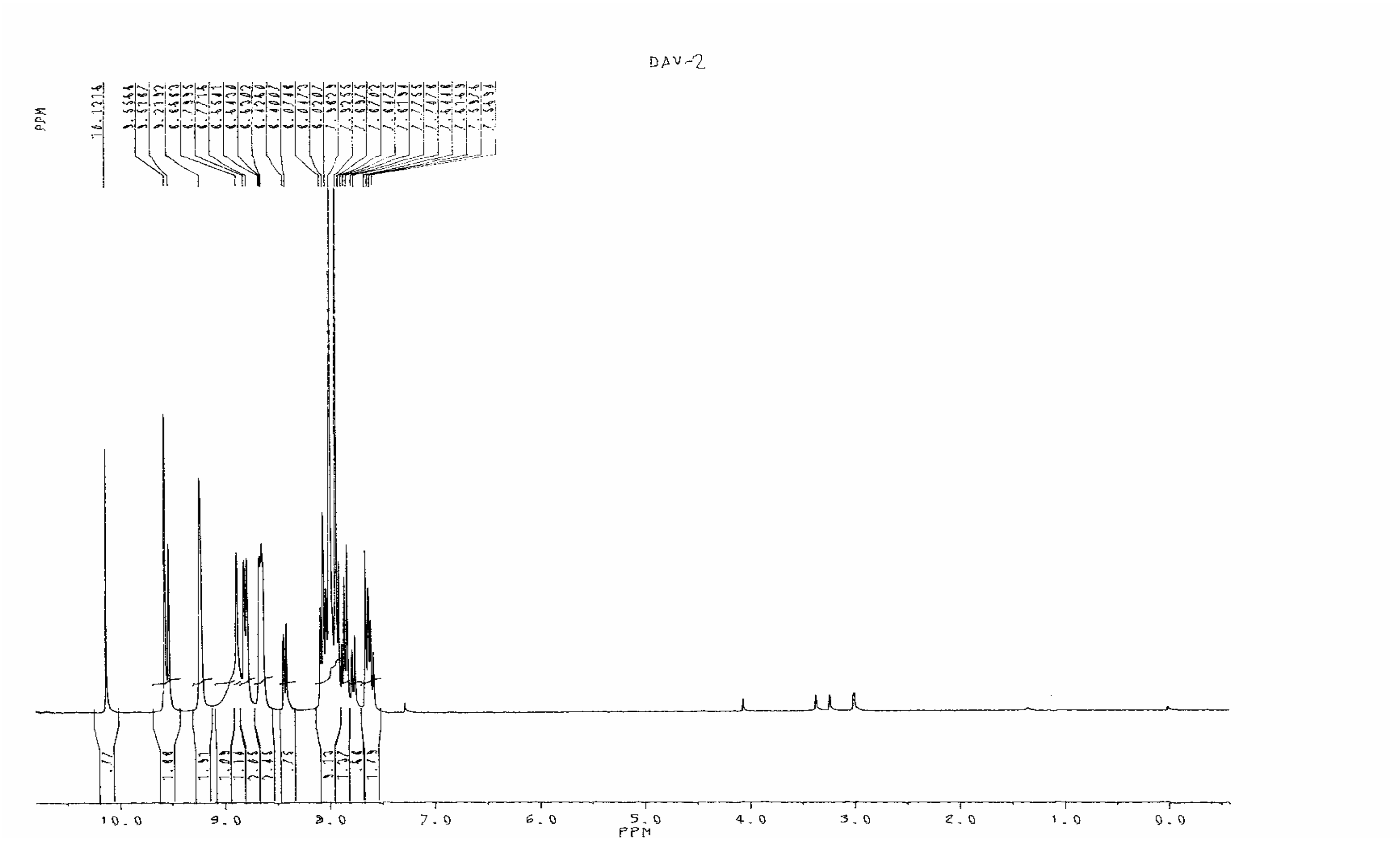
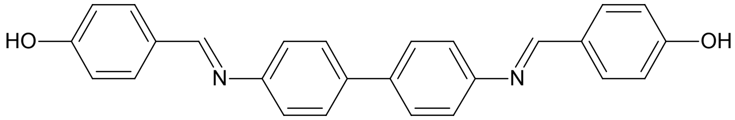


Figure 2.12 : NMR SPECTRA OF N- [(1E)-(2-NITRO PHENYL) METHYLENE]-N'-[(1Z)-(2-NITROPHENYL) METHYLENE BIPHENYL-4,4'-DIAMINE(DVA-2)

Table-2.37 *:* NMR SPECTRAL STUDY OF N-[(1E)-(4-HYDROXYPHENYL) METHYLENE]-N’-[(1Z-(4-HYDROXYPHENYL)METHYLENE BIPHENYL -4,4’-DIAMINE (DVA-3)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	7.20-7.23	4H	Doublet	Ar-H
2	7.57-7.59	2H	Doublet	CH=N
3	7.69-7.90	8H	Multiplet	Ar-H
4	8.13-8.15	4H	Doublet	Ar-H
5	8.89-8.93	2H	Singlet	-OH

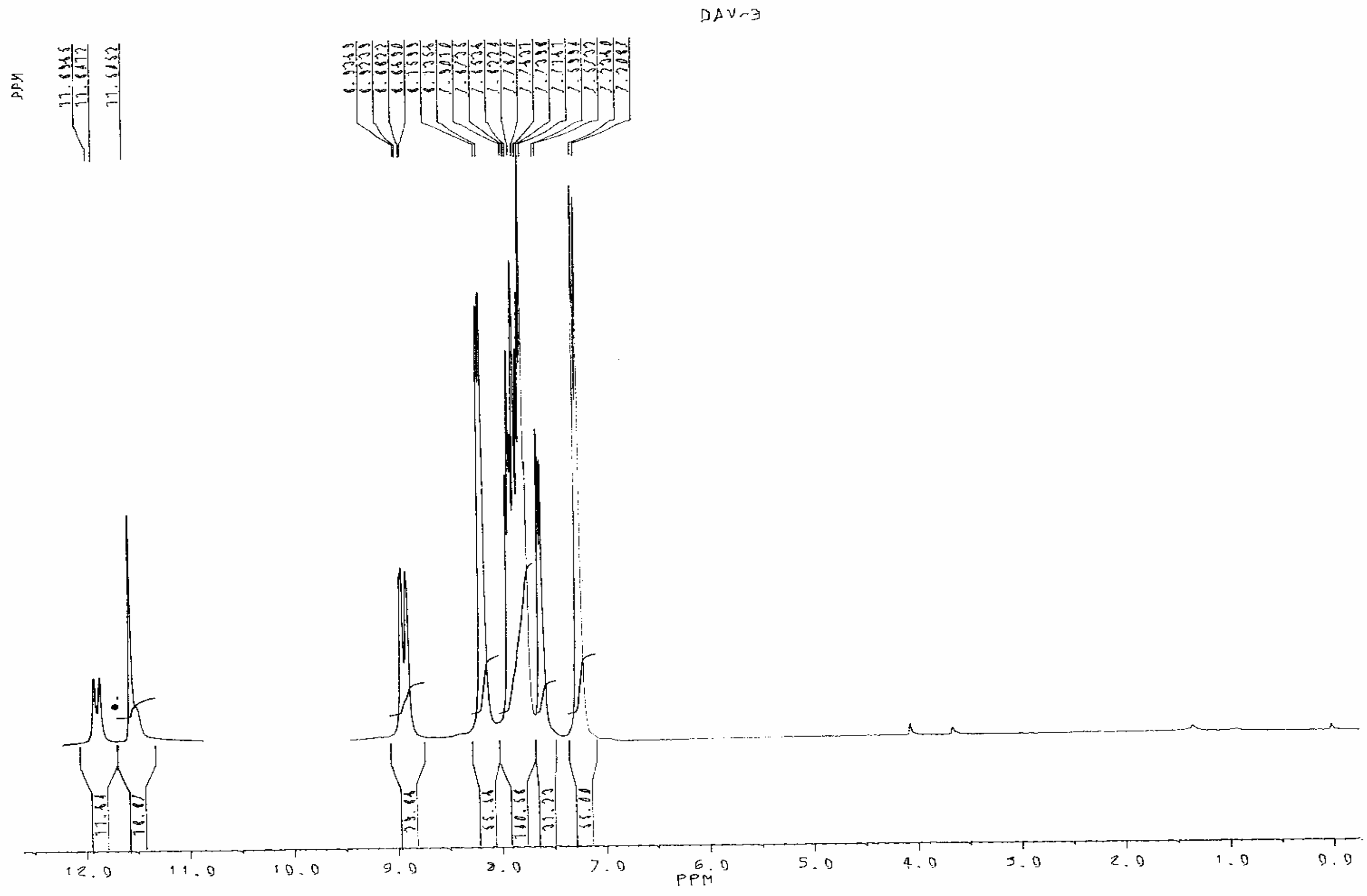
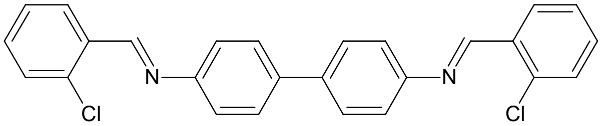


Figure 2.13 : NMR SPECTRA OF N-[(1E)-(4-HYDROXYPHENYL) METHYLENE]-N'-[(1Z-(4-HYDROX YPHENYL) METHYLENEBIPHENYL-4,4'-DIAMINE (DVA-3)

Table-2.38 : NMR SPECTRAL STUDY OF N- [(1E)-(2-CHLOROPHENYL) METHYLENE]-N’1Z)-(2-CHLORO PHENYL) METHYLENE] BIPHENYL-4,4’-DI AMINE (DVA-4)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	7.24-7.85	12H	Triplet	Ar-H
2	7.85-7.87	4H	Doublet	Ar-H
3	8.26-8.28	2H	Singlet	CH=N

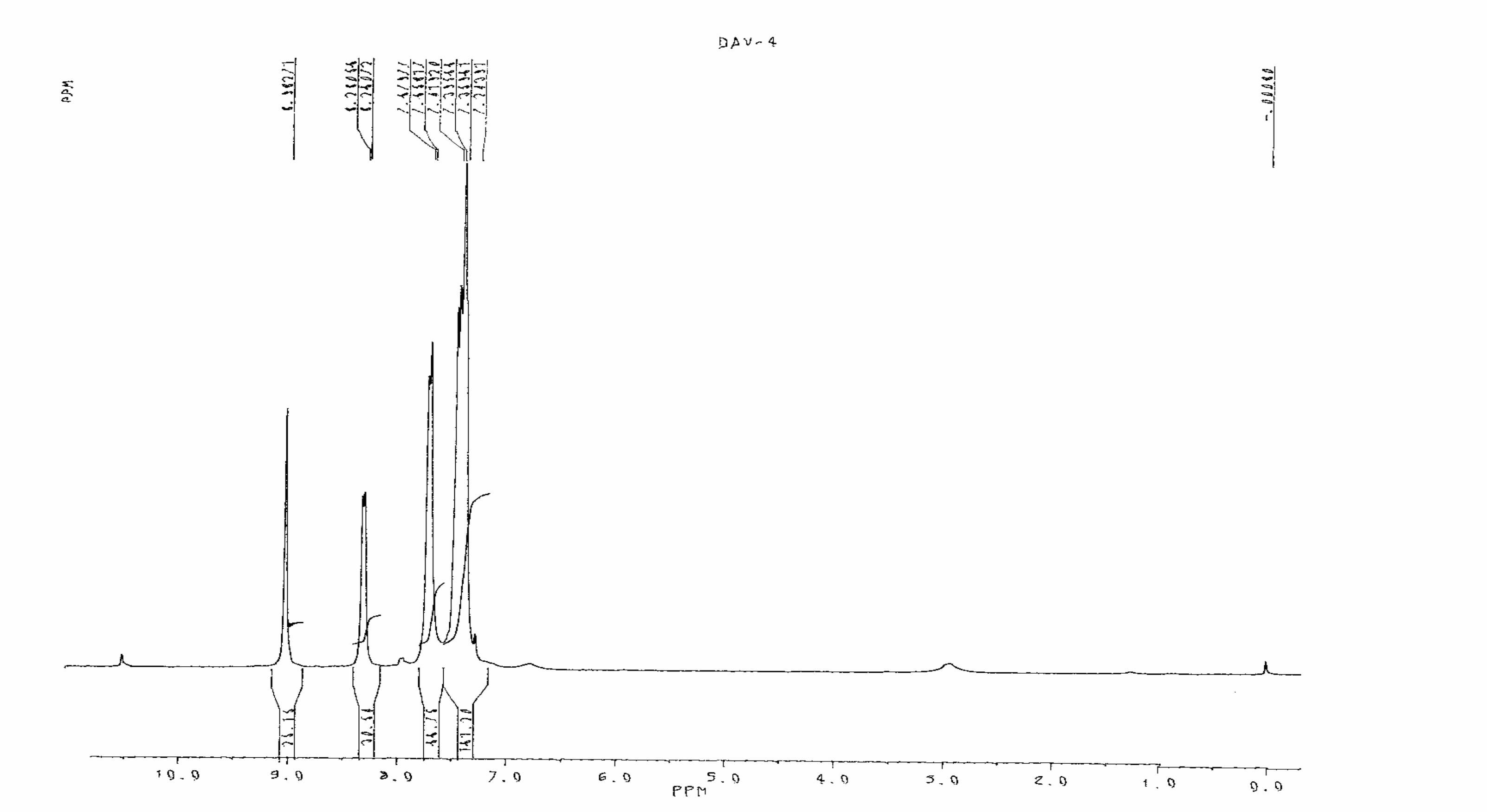
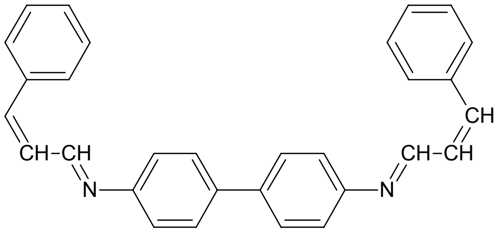


Figure 2.14 : NMR SPECTRA OF N- [(1E)-(2-CHLOROPHENYL) METHYLENE]-N’1Z)-(2-CHLORO PHENYL) METHYLENE] BIPHENYL-4,4’-DI AMINE (DVA-4)

Table-2.39 : NMR SPECTRAL STUDY OF N-[(1E)-(2-HYDROXYPHENYL) METHYLENE]-N'-[(1Z)-(2-HYDROXYPHENYL)METHYLENE BIPHENYL-4,4'-DI AMINE (DVA-5)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	7.48-7.64	6H	Triplet	-C<u>H</u>=C<u>H</u>-C<u>H</u>=
2	7.56-7.64	4H	Triplet	Ar-<u>H</u>
3	7.64-7.73	5H	Multiplet	Ar-<u>H</u>
4	7.73-7.83	4H	Multiplet	Ar-<u>H</u>
5	7.83-7.85	2H	Singlet	=C<u>H</u>-
6	8.74	2H	Doublet	=C<u>H</u>-C<u>H</u>=
7	8.09-8.90	1H	Multiplet	C<u>H</u>=N

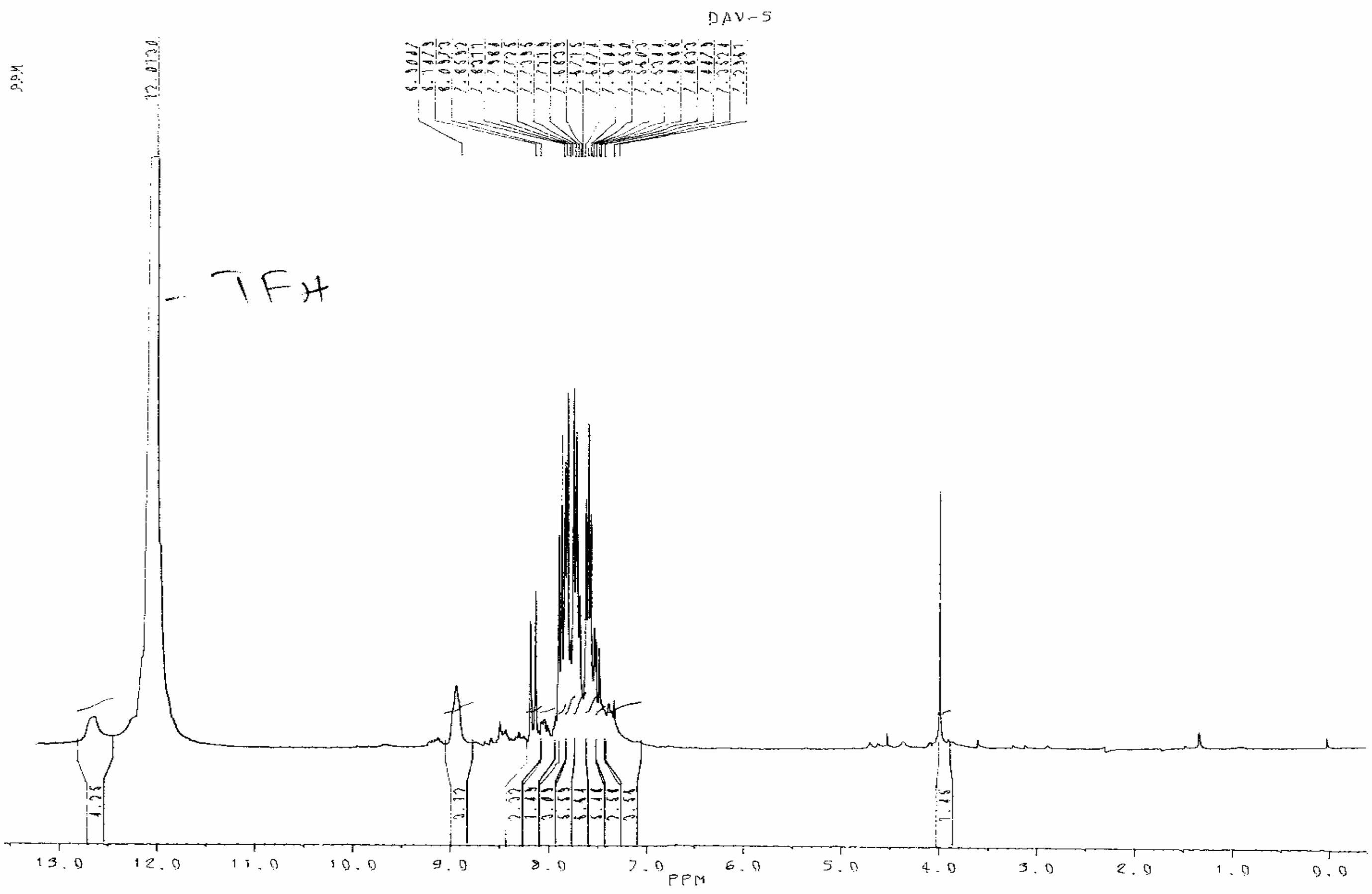
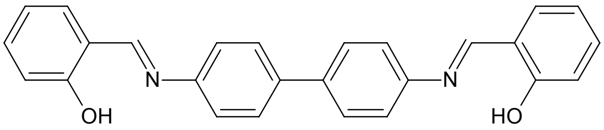


Figura 2.15: NMR SPECTRA OF N-[(1E)-(2-HYDROXYPHENYL) METHYLENE]-N'-[(1Z)-(2-HYDROXYPHENYL) METHYLENE BIPHENYL-4,4'-DI AMINE (DVA-5)

Table-2.40 : NMR SPECTRAL STUDY OF N-[(1E)-(2-CHLOROPHENYL) METHYLENE]-N’-[(1Z)-(2-HYDROXYPHENYL) METHYLENE] BIPHENYL-4,4’-DIAMINE(DVA-6)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	7.25-7.92	14H	Multiplet	Ar-H
2	9.02-9.07	2H	Doublet	-OH
3	7.30-7.33	2H	Multiplet	CH=N

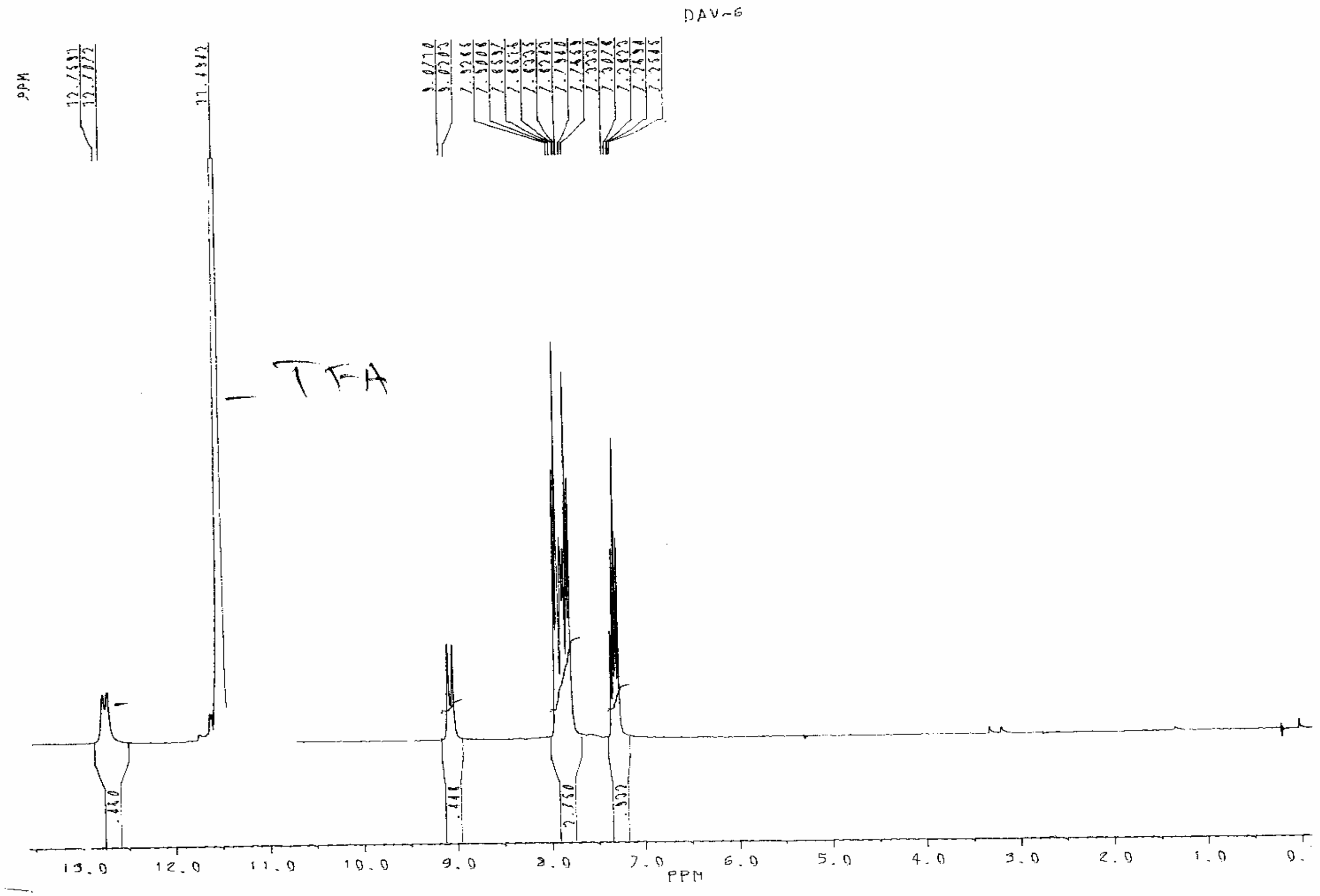
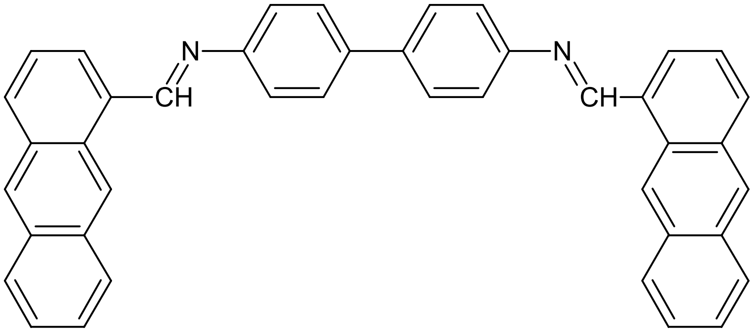


Figure 2.16 : NMR SPECTRA OF N-[(1E)-(2-HYDROXYPHENYL) METHYLENE]-N'-[(1Z)-(2-CHLORO PHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-6)

Table-2.41 : NMR SPECTRAL STUDY OF N-[(1E)-ANTHRYLMETHYLENE]-N'-[(1Z)-ANTHRYL METHYLENE] BIPHENYL-4,4'-DIAMINE (DVA-7)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	7.06-7.66	18H	Multiplet	Ar-H
2	8.70	2H	Singlet	CH=N
3	7.68-7.66	2H	Multiplet	Ar-H
4	8.5-8.7	6H	Multiplet	Ar-H

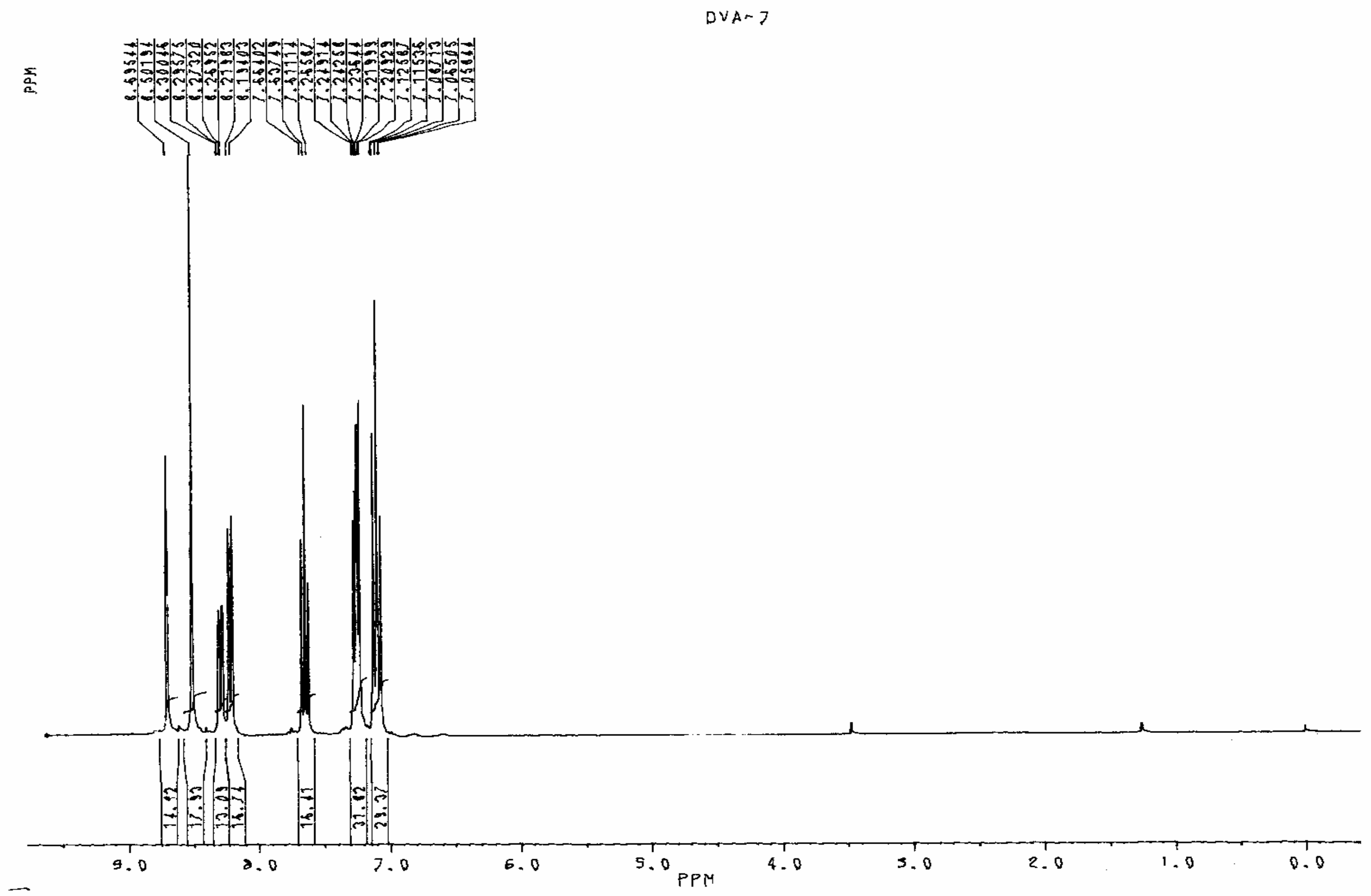
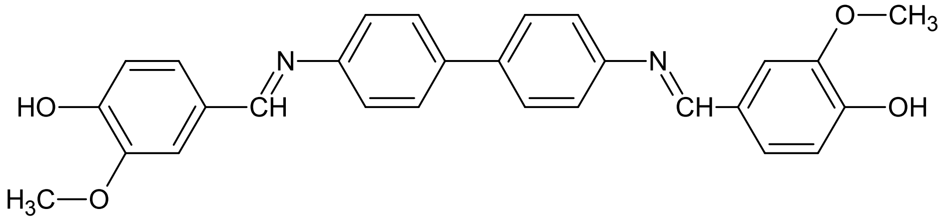


Figure 2.17: NMR SPECTRA OF N-[(1E)-ANTHRYLMETHYLENE]-N'-[(1Z)-ANTHRYL METHYLENE] BIPHENYL-4,4'-DIAMINE (DVA-7)

Table-2.42 : NMR SPECTRAL STUDY OF N-[(1E)-(3-METHOXY,4-HYDROXY PHENYL)METHYLENE]-N'-[(1Z)-(3-METHOXY,4-HYDROXY PHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE (DVA-8)

Structure



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	3.73	6H	Singlet	$-O-C\underline{H}_3$
2	5.0	2H	Singlet	$-O\underline{H}$
3	8.39	2H	Singlet	$-C\underline{H}=N-$
4	7.3-7.5	8H	Multiplet	$Ar-\underline{H}$
5	6.65-7.01	6H	Multiplet	Ar-H

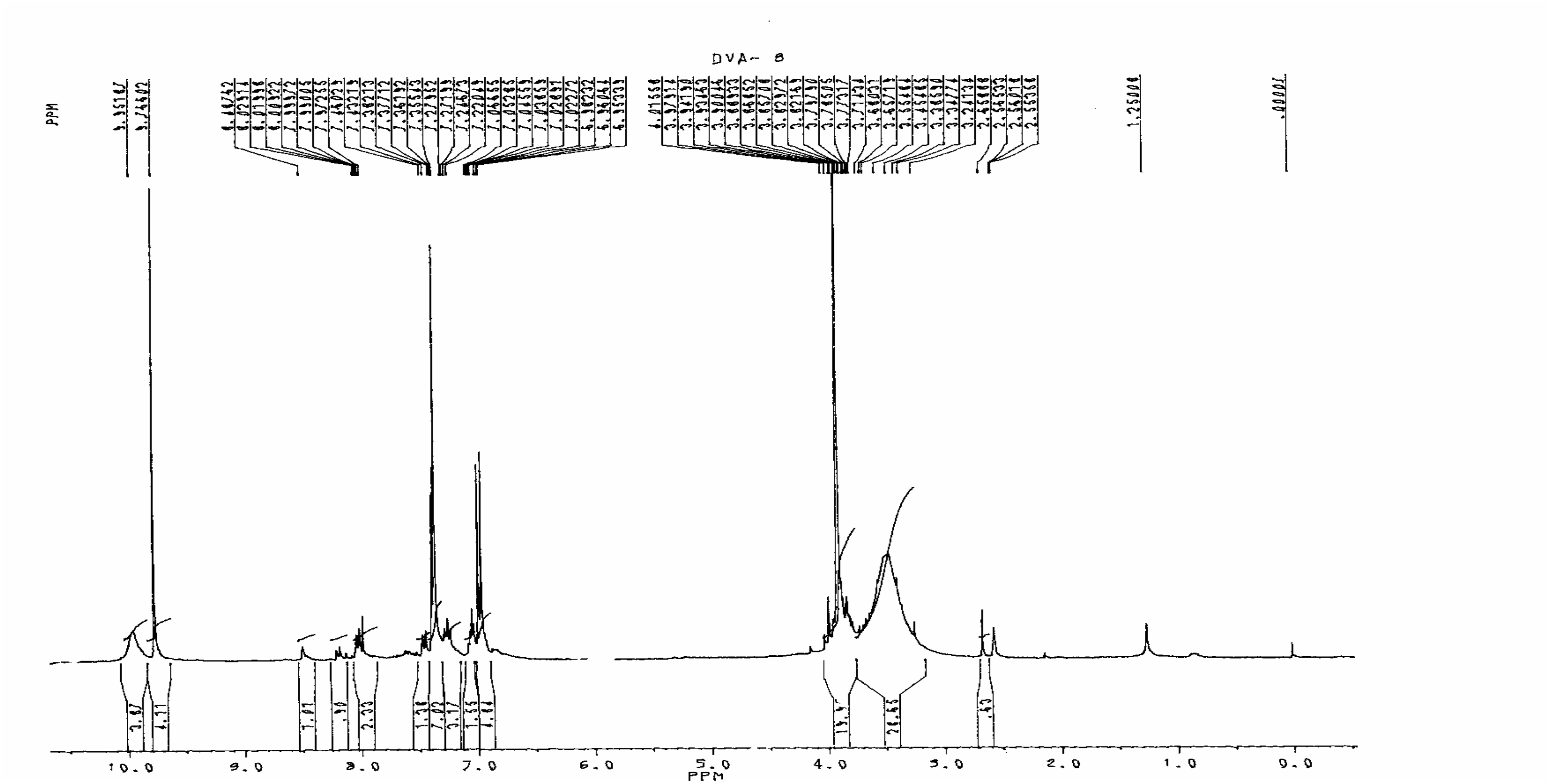
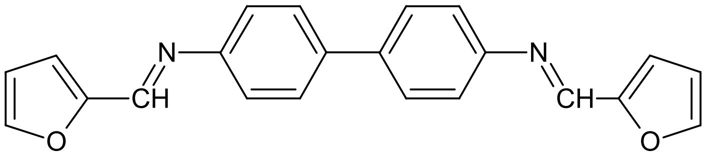


Figure 2.18 : NMR SPECTRA OF N-[(1E)-(3-METHOXY,4-HYDROXYPHENYL)METHYLENE]-N'-[(1Z)-(3-METHOXY,4-HYDROXYPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE (DVA-8)

Table-2.43 : NMR SPECTRAL STUDY OF N-[(1E)-2-FURYLMETHYLENE]-N'-[(1Z)-2-FURYLMETHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-9)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	6.4-6.76	6H	Singlet	Ar-<u>H</u>
2	7.02-7.66	8H	Multiplet	Ar-<u>H</u>
3	7.96	2H	Singlet	CH=<u>N</u>

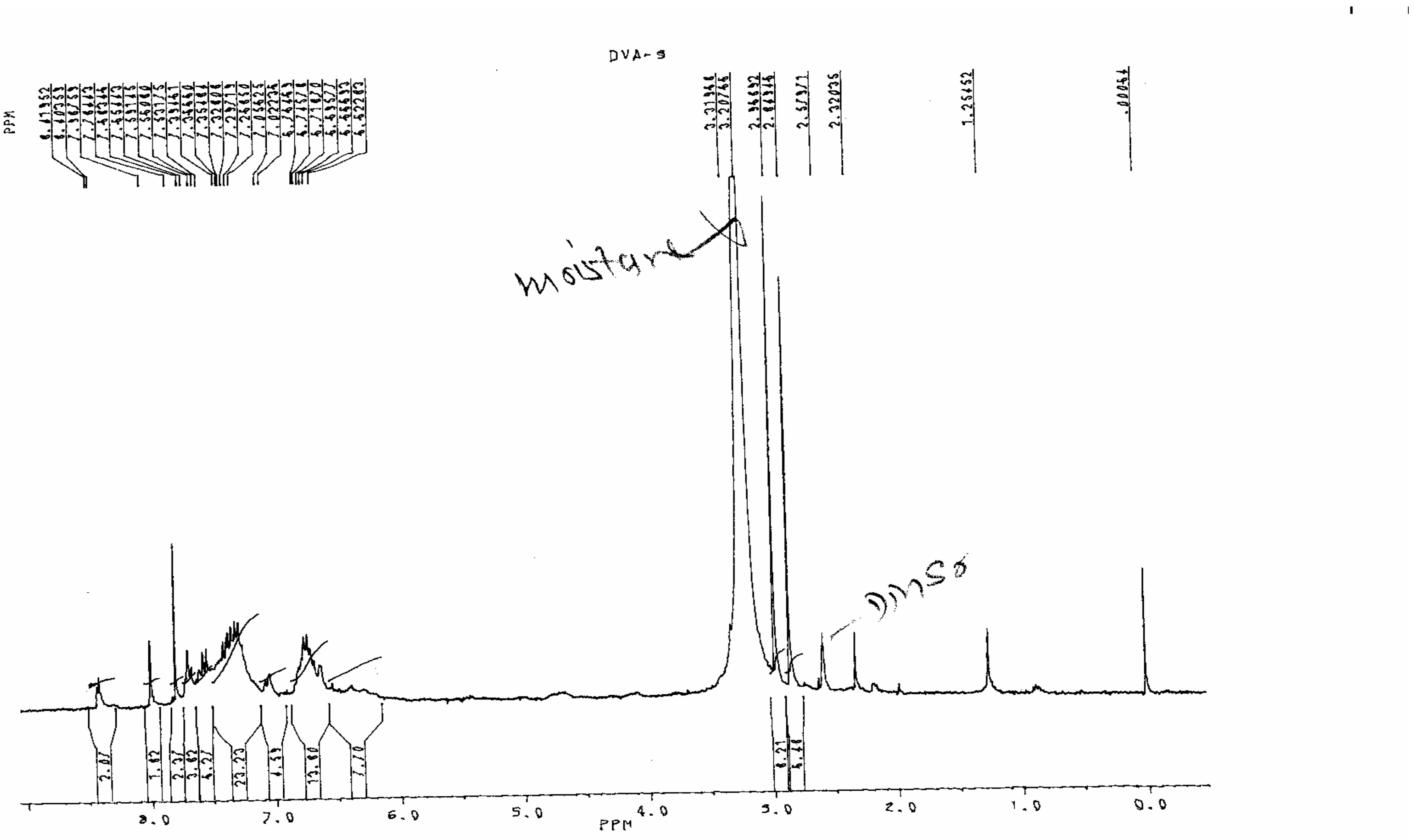
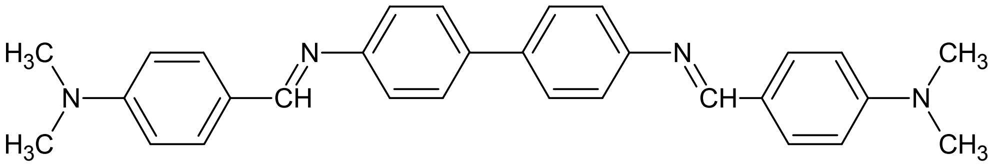


Figure 2.19 : NMR SPECTRA OF N-[(1E)-2-FURYLMETHYLENE]-N'-[(1Z)-2-FURYLMETHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-9)

Table-2.44 : NMRSPECTRAL STUDY OF N-[(1E)-(N-N-DIMETHYL) METHYLENE] -N’-[(1Z)-(N-N-DIMETHYL) METHYLENE] BIPHENYL4,4’DIAMINE (DVA-10)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	2.93-3.13	12H	Singlet	-C<u>H</u>$_3$
2	6.70-6.79	8H	Multiplet	Ar-<u>H</u>
3	7.54-7.72	8H	Multiplet	Ar-<u>H</u>
4	8.47	2H	Singlet	N=C<u>H</u>

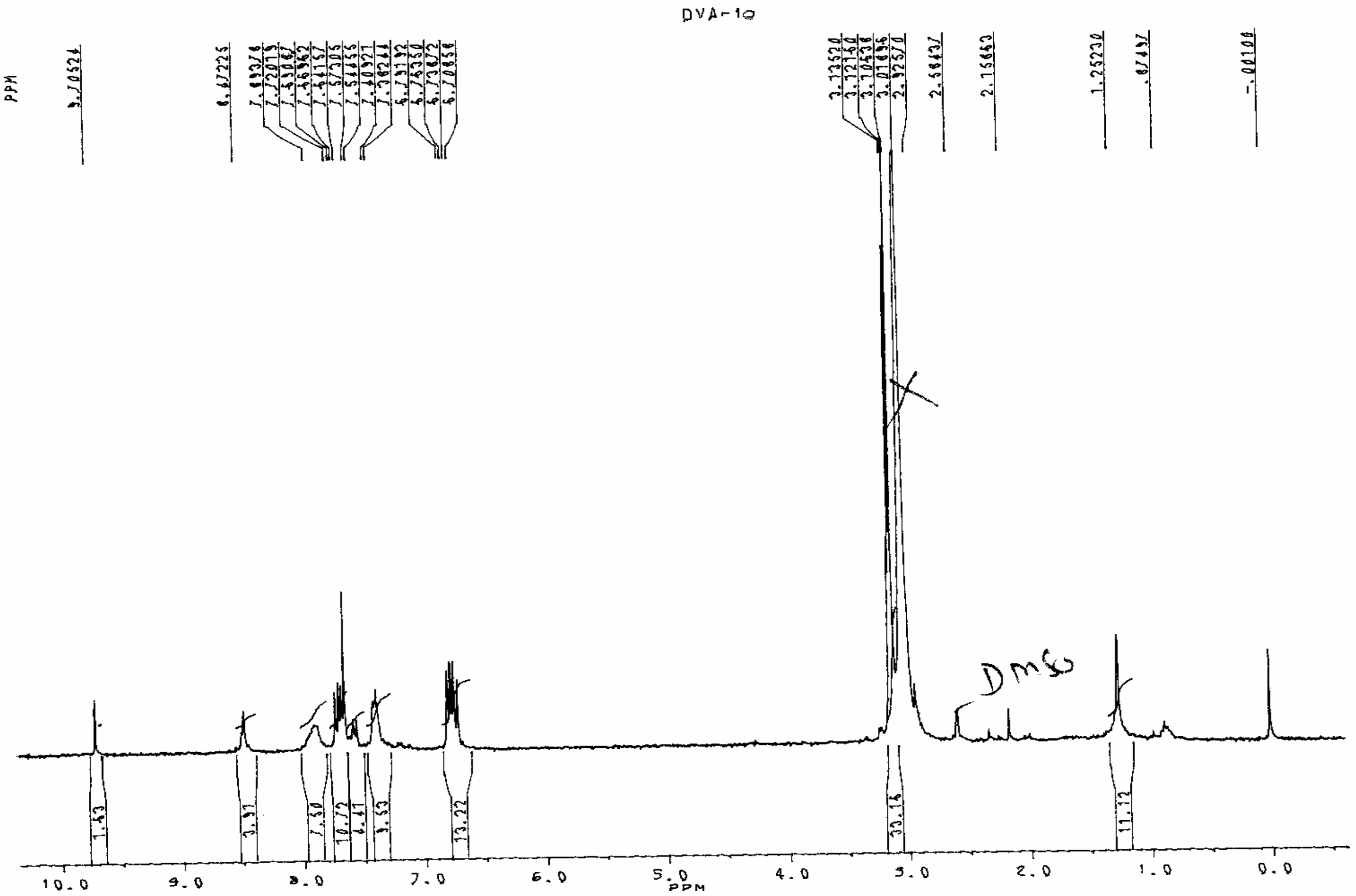
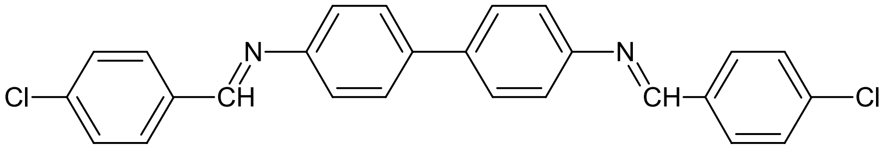


Figure 2.20 : NMR SPECTRA OF N-[(1E)-(N-N-DIMETHYL) METHYLENE]-N'-[(1Z)-(N-N-DIMETHYL) METHYLENE] BIPHENYL4,4'DIAMINE (DVA-10)

Table-2.45 : NMR SPECTRAL STUDY OF N-[(1E)-(4-CHLOROPHENYL) METHYLENE]-N'-[(1Z)-(4-CHLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-11)

Structure



Signal No.	Signal position (δ ppm)	Relative No. of protons	Multiplicity	Inference
1	7.50-7.55	8H	Multiplet	Ar-<u>H</u>
2	7.76-7.86	8H	Multiplet	Ar-<u>H</u>
3	9.96	2H	Singlet	C<u>H</u>=N

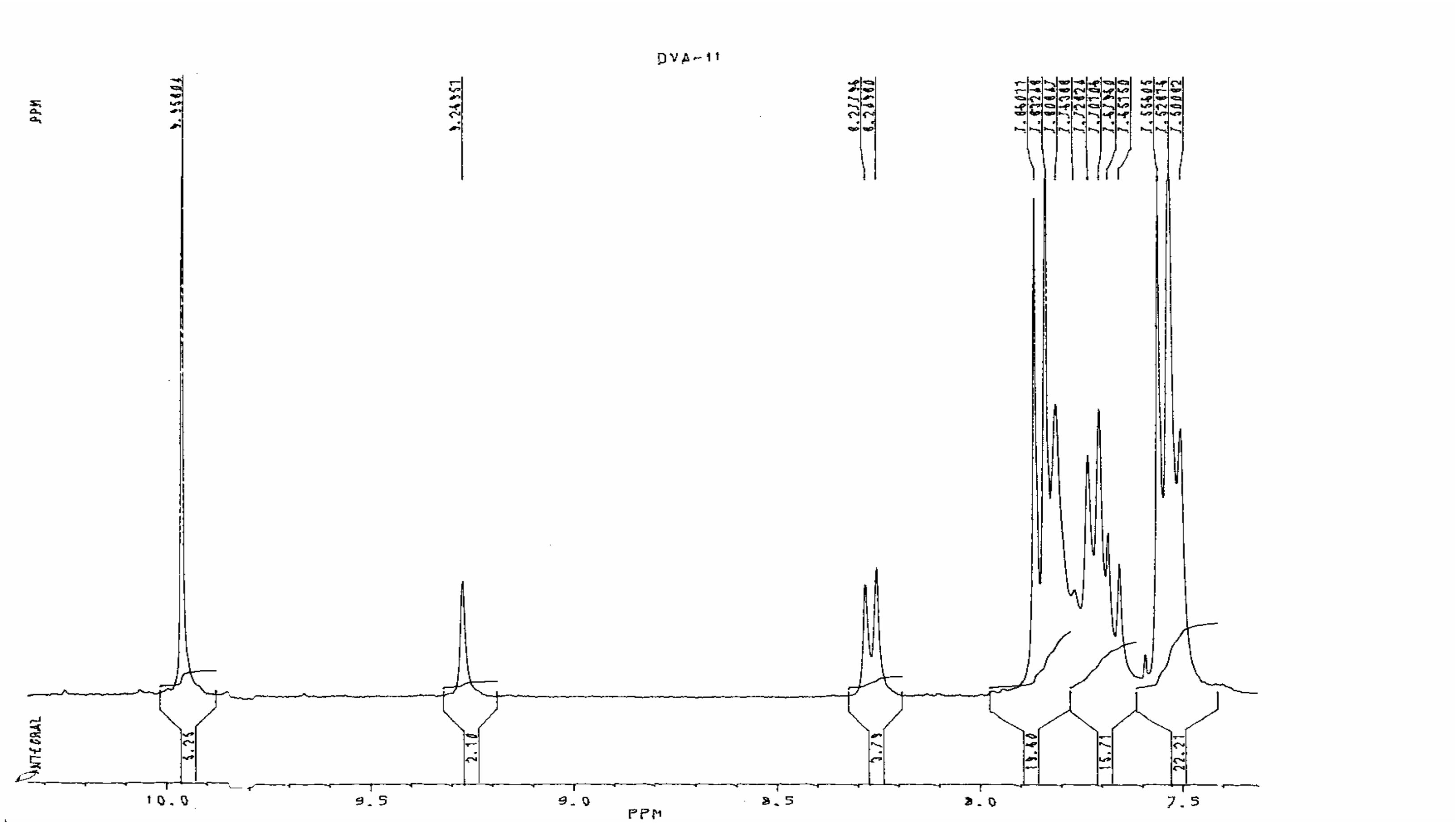
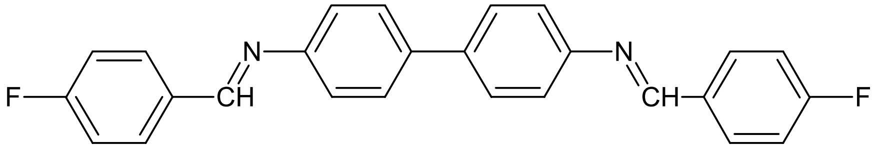


Figure 2.21 : NMR SPECTRA OF N-[(1E)-(4-CHLOROPHENYL) METHYLENE]-N'-[(1Z)-(4-CHLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-11)

Table-2.46 : NMR SPECTRAL STUDY OF N-[(1E)-(4-FLOROPHENYL) METHYLENE]-N’[(1Z)-(4-FLOROPHENYL)METHYLENE] BIPHENYL-4,4’-DIAMINE(DVA-12)

Structure



Signal No.	**Signal position (δ ppm)**	**Relative No. of protons**	**Multiplicity**	**Inference**
1	7.25-8.06	16H	Multiplet	Ar-H
2	8.30-8.34	2H	Singlet	CH=N

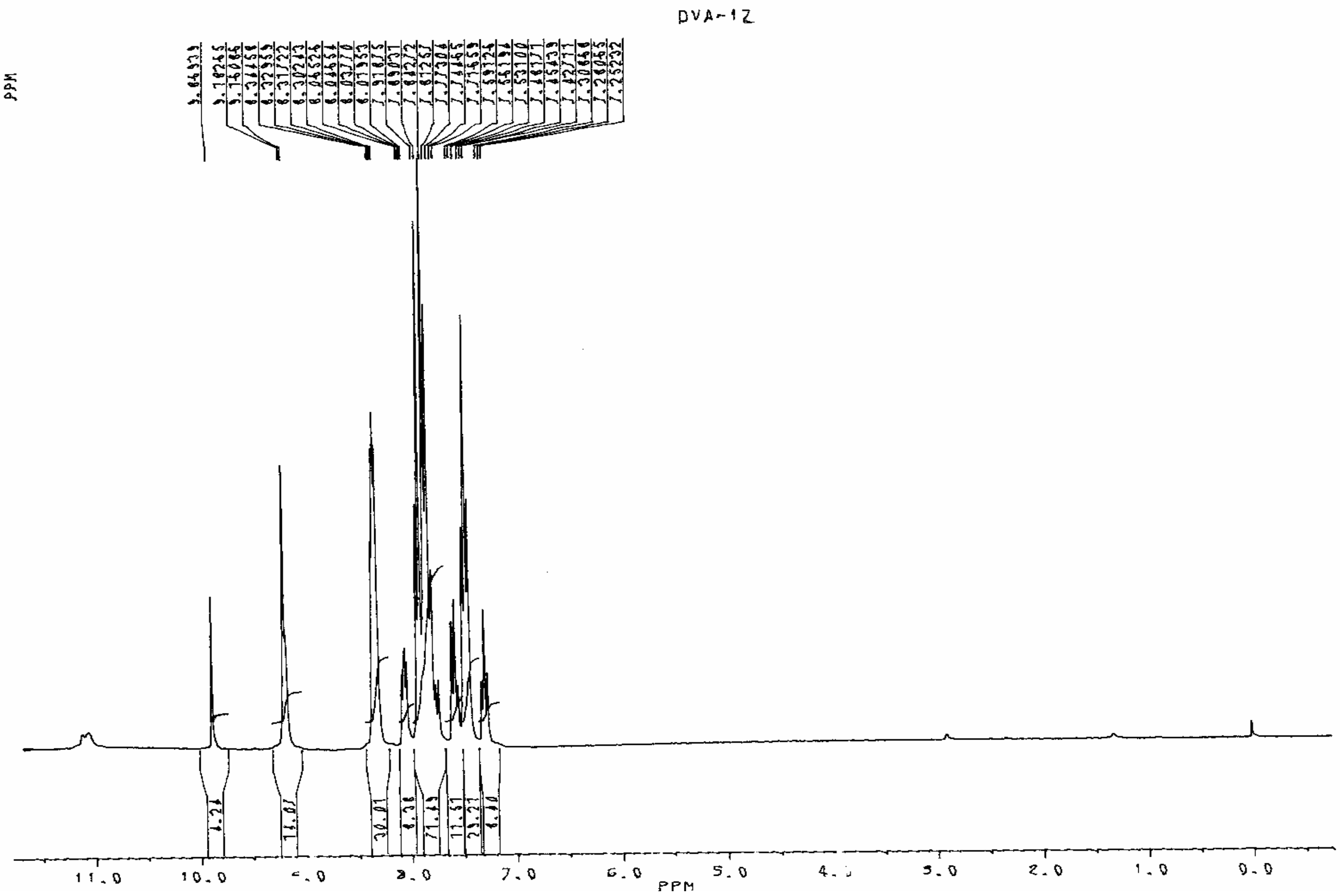


Figure 2.22 : NMR SPECTRA OF N-[(1E)-(4-FLOROPHENYL) METHYLENE]-N'[(1Z)-(4-FLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-12)

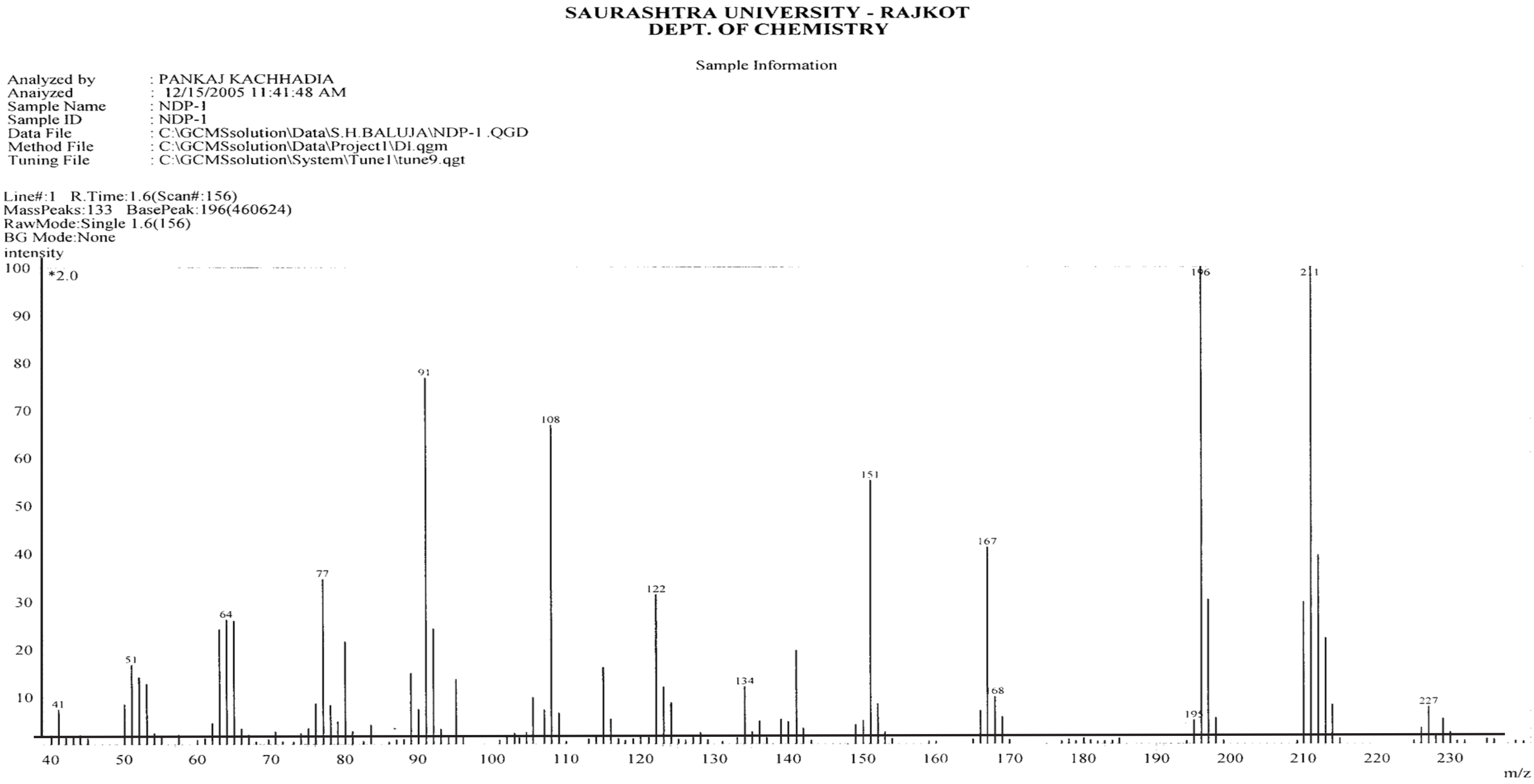
Mass spectroscopy

Mass spectrometry is perhaps the most widely applicable of all the analytical tools available to the scientist in the sense that the technique is capable of providing information about (1) the elemental composition of samples of matter (2) the structure of inorganic, organic and biological molecules (3) the qualitative and quantitative composition of solid surfaces and (5) isotopic ratios of atoms in samples In a mass spectrometer the substance under investigation is bombarded with an electron beam and the instrument quantitatively records the result as a spectrum of positive ion fragments. The probability of cleavage of a particular bond is related to the bond strength, to the stability of the fragments. A mass spectrum is a presentation of mass/charge versus intensities or relative concentration. The molecular ion peak is usually the peak of highest m/e except for isotope peaks.

It gives information about the C-skeleton from fragment peaks, functional group from high m/e peaks and characteristic ion series, to measure distinction between cis and trans isomers. Further biochemical reaction, in measurement of ionization potential of bond strengths, in quantitative analysis of mixtures, and also to studies of polymeric compounds.

Mass spectra of á-napthylamine Schiff bases and benzidine Schiff bases were taken on GCMS – QP2010 SHIMADZO and FEB-MASS Spectrometer respectively.

Figure 2.23: MASS SPECTRA OF N- [(1E) – PHENYL METHYLENE] NAPHTHALENE-1-AMINE (NDP-1)



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Sample Information

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Analyzed	: 12/15/2005 11:41:48 AM
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Scheme 2.1 : MASS SPECTRAL STUDY OF N-[(1E)– PHENYL METHYLENE] NAPHTHALENE-1-AMINE (NDP-1)

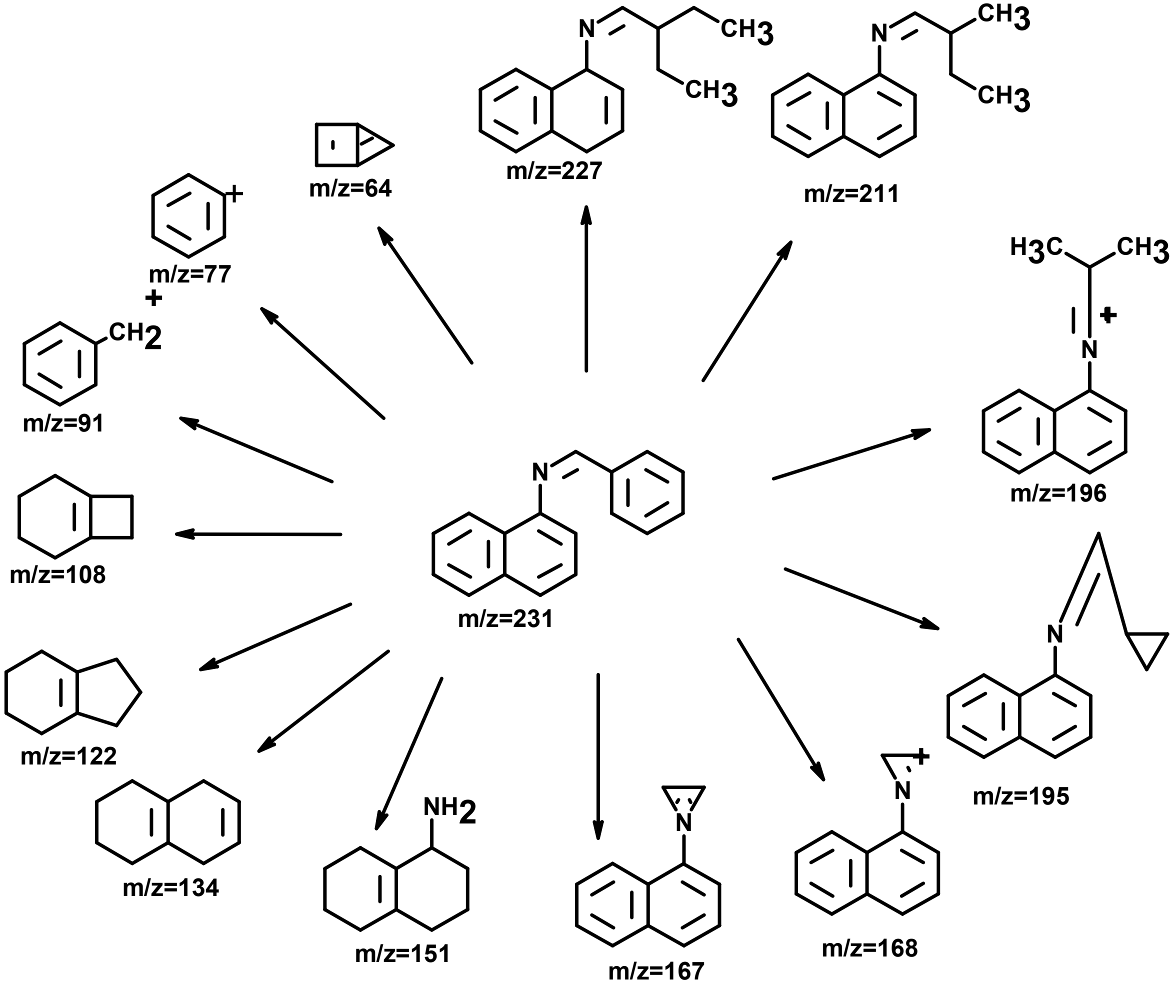

Figure 2.24: MASS SPECTRA OF [2-(E)-(1-NAPHTHYLIMINO) METHYL] PHENOL (NDP-2)

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Sample Information

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Analyzed : 12/15/2005 12:14:44 PM
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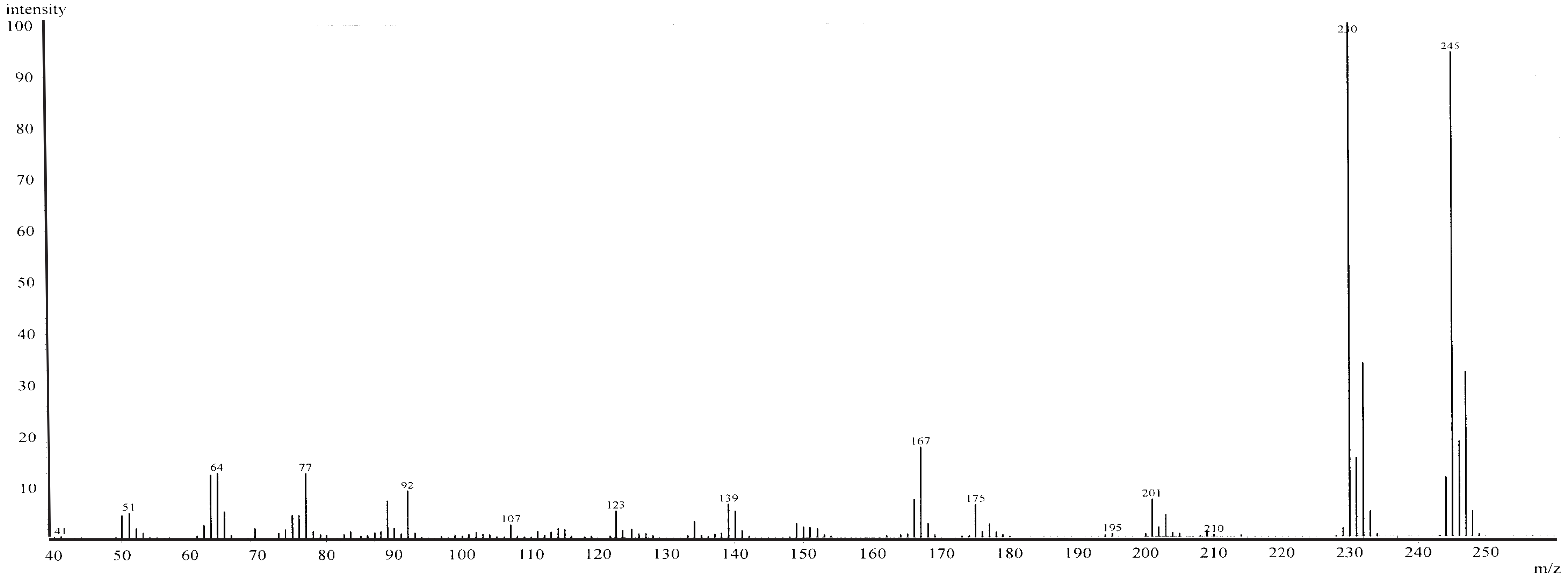


Scheme 2.2 : MASS SPECTRAL STUDY OF [2-(E)-(1-NAPHTHYLIMINO) METHYL] PHENOL (NDP-2)

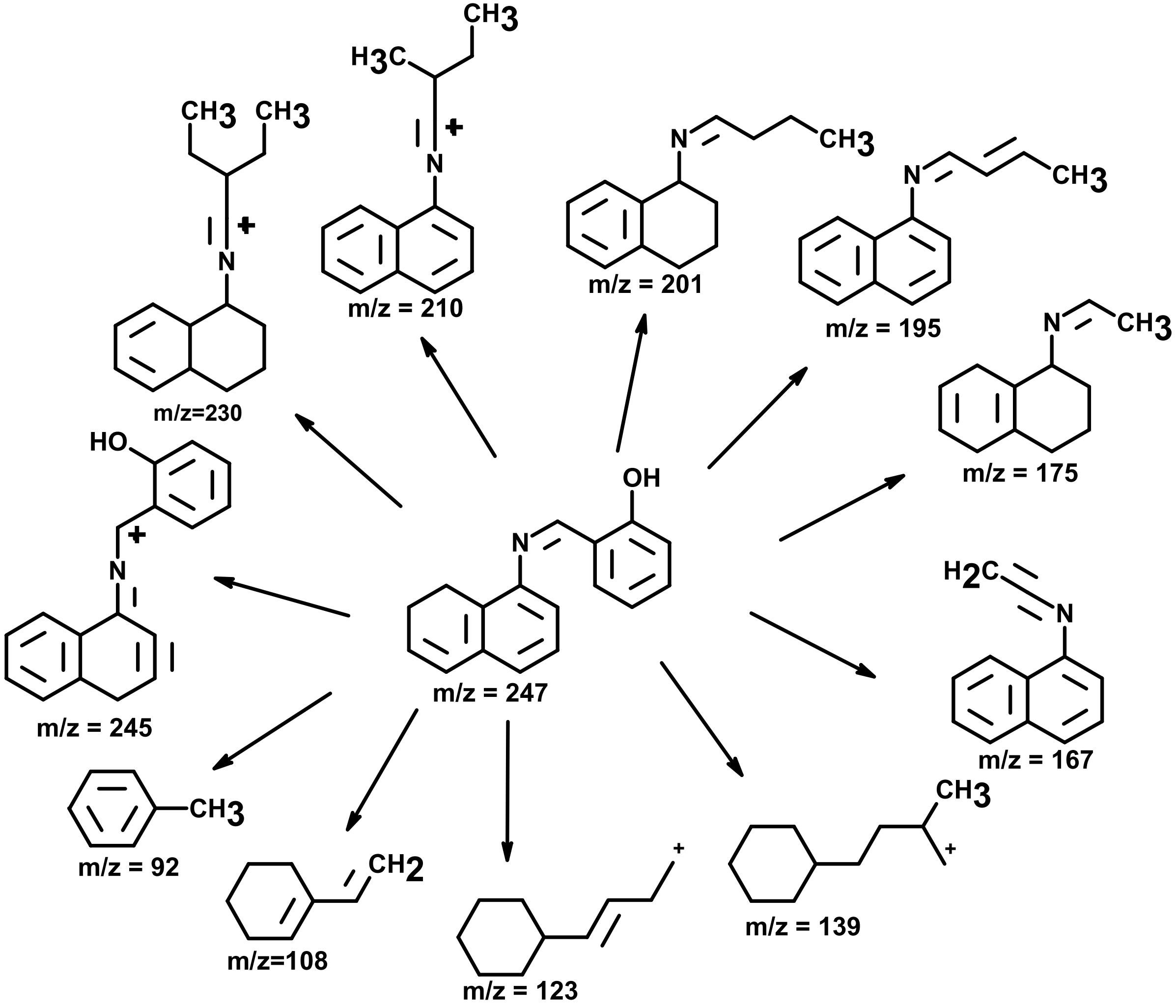
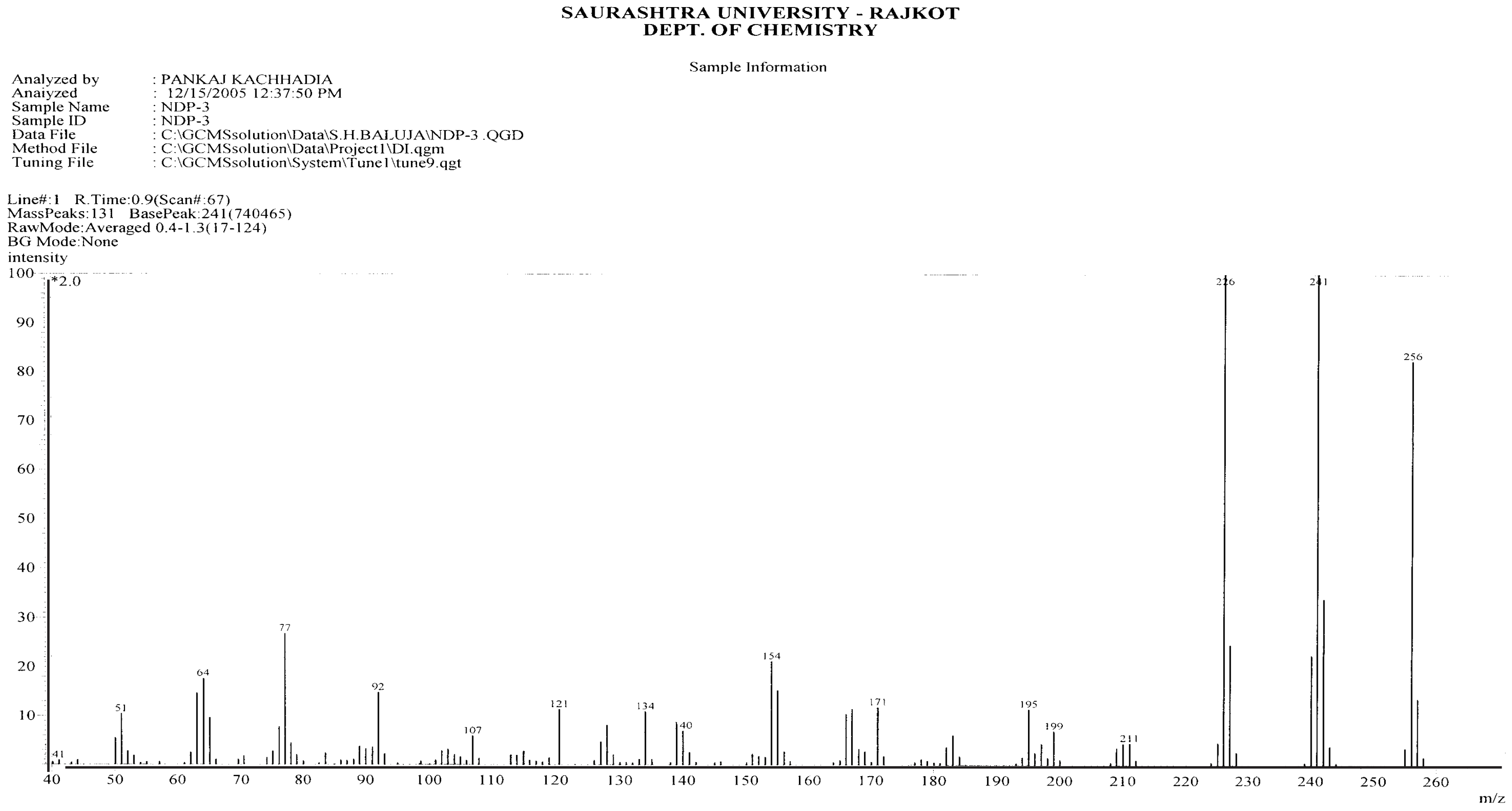


Figure 2.25 : MASS SPECTRA OF N-[(1E)-(4-METHOXY PHENYL) METHYLENE]-N-1-NAPHTHYLAMINE(NDP-3)



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Sample Information

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Scheme 2.3 : MASS SPECTRAL STUDY OF N-[(1E)-(4-METHOXY PHENYL) METHYLENE]-N-1-NAPHTHYL AMINE (NDP-3)

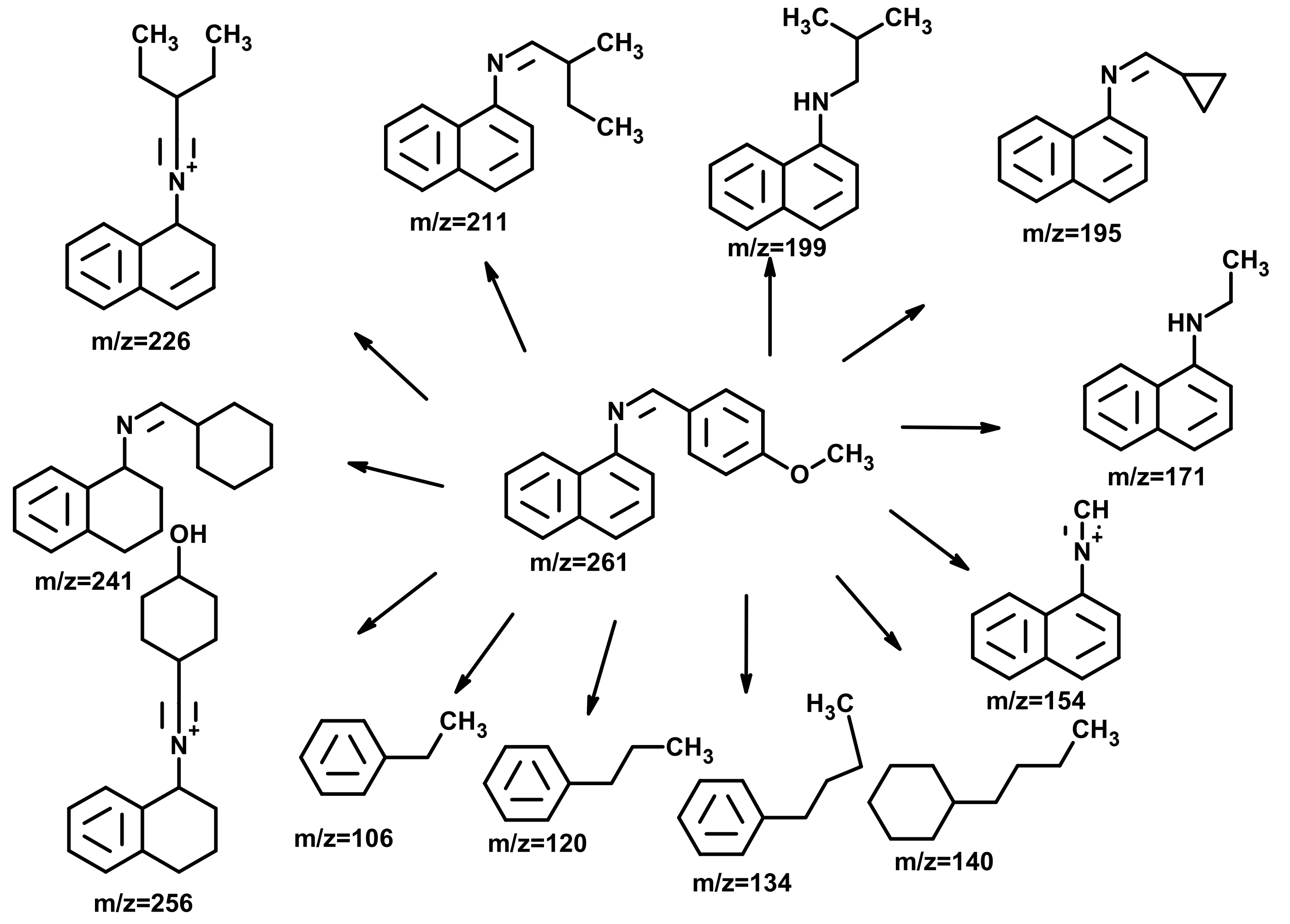
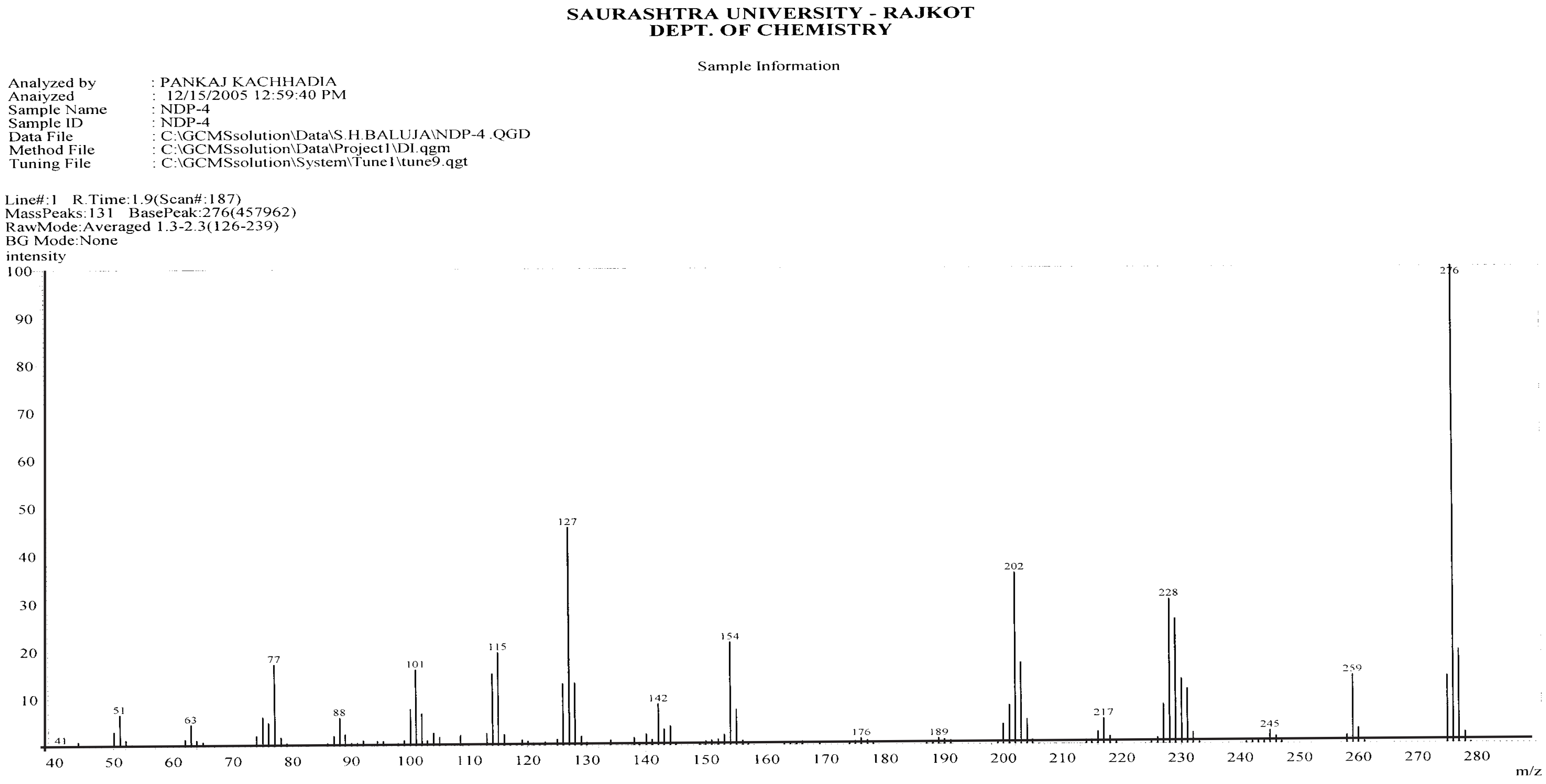


Figure 2.25 : MASS SPECTRA OF N-[(1E)-(3-NITRO PHENYL) METHYLENE] NAPHTHALENE-1-AMINE(NDP-4)



SAURASHTRA UNIVERSITY - RAJKOT
DEPT. OF CHEMISTRY

Sample Information

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Analyzed : 12/15/2005 12:59:40 PM
Sample Name : NDP-4
Sample ID : NDP-4
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Method File : C:\GCMSsolution\Data\Project1\DI.qgm
Tuning File : C:\GCMSsolution\System\Tune1\tune9.qgt

Line#:1 R.Time:1.9(Scan#:187)
MassPeaks:131 BasePeak:276(457962)
RawMode:Averaged 1.3-2.3(126-239)
BG Mode:None

Scheme 2.4 : MASS SPECTRAL STUDY OF N-[(1E)-(3-NITROPHENYL)METHYLENE] NAPHTHALENE-1-AMINE (NDP-4)

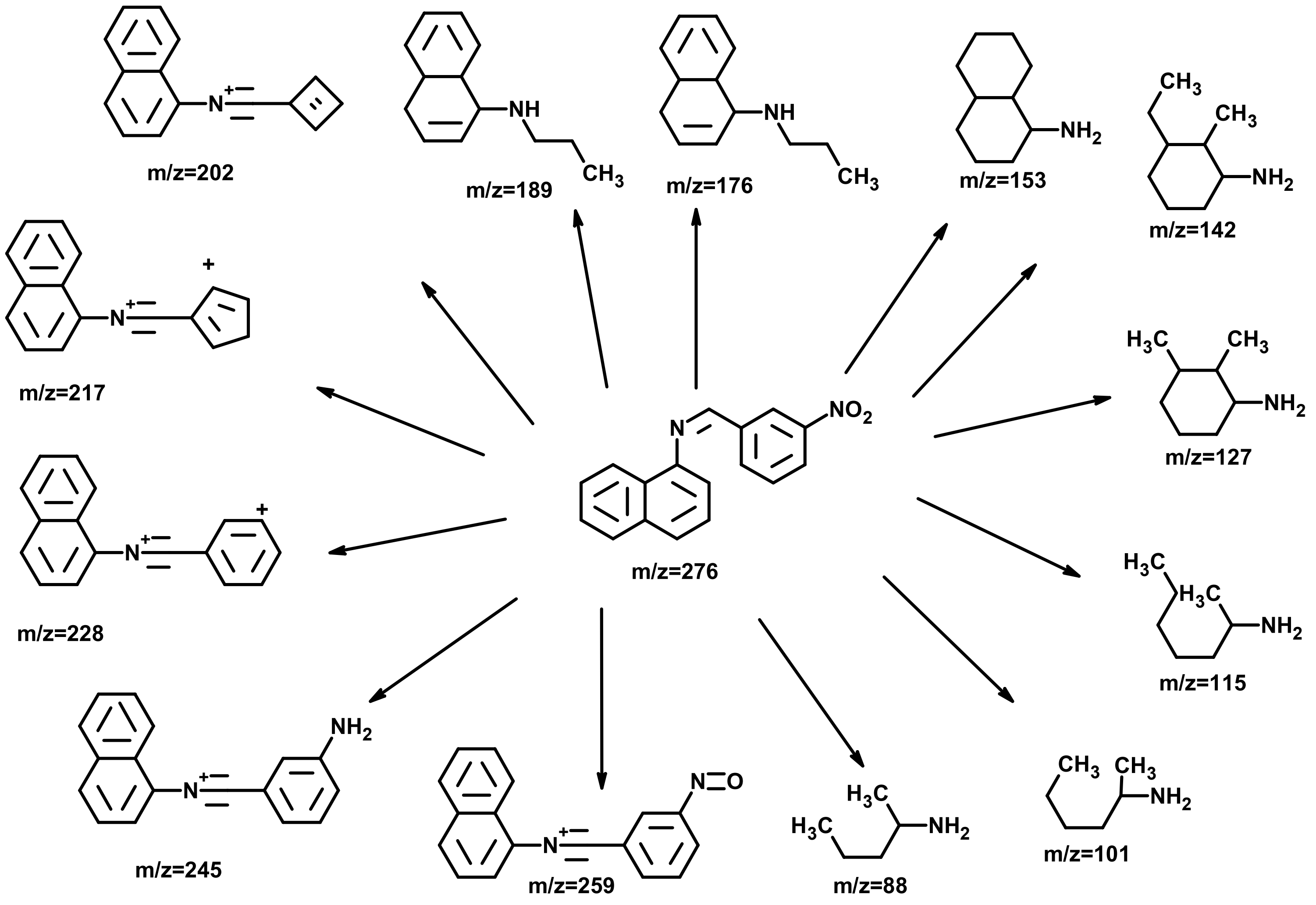
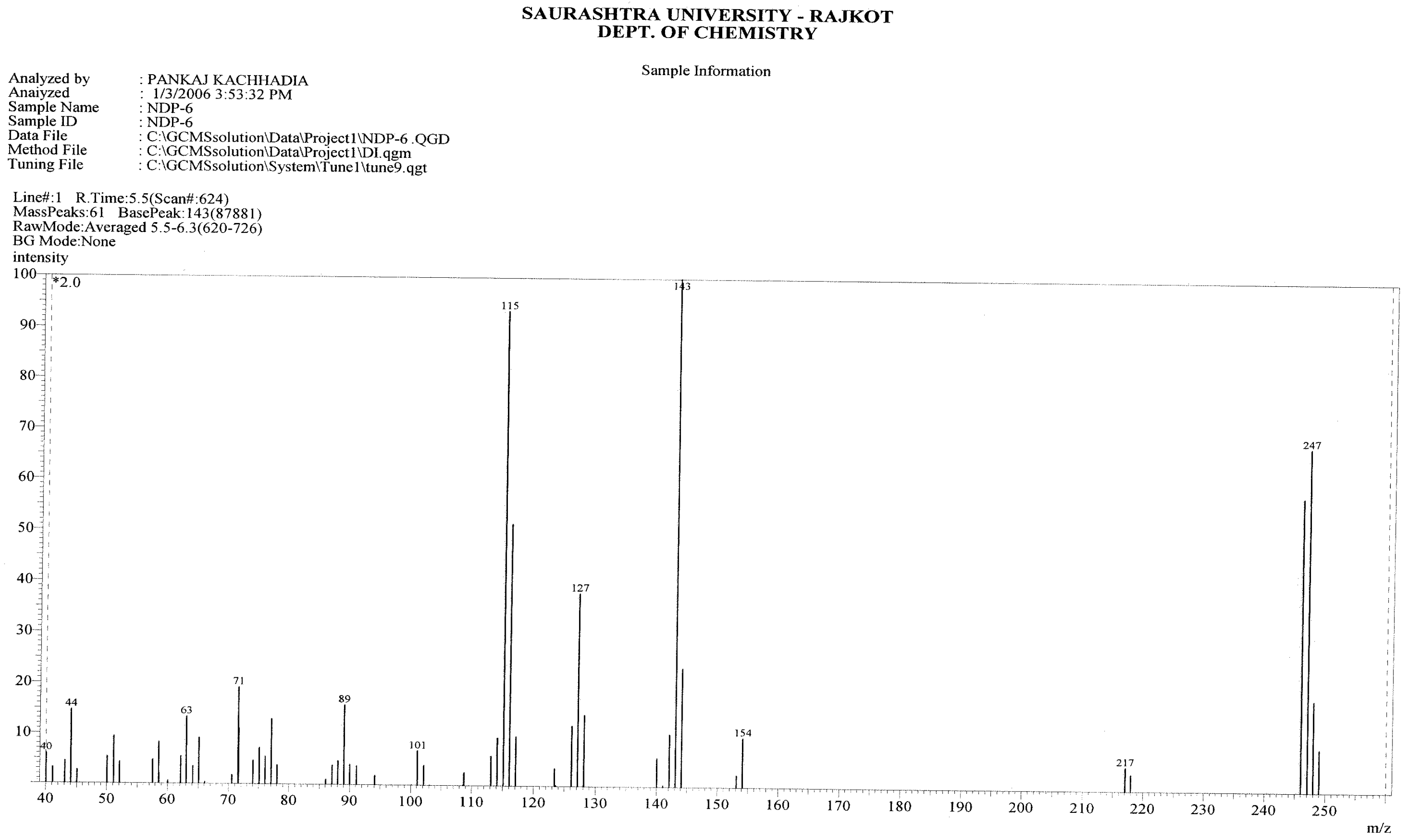


Figure 2.26: MASS SPECTRA OF 4-[(1E)-(1-NAPHTHYLIMINO) METHYL] PHENOL(NDP-6)



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Sample Information

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Anaiyzed	: 1/3/2006 3:53:32 PM
Sample Name	: NDP-6
Sample ID	: NDP-6
Data File	: C:\GCMSsolution\Data\Project1\NDP-6 .QGD
Method File	: C:\GCMSsolution\Data\Project1\DI.qgm
Tuning File	: C:\GCMSsolution\System\Tune1\tune9.qgt

Line#:1 R.Time:5.5(Scan#:624)
MassPeaks:61 BasePeak:143(87881)
RawMode:Averaged 5.5-6.3(620-726)
BG Mode:None

Scheme 2.6 : MASS SPECTRAL STUDY OF 4-[(1E)-(1-NAPHTHYLIMINO) METHYL] PHENOL(NDP-6)

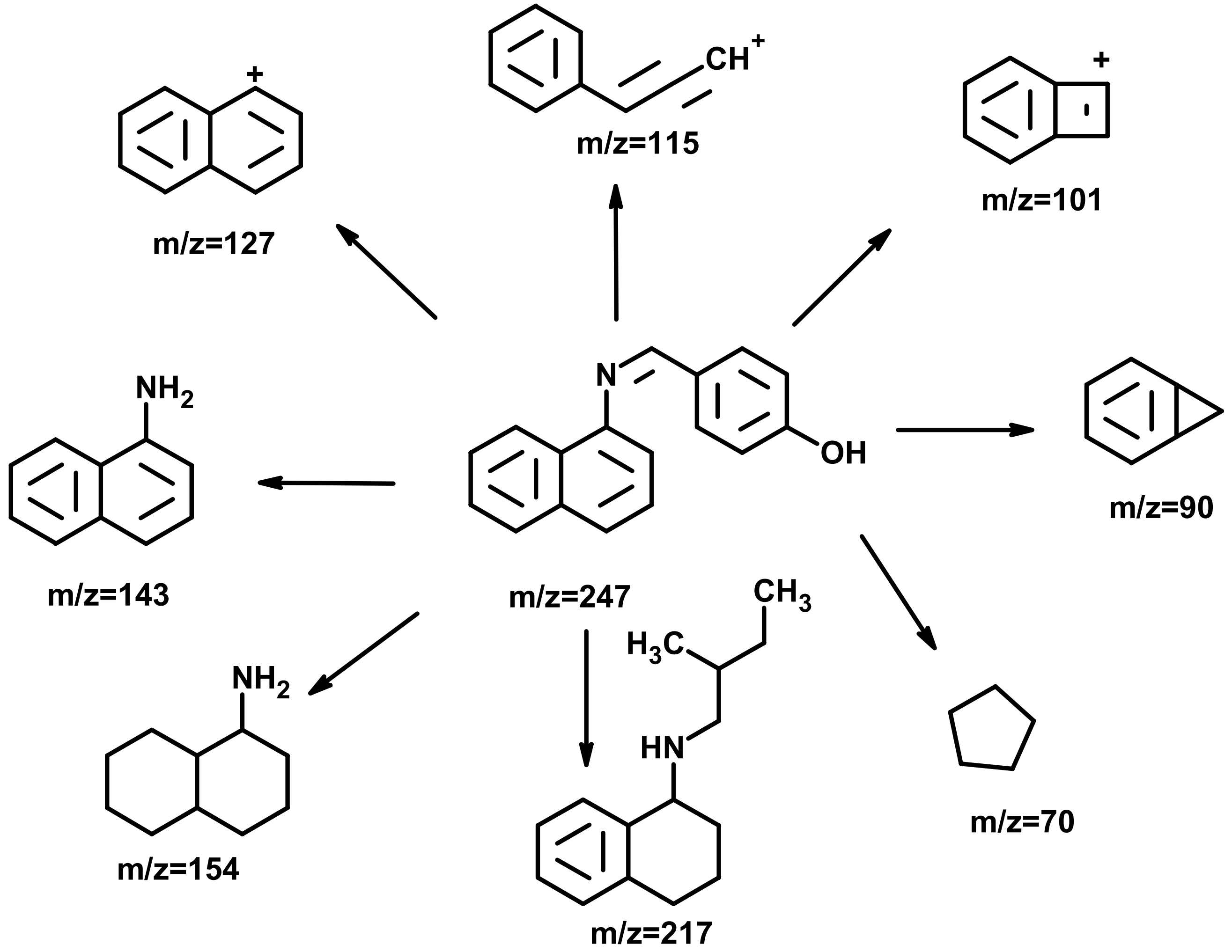
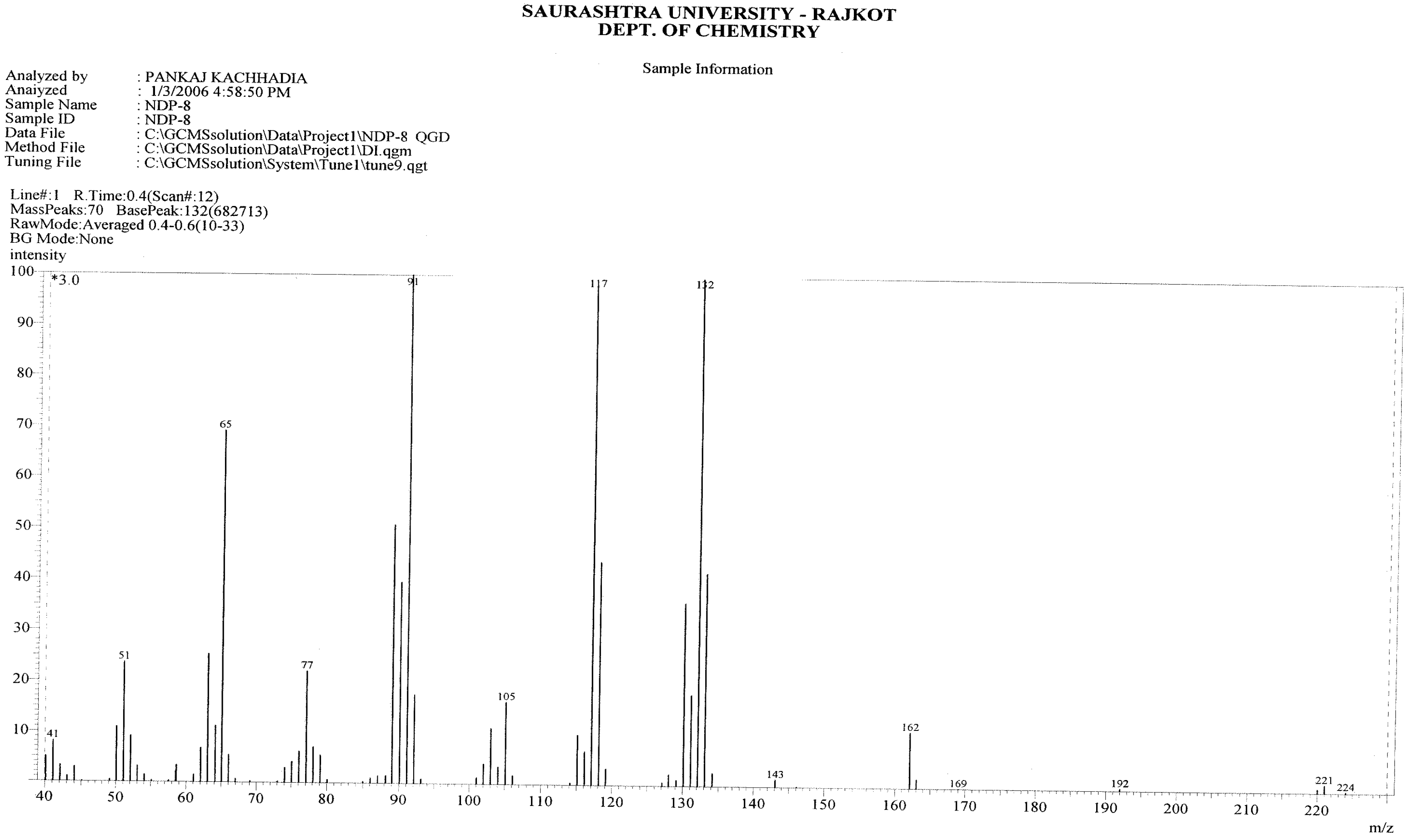


Figure 2.27: MASS SPECTRA OF N-[(1Z)-2-FURYL METHYLENE]-N-1-NAPHTHYL AMINE(NDP-8)



SAURASHTRA UNIVERSITY - RAJKOT
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Sample Information

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Analyzed : 1/3/2006 4:58:50 PM
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Sample ID : NDP-8
Data File : C:\GCMSsolution\Data\Project1\NDP-8 QGD
Method File : C:\GCMSsolution\Data\Project1\DI.qgm
Tuning File : C:\GCMSsolution\System\Tune1\tune9.qgt

Line#:1 R.Time:0.4(Scan#:12)
MassPeaks:70 BasePeak:132(682713)
RawMode:Averaged 0.4-0.6(10-33)
BG Mode:None

Scheme 2.6 : MASS SPECTRAL STUDY OF N-[(1Z)-2-FURYLMETHYLENE]-N-1-NAPHTHYL AMINE(NDP-8)

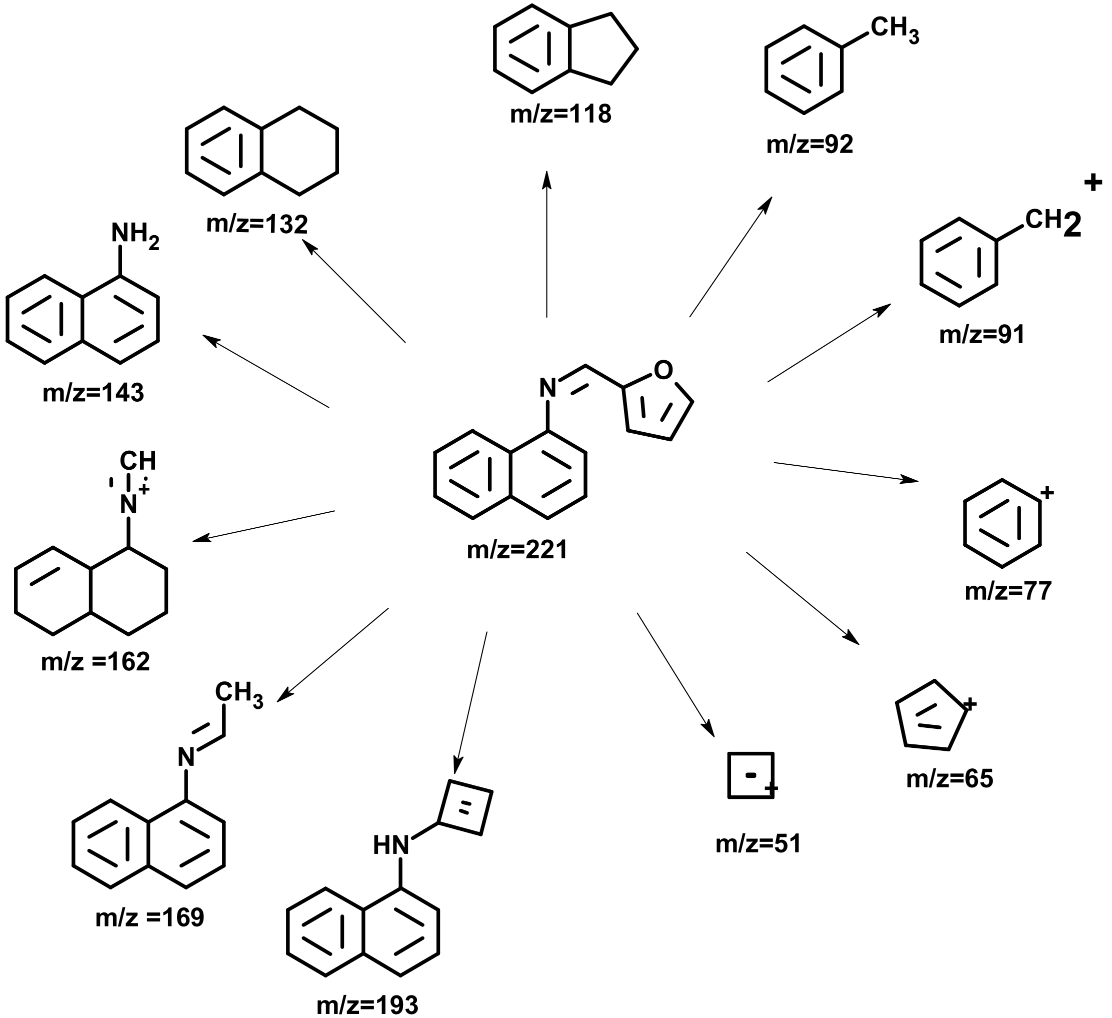
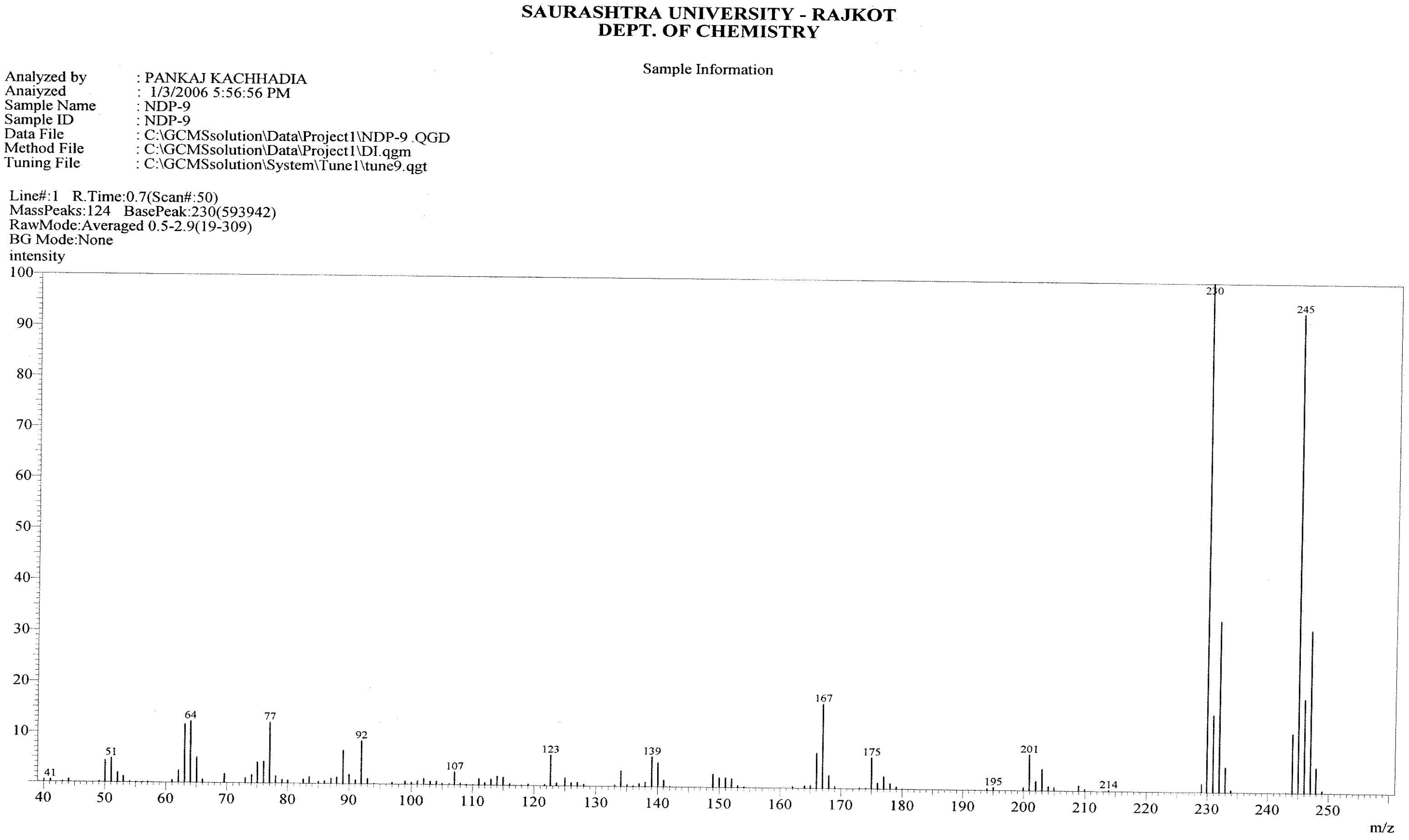


Figure 2.27: MASS SPECTRA OF [(1E)-(4-FLORO PHENYL) ETHYLENE]-N-1- NAPHTHYL AMINE(NDP-9)



SAURASHTRA UNIVERSITY - RAJKOT
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Sample Information

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Analyzed : 1/3/2006 5:56:56 PM
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Sample ID : NDP-9
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Method File : C:\GCMSsolution\Data\Project1\DI.qgm
Tuning File : C:\GCMSsolution\System\Tune1\tune9.qgt

Line#:1 R.Time:0.7(Scan#:50)
MassPeaks:124 BasePeak:230(593942)
RawMode:Averaged 0.5-2.9(19-309)
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Scheme 2.7 : MASS SPECTRAL STUDY OF [(1E)-(4-FLORO PHENYL) METHYLENE]-N-1-NAPHTHYL AMINE(NDP-9)

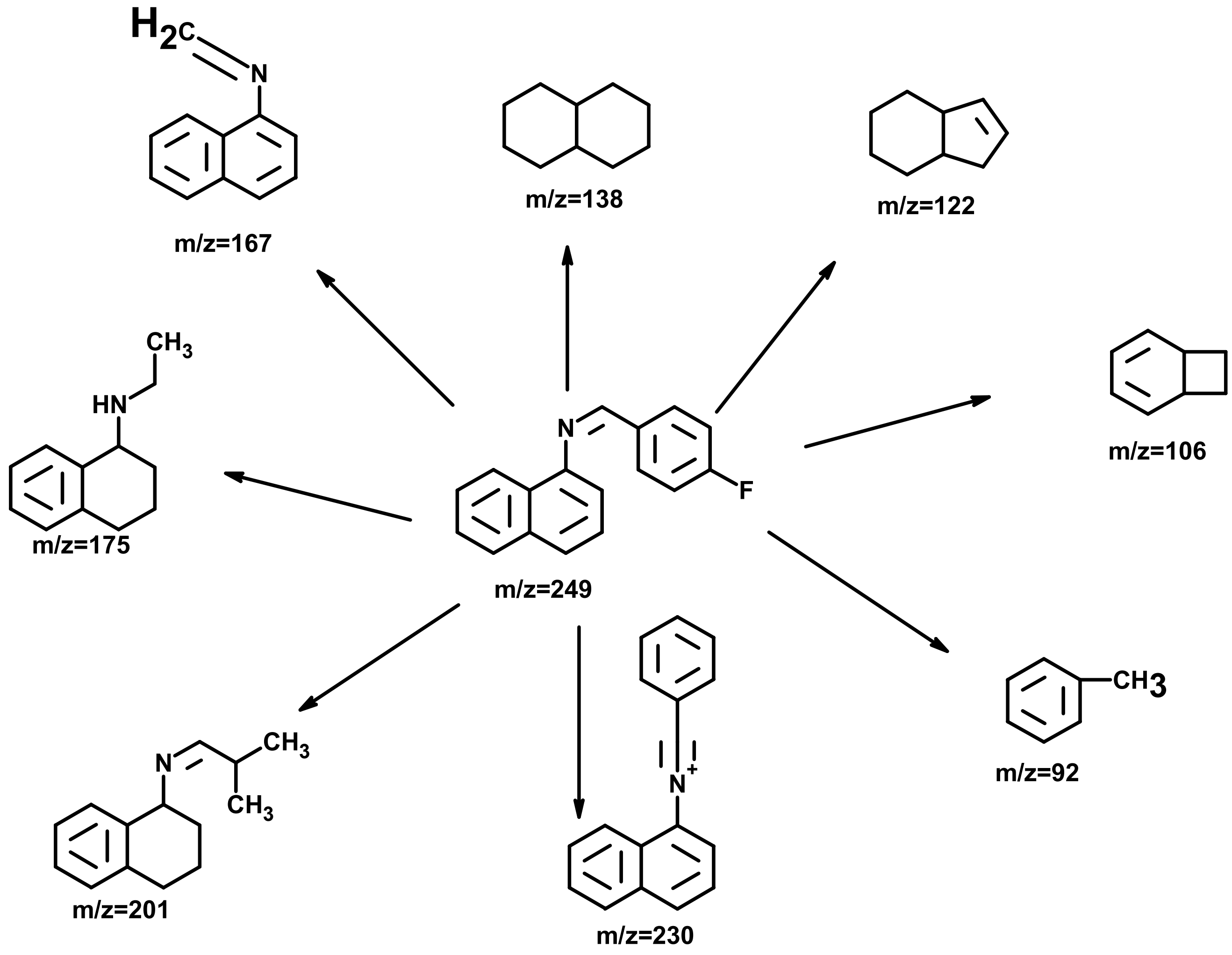
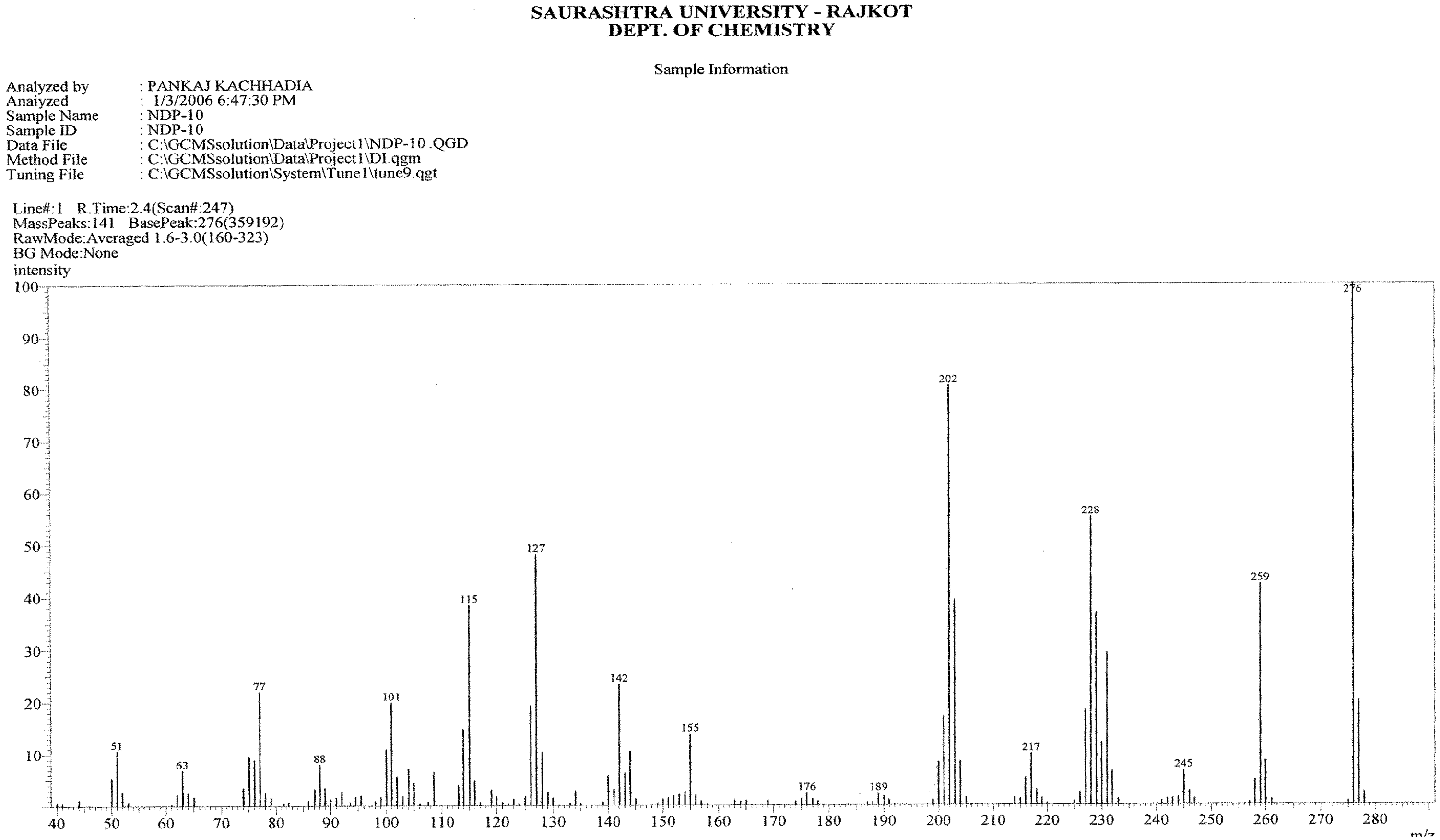


Figure 2.28 : MASS SPECTRA OF N-[(1E)-(2-NITRO PHENYL) METHYLENE] NAPHTHALENE-1-AMINE(NDP-10)



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Sample Information

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Anaiyzed : 1/3/2006 6:47:30 PM
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Sample ID : NDP-10
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Method File : C:\GCMSsolution\Data\Project1\DI.qgm
Tuning File : C:\GCMSsolution\System\Tune1\tune9.qgt

Line#:1 R.Time:2.4(Scan#:247)
MassPeaks:141 BasePeak:276(359192)
RawMode:Averaged 1.6-3.0(160-323)
BG Mode:None

Scheme 2.8 : MASS SPECTRAL STUDY OF N-[(1E)-(2-NITRO PHENYL) METHYLENE] NAPHTHALENE-1-AMINE(NDP-10)

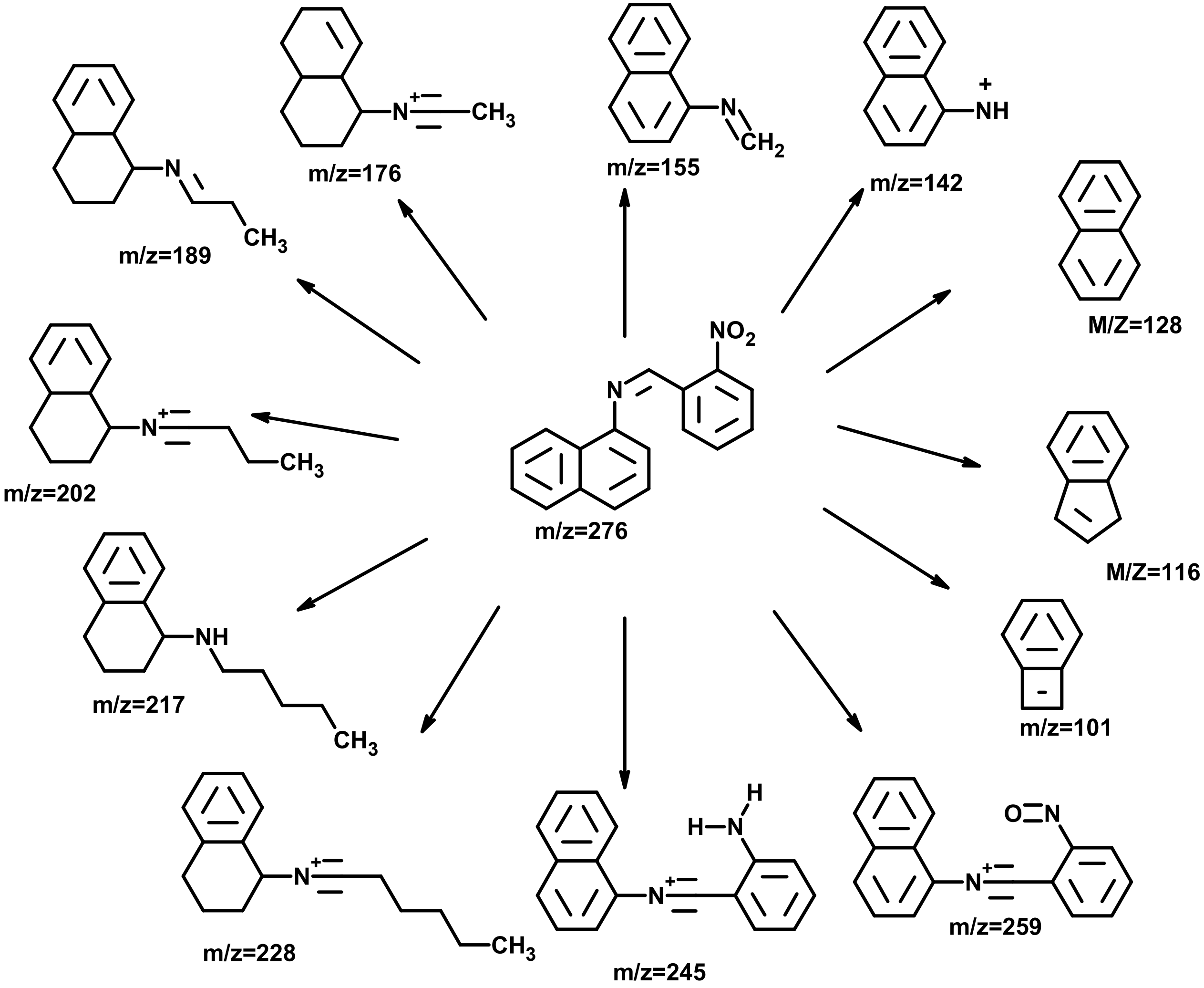
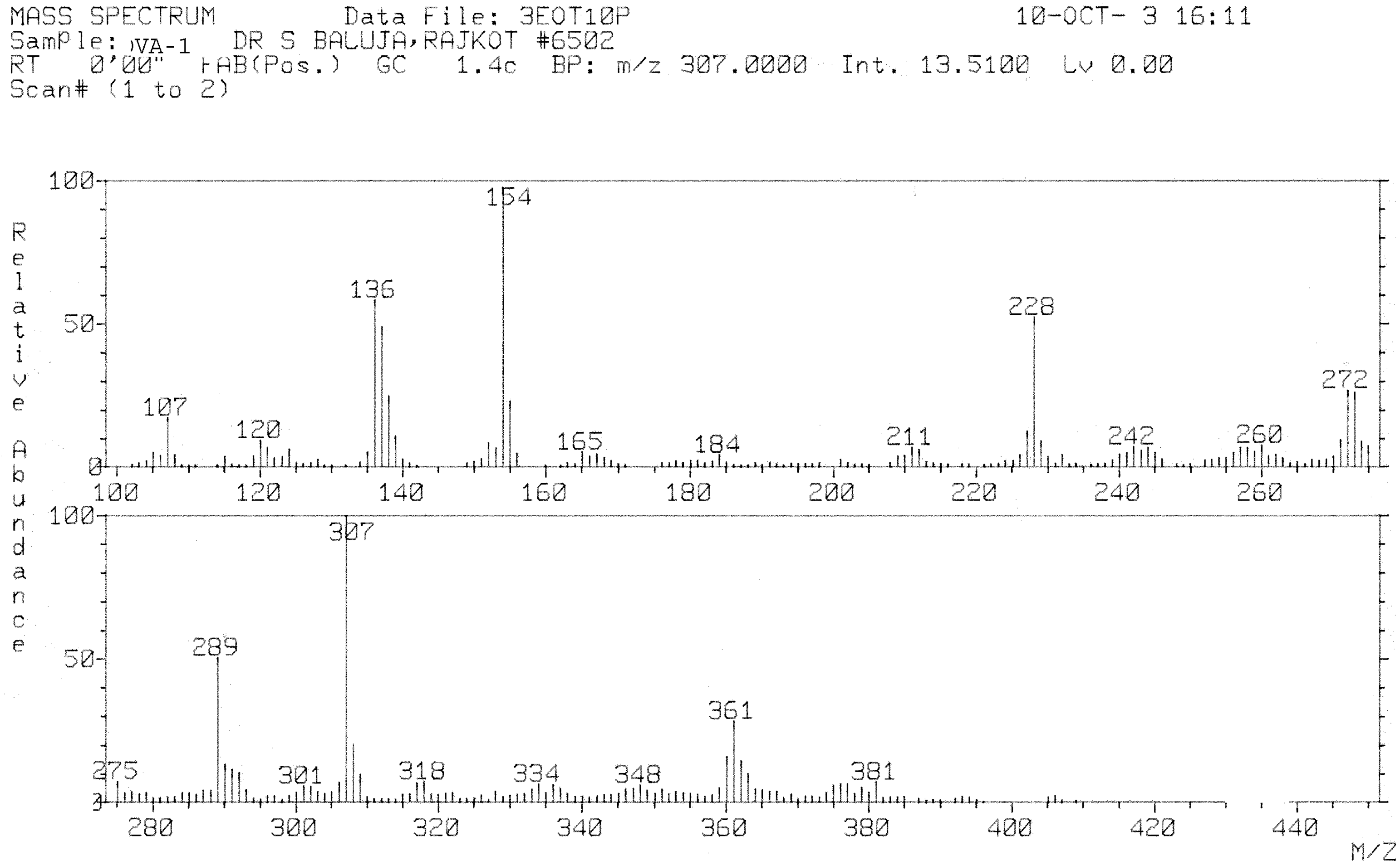


Figure 2.29 : MASS SPECTRA OF N-[(1E)-PHENYLMETHYLENE]-N'-[(1Z)-PHENYLMETHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-1)



MASS SPECTRUM Data File: 3EOT10P 10-OCT- 3 16:11
Sample:)VA-1 DR S BALUJA,RAJKOT #6502
RT 0'00" FAB(Pos.) GC 1.4c BP: m/z 307.0000 Int. 13.5100 Lv 0.00
Scan# (1 to 2)

Scheme 2.8 : MASS SPECTRAL STUDY OF OF N-[(1E)-PHENYLMETHYLENE]-N’-[(1Z)-PHENYLMETHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-1)

Figure 2.30 : MASS SPECTRA OF N-[(1E)-(2-NITROPHENYL)METHYLENE]-N'-[(1Z)-(2-NITROPHENYL)METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-2)

```
MASS SPECTRUM        Data File: 3EOT21M                              21-OCT- 3 10:57
Sample: DAV- 2 DR S BALUJA,RAJKOT #6532
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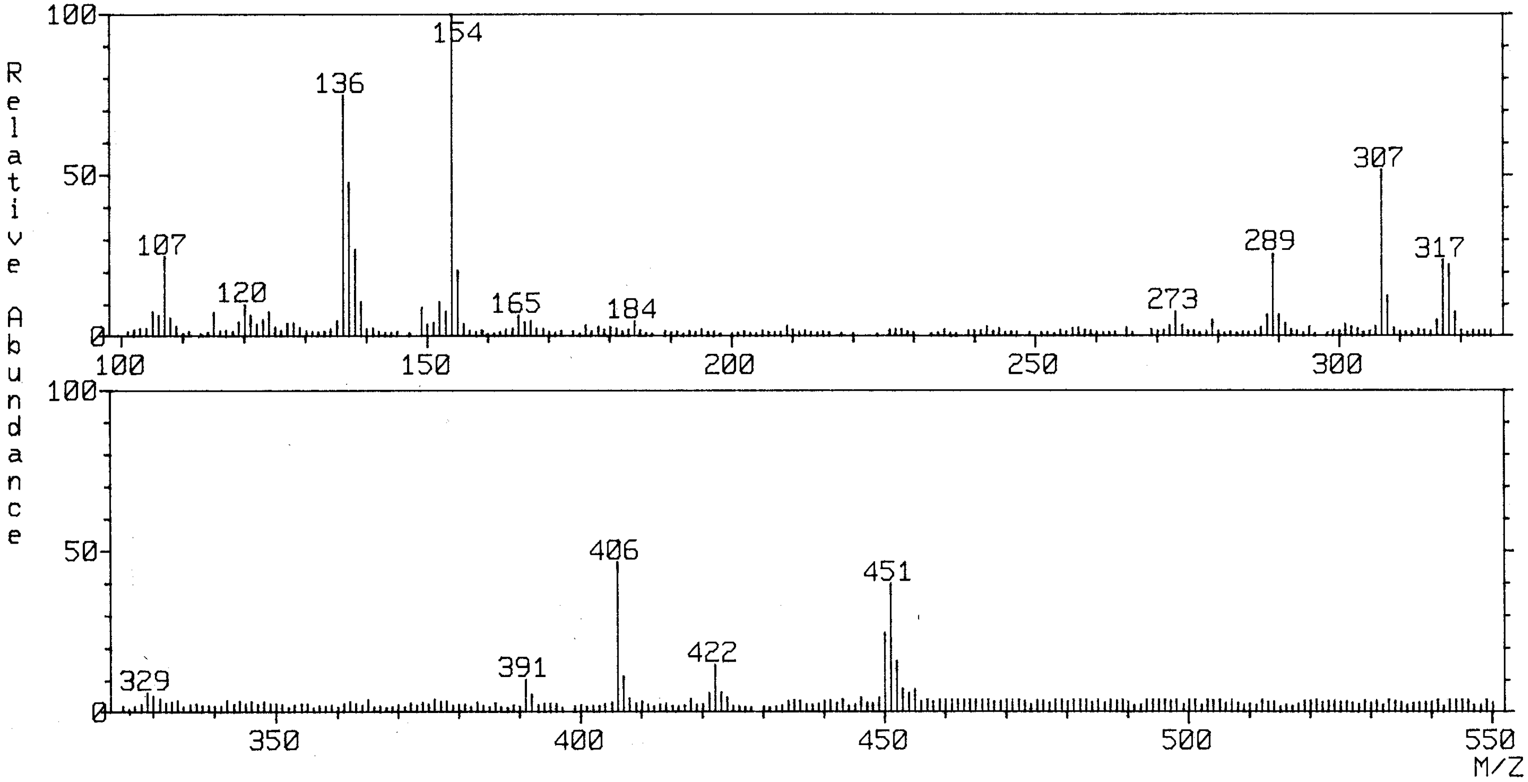
Scan# (4)
```



Scheme 2.9 : MASS SPECTRAL STUDY OF N-[(1E)-(2-NITROPHENYL)METHYLENE]-N’-[(1Z)-(2-NITROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-2)

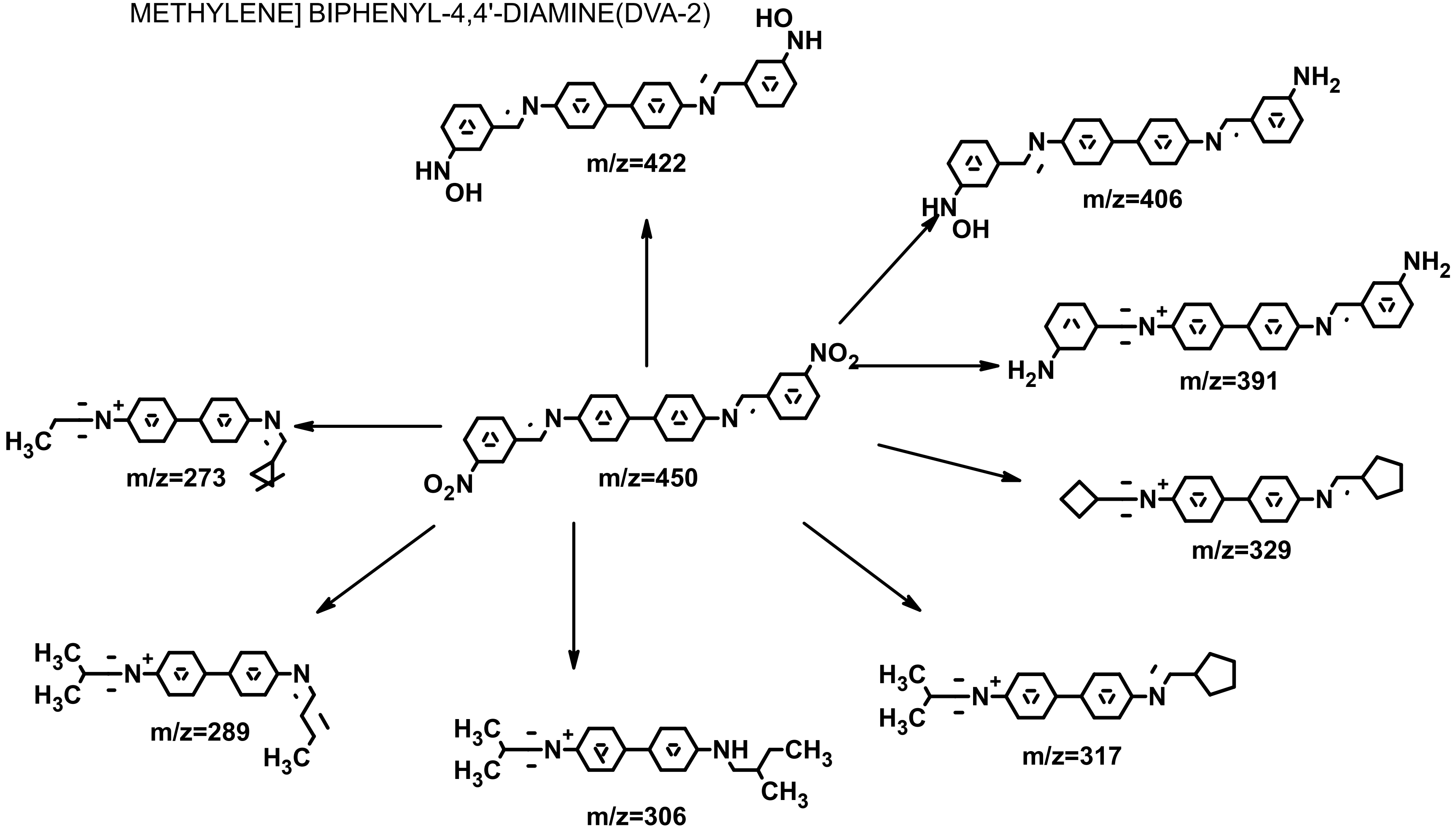
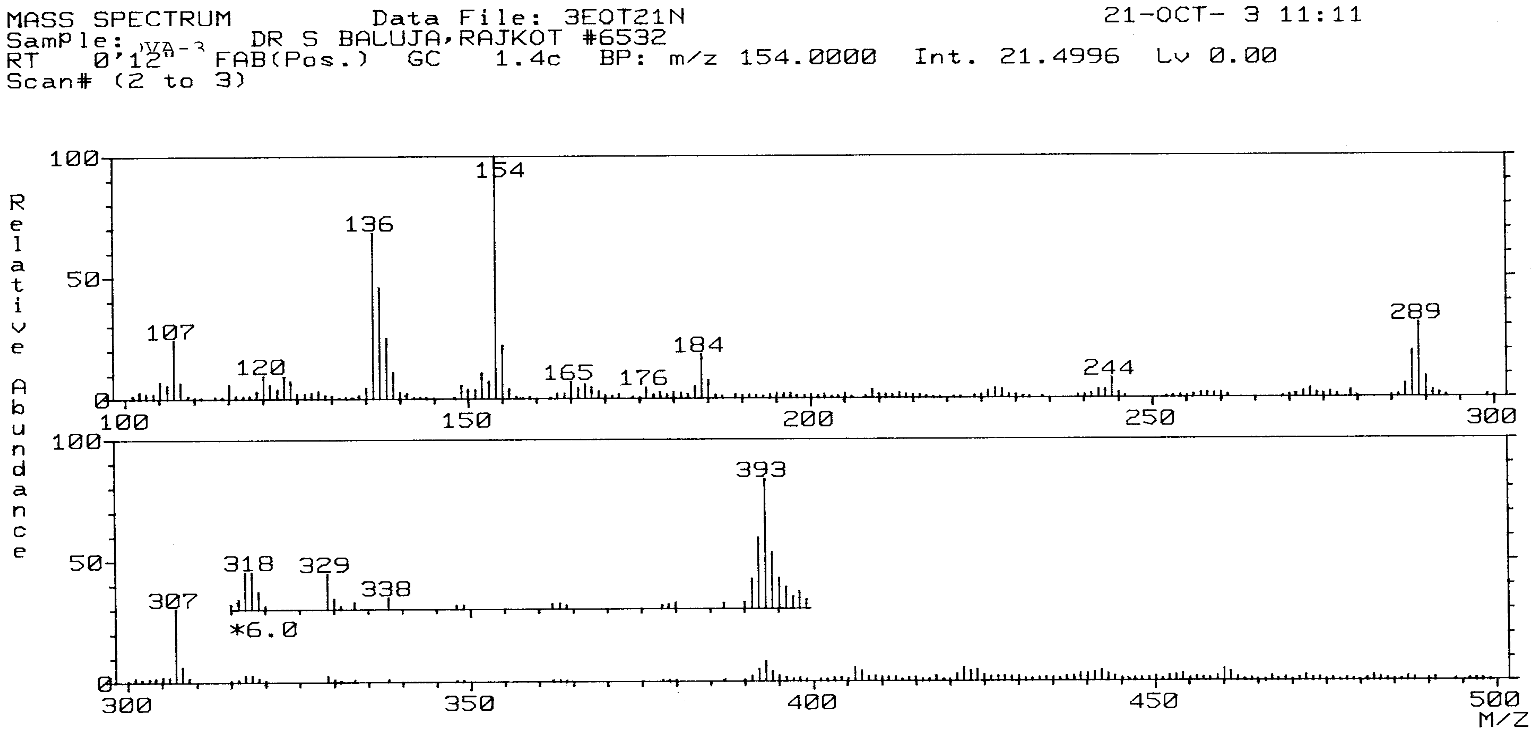


Figure 2.30 : MASS SPECTRA OF N-[(1E)-(4-HYDROXYPHENYL)METHYLENE]-N’-[(1Z)-(2-HYDROXYPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-3)



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RT   0'12"  FAB(Pos.)   GC    1.4c   BP: m/z 154.0000   Int. 21.4996   Lv 0.00
Scan# (2 to 3)
```

Scheme 2.9 : MASS SPECTRAL STUDY OF N-[(1E)-(4-HYDROXYPHENYL)METHYLENE]-N’-[(1Z)-(2-HYDROXYPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-3)

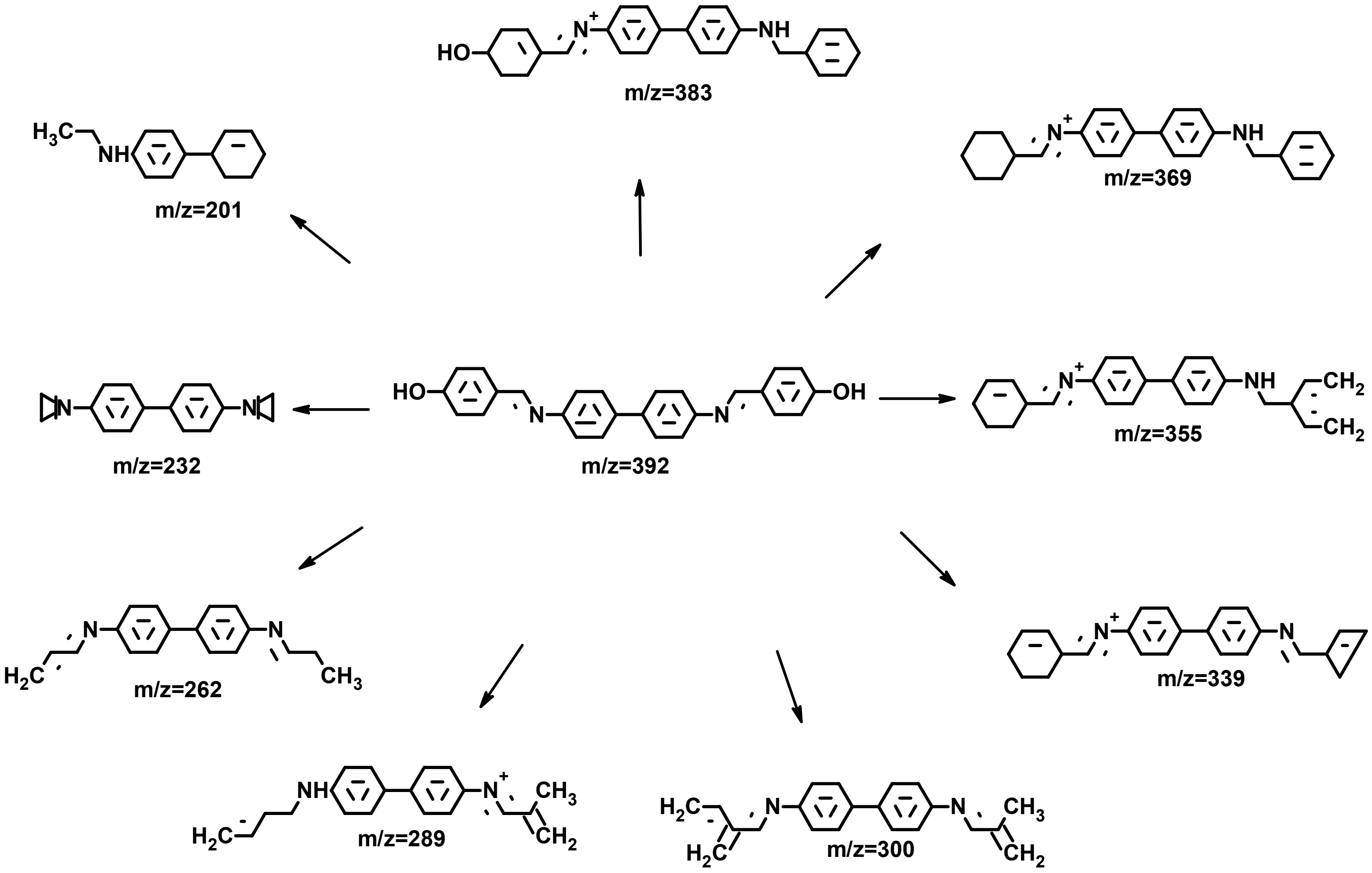
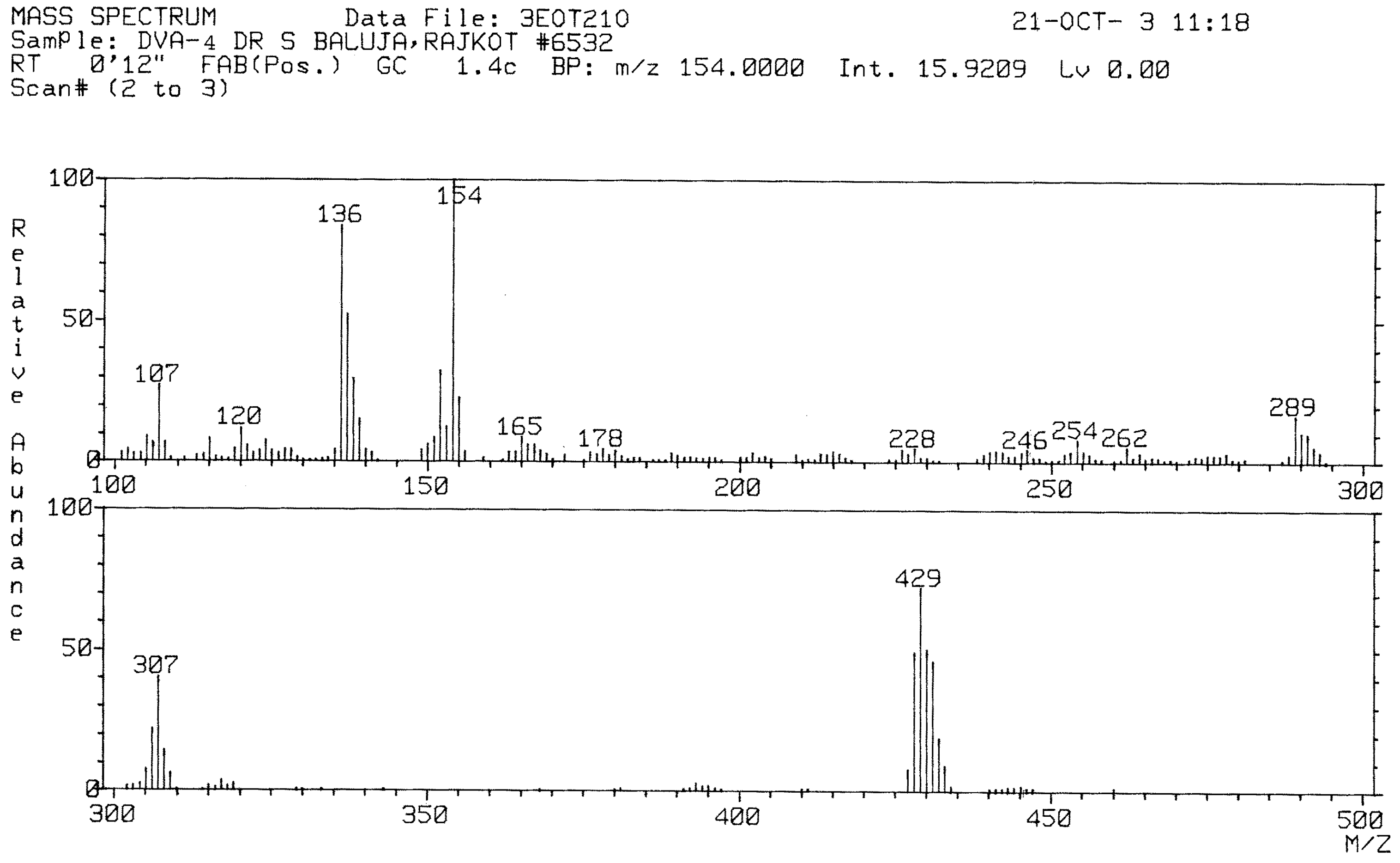


Figure 2.31 : MASS SPECTRA OF N-[(1E)-(2-CHLOROPHENYL)METHYLENE]-N'-[(1Z)-(2-CHLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-4)



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Sample: DVA-4 DR S BALUJA,RAJKOT #6532
RT   0'12"  FAB(Pos.)  GC   1.4c  BP: m/z 154.0000  Int. 15.9209  Lv 0.00
Scan# (2 to 3)
```

Scheme 2.9 : MASS SPECTRAL STUDY OF N-[(1E)-(2-CHLOROPHENYL)METHYLENE]-N’-[(1Z)-(2-CHLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-4)

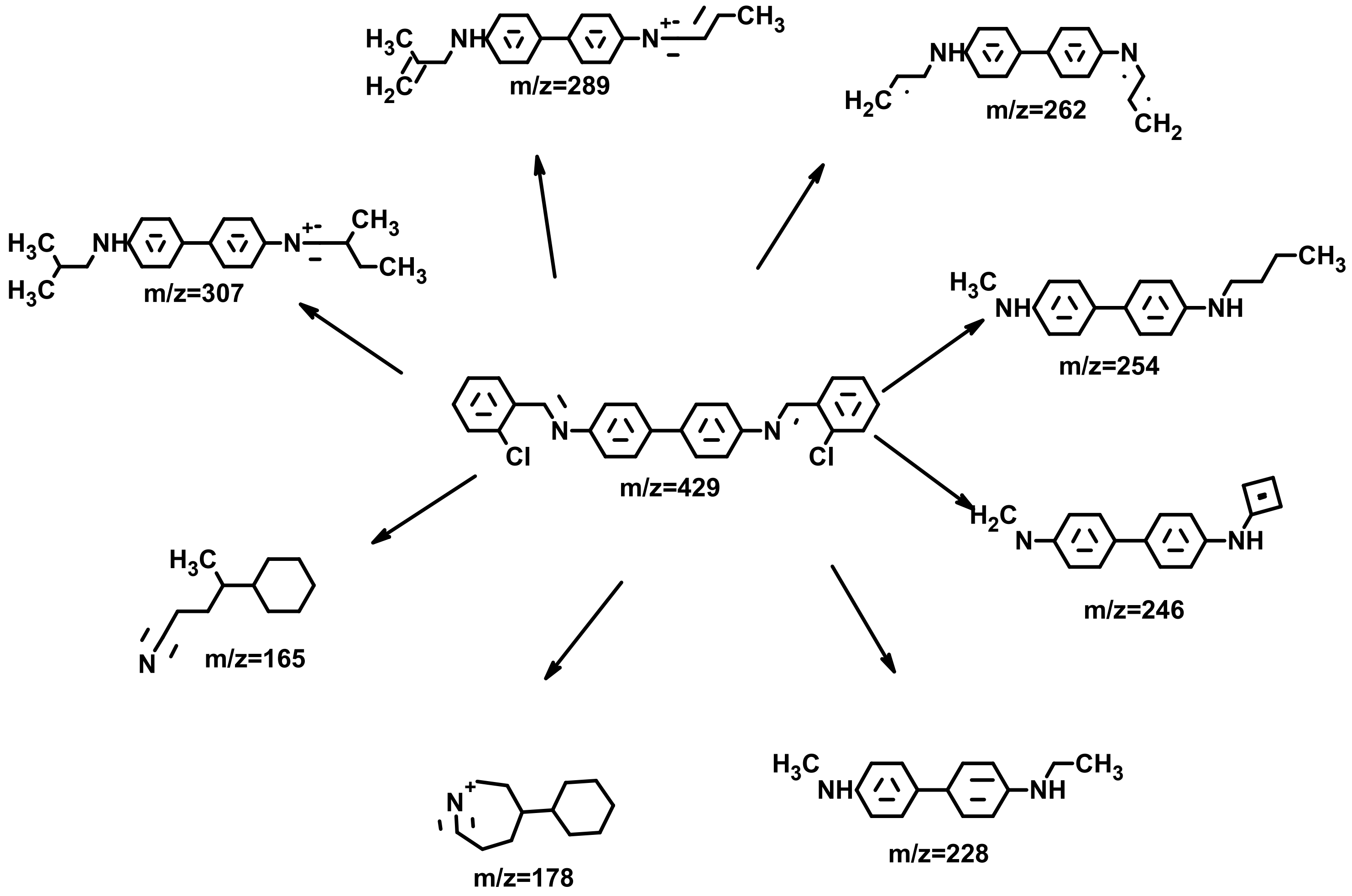
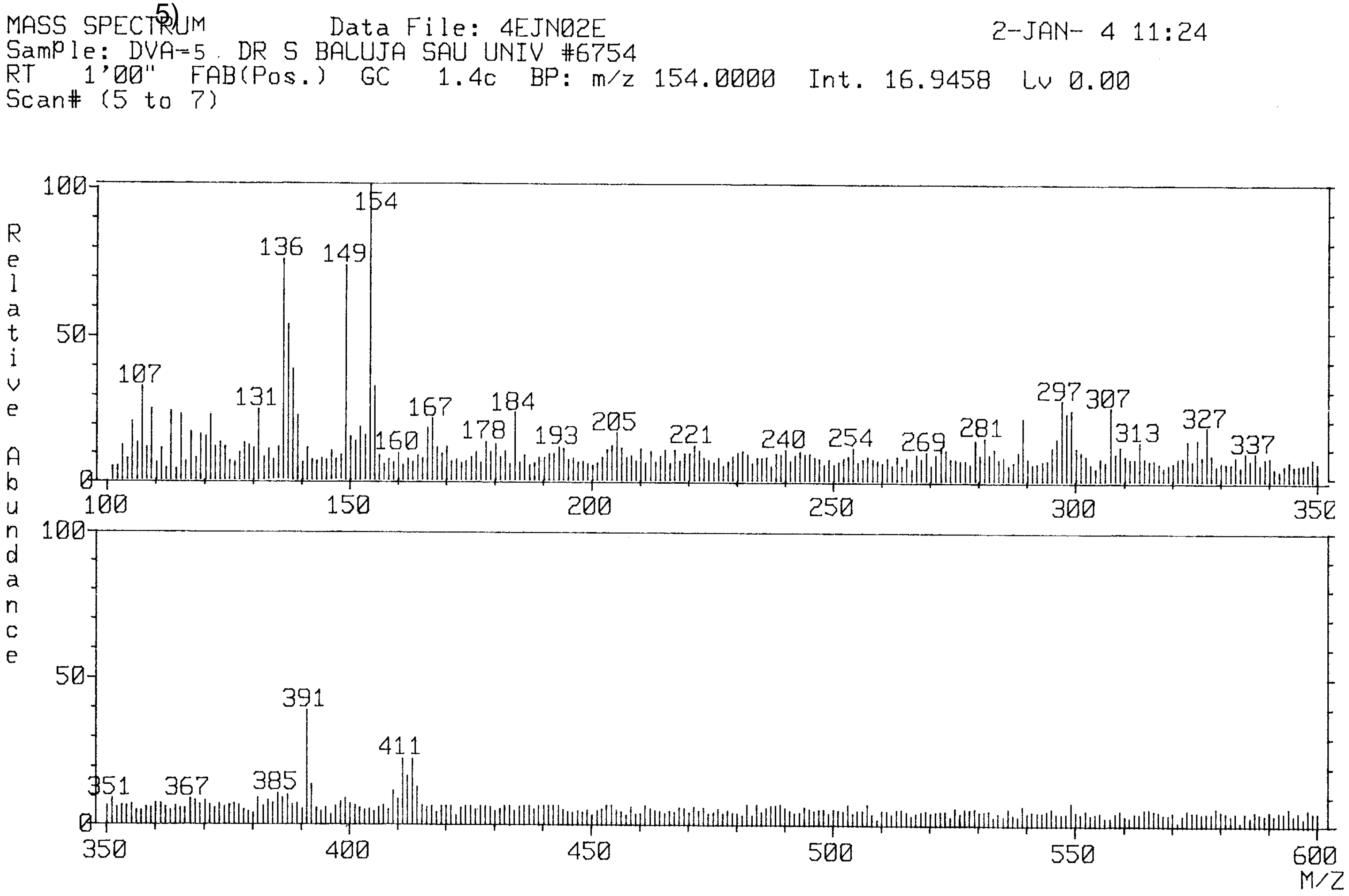


Figure 2.32 : N-[(1E)-(2-PHENYLVINYL)]-N'-[(1Z)-(2-PHENYLVINYL)]BIPHENYL-4,4'-DIAMINE(DVA-5)



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Sample: DVA-5 . DR S BALUJA SAU UNIV #6754
RT   1'00"  FAB(Pos.)  GC   1.4c  BP: m/z 154.0000  Int. 16.9458  Lv 0.00
Scan# (5 to 7)
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Scheme 2.10 : N-[(1E)-(2-PHENYLVINYL)]-N'-[(1Z)-(2-PHENYLVINYL)]BIPHENYL-4,4'-DIAMINE (DVA-5)

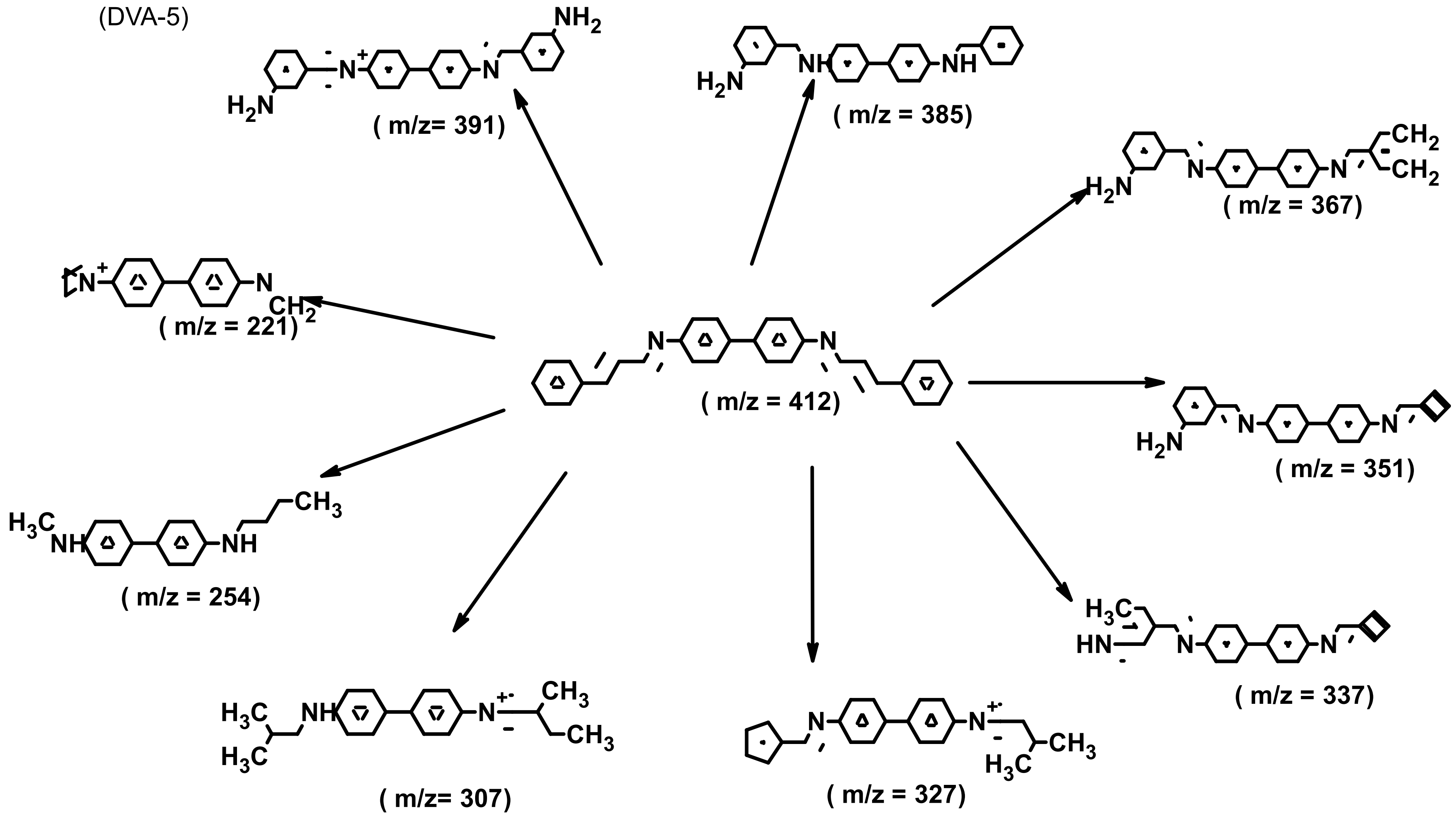
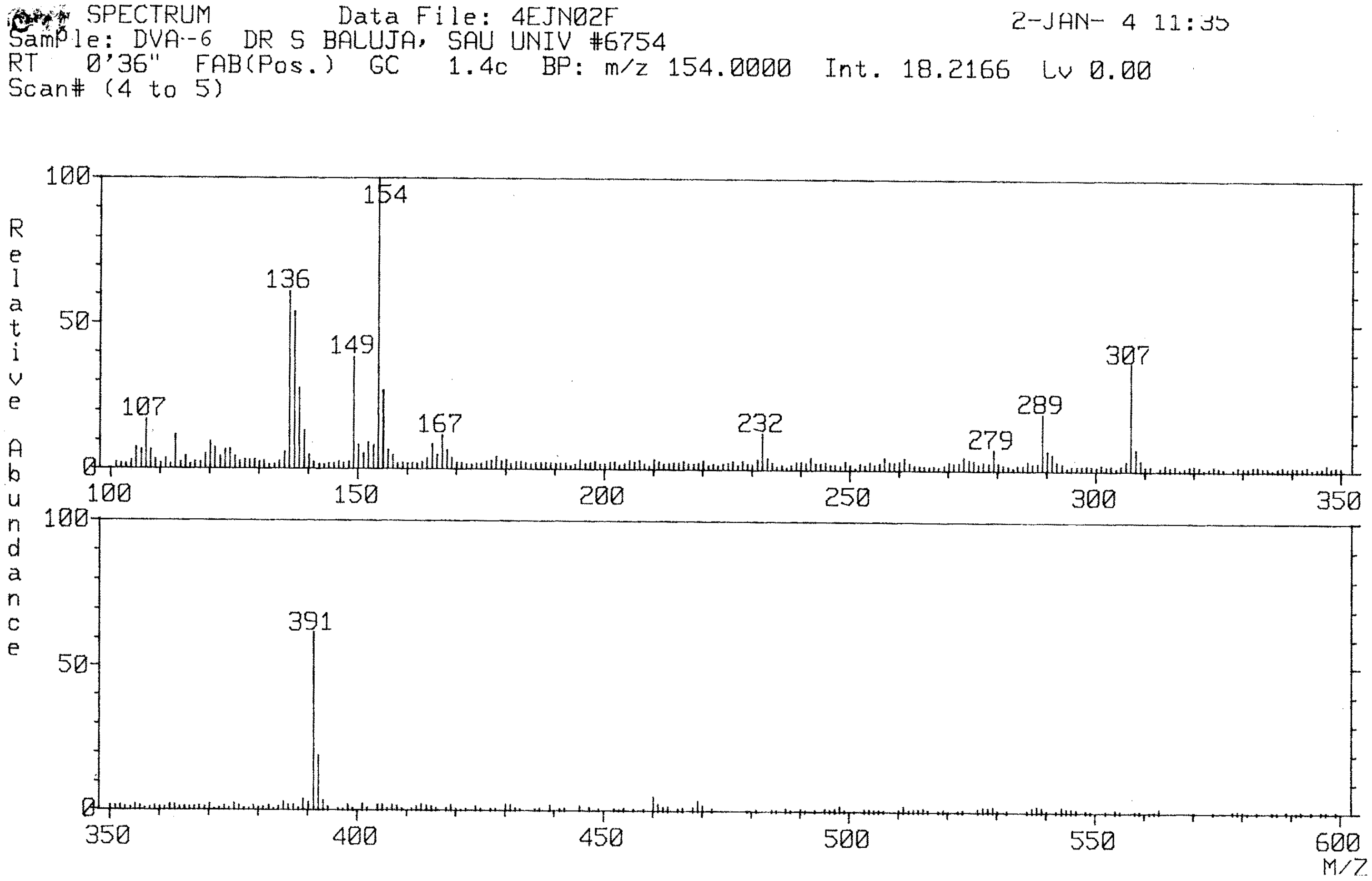


Figure 2.32 : MASS SPECTRA OF N-[(1E)-(2-HYDROXYPHENYL)METHYLENE]-N’-[(1Z)-(2-HYDROXYPHENYL) METHYLENE] BIPHENYL-4,4' -DIAMINE(DVA-6)



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RT   0'36"  FAB(Pos.)  GC   1.4c  BP: m/z 154.0000  Int. 18.2166  Lv 0.00
Scan# (4 to 5)
```

Scheme 2.11 : MASS SPECTRAL STUDY OF N-[(1E)-(2-HYDROXYPHENYL)METHYLENE]-N’-[(1Z)-(2-HYDROXYPHENYL) METHYLENE] BIPHENYL-4,4' -DIAMINE(DVA-6)

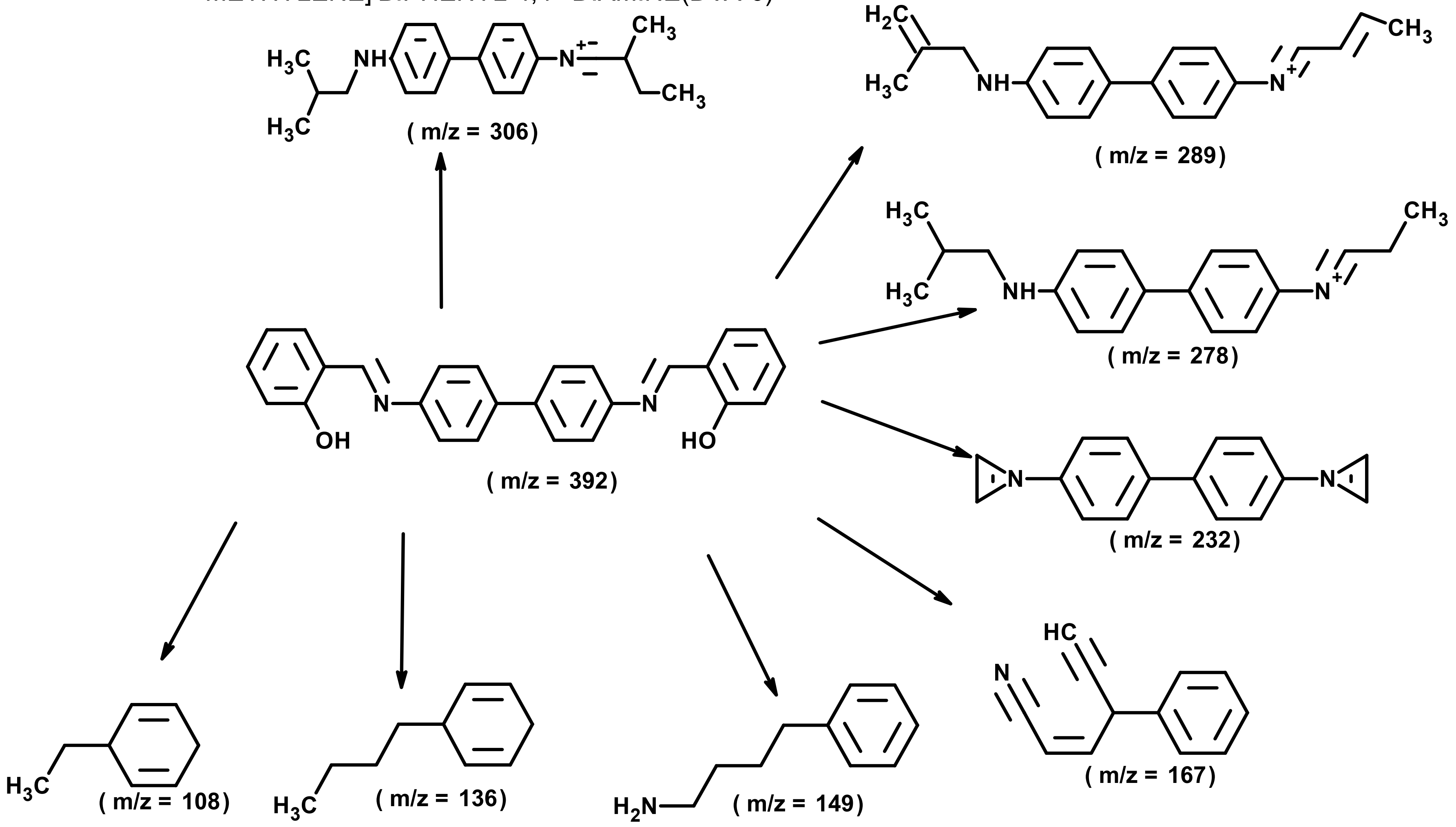
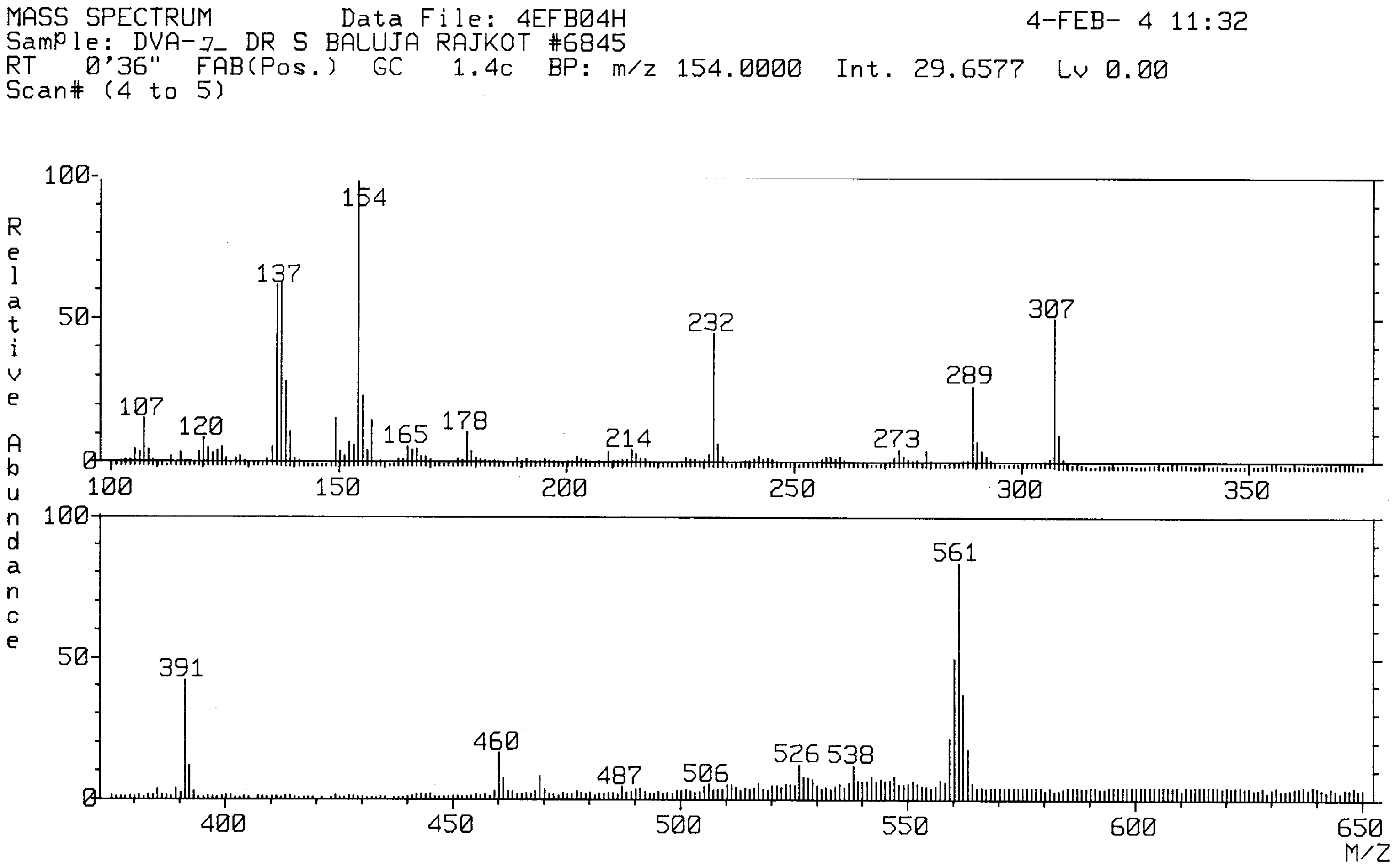


Figure 2.33 : MASS SPECTRA OF N-[(1E)-ANTHRYLMETHYLENE]-N’-[(1Z)-ANTHRYLMETHYLENE] BIPHENYL - 4,4'-DIAMINE(DVA-7)



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Scan# (4 to 5)
```

Scheme 2.12 : MASS SPECTRAL STUDY OF OF N-[(1E)-ANTHRYLMETHYLENE]-N'-[(1Z)-ANTHRYLMETHYLENE] BIPHENYL - 4,4'-DIAMINE(DVA-7)

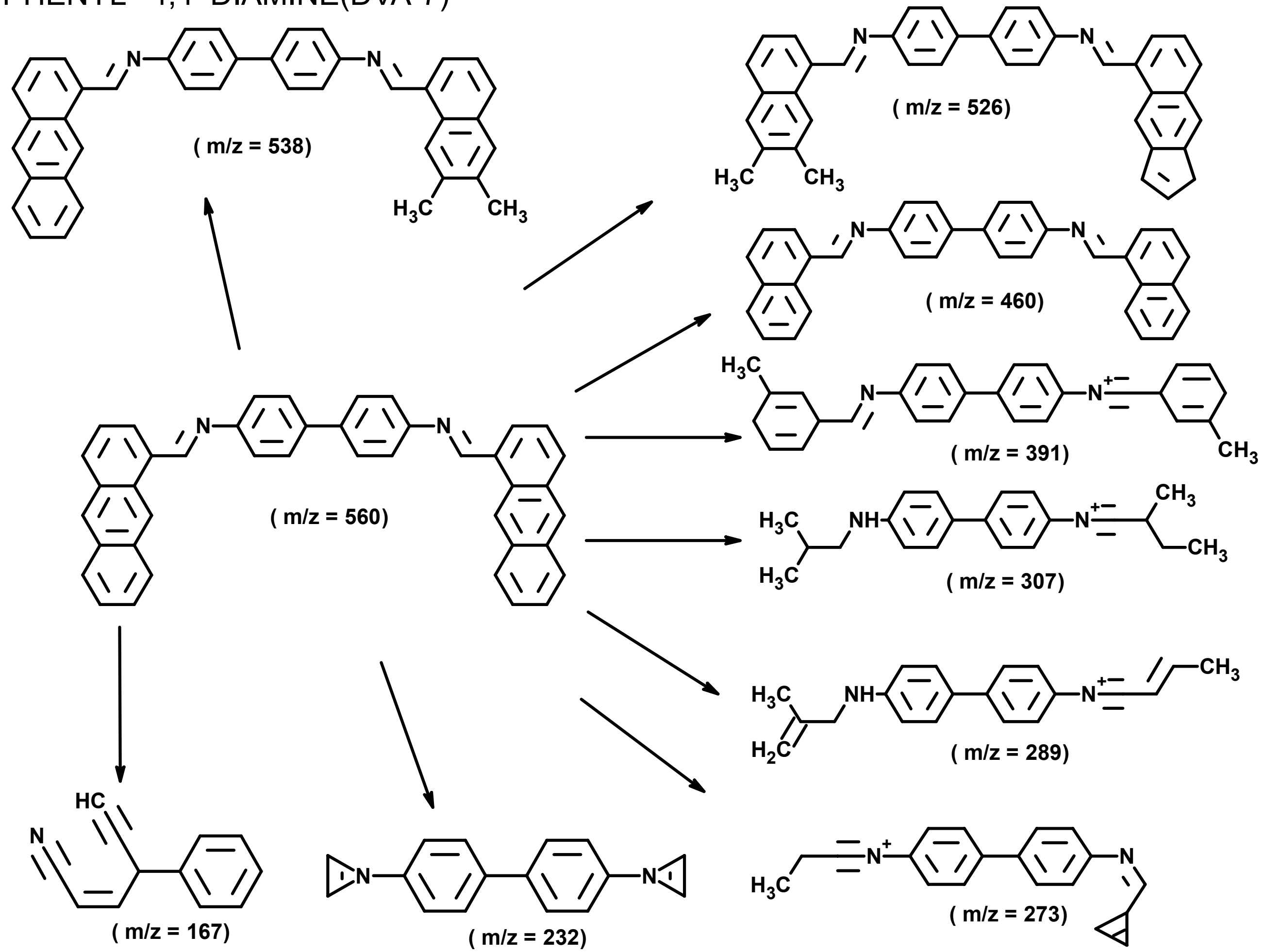
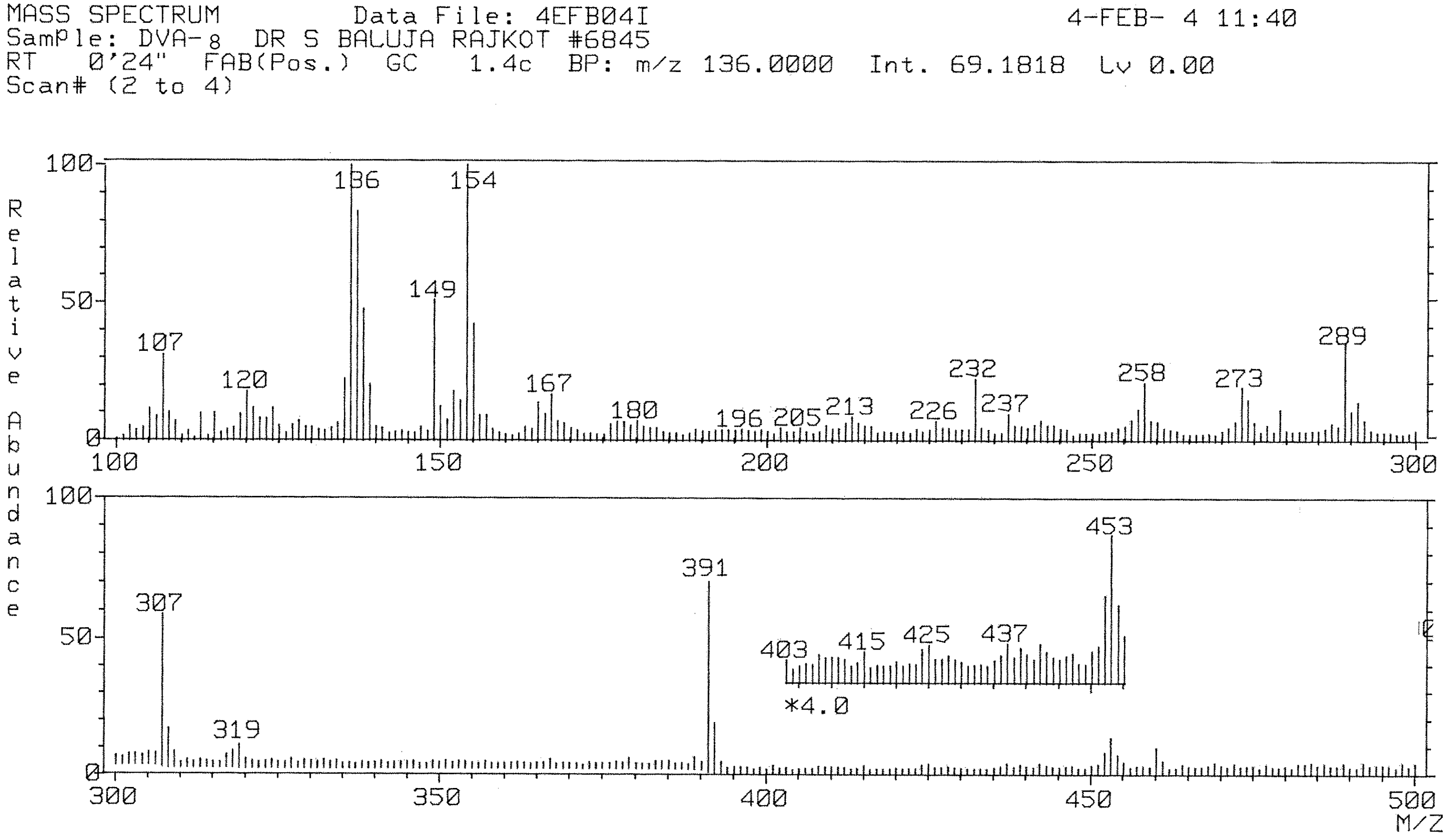


Figure 2.34 : MASS SPECTRA OF N-[(1E)-(3-METHOXY,4-HYDROXYPHENYL)METHYLENE]-N’-[(1Z)-(3-METHOXY, 4-HYDROXY PHENYL)METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-8)



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Sample: DVA-8  DR S BALUJA RAJKOT #6845
RT   0'24"  FAB(Pos.)  GC   1.4c  BP: m/z 136.0000  Int. 69.1818  Lv 0.00
Scan# (2 to 4)
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Scheme 2.12 : MASS SPECTRAL STUDY OF OF N-[(1E)-(3-METHOXY,4-HYDROXYPHENYL)METHYLENE]-N’-[(1Z)-(3-METHOXY,4-HYDROXY PHENYL)METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-8)

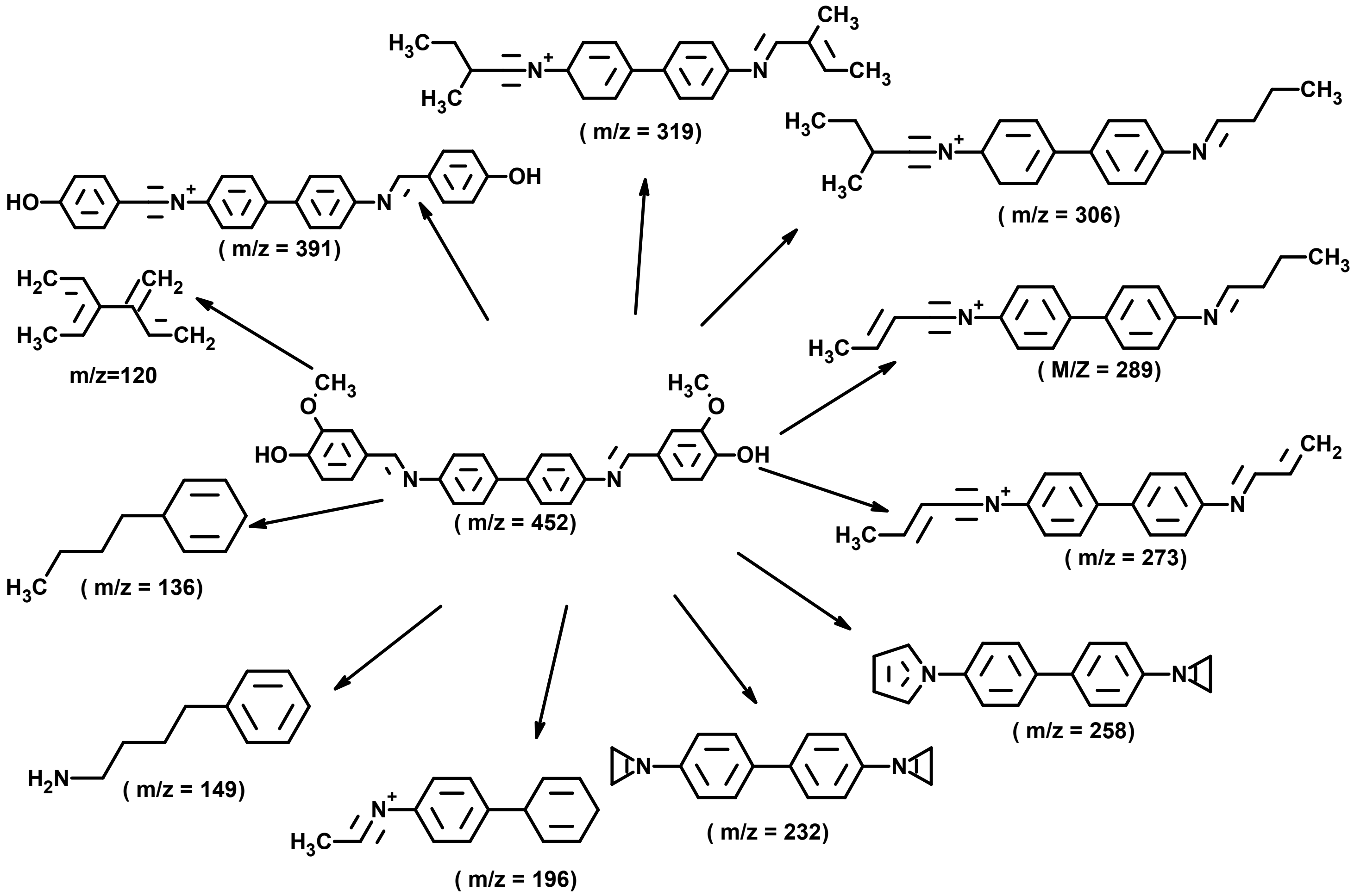

Figure 2.35 : MASS SPECTRA OF N-[(1E)-2-FURYLMETHYLENE]-N’-[(1Z)-2-FURYLMETHYLENE]BIPHENYL-4,4'-DIAMINE (DVA-9)

```
MASS SPECTRUM        Data File: 4EFB04J                        4-FEB- 4 11:54
Sample: DVA- 9 DR S BALUJA RAJKOT #6845
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Scan# (2 to 4)
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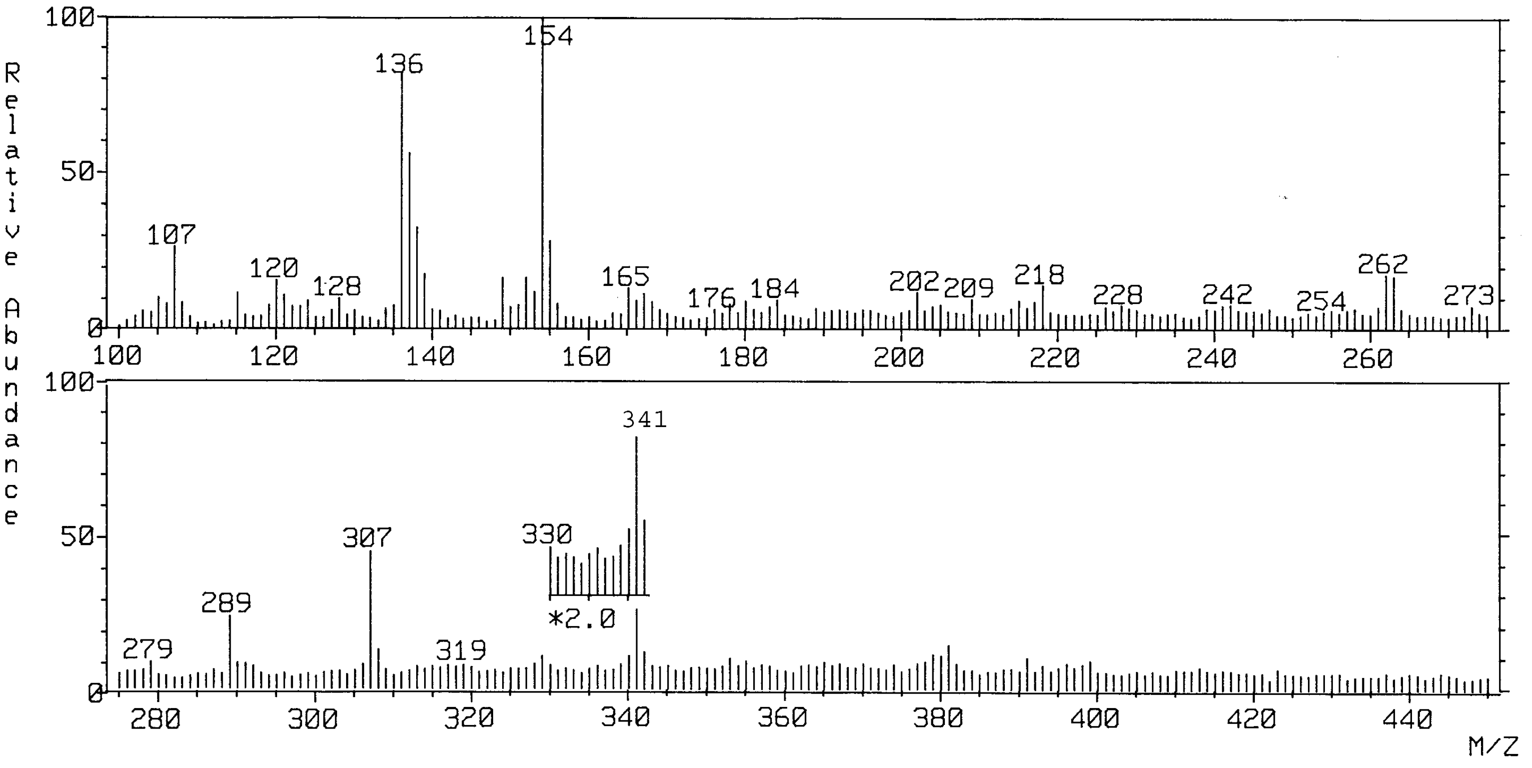

Scheme 2.13 : MASS SPECTRAL STUDY OF N-[(1E)-2-FURYLMETHYLENE]-N’-[(1Z)-2-FURYLMETHYLENE]BIPHENYL-4,4'-DIAMINE (DVA-9)

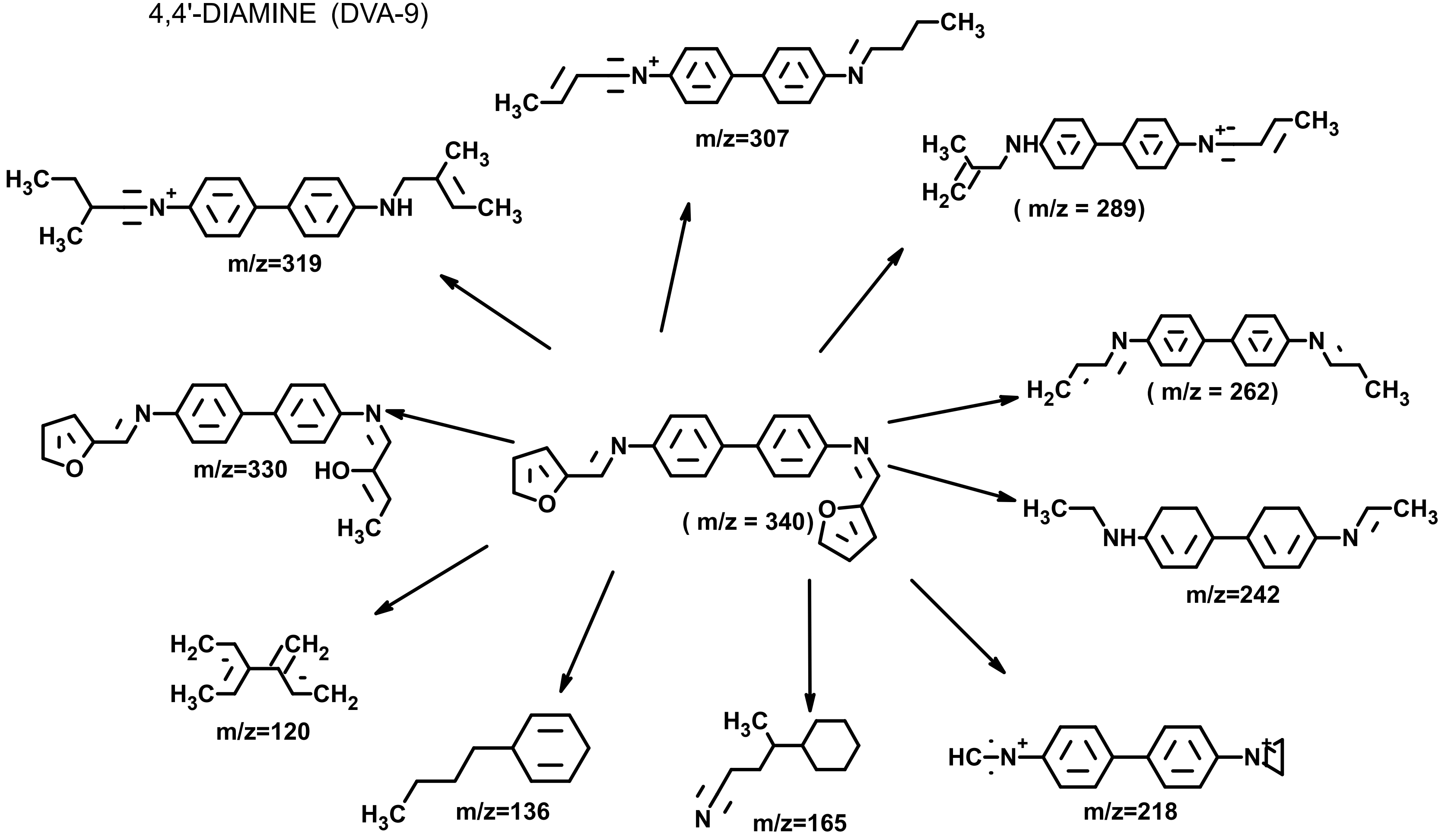

Figure 2.36 : MASS SPECTRA OF N-[(1E)-(N-N-DIMETHY)METHYLENE]-N’-[(1Z)-(N-N-DIMETHY) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-10)

```
MASS SPECTRUM        Data File: 4EFB04K                            4-FEB- 4 12:04
Sample: DVA-10 DR S BALUJA RAJKOT #6845
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Scan# (3 to 4)
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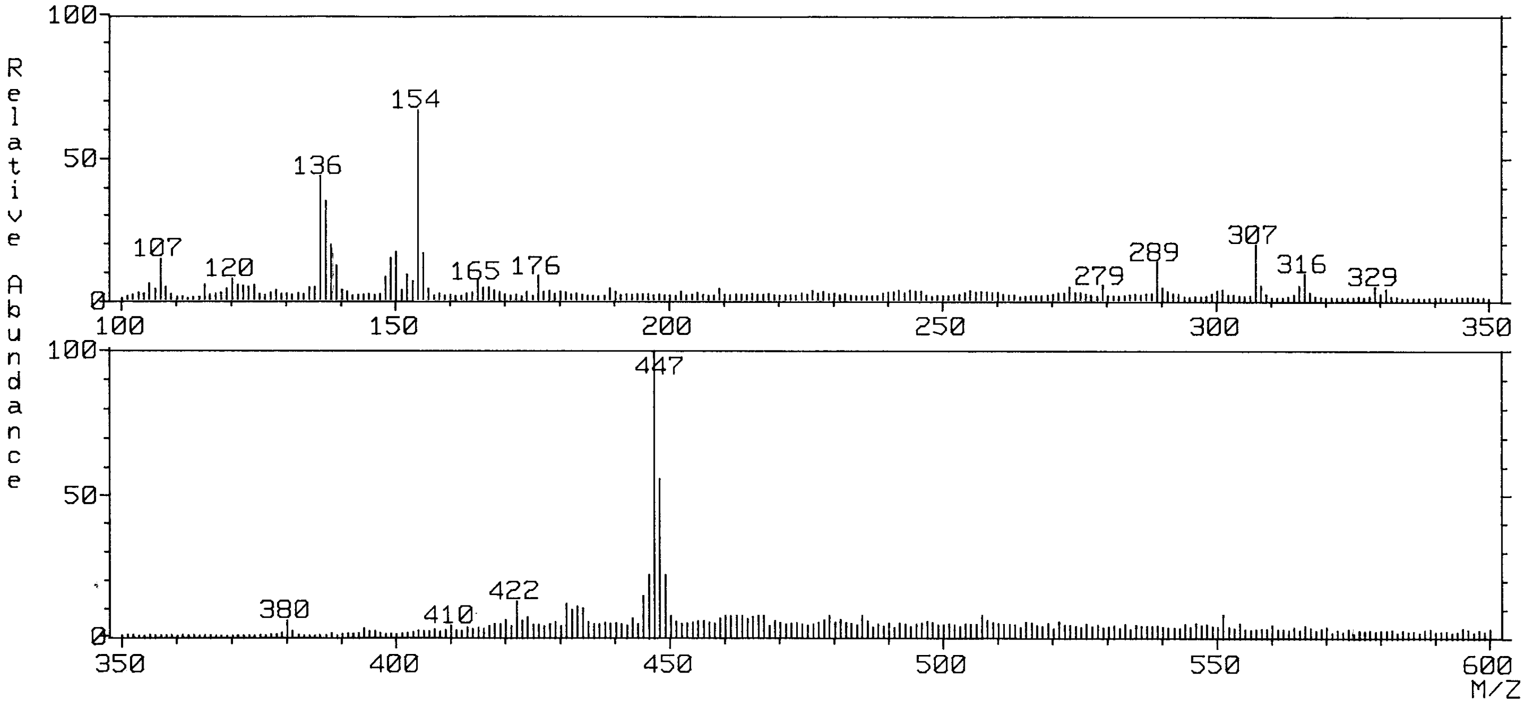

Scheme 2.14 : MASS SPECTRAL STUDY OF N-[(1E)-(N-N-DIMETHY)METHYLENE]-N’-[(1Z)-(N-N-DIMETHY) METHYLENE] BIPHENYL- 4,4'-DIAMINE(DVA-10)

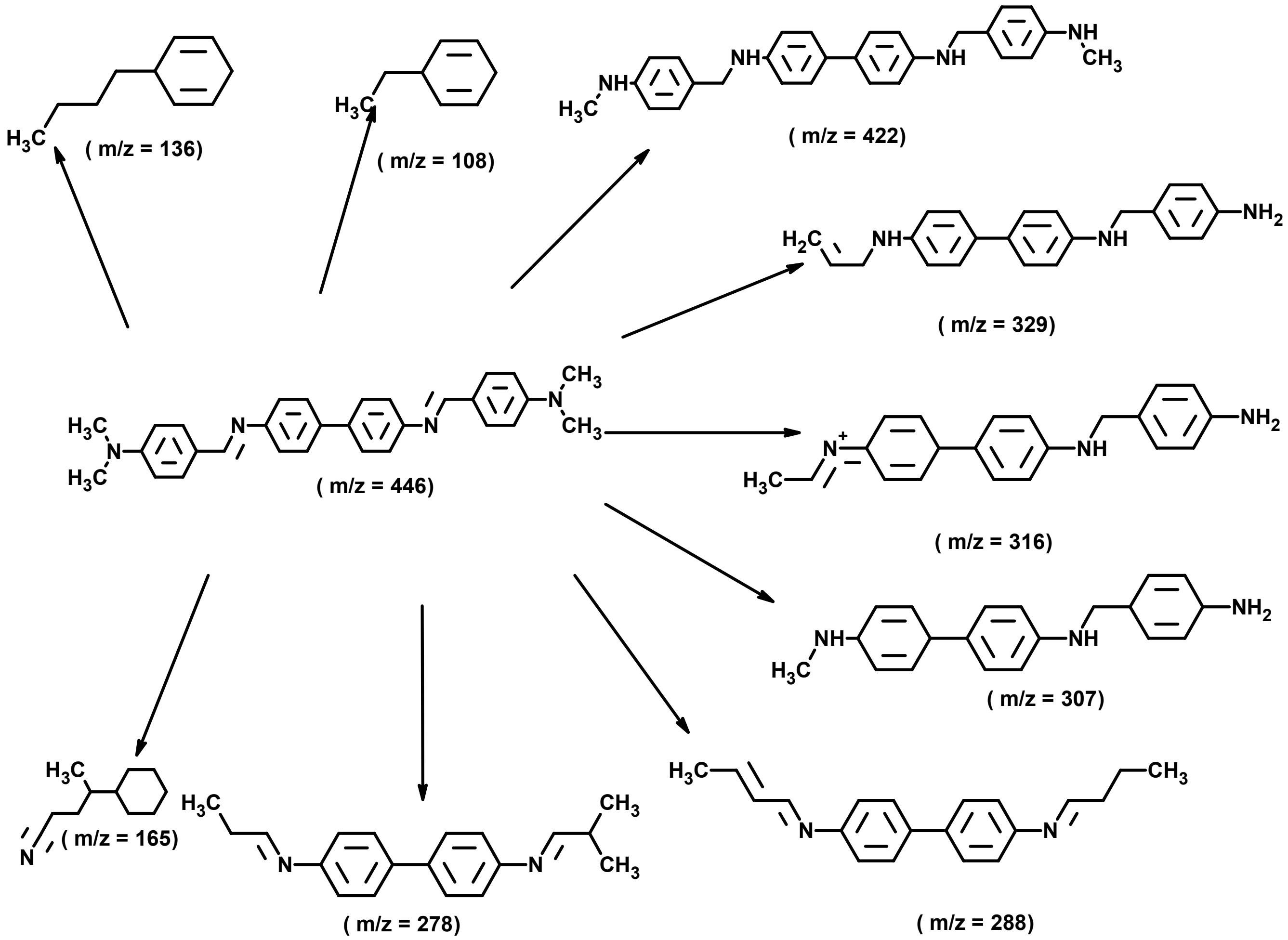

Figure 2.37 : MASS SPECTRA OF N-[(1E)-(4-CHLOROPHENYL)METHYLENE]-N'-[(1Z)-(4-CHLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-11)

```
MASS SPECTRUM          Data File: 4EFB04L                               4-FEB- 4 12:27
Sample: DVA- 11 DR S BALUJA RAJKOT #6845
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Scan# (1 to 2)
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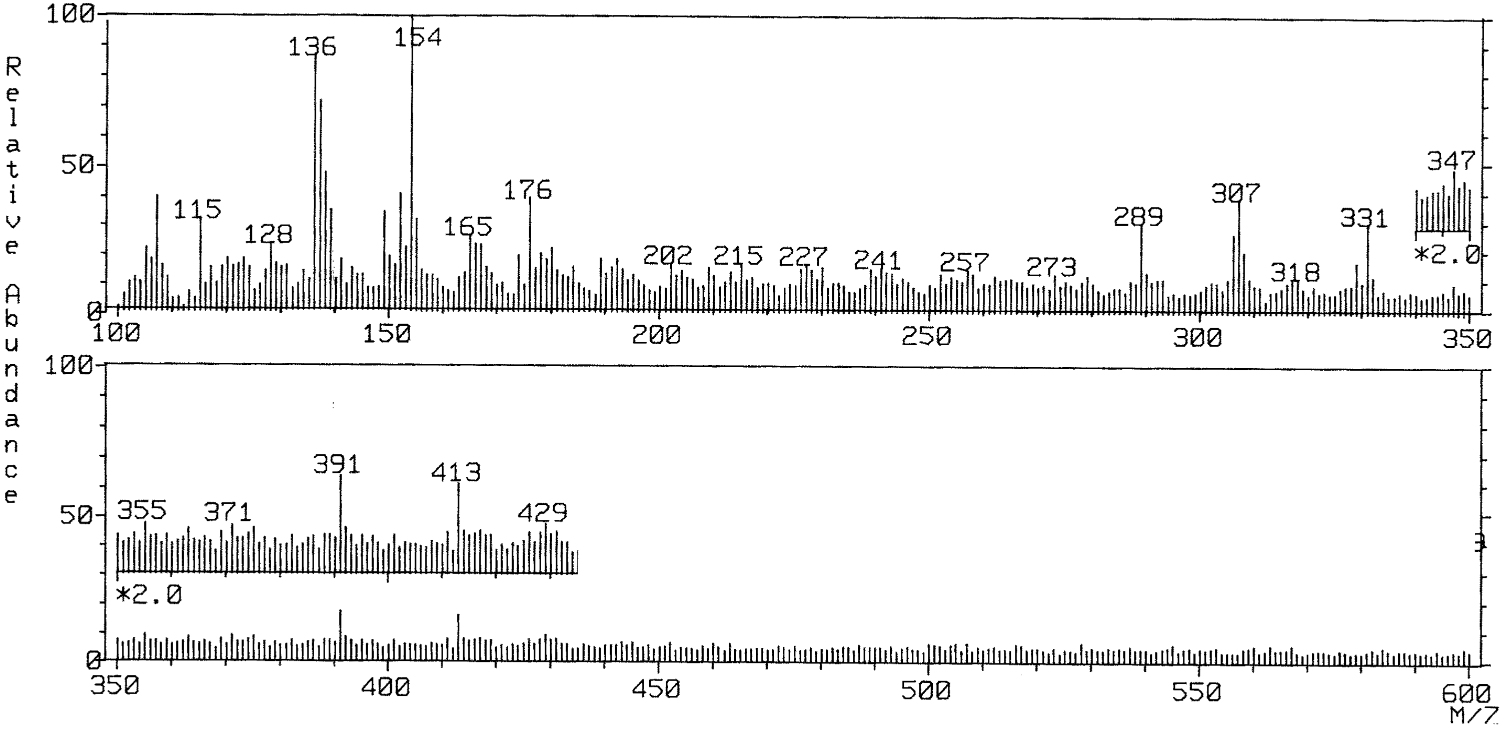


Scheme 2.15 : MASS SPECTRAL STUDY OF N-[(1E)-(4-CHLOROPHENYL)METHYLENE]-N’-[(1Z)-(4-CHLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-11)

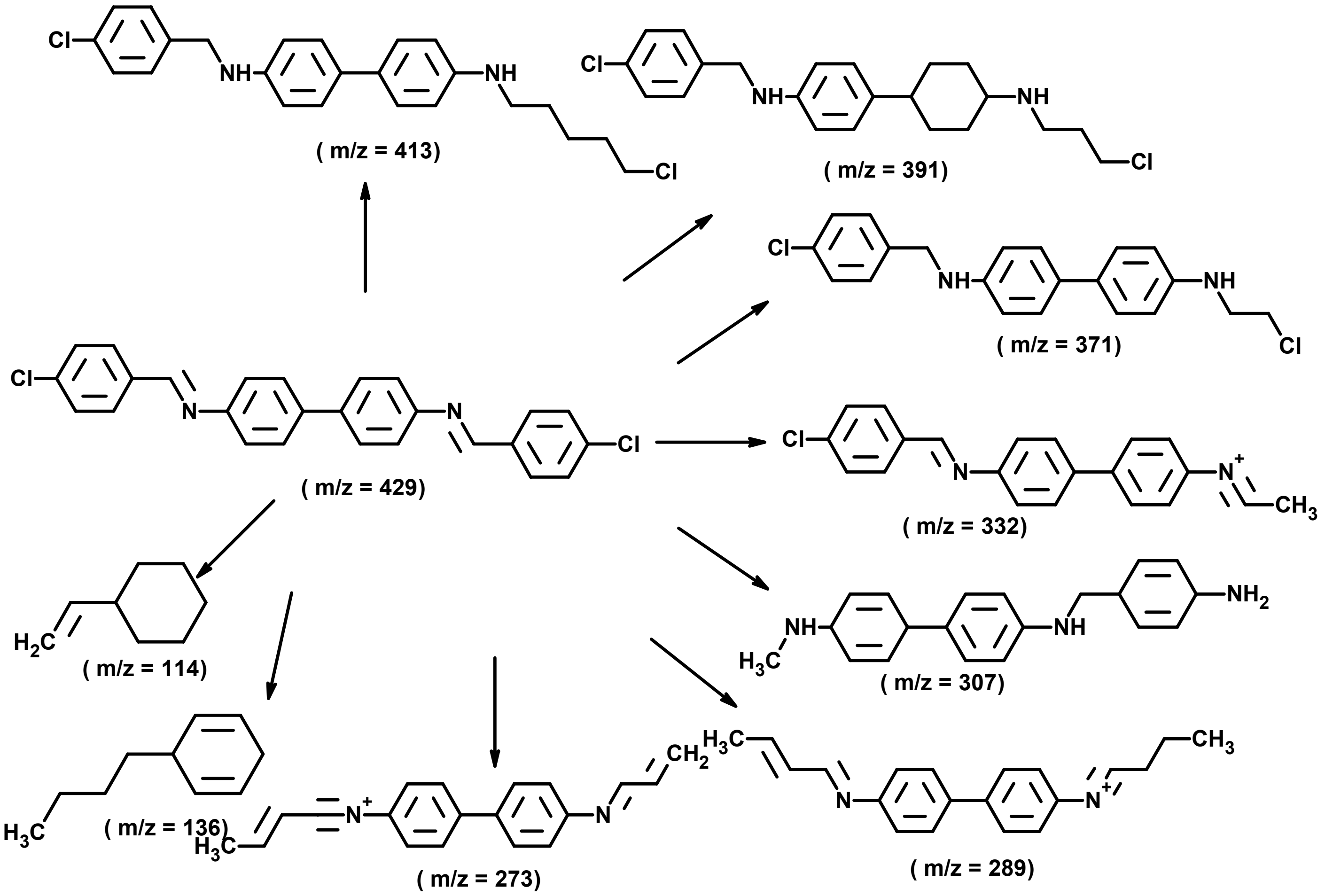
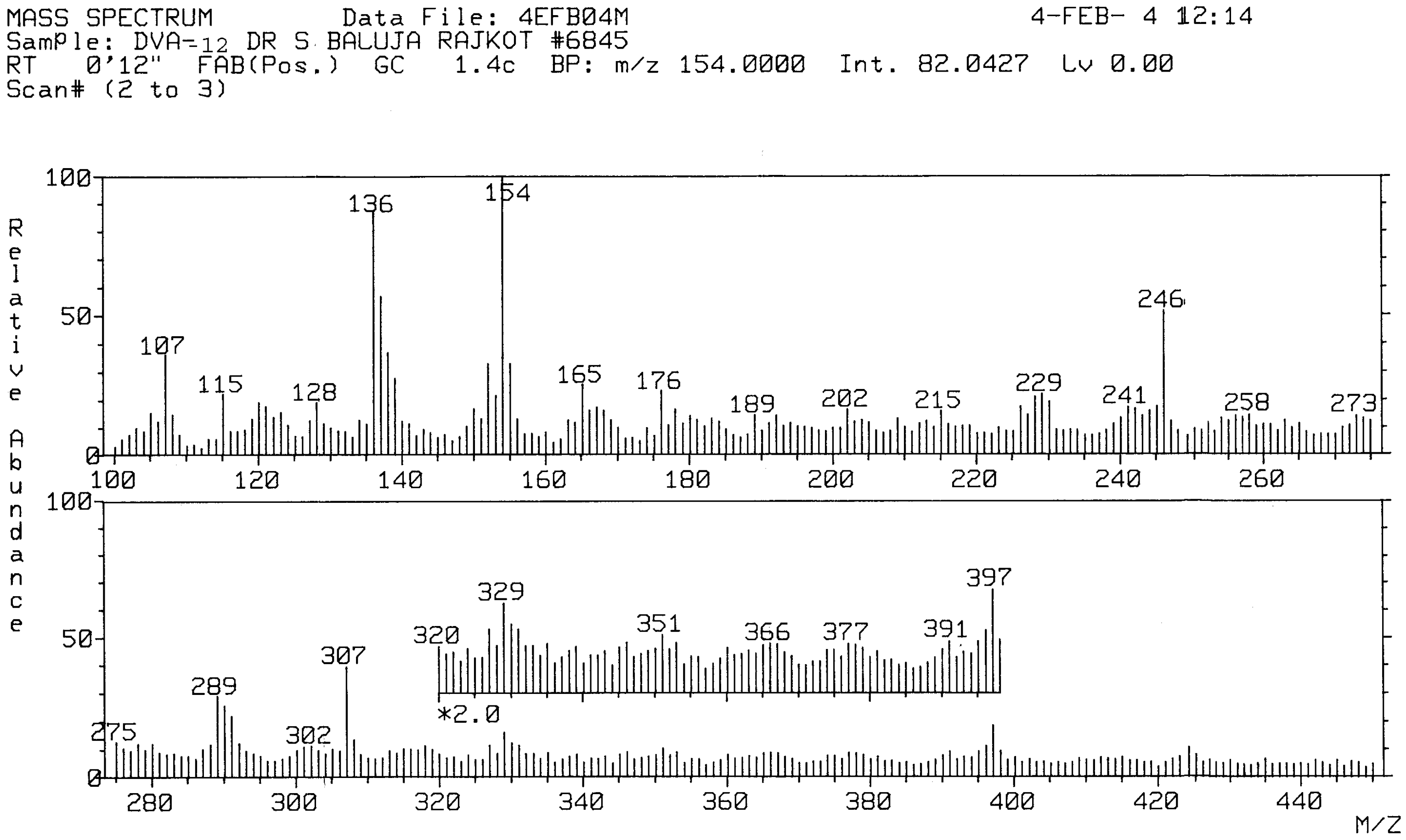


Figure 2.37 : MASS SPECTRA OF N-[(1E)-(4-FLOROPHENYL)METHYLENE]-N’-[(1Z)-(4-FLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-12)



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Scan# (2 to 3)
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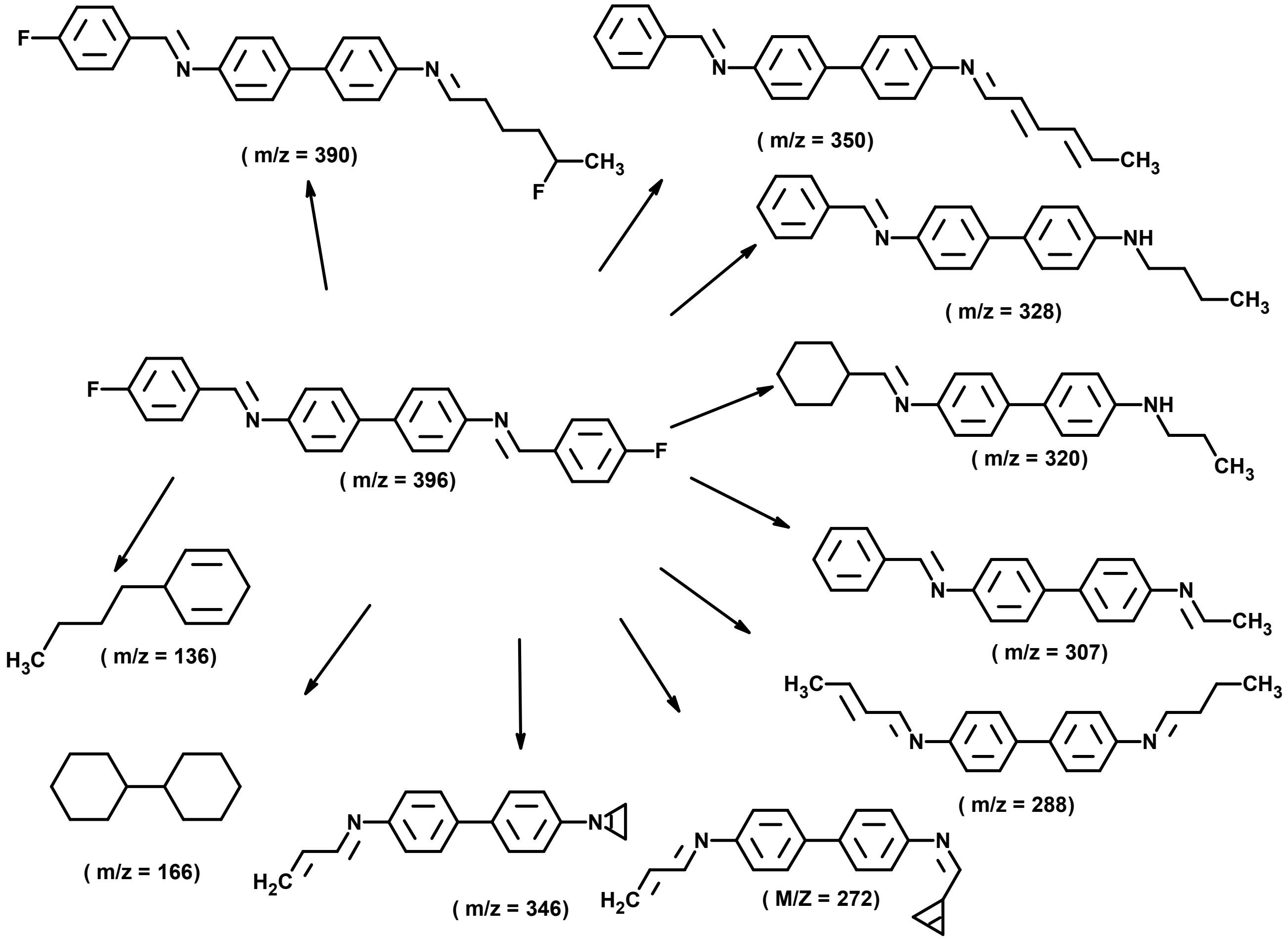
Scheme 2.16 : MASS SPECTRAL STUDY OF N-[(1E)-(4-FLOROPHENYL)METHYLENE]-N’-[(1Z)-(4-FLOROPHENYL) METHYLENE] BIPHENYL-4,4'-DIAMINE(DVA-12)



INTRODUCTION

The refractive index is a characteristic property of a substances, which depends upon temperature and the wavelength of the light used. By measuring the refractive index, one can determine the structure and purity of compounds. Further, it is also useful in the evaluation of different thermodynamic properties of chemical compound with the help of density, molecular weight and specific volume. The number of atoms, groups, radicals and bonds present in the compound can also be calculated by refractive index measurement.

Literature survey shows that much work has been reported for liquid mixtures(1-10), solutions of organic, inorganic and polymeric materials(11-23).

In the present chapter, the refractive index and density of some Schiff bases derived from α-naphthalamine are measured in dimethyl formamide (DMF) and tetrahydrofuran (THF) at 313.15 K.

EXPERIMENTAL

The solvents used in the present study were dimethyl formamide (DMF) and tetrahydrofuran (THF), which were fractionally distilled prior to use by standard methods(24).

All the Schiff bases were recrystalized from methanol. For each Schiff base except NDP-8, a series of solutions of different concentrations were prepared in both the solvents. NDP-8 is almost black so its refractive index measurement was not possible even in very dilute solution.

The density and refractive index of all the solutions were measured by Pyknometer and Abbe Refractometer respectively at 313.15 K. All these experimental values are given in Table 3.1.1 and 3.1.2.

RESULTS AND DISCUSSION

From the concentrations of solutions, g_1 and g_2 i.e., weight fractions of solvent and solute respectively were calculated. These values are also given in Tables 3.1.1 and 3.1.2 along with experimental refractive index and density of solutions.

The density of solution (ρ_{12}) is related to density of pure solvent (ρ_1) and density of solute (ρ_2) by the equation:

$$1/\rho_{12} = g_1/\rho_1 + g_2/\rho_2 \qquad \text{-----(3.1.1)}$$

The density of all the Schiff bases was determined from the slope of the plot of $1/g_1\rho_{12}$ verses g_2/g_1. Figure 3.1.1 shows the plot of $1/g_1\rho_{12}$ verses g_2/g_1 for NDP-1 in DMF and THF. The inverse of slope gives ρ_2. The calculated densities for all Schiff bases are given in Table 3.1.3. It is evident from Table 3.1.3 that for the same Schiff base, density is different in the two solvents.

The density of these compounds have also evaluated by the equation(24)

$$\rho = KM/(N_A\Sigma\Delta V_i) \qquad \text{-----(3.1.2)}$$

where ρ the density of the compound, K is packing fraction (0.599), M is the molecular weight of the compound, N_A is the Avogadros number and ΔV_i is the volume increment of the atoms and atomic groups present in the compound.

ΔV_i for atoms and groups of atoms used in the present study are reported in Table 3.1.4. The densities calculated from equation (3.1.2) are given in Table 3.1.3. Again, the evaluated densities by equation (3.1.2) are different than those calculated from the slope of the plot of $1/g_1\rho_{12}$ verses g_2/g_1 (Figure 3.1.1) in DMF and THF. This suggests that solvent plays an important role. Due to polar group in the compound or in solvent, density is affected due to intermolecular interactions.

Table 3.1.1: The density (ρ_{12}) and refractive index (n) of Schiff bases in DMF at 313.15 K.

Conc. (M)	ρ_{12}	g_1	g_2	n
NDP-1				
0.01	0.9338	0.9975	0.0025	1.411
0.02	0.9341	0.9951	0.0049	1.412
0.04	0.9344	0.9902	0.0098	1.413
0.06	0.9345	0.9852	0.0147	1.414
0.08	0.9366	0.9804	0.0196	1.416
0.10	0.9371	0.9754	0.0246	1.420
NDP -2				
0.01	0.9343	0.9974	0.0026	1.410
0.02	0.9356	0.9947	0.0052	1.411
0.04	0.9364	0.9895	0.0105	1.412
0.06	0.9386	0.9843	0.0157	1.413
0.08	0.9391	0.9391	0.0209	1.414
0.10	0.9400	0.9739	0.0261	1.415
NDP -3				
0.01	0.9283	0.9972	0.0028	1.412
0.02	0.9390	0.9945	0.0055	1.412
0.04	0.9394	0.9889	0.0111	1.413
0.06	0.9396	0.9834	0.0166	1.414
0.08	0.9410	0.9756	0.0244	1.415
0.10	0.9412	0.9724	0.0276	1.417
NDP-4				
0.01	0.9413	0.9971	0.0029	1.413
0.02	0.9440	0.9942	0.0058	1.414
0.04	0.9442	0.9884	0.0116	1.416
0.06	0.9443	0.9826	0.0174	1.417
0.08	0.9450	0.9768	0.0232	1.419
0.10	0.9480	0.9710	0.0292	1.420
NDP -5				
0.01	0.9390	0.9971	0.0029	1.412
0.02	0.9403	0.9942	0.0058	1.413
0.04	0.9409	0.9884	0.0116	1.417
0.06	0.9419	0.9826	0.0174	1.418
0.08	0.9445	0.9769	0.0231	1.420
0.10	0.9446	0.9711	0.0289	1.421

Continue …(Table 3.1.1)

Conc. (M)	ρ_{12}	g_1	g_2	**n**
NDP -6				
0.01	0.9357	0.9974	0.0026	1.411
0.02	0.9363	0.9948	0.0052	1.413
0.04	0.9393	0.9895	0.0105	1.415
0.06	0.9410	0.9843	0.0157	1.416
0.08	0.9418	0.9791	0.0209	1.417
0.10	0.9431	0.9740	0.0260	1.418
NDP -7				
0.01	0.9367	0.9972	0.0028	1.412
0.02	0.9390	0.9944	0.0056	1.414
0.04	0.9418	0.9888	0.0112	1.415
0.06	0.9431	0.9832	0.0168	1.417
0.08	0.9437	0.9776	0.0244	1.419
0.10	0.9441	0.9720	0.0280	1.420
NDP-9				
0.01	0.9372	0.9974	0.0026	1.411
0.02	0.9375	0.9947	0.0053	1.412
0.04	0.9387	0.9895	0.0105	1.413
0.06	0.9393	0.9842	0.0158	1.414
0.08	0.9407	0.9790	0.0210	1.415
0.10	0.9421	0.9738	0.0262	1.416
NDP-10				
0.01	0.9368	0.9971	0.0029	1.411
0.02	0.9376	0.9941	0.0059	1.413
0.04	0.9418	0.9883	0.0117	1.414
0.06	0.9431	0.9825	0.0175	1.415
0.08	0.9446	0.9768	0.0232	1.416
0.10	0.9453	0.9710	0.0290	1.419

Table 3.1.2 : The density (ρ_{12}) and refractive index (n) of Schiff bases in THF at 313.15 K.

Conc. (M)	ρ_{12}	g_1	g_2	n
NDP-1				
0.01	0.8678	0.9973	0.0026	1.386
0.02	0.8729	0.9947	0.0053	1.386
0.04	0.8738	0.9895	0.0105	1.387
0.06	0.8747	0.9842	0.0157	1.387
0.08	0.8752	0.9790	0.0210	1.388
0.10	0.8763	0.9738	0.0260	1.389
NDP-2				
0.01	0.8702	0.9972	0.0028	1.387
0.02	0.8711	0.9944	0.0056	1.388
0.04	0.8717	0.9887	0.0114	1.389
0.06	0.8731	0.9831	0.0172	1.390
0.08	0.8744	0.9775	0.0230	1.392
0.10	0.8757	0.9719	0.0288	1.394
NDP-3				
0.01	0.8714	0.9970	0.0030	1.387
0.02	0.8716	0.9940	0.0059	1.387
0.04	0.8718	0.9881	0.0119	1.388
0.06	0.8719	0.9821	0.0179	1.390
0.08	0.8730	0.9762	0.0238	1.391
0.10	0.8743	0.9703	0.0297	1.392
NDP-4				
0.01	0.8715	0.9968	0.0031	1.388
0.02	0.8717	0.9937	0.0063	1.389
0.04	0.8718	0.9874	0.0126	1.390
0.06	0.8719	0.9896	0.0189	1.391
0.08	0.8726	0.9748	0.0251	1.392
0.10	0.8741	0.9685	0.0314	1.393

Continue…(Table 3.1.2)

Conc. (M)	ρ_{12}	g_1	g_2	n
		NDP-5		
0.01	0.8715	0.9732	0.0031	1.387
0.02	0.8716	0.9937	0.0062	1.388
0.04	0.8717	0.9875	0.0125	1.389
0.06	0.8724	0.9812	0.0187	1.390
0.08	0.8734	0.9750	0.0249	1.392
0.10	0.8754	0.9689	0.0311	1.393
		NDP-6		
0.01	0.8856	0.9972	0.0028	1.387
0.02	0.8867	0.9945	0.0055	1.387
0.04	0.8875	0.9870	0.0103	1.388
0.06	0.8905	0.9834	0.0165	1.389
0.08	0.8910	0.9779	0.0220	1.390
0.10	0.8915	0.9724	0.0275	1.391
		NDP-7		
0.01	0.8595	0.9969	0.0031	1.387
0.02	0.8596	0.9938	0.0061	1.388
0.04	0.8608	0.9877	0.0123	1.389
0.06	0.8609	0.9816	0.0184	1.390
0.08	0.8632	0.9755	0.0245	1.391
0.10	0.8645	0.9695	0.0305	1.393
		NDP-9		
0.01	0.8585	0.9971	0.0029	1.387
0.02	0.8591	0.9943	0.0057	1.387
0.04	0.8603	0.9885	0.0115	1.388
0.06	0.8607	0.9828	0.0172	1.389
0.08	0.8615	0.9771	0.0229	1.390
0.10	0.8625	0.9714	0.0286	1.391
		NDP-10		
0.01	0.8600	0.9968	0.0032	1.387
0.02	0.8607	0.9936	0.0064	1.388
0.04	0.8609	0.9872	0.0127	1.389
0.06	0.8619	0.9809	0.0191	1.390
0.08	0.8619	0.9746	0.0254	1.391
0.10	0.8654	0.9683	0.0317	1.392

Figure 3.1.1 : The variation of $1/\rho_{12}g_1$ with g_2/g_1 for NDP-1 in (A) DMF and (B) THF at 313.15 K

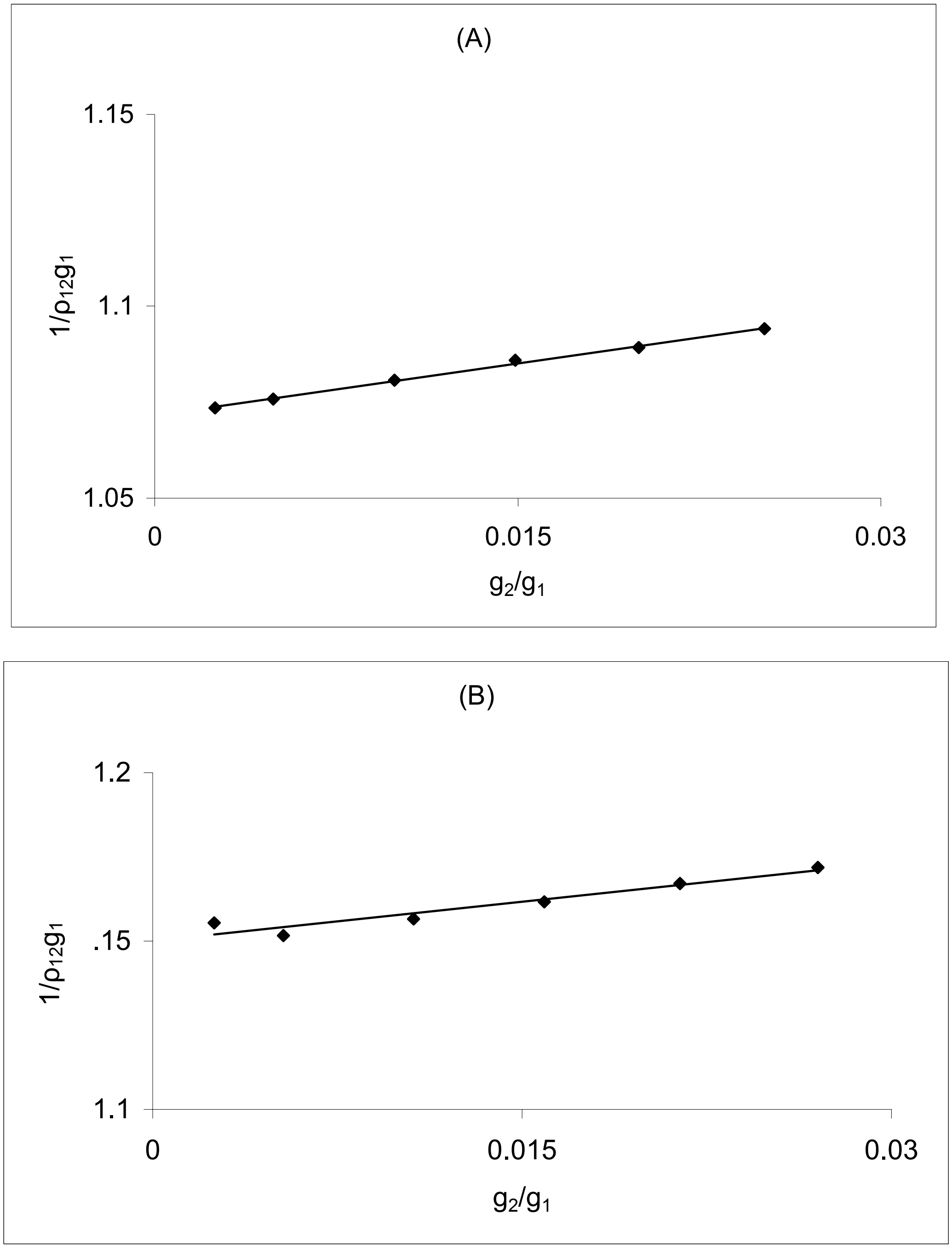


Table 3.1.3 : Experimental and calculated densities of Schiff bases in DMF and THF solutions at 313.15 K

Compound code	Density g/cm^3 [from equ. 3.1.2]	Density g/cm^3 [from Fig. 3.1.1]		Refractive index	
		DMF	THF	DMF	THF
NDP-1	0.9799	1.1476	1.0679	1.3604	1.2518
NDP-2	1.0368	1.3254	1.1932	1.1819	1.5987
NDP-3	1.0150	1.2676	1.0715	1.1236	1.3444
NDP-4	1.0995	1.2448	0.9016	1.1499	1.5601
NDP-5	0.9601	1.2371	1.0769	1.5149	1.4061
NDP-6	1.0456	1.4679	1.0000	1.4344	1.8675
NDP-7	1.1460	1.8988	1.1404	1.2222	1.9321
NDP-9	1.0750	1.1429	1.2000	1.1727	1.8600
NDP-10	1.0995	1.3043	1.1667	1.0921	1.8094

Table 3.1.4 : Volume increments of some atoms and groups of atoms.

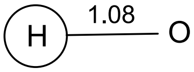
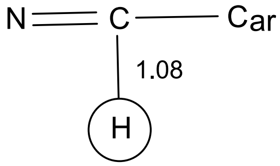
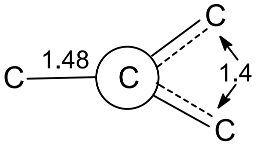
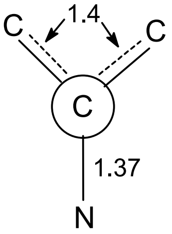
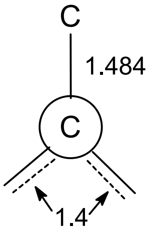
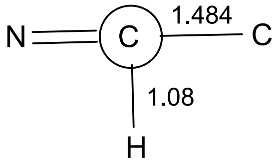
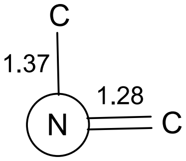
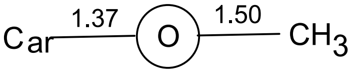
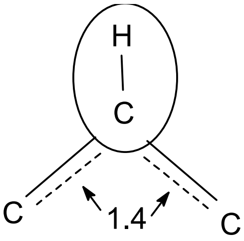
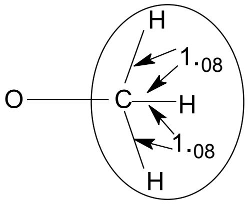
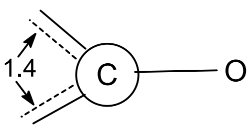
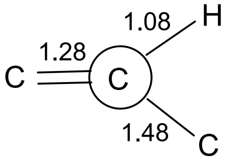
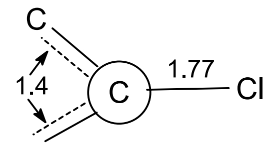
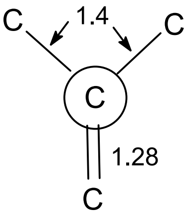
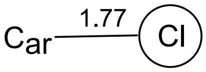
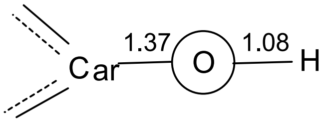
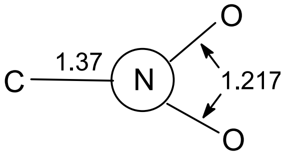
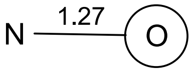
Atom or Atomic group	Volume Increment ΔV_i $(A^0)^3$	Atom or Atomic group	Volume Increment ΔV_i $(A^0)^3$
	3.52		1.25
	8.40		1.02
	8.40		3.60
	5.62		2.66
	14.70		26.30
	11.65		11.36

Table 3.1.4. (contd.)

	10.10		7.84
	19.35		5.6
	7.46		7.29

Thus, the deviation in experimental density values (calculated from slope of plot of $1/g_1\rho_1$ verses g_2/g_1) and theoretical values (calculated from equation (3.1.2)) suggest the presence of intermolecular interactions between solute and solvent molecules. This is further confirmed by ultrasonic studies explained in section-V **.**

Using Lorentz and Lorentz(25) relations (3.1.3) and (3.1.4), the molar refraction (MRD) of pure liquids and solutions can be determined.

For pure liquid :

$$(MRD) = [(n^2 - 1)/(n^2 + 2)]\ M/\rho \qquad \text{-----(3.1.3)}$$

where n is refractive index and M is the molecular weight of the solution.

For solutions:

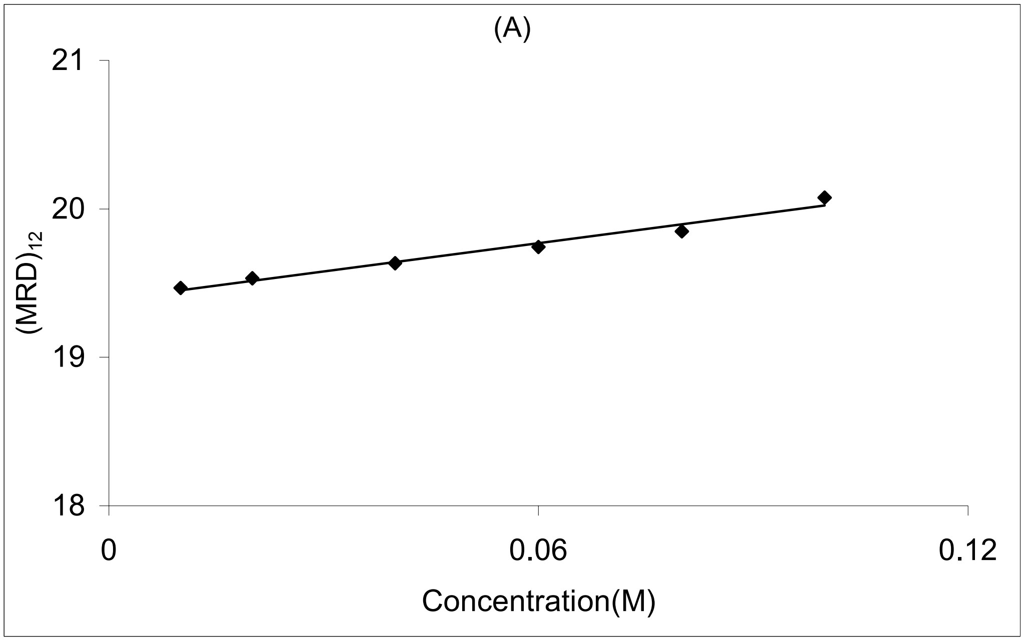
$$(MRD)_{12} = [(n^2_{12} - 1)/(n^2_{12} + 2)][(X_1M_1 + X_2M_2) / \rho_{12}] \qquad \text{-----(3.1.4)}$$

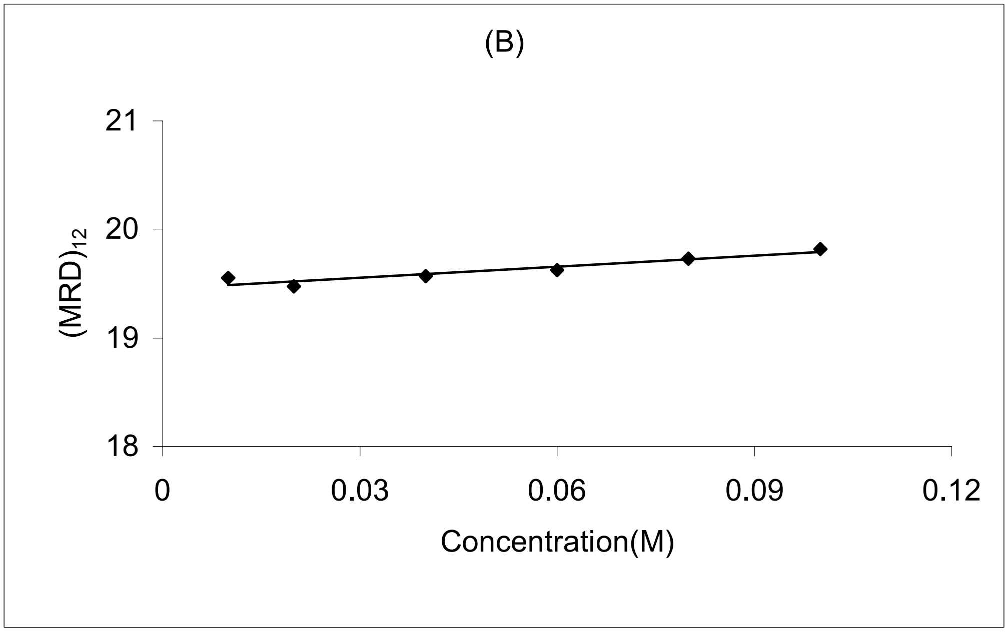
where n_{12} and ρ_{12} are refractive index and density of the solution respectively. X_1 and X_2 are the mole fractions and M_1 and M_2 are the molecular weights of the solvent and solute respectively.

Figure 3.1.2 shows the plot of calculated $(MRD)_{12}$ against concentration for NDP-1 in the two solvents DMF and THF. It is evident from figure that $(MRD)_{12}$ increases with increase in concentration. From the values of the molar refraction of solutions and pure solvent, molar refraction of Schiff bases ($(MRD)_2$) were determined by the following equation:

$$(MRD)_{12} = X_1 (MRD)_1 + X_2 (MRD)_2 \qquad \text{----- (3.1.5)}$$

Figure 3.1.2 : The variation of $(MRD)_{12}$ with concentration for NDP-1 in (A) DMF and (B) THF at 313.15 K





From the density and molar refraction $(MRD)_2$ data,, the refractive index (n) of each Schiff bases were calculated and are given in Table 3.1.3. The calculated values of refractive index are also found to be different in different solvents. This again proves that in different solvents, intermolecular interactions are different, which also affect refractive index. In some solvents, aggregation or hydrogen bonding takes place whereas in others, breakage of bonds takes place. As refractive index and molar refraction depends not only upon atomic refractions but also upon single, double or triple bonds(26), these parameters are affected by the type of interactions taking place in solution. However, it is reported that bond refraction is more effective than atomic refraction(27,28). Further, bond polarity also causes changes in molar refraction(29). This again suggests the effect of solvent on refractive index and molar refraction of the solute.

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INTRODUCTION

The addition of some solutes to a solvent will raise the temperature of the solution, while others may lower the temperature and still others will have no noticeable effect. This behavior depends on the nature of solute in a particular solvent. The heat change accompanying the dissolution of one gram mole of a solute in such large excess of a solution, so that no more heat change occurs when solvent is added further, is called heat of solution. It is equal to the difference between the energy that must be supplied to break up the crystals of the solute and the energy that is released when the solute particles are taken into solution by the solvent. If the heat is absorbed, i.e., the solution is cooler, ΔH is given a positive sign. If the heat is evolved, i.e., the solution is warmer, ΔH is given a negative sign.

Literature survey shows that thermodynamic properties of several organic and inorganic compounds have been proved to be useful for industrial applications and are studied by several workers in various pure and mixed solvents(1-15). The heat of solution for many polymer and complexes have also been reported(16-20).

In the present work, heat of solution for all the Schiff bases derived from α-naphthalamine were determined at different temperatures (303.15-323.15 K) in tetrahydrofuran (THF) and 1,4-dioxane.

EXPERIMENTAL

The solvents used for the measurements were purified and fractionally distilled prior to use by the method reported in the literature(21). All the Schiff bases were recrystalized. The solubility of each Schiff base was determined by transferring 25ml of saturated solution into a pre-weighted 50 ml beaker. The weight of beaker along with solution was taken and the solvent was evaporated to dryness till constant weight is obtained. This gives weight of solute present in 25 ml saturated solution. Three replicate measurements were carried out at a particular temperature and average value of weight was determined. The experiment was repeated at 313.15 K and 323.15 K also. Subtraction of weight of solute from the weight of solution gives the weight of solvent in 25 ml saturated solution. Finally, the moles of solute and solvent were determined in one liter of saturated solution.

RESULTS AND DISCUSSION

Tables 3.2.1 and 3.2.2 shows the solubility (N_2) of all the Schiff bases in 1,4-dioxane and THF at different temperatures. It is evident from Tables 3.2.1 and 3.2.2 that solubility of all Schiff bases increases with temperature in both the solvents. In general, the order of solubility in 1,4-dioxane is: NDP-2 > NDP-4 > NDP-3 > NDP-5 > NDP-1 > NDP-7 > NDP-8 ≈ NDP-9 > NDP-6 > NDP-10. Whereas in THF, it is of the order: NDP-10 > NDP-9 >NDP-4 > NDP-2 > NDP-8 > NDP-1 > NDP-6 > NDP-3 > NDP-7>NDP-5.

Thus, NDP-2 is more soluble in 1,4-dioxane than THF whereas NDP-10 is more soluble in THF than in 1,4-dioxane. All Schiff bases have common central moiety with different side chains. Thus, different substituents in side chains affect the solubility in different solvents which are of different polarity and dielectric constants.

The variation of solubility with temperature is given by:

$$[(\partial \ln N_2) / \partial T]_P = \Delta H_S / RT^2 \qquad \text{------(3.2.1)}$$

where N_2 is the solubility or mole fraction, T is temperature, ΔH_S is the heat of solution and R is gas constant. Integration of equation (3.2.1) between temperature limits from T and T_m gives:

$$\ln N_2 = \Delta H_S / R\,[(T - T_m) / T.T_m] \qquad \text{------(3.2.2)}$$

where T and T_m are the temperature of the experiment and melting temperature of the Schiff bases. Figure 3.2.1 shows the variation of in N_2 with 1/T for NDP-7 in THF and 1,4-dioxane. From the slope of the plot, heat of solution was calculated for all the solutions and is reported in Tables 3.2.1 and 3.2.2. It is observed that the values of heat of solution are positive for all the Schiff bases. Further, all the values increases with temperature in both the solvents. The positive values of heat of solution indicate endothermic behavior of these bases in both the solvents.

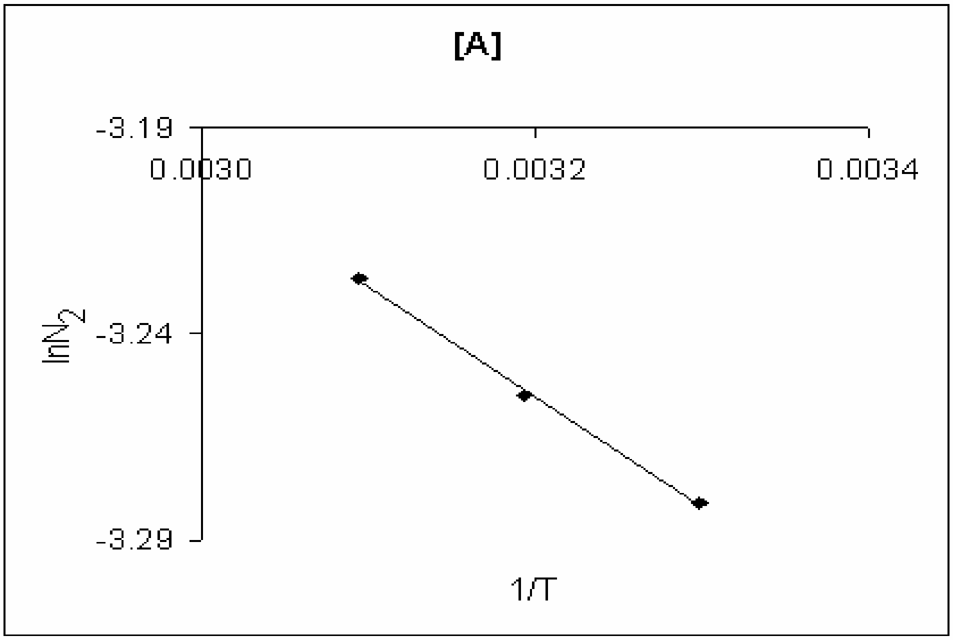
Table 3.2.1: The solubility and heat of solution of Schiff bases in 1, 4- dioxane at different temperatures.

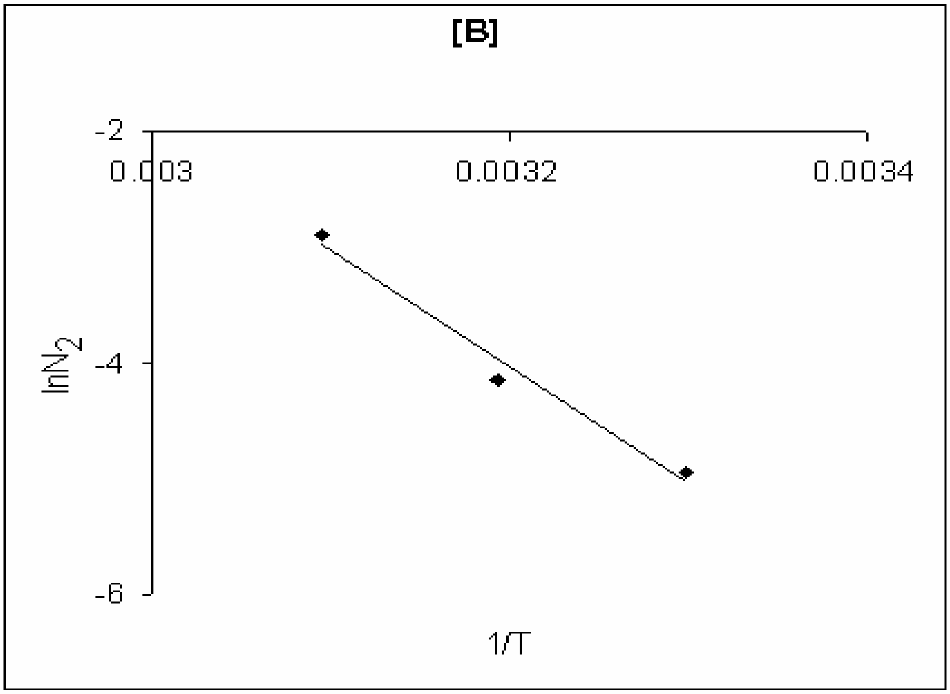
Temp. K	**N_2 $.10^3$**	**ΔH_s (Kcal/mol)**	**N_2 $.10^3$**	**ΔH_s (Kcal/mol)**
	NDP-1		**NDP-6**	
303.15	0.0598	11.0504	0.0257	6.0460
313.15	0.0603	13.9105	0.0267	6.5579
323.15	0.0647	19.0964	0.0268	7.2009
	NDP-2		**NDP-7**	
303.15	0.1094	8.1827	0.0376	8.4892
313.15	0.1146	9.9640	0.0386	9.7688
323.15	0.1151	12.8927	0.0396	11.3739
	NDP-3		**NDP-8**	
303.15	0.0643	11.9195	0.0247	6.3764
313.15	0.0708	12.0500	0.0277	6.7965
323.15	0.0715	12.4563	0.0326	7.1683
	NDP-4		**NDP-9**	
303.15	0.0622	11.8183	0.0269	14.1845
313.15	0.1122	12.0219	0.0288	17.5625
323.15	0.1176	16.1829	0.0289	23.3247
	NDP-5		**NDP-10**	
303.15	0.0585	6.8945	0.0054	16.0092
313.15	0.0619	7.7535	0.0054	19.1172
323.15	0.0668	8.7595	0.0087	21.2565

Table 3.2.2: The solubility and heat of solution of Schiff bases in THF at different temperatures.

Temp. K	N_2 .10^3	ΔH_s (Kcal/mol)	N_2 .10^3	ΔH_s (Kcal/mol)
	NDP-1		**NDP-6**	
303.15	0.0410	12.5268	0.0298	5.0860
313.15	0.0527	14.5776	0.0518	6.4285
323.15	0.0558	18.9634	0.0523	6.4325
	NDP-2		**NDP-7**	
303.15	0.0399	11.9134	0.0720	10.7135
313.15	0.0461	14.1525	0.0159	12.4310
323.15	0.0920	14.2271	0.0550	12.5960
	NDP-3		**NDP-8**	
303.15	0.0329	10.4782	0.0208	6.6725
313.15	0.0381	12.9876	0.0562	6.6881
323.15	0.0509	13.3570	0.0844	7.0530
	NDP-4		**NDP-9**	
303.15	0.1092	9.618	0.0784	9.9872
313.15	0.0478	16.7074	0.0876	10.5750
323.15	0.0778	19.3045	0.1242	13.7275
	NDP-5		**NDP-10**	
303.15	0.0117	10.8037	0.0970	8.3387
313.15	0.0426	13.7060	0.1164	9.2997
323.15	0.0428	13.6850	0.1466	10.1863

Fig. 3.2.1 : The variation of ln N_2 against 1/T for NDP-7 [A] THF and [B] 1,4-dioxane.





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INTRODUCTION

Electronic conductance is a property of ionic solutions which have been used as direct and indirect method of physicochemical analysis. By measuring conductance, the equilibrium constant, degree of hydrolysis, solubility products, dissociation constants, rate of reactions, basicity of organic acids, relative strength of two acids or bases and other properties of electrolytic solutions can be determined. An indirect conductometric screening method have also been reported to the antibiotic residues in bowing kidneys(1). Various workers have studied conductance of organic and inorganic compounds in aqueous and non aqueous solutions(2-12). Further, conductance study of association phenomena of some metal complex solutions at different temperatures have also been studied by different workers(13-17). Nandi and Hazra reported conductance of alkali metal chlorides and bromides in aqueous binary mixture of 2-methoxy ethanol(18-19). Conductivity in crown ether was also reported by Allcock and co-workers(20). Later on, Rani and Panigrahi also used conductometric technique to study solubilization of dibasic acids in sodium lauryl sulphate micelles(21). Tasic et al(22) measured conductance of aqeous solutions of some cyclo hexyl sulfamates. However, scanty work has been reported on Schiff bases(23-27).

In the present chapter, conductance of some Schiff base of α-naphthylamine are measured in dimethylformamide (DMF) and dimethylsulphoxide (DMSO) at 313.15 K.

EXPERIMENTAL

All the solvents used, were distilled prior to use. The solutions of different concentrations were prepared for each Schiff base in DMF and DMSO and the conductance of each solution was measured by using Systronics Conductivity Meter (Model No. 306) having cell constant 0.84 cm^{-1} at 313.15 K The conductance of each solution was corrected by subtracting the conductance of pure solvent.

RESULTS AND DISCUSSION

The measured conductance (C), after correction, was used to determine the specific conductance (κ), which is used for the calculation of equivalent conductance (λ_C). The following equations are used:

$$C = \kappa / \theta \qquad \text{-----(3.3.1)}$$

$$\lambda_C = 1000\ \kappa / c \qquad \text{----- (3.3.2)}$$

where c is the concentration (g.equi/lit).

The equivalent conductance of all Schiff bases in DMF and DMSO solutions at 313.15 K are reported in Tables 3.3.1 and 3.3.2 along with uncorrected measured conductance values. It is evident from Tables 3.3.1 and 3.3.2 that for all Schiff bases, equivalent conductance increases with dilution in both the solvents. However, at lower concentration range, there is change in the order in some cases in both the solvents.

It is observed that in DMF, overall equivalent conductance is maximum for NDP-2 over the wide range of concentration where as minimum λ_C is observed in NDP-6. In DMSO, no regular trend is observed. Overall, highest λ_C value is observed in NDP-5 whereas low λ_C is observed in NDP-2 and NDP-7. This ensures that conducting behavior of Schiff base depends on solvent and nature of solute under study rather than on its molecular weight (28).

In the studied Schiff bases, central moiety is same but different substituents are present as side chain. These different substituents interact differently in different solvents, which causes different conductance in different solvents. The dielectric constant and dipole moment of solvents play an important role in conductance of solutions.

The equivalent conductance is plotted against √c for all Schiff bases in both DMF and DMSO (Figures 3.3.1). It is clear from these figures that almost all Schiff bases are weak electrolytes in nature except NDP-1 and NDP-6.

Table 3.3.1: The conductance (C) and equivalent conductance (λ_C) of Schiff bases in DMF at 313.15 K.

Conc. c (gm/lit)	$C.10^5$ $(\Omega)^{-1}$	λ_C $(cm^2/\Omega.equiv.)$	$C.10^5$ $(\Omega)^{-1}$	λ_C $(cm^2/\Omega.equiv.)$	$C.10^5$ $(\Omega)^{-1}$	λ_C $(cm^2/\Omega.equiv.)$	$C.10^5$ $(\Omega)^{-1}$	λ_C $(cm^2/\Omega.equiv.)$	$C.10^5$ $(\Omega)^{-1}$	λ_C $(cm^2/\Omega.equiv.)$
	NDP-1		**NDP-2**		**NDP-3**		**NDP-4**		**NDP-5**	
0.00	2.2	-	2.2	-	2.2	-	2.2	-	2.2	-
0.002	2.5	1.26	3.9	7.14	3.3	4.62	3.0	3.36	3.0	3.36
0.004	2.8	1.26	4.2	4.20	3.4	2.52	3.2	2.10	3.2	2.10
0.006	3.0	1.12	4.4	3.08	3.5	1.82	3.3	1.54	3.3	1.54
0.008	3.2	1.05	4.5	2.42	3.5	1.37	3.4	1.26	3.7	1.58
0.01	3.3	0.84	4.7	2.10	3.6	1.01	3.4	1.01	4.1	1.60
0.02	3.9	0.72	5.1	1.22	3.7	0.55	3.5	0.55	6.1	1.63
0.04	5.1	0.61	6.2	0.84	3.7	0.32	3.8	0.34	12.0	2.06
0.06	5.5	0.46	6.8	0.64	3.8	0.20	4.1	0.27	14.7	1.76
0.08	5.6	0.37	6.9	0.49	3.9	0.13	4.3	0.22	18.5	1.71
0.10	7.7	0.46	8.6	0.54	4.1	0.08	4.4	0.18	21.8	1.65
	NDP-6		**NDP-7**		**NDP-8**		**NDP-9**		**NDP-10**	
0.002	2.5	0.84	3.2	4.20	3.6	5.88	3.1	3.78	3.2	4.20
0.004	2.6	0.84	3.3	2.31	4.0	3.78	3.2	2.10	3.3	2.31
0.006	2.7	0.70	3.4	1.68	4.3	2.94	3.2	1.40	3.3	1.54
0.008	2.8	0.63	3.5	1.37	4.6	2.52	3.3	1.16	3.3	1.16
0.01	2.8	0.50	3.6	1.18	4.9	2.27	3.5	1.01	3.2	0.84
0.02	3.1	0.38	3.9	0.71	8.3	2.56	3.7	0.59	3.3	0.46
0.04	3.2	0.21	4.0	0.25	8.5	1.32	3.9	0.36	3.4	0.25
0.06	3.4	0.17	4.3	0.29	10.6	1.18	4.5	0.32	3.7	0.21
0.08	3.9	0.18	5.8	0.38	11.9	1.02	5.0	0.29	3.9	0.18
0.10	4.1	0.16	7.0	0.40	13.1	0.92	8.8	0.55	9.0	0.57

Table 3.3.2 : The conductance (C) and equivalent conductance (λ_C) of Schiff bases in DMSO at 313.15 K.

Conc. c (gm/lit)	$C.10^5$ $(\Omega)^{-1}$	λ_C (cm^2/Ω.equiv.)	$C.10^5$ $(\Omega)^{-1}$	λ_C (cm^2/Ω.equiv.)	$C.10^5$ $(\Omega)^{-1}$	λ_C (cm^2/Ω.equiv.)	$C.10^5$ $(\Omega)^{-1}$	λ_C (cm^2/Ω.equiv.)	$C.10^5$ $(\Omega)^{-1}$	λ_C (cm^2/Ω.equiv.)
	NDP-1		**NDP-2**		**NDP-3**		**NDP-4**		**NDP-5**	
0.000	0.7	-	0.7	-	0.7	-	0.7	-	0.7	-
0.002	0.8	0.42	1.0	1.26	1.0	1.26	1.0	1.26	1.2	2.10
0.004	1.0	0.63	1.1	0.84	1.2	1.05	1.2	1.05	1.3	1.05
0.006	1.1	0.56	1.3	0.84	1.5	1.12	1.4	0.98	1.4	0.98
0.008	1.2	0.53	1.4	0.74	1.8	1.15	1.5	0.84	1.5	0.84
0.01	2.0	0.56	1.5	0.76	2.6	1.60	1.6	0.67	1.7	0.84
0.02	2.1	0.59	1.6	0.38	2.8	0.88	1.8	0.46	1.9	0.50
0.04	2.6	0.40	1.8	0.23	3.0	0.48	2.0	0.27	2.0	0.27
0.06	3.0	0.32	1.9	0.17	3.1	0.34	2.5	0.25	3.0	0.32
0.08	3.4	0.28	2.5	0.19	3.2	0.26	3.1	0.25	3.1	0.25
0.10	3.6	0.24	3.1	0.20	4.1	0.29	3.8	0.26	4.7	0.34
	NDP-6		**NDP-7**		**NDP-8**		**NDP-9**		**NDP-10**	
0.002	0.9	0.84	0.8	0.42	0.9	0.84	0.9	0.84	0.8	0.42
0.004	1.0	0.63	0.9	0.42	1.5	1.68	1.0	0.63	0.9	0.21
0.006	1.1	0.56	1.0	0.42	2.7	2.80	2.5	2.52	1.0	0.28
0.008	1.2	0.42	1.3	0.63	3.3	2.73	2.6	1.99	1.1	0.42
0.01	1.3	0.50	1.6	0.76	4.0	2.77	3.1	2.02	1.5	0.50
0.02	1.4	0.29	1.7	0.42	4.1	1.43	3.9	1.34	2.7	0.84
0.04	1.5	0.16	1.9	0.25	4.3	0.76	4.9	0.88	3.5	0.59
0.06	1.6	0.13	2.0	0.18	5.3	0.64	5.3	0.64	4.9	0.59
0.08	1.7	0.11	2.5	0.19	5.9	0.55	6.4	0.60	5.1	0.46
0.10	1.9	0.10	3.5	0.24	6.0	0.61	7.0	0.53	6.3	0.47

Figure 3.3.1 : Variation of equivalent conductance (λc) with √c for Schiff bases in DMF and DMSO at 313.15 K.

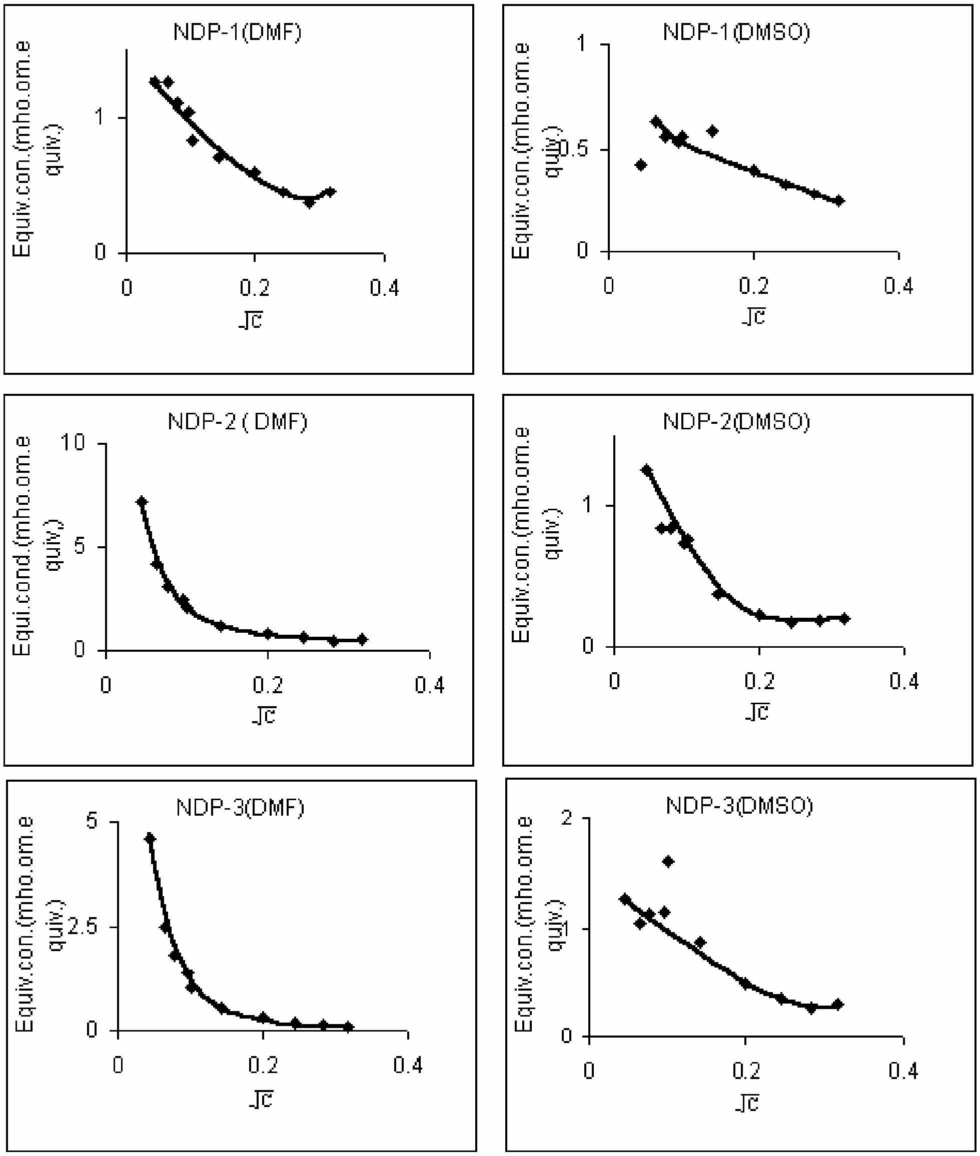


Figure 3.3.1 (contd…)

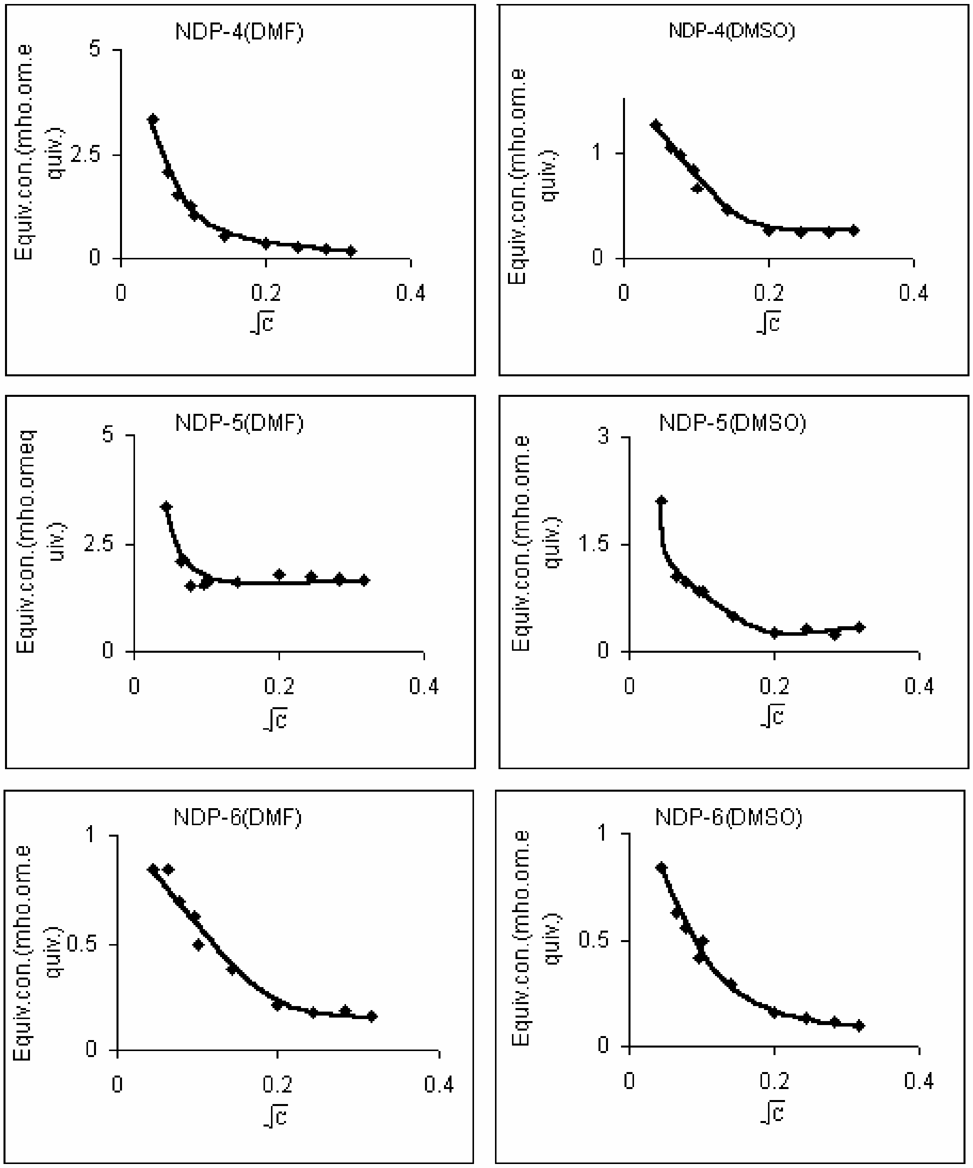
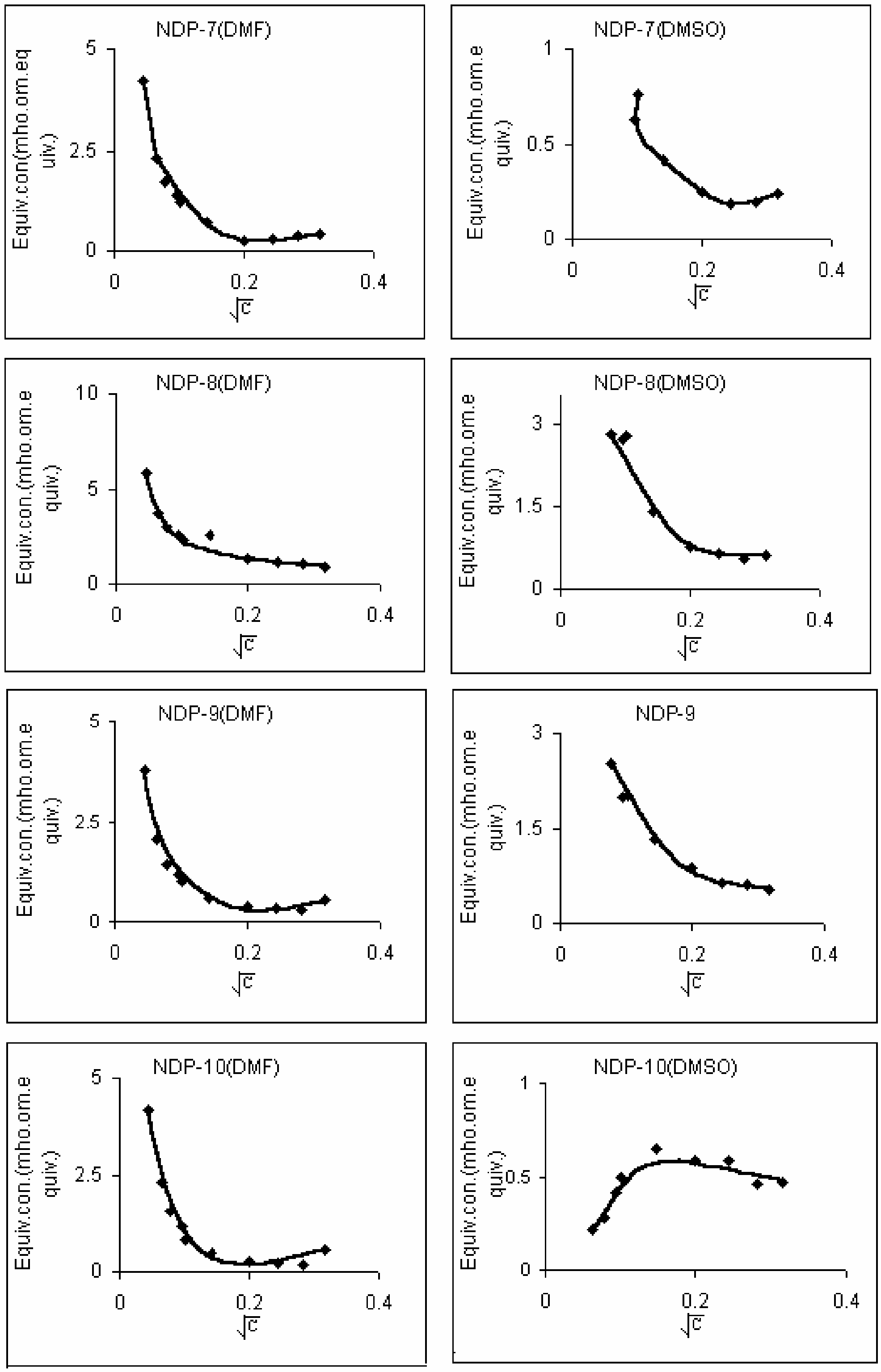


Figure 3.3.1 (contd…)



NDP-1 has benzaldehyde as side chain whereas NDP-6 contains p-hydroxy benzaldehyde as side chain.

For weak electrolytes, the equivalent conductance at infinite dilution(λ_0) can not be calculated by extrapolation of λ_C verses $\sqrt{c}$ plots. However, for NDP-1, NDP-4 and NDP-6, values of λ_0 are evaluated by extrapolation and are given in Table 3.3.3.

By an alternative procedure$^{(12)}$, λ_0 values were tried to calculate for weak electrolytes. In this procedure, λ_0 is related to conductivities by using the equation:

$$\kappa = \kappa_0 + \lambda_0 c + c\,\phi(c) \qquad \text{.... (3.3.2)}$$

where κ and κ_0 are the electrolytic conductivities of the solutions and solvent respectively. c is the equivalent concentration and the function $\phi(c)$ denotes the effect of interionic interactions.

The differential form of equation (3.3.2) is:

$$d\kappa/dc = d\kappa_0/dc + \lambda_0 + d/dc\,[c\,\phi(c)] \qquad \text{....(3.3.3)}$$

The slope $d\kappa/dc$ of the plot of κ verses c approximates the limiting conductivity (λ_0), provided other derivatives $d\kappa_0/dc$ and $d[c\phi(c)]/dc$ in equation (3.3.3) are neglected as compared to λ_0.

Figures 3.3.2 show the variation of corrected conductance with concentration for all Schiff bases in both DMF and DMSO at 313.15 K. It is clear from the figures that in lower concentration range, conductance varies almost linearly with concentration for all the Schiff bases, At higher concentrations, non-linearity is observed for most of the Schiff bases in both the solvents.

As interionic interactions are present in all the systems over the wide range of concentrations, so the derivative $d[c\phi(c)]/dc$ cannot be ignored in

Figure 3.3.2 : Variation of conductance with concentration for Schiff bases in DMF and DMSO at 313.15 K

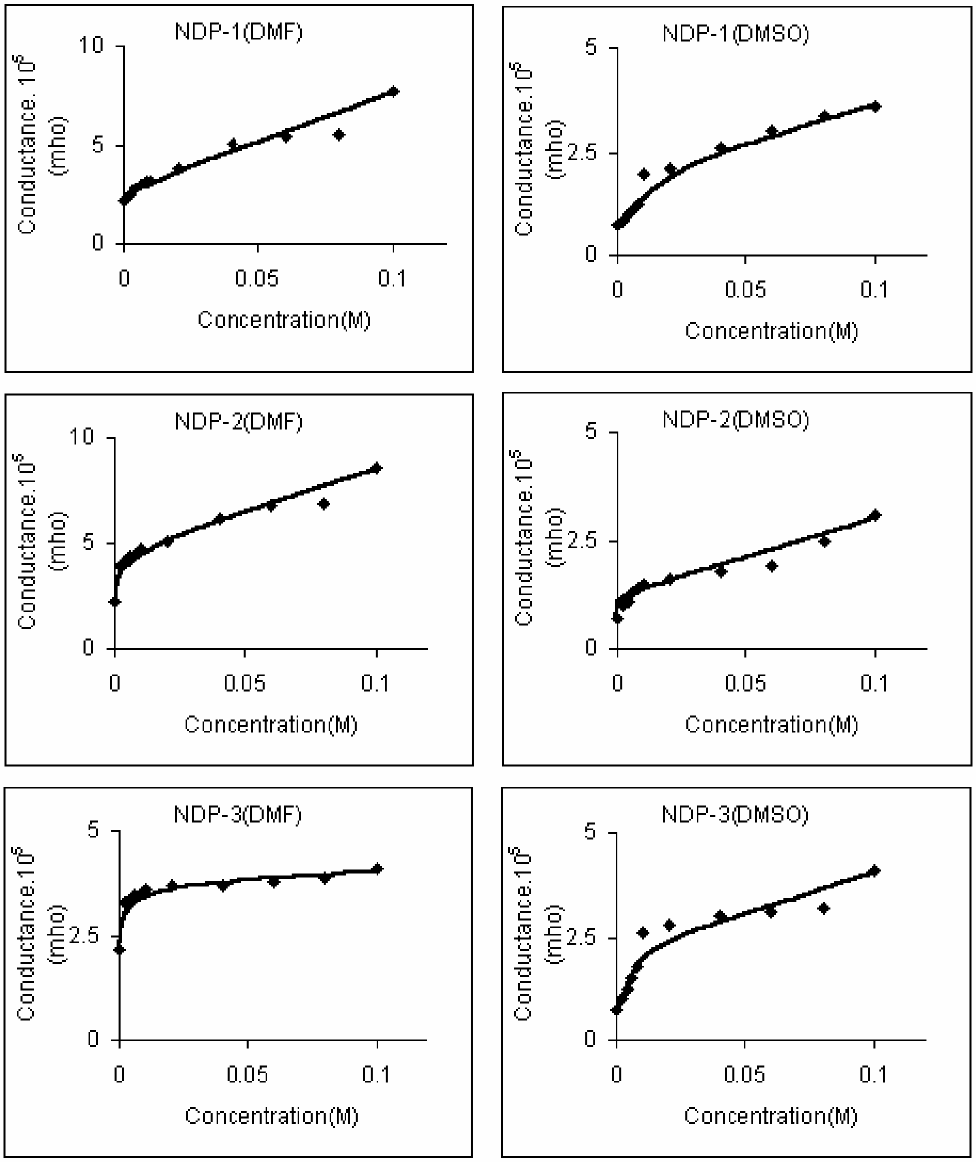


Figure 3.3.2 contd...

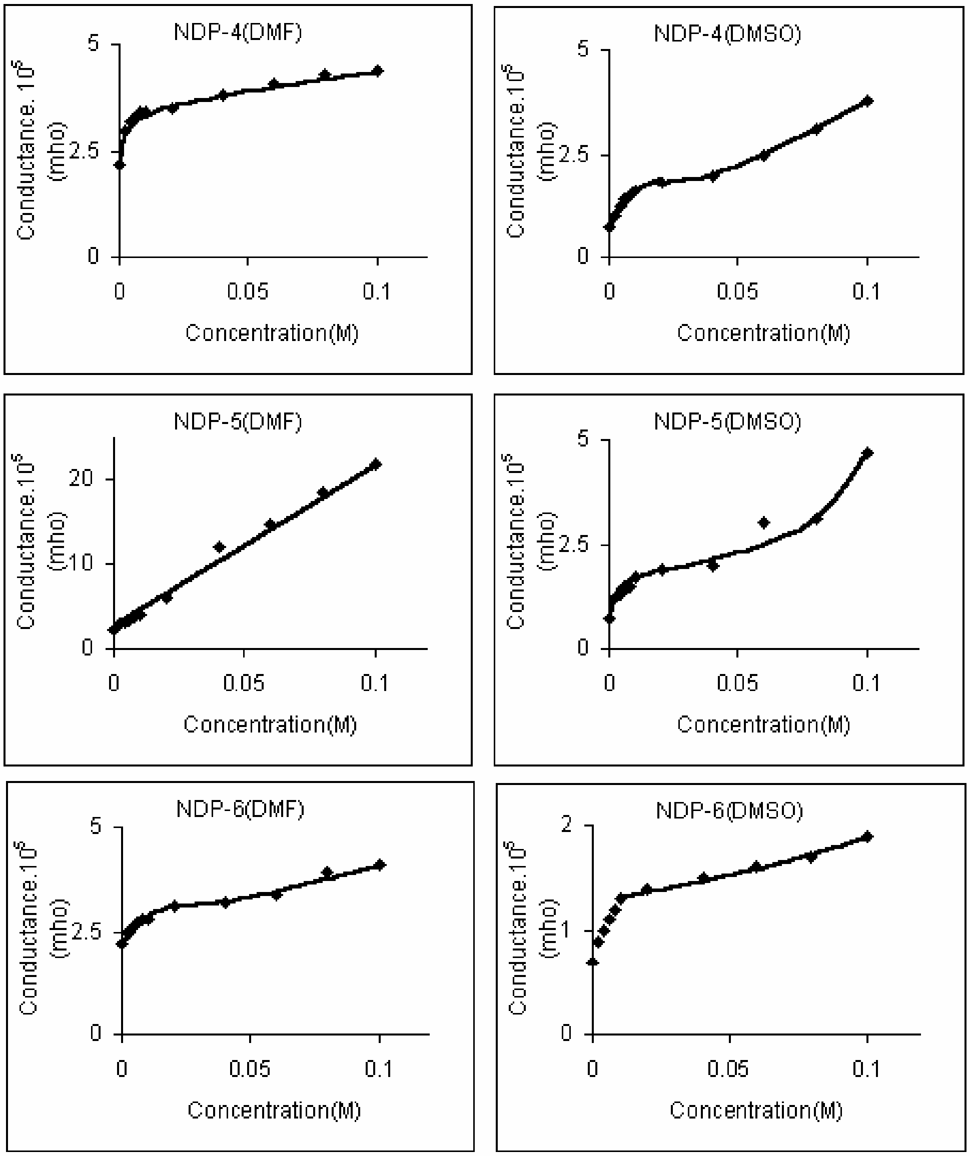


Figure 3.3.2 contd..

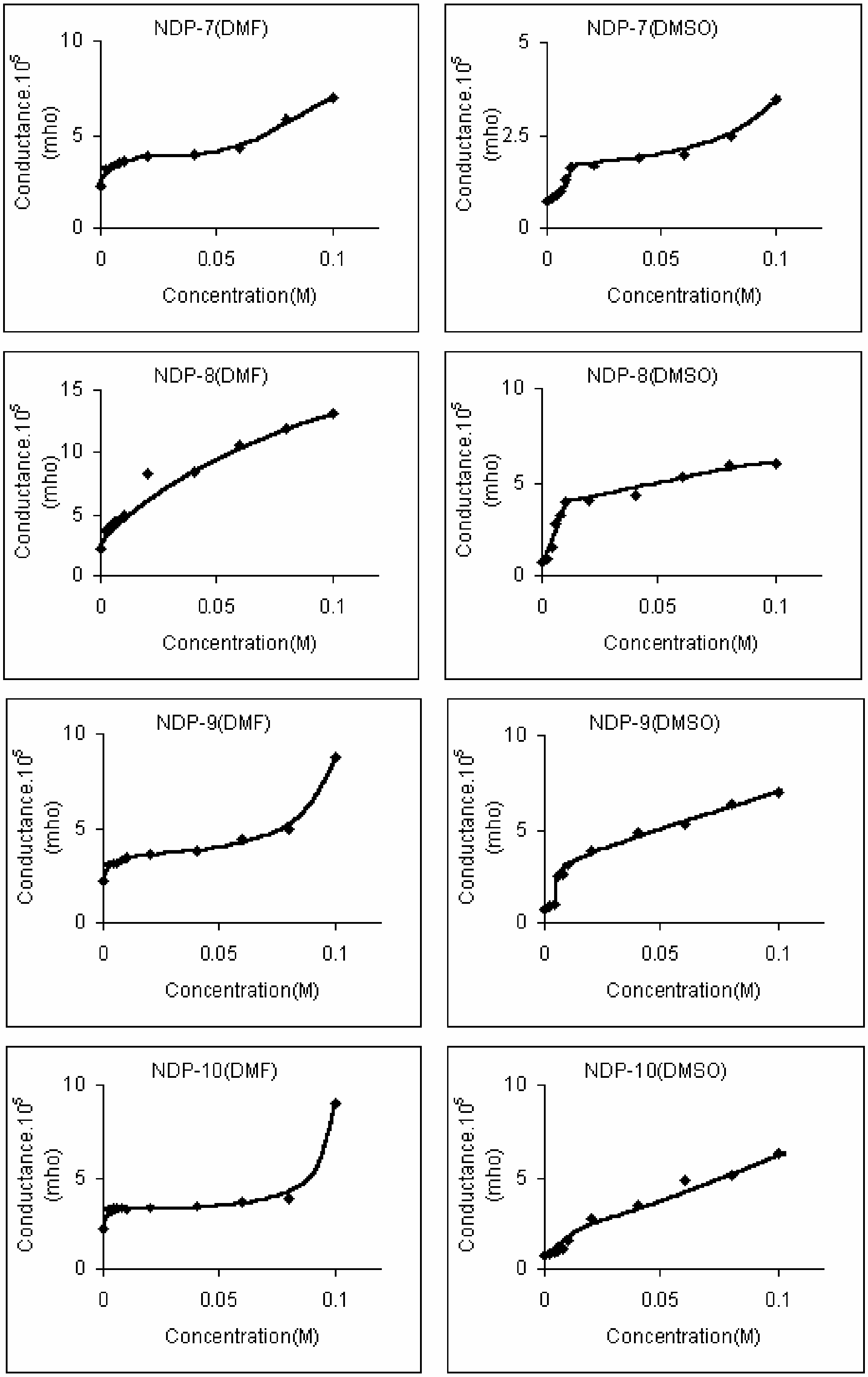


Table 3.3.3 : The limiting equivalent conductance(λ_0) for all Schiff bases in DMF and DMSO at 313.15 K

Comp. Code	DMF		DMSO	
	λ_0 ($cm^2/\Omega equiv.$)	$\lambda_0 \times 10^3$ ($cm^2/\Omega equiv.$) calc. by eq. (2)	λ_0 ($cm^2/\Omega equiv.$)	$\lambda_0 \times 10^3$ ($cm^2/\Omega equiv.$) calc. by eq. (2)
NDP-1	1.50	1.45	-	0.69
NDP-2	-	1.15	1.6	1.17
NDP-3	-	0.50	1.5	1.20
NDP-4	6	0.80	1.6	1.00
NDP-5	-	1.00	-	0.60
NDP-6	1.1	0.60	1.2	0.50
NDP-7	-	0.50	-	0.40
NDP-8	-	1.67	-	0.50
NDP-9	-	0.50	4.0	2.50
NDP-0	-	0.20	-	1.00

Comparison to λ_0. However, limiting equivalent conductivities were evaluated from the limiting slope of small linear portions of the κ verses c curve, assuming that the interionic interactions in this range of concentration are limited. For all the systems, the calculated λ_0 values are given in Table 3.3.3.

It is evident from Table 3.3.3 that the λ_0 values calculated from λ_C verses $\sqrt{c}$ plots are quite different than those calculated from equation (3.3.2) for NDP-4 and NDP-6. Thus, for these Schiff bases, equation (3.3.2) is not valid for the evaluation of λ_0.

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INTRODUCTION

The dissociation constants are used to measure the strength of acid and bases. They are also known as acidity constant, ionization constant or formation constant.

Various physical methods have been reported(1-5) for the measurement of dissociation constant of acids such as potentiometry including pH metry, spectrophotometry, conductometry, solubility measurements, cryoscopy etc.

For very weak acids having pK range 11 to 14, electrical conductance is used for the measurement of dissociation constant but it is time-consuming(6). For very high or very low acid strengths, spectrophotometer method is considered to be an ideal method but this method is also more time consuming. It is applicable if at least one of the species at equilibrium absorbs characteristically in the ultraviolet or visible region and the relevant ionic species show absorption maxima at different wavelengths.

The use of Raman spectra and nuclear magnetic constants are also known to be used for a number of acids, which are regarded as strong in aqueous solution (7).

By using UV visible and multinuclear NMR spectroscopy, formation constant of some compounds have also been studied(8).

The solubility method for determining dissociation constant is not so accurate as conductometry, spectrophotometery or potentiometry, but is useful in those cases, where the substance is too insoluble in water for conductance or potentiometric methods or the molecular or ionic ultraviolet spectra are either too similar or totally lacking.

Recently, Ikuta and Hirokawa(9) have reported an apparatus and method for determining acid dissociation constant using electrophoresis.

Potentiometry is most popular method used for the determination of dissociation constants of acids of pK_a range from 2 to 11 units(6). Further, it is economical in time. For this measurement, glass and calomel electrodes have been used and carbonate free potassium hydroxide is the best alkali to use as a titrant.

The potential generated by the hydrogen ions, in the solution of an acid in a given medium is measured by an electronic potentiometer assembly. The relationship between the potential of glass electrode and the pH of the solution has the general form:

$$-\log [H^+] = pH = E_0 - E_c / 0.0591 \text{ at } 25^0C$$

where E_0 is the observed potential and E_c is the potential of the calomel electrode. The various terms, in above equation change with time. So, this electrode cannot be used as a primary standard. However, it provides a convenient way of comparing the pH of a series of solutions. So, it is calibrated before and after use with a pair of known buffers, the pH of one of which must lie near to the pH region to be measured. The calibrated pH-meter gives quite accurate results.

The activity of the hydrogen ions is measured directly by pH metry. So, one can get reliable values of dissociation constant by this method. However, there are certain difficulties in mixed aqueous media and non-aqueous media.

The dissociation or formation constant provides useful information about structure, tautomeric equilibria, solvent-solute interactions etc(10). Further, the nature of the functional groups can be determined by simple comparison of acidity or dissociation constant of the unknown compound with those of known compounds.

For water-insoluble compounds, the formation constant and other thermodynamic properties are measured in purely non-aqueous organic solvent or in a mixture of two solvents, one of which may be water. A solvent mixture containing water and water-miscible organic solvent is known as mixed aqueous medium. A number of works has been done in non-aqueous and mixed-aqueous media (11-17).

A Literature survey shows that the dissociation constant of many substances have been studied by various workers(18-23). The dissociation constants of some alkyl pyridines in aqueous solution have also been reported (24). Marshall and Grunwald(25) have measured thermodynamic parameters for the ionization reactions of acetic and chloroacetic acid in ethanol – water mixture. The dissociation constants of acetic acid, tri chloro acetic acid, benzoic acid and salicylic acids in aqueous ethanol have also been studied by potentiometry(26). The dissociation constants of many other compounds have also been studied in mixed solvents(27-31). Muhammad et al.(32) have studied dissociation constant of long chain fatty acids in methanol water and ethanol water mixtures. The effect of solvent on formation constant was also studied by Fedorov et al(33). The acidity constants of benzidine and N, N- dimethylbenzidine have also been reported(34). Donoso et al also reported ionization constants of some Schiff bases(35). Gaus et al investigated formation constant by a computer programme(36). Cao et al studied dissociation constant of some novel polydentate ligands(37). Boraei and Ahmed (38) studied formation constant of transition metal ion mixed complexes of tricine and 8-hydroxy quinoline. Ghaseni et al.(39) studied acidity constant of 4-(2-pyridylazo)resorcinol in acetonitrile-water mixtures. The acidity constants of some tetradentate tripodal ligands and their complexes have also been reported(40). Partanen and Covington determined the dissociation constants of propionic acid and n-butyric acids by using electrochemical cell(41). Dlugosz and Antosiewicz studied the impact of protonation equilibria on protein structure(42).

In the present work, the dissociation constant of some Schiff bases are studied in 1, 4- dioxane-water (60:40 v/v) mixture at 313.15 K.

EXPERIMENTAL

The chemicals used were of B.D.H Analar grade. All solutions used for the titration are prepared using distilled water. Following are the concentrations of the solutions used for the titration.

Solutions	**Concentration (M)**
Nitric acid	0.1
Sodium hydroxide	0.5, 0.1
Sodium nitrate	1.0
Schiff base (in 1,4-dioxane)	0.1

Standardization of nitric acid and sodium hydroxide were done by titrating with 0.1 N NaOH and 0.05 M succinic acid solution respectively.

The 1, 4-dioxane used was of S. Merck and was purified by the reported method [50].

0.05 M potassium hydrogen phthalate and 0.01 M Borax buffer solutions used for the calibration of pH meter.

A Systronic pH meter (Model No. EQ 664) was used for the pH determination. The systronic glass electrode and a saturated calomel electrode were used as indicator and reference electrodes respectively.

Before measurement, the pH meter was calibrated with buffer solution of known pH.

Calvin Bjerrum pH titration

The following sets of mixtures were prepared for titration:

(I) 0.8 ml HNO_3 (0.1M) + 11.20 ml water + 24.00 ml 1, 4-dioxane + 4.0 ml $NaNO_3$ (1.0 M).

(ii) 0.8 ml HNO_3 (0.1M) + 11.20 ml water + 22.0 ml 1, 4-dioxane + 2.0 ml ligand solution (0.1M) + 4.0 ml $NaNO_3$ (1.0 M).

Thus, total volume (V^0) in each set = 40.0 ml and 1, 4-dioxane: water ratio 60:40 (v/v).

The above mentioned solutions were allowed to attain a constant temperature (313.15 K) and then titrated against standard NaOH solution (0.5 M) under an inert atmosphere of nitrogen. The change in the pH of the solution with each addition of alkali was recorded and is given in Tables 3.4.1 and 3.4.2.

Theory

In the present work, the ligands are Schiff bases of two general types: HL and H_2L. NDP-2 and NDP-6 bases are of H_2L type whereas other bases are of HL type. Thus, the equilibria are,

$$L + H \leftrightarrow HL$$

and

$$L + H \leftrightarrow HL$$

$$HL + H \leftrightarrow H_2L$$

In general, these equations can be represented as:

$$LH_{j-1} + H \leftrightarrow LH_j$$

The thermodynamic proton-ligand stability constant (TK_j^H)is given by:

$$TK_j^H = \frac{\left[LH_j\right]}{\left\{\left[LH_{j-1}\right]\left[H\right]\right\}} \qquad \text{.....(3.4.1)}$$

TK_j^H is reciprocal of the thermodynamic dissociation constant of the acid LH_j dissociating as:

$$LH_j = LH_{j-1} + H$$

The overall thermodynamic proton-ligand stability constant β_j^H is given by:

$$T\beta_j^H = [LH_j] / [L].[H] \qquad \text{..... (3.4.2)}$$

and it refers to the reaction:

$$L + JH \leftrightarrow LH_j$$

The stoichiometric proton-ligand stability constant is given by:

$$K_j^{\ H} = \frac{\left[LH_j\right]}{\left\{\left[LH_{j-1}\right]\left[H\right]\right\}} \qquad \text{..... (3.4.3)}$$

and

$$\beta_j^{\ H} = \frac{\left[LH_j\right]}{\left[L\right]\left[H\right]^j} \qquad \text{........ (3.4.4)}$$

In the presence of several complexes, it is difficult to determine these thermodynamic constants, so, an inert electrolyte is used to determine the stability constant in a particular salt medium. Sodium nitrate is mostly preferred as supporting electrolyte, because of very slight complexing tendency of nitrate ion. Generally, the competition between nitrate ion and the ligand under study is of minor importance. The molar concentrations are used in place of activities.

For the determination of dissociation constants, Bjerrum(43) introduced a relation for the determination of **n**$_H$, which is defined as average number of hydrogen bound to each ligand.

$\bar{n}_H$ = {K_1^H [H] + 2K_1^H K_2^H $[H]^2$ + ...JK_1^H K_2^H [H] ... K_j^H $[H]^j$} / {1 + K_1^H[H] + K_1^H K_2^H $[H]^2$ + ... K_1^H K_2^H ..... K_j^H $[H]^j$ .... (3.4.5)

From equation (3.4.4), we can write

$$\bar{n}_H = \Sigma\, j\, \beta_j^H\, [H]^j \,/\, \Sigma\, \beta_j^H\, [H]^j \quad ; (\beta_0^H = 1) \qquad \text{....... (3.4.6)}$$

Equation (3.4.6) is called Bjerrum formation function of the system.

The dissociation or formation constants can be evaluated from experimental data by the following three steps: (i) evaluation of formation curve of the system (ii) calculation of stoichiometric K`s of the system by direct solution of the formation function and (iii) conversion of stoichiometric constants into thermodynamic constants.

When the system consists of a ligand, which is a conjugated base of a weak acid, the "Bjerrum-Calvin pH titration technique" introduced by Bjerrum(43) has been widely used. In this technique, concentration of H^+ ions is measured potentiometrically. Thus, a large amount of data can be obtained in a short period of time. However, the Irving and Rossotti method(44) has some advantages such as: (i)This method is valid for both pure water and for the mixed solvents. (ii) In this method, it is not necessary to convert the pH-meter reading in to stochiometric hydrogen ion concentration. (iii) It is not necessary to know the stochiometric concentration of neutral salt added to maintain the ionic strength constant.

Due to these advantages, this method is used in the present work. In this method, the pH-meter is standardized using an aqueous buffer and the meter reading B is plotted against volume of alkali used to titrate:

(1) a mixture containing a mineral acid, a chelating agent and a neutral electrolyte to keep ionic strength constant.

(2) a mixture same as above but without the chelating agent.

The possible hydrolysis reactions are ignored because (i) fresh reagent solutions were used in pH titrations (ii) titration times were of the order of one hour (iii) there were no observable drifts with time in the meter readings and (v) the concentrations of the mineral acid or alkali in the solutions were small.

After each addition of standard alkali, the pH meter reading (B) is noted using a glass electrode-saturated calomel electrode combination. The same total initial volume of the mixture is used in the above two titrations at the same constant temperature under an inert atmosphere of purified nitrogen. The same standard alkali is used in the two titrations. The titration curves obtained in the above two titrations are designated as the reagent or ligand titration curve and the acid titration curve respectively.

The use of a pH-meter calibrated with an aqueous buffer is restricted to aqueous solutions. For the mixed aqueous media, especially aqueous dioxane solutions, Van Uitert and Haas(45) gave a relation between the glass electrode reading B in dioxane-water medium and the stoichiometric hydrogen ion concentration of the same in mixture of varied composition and ionic strength. They reported the relation:

$$- \log [H] = B + \log f + \log U^0_H \qquad \text{………} (3.4.7)$$

where f is the activity coefficient of the hydrogen ions in the solvent mixture under consideration at the same temperature and ionic strength, and U^0_H is a correction factor at zero ionic strength, which depends only on the solvent composition and temperature. U^0_H is taken as unity in aqueous media. The values of U^0_H and f are reported in literature(45). The meter reading in any aqueous dioxane solution can, therefore, be converted into hydrogen ion concentration using equation (3.4.7), provided that correction factor for the appropriate solvent, salt medium, and temperature, has been determined.

Equation (3.4.7) can be written as:

$$1/\text{ antilog } B = [H]\, f\, U^0_H \qquad \ldots\ldots\ldots (3.4.8)$$

$$\therefore\ [H] = 1/\, f\, U^0_H \,.\, [1/\text{antilog } B] \qquad \ldots\ldots\ldots\ldots (3.4.9)$$

Substituting for [H] in equation (3.4.5) we get,

$$\bar{n}_H = (K_1^H/f\, U^0_H)[1/\text{antilog } B] + \ldots + ((JK_1^H K_2^H \ldots K_J^H)/(f\, U^0_H)^J)[1/\text{antilog } B]^J/(1+K_1^H/f\, U^0_H))[1/\text{antilog } B]+ \ldots + ((K_1^H K_2^H \ldots K_J^H)/(fU^0_H)J)[1/\text{antilog} B] \qquad \ldots\ldots\ldots (3.4.10)$$

$$K_j^H = f\, U^0_H \,.\, p_{Kj}^H \qquad \ldots\ldots\ldots (3.4.11)$$

$$\beta_j^H = f\, U^0_H \,.\, p_{\square j}^H \qquad \ldots\ldots\ldots (3.4.12)$$

The proton-ligand stability constant, p_{Kj}^H can be obtained by the following methods:

1. Interpolation at half $\bar{n}_H$ values:

At the following $\bar{n}_H$ values, log K_1 and log K_2 can be determined:

$$\log K_1 = (\bar{n}_H)_{0.5} \qquad \ldots\ldots\ldots (3.4.13)$$

$$\log K_2 = (\bar{n}_H)_{1.5} \qquad \ldots\ldots\ldots (3.4.14)$$

2. Mid point slope method:

For H_2L type ligands:

$$K_1 K_2 [L]^2 = 1$$

or $$\log K_1 K_2 = 2 \, pL_1 \quad \text{……….} \ (3.4.15)$$

From the measured mid-point slope, D, the ratio K_1/K_2 can be calculated by eq. (3.4.16):

$$D = -4.606 / (2 + \sqrt{(K_1/K_2)}) \quad \text{……….} \ (3.4.16)$$

The individual values of K_1 and K_2 were obtained by using K_1/K_2 values and relation (3.4.15).

3. The least square method [54]:

This method is based on the following equation:

$$[\bar{n}_H / (\bar{n}_H - 1)] \, . \, [1/[L]] = [(2- \bar{n}_H \ [L])/(\bar{n}_H - 1). \, K_1 K_2] - K_1 \quad \text{……….} \ (3.4.17)$$

Equation (3.4.17) is an equation of a straight line, where slope is equal to $K_1 K_2$ and the intercept is - K_1. Usually [L] values vary over several powers of ten so, it is not convenient to plot $[(\bar{n}_H /(\bar{n}_H -1)). \, 1/(L)]$ against $[(2- \bar{n}_H (L))/(\bar{n}_H -1)]$ to obtain the best straight line. Thus, the constants are evaluated by the method of least square [55]. This method uses all of the experimental data except that $\bar{n}_H = 0.95$ and $\bar{n}_H = 1.05$. The values of $[(\bar{n}_H /(\bar{n}_H -1)). \, 1/(L)]$ and $[(2-\bar{n}_H (L))/(\bar{n}_H -1)]$ are calculated for each pH reading in the titration. These values are called y and x respectively. From these x and y values, Σx, Σx^2, Σxy and Σy are calculated. These sums are used to solve the standard simultaneous equations for least squares, which are:

$$\Sigma y = na + b\Sigma x$$

$$\Sigma xy = a \, \Sigma x + b\Sigma x^2 \quad \text{……} \ (3.4.18)$$

where n is equal to the number of observations. The coefficient a is $-K_1$ and b is $K_1 K_2$. From equation (3.4.18), the means values of log K_1 and log K_1K_2 (i.e. log β_2) can be calculated. Subtraction of log K_1 from log $K_1 K_2$ gives the mean value of log K_2.

RESULTS AND DISCUSSION

From the above mentioned two titrations, two titration curves were obtained for each Schiff base. These two titrations curves are designated as the acid titration curve and ligand or reagent titration curve respectively. These titration curves are shown in Figure 3.4.1 for NDP-1 and NDP-2 bases.

From these two titration curves, the average number of proton associated with the ligand ($\bar{n}_H$) can be calculated by the equation:

$$\bar{n}_H = Y - \{(\tilde{V}'' - V')(N^0 + E^0)\} / \{(V^0 + V')\, T^0_L\} \qquad \ldots\ldots\ldots (3.4.19)$$

where Y is number of displaceable protons per ligand molecule. For NDP-2 and NDP-6, Y is taken to be 2 whereas for rest of the Schiff bases its value is 1. V' and $\tilde{V}''$ are the volume of alkali required at the same pH for both acid and ligand titration curves respectively. V^0 is the initial volume of test solution. N^0, E^0 and T^0_L are the initial concentration of the alkali, acid and ligand respectively.

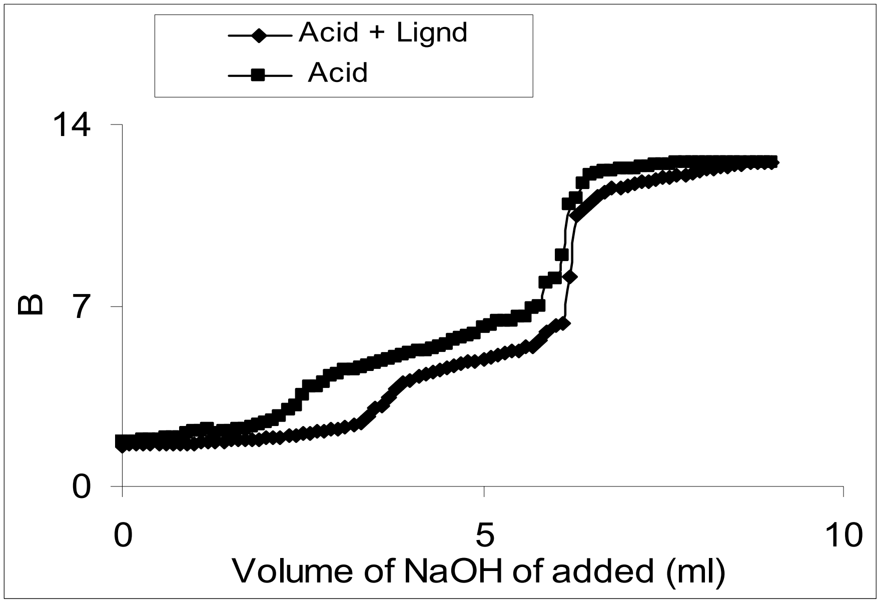
These calculated values of $\bar{n}_H$ for all the Schiff bases are given in Tables 3.4.1 and 3.4.2 respectively. The formation curves for NDP-1, NDP-3 to NDP-5, NDP-7 and NDP- 8 are shown in Figure 3.4.3 whereas for NDP-2 and NDP-6, these are shown in Figure 3.4.4. It is observed that for all the Schiff bases, except NDP-2 and NDP-6, the formation curves extend from 0 to 1. For NDP-2 and NDP-6, $\bar{n}_H$ values extend over the range from 0 to 2 indicating two dissociation steps.

The proton-ligand stability constants were obtained by solving equation (3.4.1), which becomes equation (3.4.2) for Schiff bases with one dissociation step.

$$\bar{n}_H + (\bar{n}_H - 1)\, pK_1^H\, [1/\text{ antilog } B] = 0 \qquad \ldots\ldots\ldots (3.4.20)$$

The plots of $\log(\bar{n}_H) / (\bar{n}_H - 1)$ against B is a straight line and are

Figure 3.4.1 : The plot of pH meter reading (B) against NaOH for NDP-1 and NDP-2 at 313.15 K.



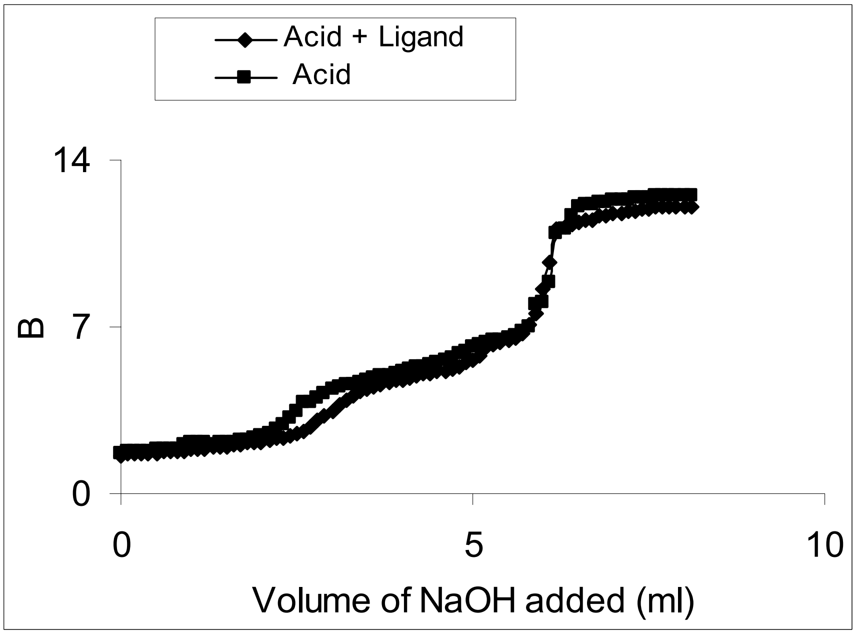


Table 3.4.1 : The pH(B), n_H, pK_1^H and other terms for NDP Schiff bases at 313.15K.

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$**)**	$\mathbf{pK_1^H}$
NDP-1					
10.4	0.1311	6.30	0.7157	0.4010	10.8010
10.5	0.1243	6.31	0.7305	0.4330	10.9330
10.6	0.1566	6.34	0.6607	0.2894	10.8894
10.7	0.1905	6.38	0.5876	0.1538	10.8538
10.8	0.2337	6.43	0.4946	-0.0094	10.7906
10.9	0.2572	6.46	0.4442	-0.0973	10.8027
11.0	0.2493	6.50	0.4617	-0.0666	10.9334
11.1	0.2581	6.55	0.4433	-0.0989	11.0011
11.2	0.2731	6.59	0.4114	-0.1555	11.0445
11.3	0.3116	6.63	0.3292	-0.3092	10.9908
11.4	0.3371	6.68	0.2750	-0.4210	10.9790

Half-integral value = pK_1^H = (B) $\bar{n}_{H\,(0.5)}$= 10.91, Average pK_1^H=10.91

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$**)**	$\mathbf{pK_1^H}$
NDP-3					
11.4	0.0380	6.36	0.9177	1.0473	12.4473
11.5	0.0712	6.38	0.8459	0.7394	12.2394
11.6	0.1106	6.39	0.7607	0.5022	12.1022
11.7	0.1320	6.42	0.7145	0.3984	12.0984
11.8	0.1633	6.44	0.6470	0.2631	12.0631
11.9	0.1813	6.47	0.6083	0.1912	12.0912
12.0	0.2588	6.50	0.4413	-0.1025	11.8975

Half-integral value = pK_1^H = (B) $\bar{n}_{H\,(0.5)}$= 12.00, Average pK_1^H=12.13

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$**)**	$\mathbf{pK_1^H}$
NDP-4					
10.4	0.13	6.30	0.7181	0.4061	10.8061
10.5	0.14	6.31	0.6965	0.3608	10.8608
10.6	0.16	6.34	0.6533	0.2752	10.8752
10.7	0.19	6.38	0.5887	0.1557	10.8557
10.8	0.22	6.43	0.5243	0.0422	10.8422
10.9	0.24	6.46	0.4814	-0.0323	10.8677
11.0	0.25	6.50	0.4602	-0.0693	10.9307
11.1	0.26	6.55	0.4392	-0.1061	10.9939
11.2	0.27	6.59	0.4182	-0.1434	11.0566
11.3	0.31	6.63	0.3325	-0.3027	10.9973
11.4	0.34	6.68	0.2687	-0.4348	10.9652

Half-integral value = pK_1^H = (B) $\bar{n}_{H\,(0.5)}$= 10.90, Average pK_1^H=10.91

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$ **)**	**pK_1^H**
NDP-5					
11.0	0.05	6.30	0.8920	0.9170	11.9170
11.1	0.03	6.32	0.9382	1.1815	12.2815
11.2	0.03	6.34	0.9385	1.1833	12.3833
11.3	0.05	6.37	0.8930	0.9217	12.2217
11.4	0.06	6.40	0.8767	0.8517	12.2517
11.5	0.09	6.45	0.8154	0.6452	12.1452
11.6	0.12	6.50	0.7385	0.4509	12.0509
11.7	0.14	6.53	0.7083	0.3852	12.0852
11.8	0.13	6.56	0.7237	0.4183	12.2183
11.9	0.13	6.58	0.7237	0.4182	12.3182
12.0	0.19	6.68	0.6019	0.1795	12.1795
12.1	0.28	6.88	0.3900	-0.1940	11.9058
12.2	0.31	7.07	0.3471	-0.2740	11.9255
12.3	0.42	7.38	0.1098	-0.9090	11.3912

Half-integral value = pK_1^H = (B) $\bar{n}_{H\ (0.5)}$= 11.90, Average pK_1^H=12.08

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$ **)**	**pK_1^H**
NDP-7					
10.8	0.18	6.06	0.6076	0.1899	11.4076
10.9	0.19	6.08	0.5860	0.1509	11.0509
11.0	0.20	6.10	0.5644	0.1125	11.1125
11.1	0.23	6.10	0.4991	-0.0015	11.0985
11.2	0.26	6.10	0.4338	-0.1157	11.0843
11.3	0.26	6.12	0.4340	-0.1153	11.1847
11.4	0.26	6.14	0.4342	-0.1150	11.2850
11.5	0.29	6.16	0.3692	-0.2326	11.2674
11.6	0.32	6.18	0.3043	-0.3591	11.2409
11.7	0.34	6.21	0.2613	-0.4513	11.2487
11.8	0.36	6.24	0.2183	-0.5540	11.2460
11.9	0.39	6.27	0.1537	-0.7408	11.1592

Half-integral value = pK_1^H = (B) $\bar{n}_{H\ (0.5))}$ = 11.10, Average pK_1^H=11.20

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$ **)**	**pK_1^H**
NDP-8					
11.2	0.07	6.36	0.8484	0.7479	11.9479
11.3	0.10	6.38	0.7835	0.5586	11.8586
11.4	0.15	6.40	0.6754	0.3182	11.7182
11.5	0.17	6.50	0.6329	0.2356	11.7356
11.6	0.22	6.61	0.5261	0.0454	11.6454
11.7	0.25	6.65	0.4619	-0.0066	11.6934
11.8	0.27	6.70	0.4195	-0.1410	11.6590
11.9	0.29	6.76	0.3773	-0.2176	11.6824
12.0	0.30	6.82	0.3567	-0.2561	11.7439
12.1	0.32	6.90	0.3150	-0.3373	11.7627

Half-integral value = pK_1^H = (B) $\bar{n}_{H\ (0.5)}$= 11.74, Average pK_1^H=11.70

Table 3.4.1 (Contd.)….

B	V”-V’	V’	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$	pK_1^H
NDP-9					
11.00	0.19	6.30	0.5871	0.1529	11.1529
11.10	0.20	6.33	0.5694	0.1214	11.2214
11.20	0.20	6.36	0.5675	0.1180	11.3180
11.30	0.21	6.38	0.5487	0.0848	11.3848
11.40	0.21	6.40	0.5456	0.0794	11.4794
11.50	0.22	6.41	0.5252	0.0437	11.5437
11.60	0.22	6.42	0.5207	0.0360	11.6360
11.70	0.22	6.45	0.5190	0.0331	11.7331
11.80	0.23	6.48	0.5014	0.0025	11.8025
11.90	0.23	6.49	0.5029	0.0050	11.9050
12.00	0.22	6.51	0.5155	0.0270	12.0270

Half-integral value = pK_1^H = (B) $\bar{n}_{H\,(0.5)}$= 11.75, Average pK_1^H=11.56

B	V”-V’	V’	$\bar{n}_H$	log $\bar{n}_H/(1-\bar{n}_H)$	pK_1^H
NDP-10					
11.0	0.11	6.43	0.7652	0.5130	11.5130
11.1	0.13	6.45	0.7266	0.4245	11.5245
11.2	0.14	6.46	0.7050	0.3784	11.5784
11.3	0.14	6.47	0.6879	0.3433	11.6433
11.4	0.16	6.48	0.6479	0.2649	11.6649
11.5	0.17	6.50	0.6434	0.2563	11.7563
11.6	0.21	6.56	0.5549	0.0958	11.6958
11.7	0.21	6.57	0.5438	0.0763	11.7763
11.8	0.24	6.60	0.4929	-0.0120	11.7876
11.9	0.32	6.70	0.3165	-0.3340	11.5657
12.0	0.39	6.79	0.1548	-0.7370	11.2627
12.1	0.36	6.79	0.2192	-0.5520	11.5482

Half-integral value = pK_1^H = (B) $\bar{n}_{H\,(0.5)}$=11.76 , Average pK_1^H=11.61

Table 3.4.2 : The pH(B), n_H, pK_1^H and other terms for NDP Schiff bases at 313.15K.

B	**V”-V’**	**V’**	$\bar{n}_H$	**log** $\bar{n}_H$ **/(1-**$\bar{n}_H$ **)**	$\mathbf{pK_2^H}$	$\mathbf{n_H/(1-n_H)}$**. antilogB .** $\mathbf{10^{-7}}$	$\mathbf{(2-n_H)/(n_H-1)}$ **. (1/antilogB) .** $\mathbf{10^{+7}}$
			NDP-2				
6.0	0.38	4.89	1.1463	-0.7662	5.2338	0.7837	58.3696
6.1	0.39	4.95	1.1359	-0.8033	5.2967	1.0521	50.4988
6.2	0.35	5.02	1.2108	-0.5734	5.6266	0.9104	23.6239
6.3	0.32	5.08	1.2813	-0.4073	5.8927	0.9088	12.8036
6.4	0.25	5.15	1.4501	-0.0871	6.3129	0.8093	4.8647
6.5	0.22	5.21	1.5167	0.0291	6.5291	0.9282	2.9573
6.6	0.21	5.38	1.5443	0.0771	6.6771	1.1296	2.1034
6.7	0.16	5.59	1.6373	0.2448	6.9448	1.2876	1.1354
6.8	0.15	5.66	1.6790	0.3253	7.1253	1.5602	0.7494
6.9	0.13	5.71	1.7186	0.4072	7.3072	1.8997	0.4929
7.0	0.05	5.75	1.8844	0.8835	7.8835	2.1308	0.1308

Table 3.4.2(contd…)

B	V''-V'	V'	$\bar{n}_H$	log $\bar{n}_H$ /(1-$\bar{n}_H$)	pK_1^H	$n_H/(n_H-1)$. antilogB . 10^{-11}	$(2-n_H)/(n_H-1)$. (1/antilogB) . 10^{+11}
NDP-2							
11.0	0.09	6.30	0.8048	0.6152	11.6152	4.1230	6.1230
11.1	0.11	6.33	0.7616	0.5044	11.6044	4.0217	4.1263
11.2	0.13	6.36	0.7185	0.4069	11.6069	4.0453	2.8724
11.3	0.18	6.37	0.6103	0.1948	11.4948	3.1248	1.7872
11.4	0.19	6.40	0.5889	0.1561	11.5561	3.5983	1.3665
11.5	0.20	6.41	0.5673	0.1176	11.6176	4.1460	1.0470
11.6	0.21	6.42	0.5458	0.0798	11.6798	4.7840	0.8042
11.7	0.22	6.45	0.5245	0.0426	11.7426	5.5284	0.6191
11.8	0.23	6.48	0.5032	0.0056	11.8056	6.3909	0.4775
11.9	0.26	6.49	0.4385	-0.1074	11.7926	6.2033	0.3501
12.0	0.265	6.50	0.4170	-0.1455	11.8545	7.1527	0.2715

Half-integral value = pK_1^H = (B) $\bar{n}_{H\,(0.5)}$= 11.80, pK_2^H = (B) $\bar{n}_{H\,(1.5)}$= 6.60, Average pK_2^H (pK_1^H) =6.30 (11.67)

Least-Square treatment : K_1^H=11.82, pK_2^H= 5.64, $pK_1^H \cdot pK_2^H$=17.46

Table 3.4.2(contd…)

B	V”-V’	V’	$\bar{n}_H$	log $\bar{n}_H$/(1-$\bar{n}_H$)	pK_2^H	$n_H/(1-n_H)$. antilogB . 10^{-7}	$(2-n_H)/(n_H-1)$. (1/antilogB) . 10^{+7}
NDP-6							
5.8	0.11	4.79	1.7534	0.4851	6.2851	0.1468	5.1869
5.9	0.11	4.80	1.7535	0.4852	6.3852	0.1849	4.1188
6.0	0.12	4.88	1.7316	0.4354	6.4354	0.2367	3.6696
6.1	0.14	4.96	1.6874	0.3422	6.4422	0.3090	3.6128
6.2	0.17	5.04	1.6211	0.2146	6.4146	0.4137	3.8500
6.3	0.18	5.13	1.5996	0.1753	6.4753	0.5323	3.3474
6.4	0.22	5.18	1.5111	0.0193	6.4193	0.7426	3.8080
6.5	0.20	5.30	1.5567	0.0990	6.5990	0.8842	2.5178
6.6	0.20	5.37	1.5574	0.1002	6.7002	1.1123	1.9944
6.7	0.21	5.44	1.5360	0.0627	6.7627	1.4362	1.7272
6.8	0.22	5.46	1.5141	0.0245	6.8245	1.8577	1.4965
6.9	0.23	5.48	1.4923	-0.0135	6.8865	2.4080	1.2985
7.0	0.23	5.52	1.4927	-0.0127	6.9873	3.0296	1.0296

Table 3.4.2(contd…)

B	V”-V’	V’	$\bar{n}_H$	log $\bar{n}_H$ /(1-$\bar{n}_H$)	pK_1^H	$n_H/(1-n_H)$. antilogB . 10^{-12}	$(2-n_H)/(n_H-1)$. (1/antilogB) . 10^{+12}
NDP-6							
11.2	0.04	6.32	0.9133	1.0190	12.2190	1.6695	79.0830
11.3	0.05	6.33	0.8916	0.9029	12.2030	1.6419	51.2659
11.4	0.06	6.34	0.8700	0.8141	12.2140	1.6811	34.6055
11.5	0.08	6.37	0.8268	0.6788	12.1790	1.5094	21.4185
11.6	0.11	6.40	0.7620	0.5053	12.1050	1.2745	13.0652
11.7	0.13	6.42	0.7188	0.4077	12.1080	1.2813	9.0914
11.8	0.16	6.44	0.6541	0.2767	12.0770	1.1931	6.1667
11.9	0.18	6.47	0.6111	0.1962	12.0960	1.2482	4.4961
12.0	0.20	6.50	0.5682	0.1192	12.1190	1.3157	3.3157
12.1	0.16	6.60	0.6553	0.1208	12.2210	2.3930	3.0987
12.2	0.11	6.69	0.7635	0.0469	12.2470	5.1155	3.2984
12.3	0.25	6.79	0.4636	-0.0633	12.2370	1.7242	1.4354

Half-integral value = pK_1^H = (B) $\bar{n}_{H\ (0.5)}$= 12.21 , log pK_2^H = (B) $\bar{n}_{H\ (1.5)}$= 6.45 , Average pK_2^H (pK_1^H) =6.59(12.17)

Least-Square treatment :pK_1^H=11.95, pK_2^H=5.72 , $pK_1^H \cdot pK_2^H$=17.63

shown in Figure 3.4.5. From these plots, log pK_1^H values were calculated at several B by the following equation:

$$\log pK_1^H = B + \log [(\bar{n}_H) / (\bar{n}_H - 1)] \qquad \text{……… (3.4.21)}$$

From these log pK_1^H values, the average value of pK_1^H can be calculated and are given in Table 3.4.1 along with pH meter reading (B), $\bar{n}_H$ and other terms used in the calculation.

For NDP-2 and NDP-6, the proton-ligand constants were calculated by solving equation (3.4.1). For all the points below $\bar{n}_H$ =1, the following equation was used.

$$\log pK_1^H = B + \log (\bar{n}_H) / (\bar{n}_H - 1) \qquad \text{……… (3.4.22)}$$

where as for all the points above $\bar{n}_H$ =1, the equation used was:

$$\log pK_2^H = B + \log [(\bar{n}_H - 1) / (2 - \bar{n}_H)] \qquad \text{……… (3.4.23)}$$

The plots of log $[(\bar{n}_H) / (1-\bar{n}_H)]$ against B gives a straight line and are shown in Figure 3.4.5. From the average log pK_1^H (or log pK_2^H) values calculated for a system, the average value was calculated. The dissociation constants of Schiff bases were also evaluated by half-integral method. The values of log pK_1^H and log pK_2^H calculated by these methods are given in Table 3.4.2. It is observed that the values calculated by these two methods are in good agreement.

Out of all Schiff bases studied, NDP-2 and NDP-6 are of H_2L type whereas others are of HL type. The comparison of pK_1^H values of HL type Schiff bases shows that NDP-1, NDP-4 and NDP-5 are more acidic than other bases. Minimum acidic character is observed for NDP-3 containing methoxy group. This suggests that the presence of methoxy group decreases the acidity due to positive inductive effect.

Further, the position of group at ortho or para position also affects the dissociation constant as shown by NDP-4 and NDP-10. Both these Schiff bases contain –NO_2 group. The presence of –NO_2 group at para position as in NDP-4, increases the acidic character in comparison to NDP-10 containing same group at ortho position. It is reported that the substitution of NO_2 at para position in 2-hydroxy acetophenone caused a larger acidity(46).

Comparison of NDP-2 and NDP-6 shows that NDP-2 is more acidic than NDP-6. Again, the position of group is found to affect the acidic character. But, in this case, reverse nature is observed. In NDP-2, -OH group is at ortho position which causes increase in acidity than that in para position as in NDP-6. This suggests that both the position and type of group affect the acidic character of a compound.

Figure 3.4.3 : The plot of $\bar{n}_H$ against B for Schiff bases at 313.15 K.

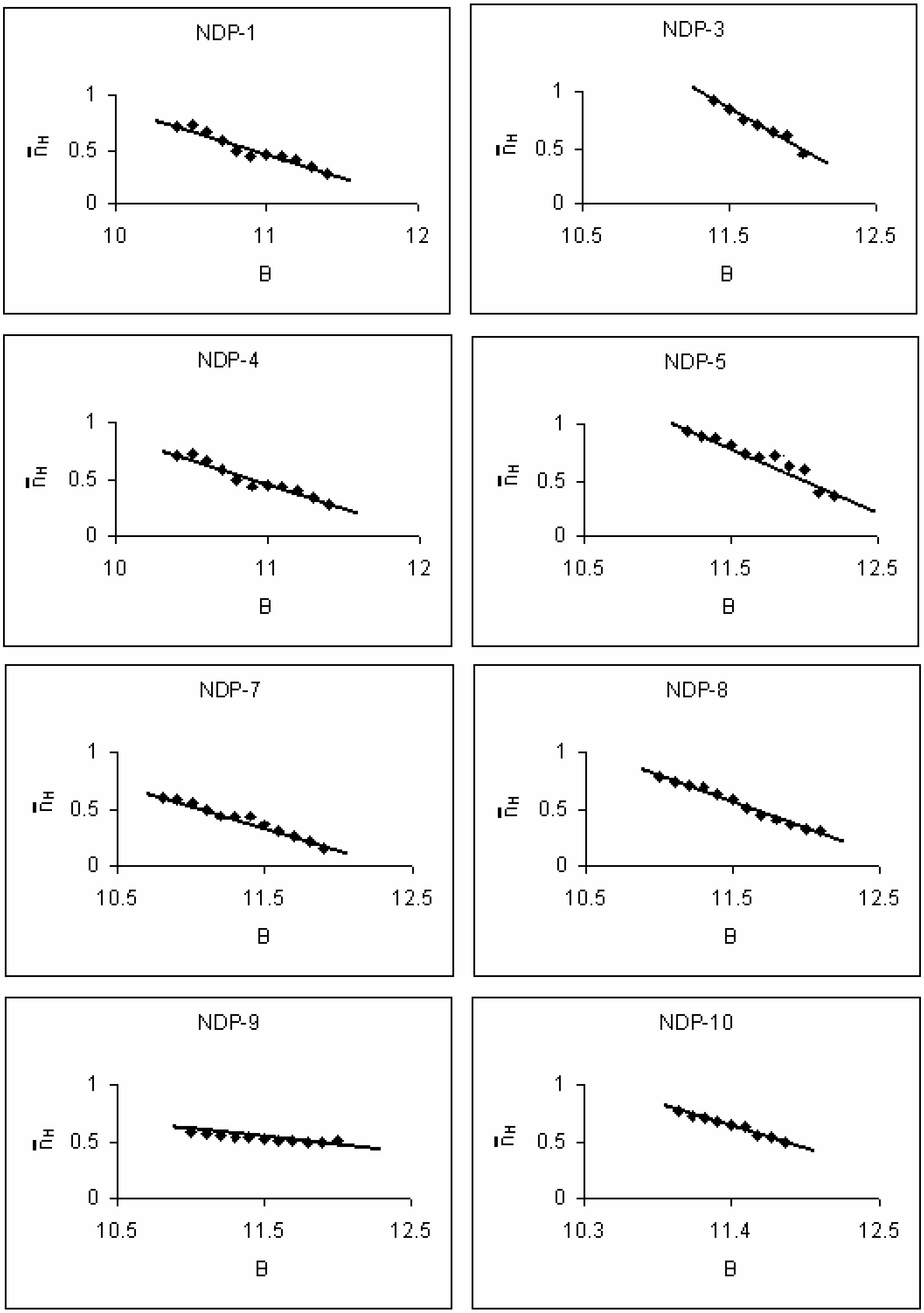


Figure 3.4.4 : The plot of $\bar{n}_H$ against B for NDP-2 Schiff bases at 313.15 K.

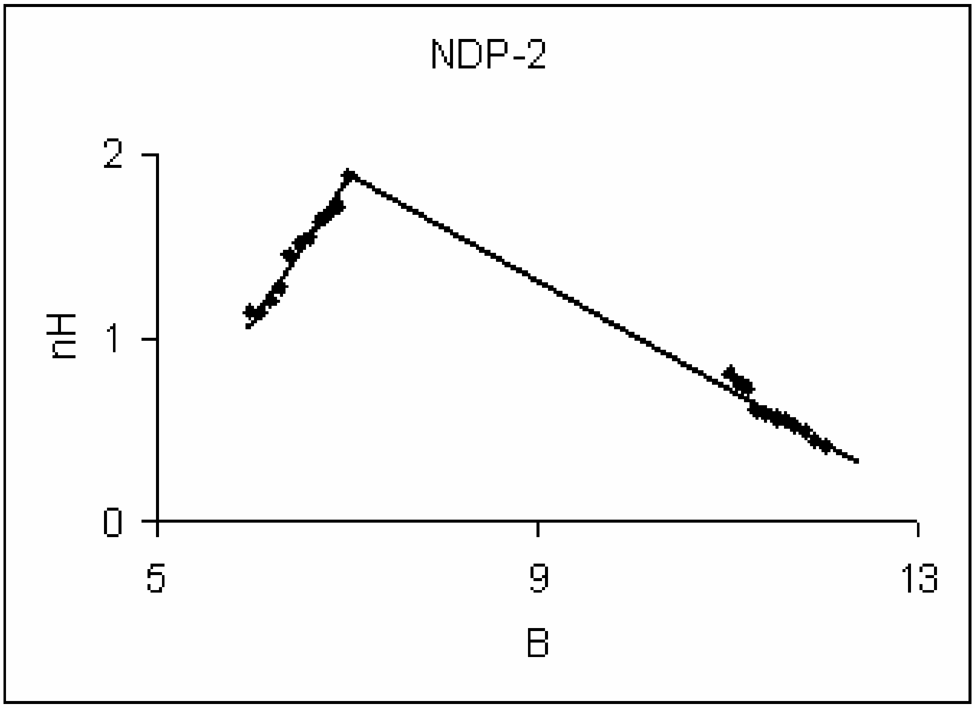
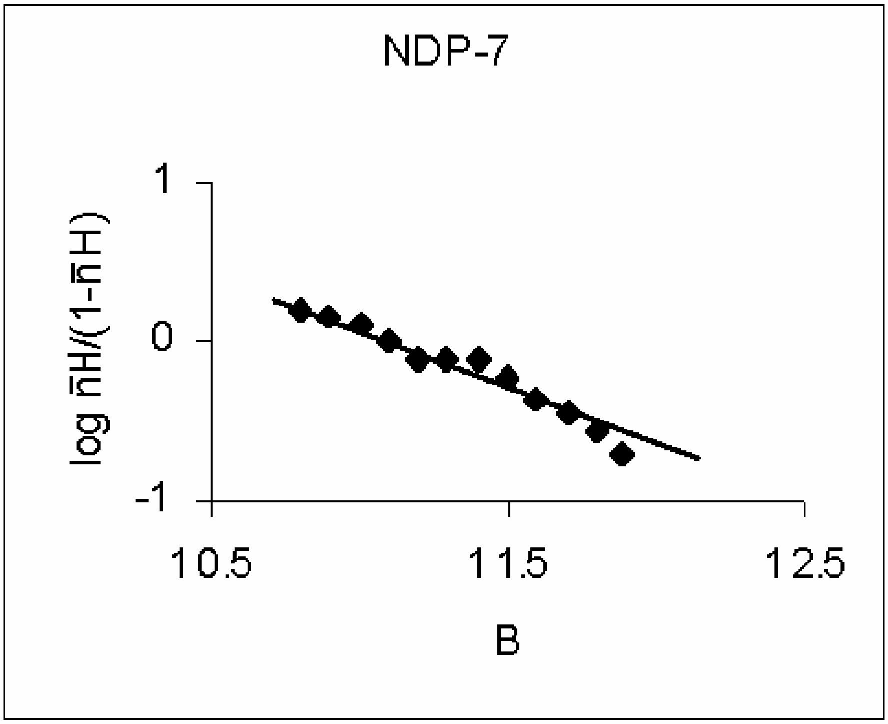


Figure 3.4.5 : The plot of log $\bar{n}_H$ /(1-$\bar{n}_H$) against B for NDP-7 and NDP-8 at 313.15 K.



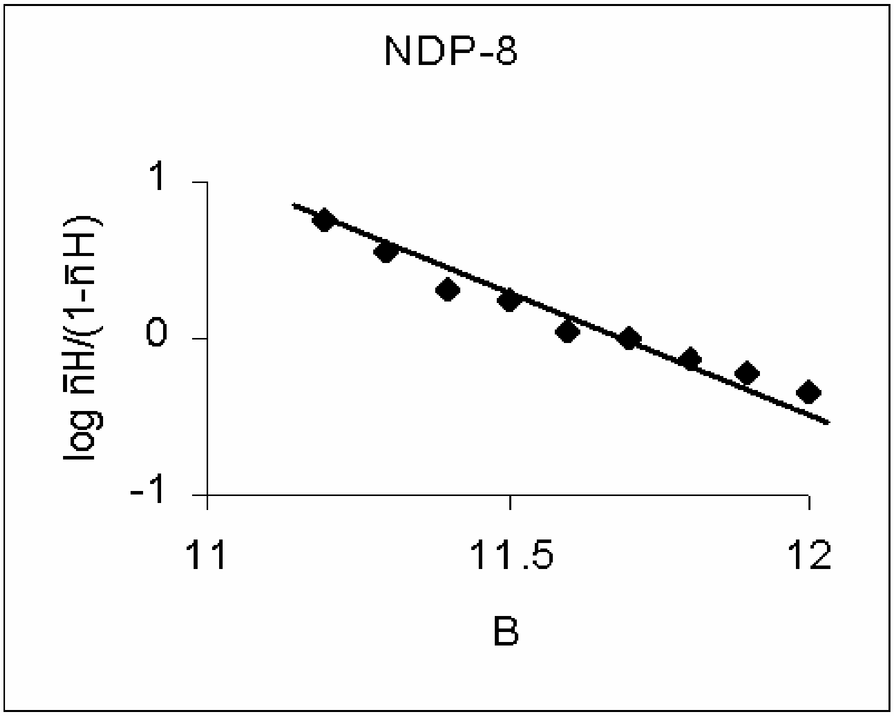


Table 3.4.3 : The log pK_1^H, log pK_2^H and log values for all Schiff bases calculated by different methods.

	pK_1^H			**pK_2^H**			**log β_2**		
Compd. Code	**by Half-integral method**	**by Point-wise calculation method**	**by Least-Square method**	**by Half-integral method**	**by Point-wise calculation method**	**by Least-Square method**	**by Half-integral method**	**by Point- wise calculation method**	**by Least-Square method**
NDP - 1	10.91	10.91	-	-	-	-	-	-	-
NDP-2	11.80	11.67	11.82	6.60	6.30	5.64	-	-	17.45
NDP - 3	12.00	12.13	-	-	-	-	-	-	-
NDP - 4	10.90	10.91	-	-	-	-	-	-	-
NDP - 5	11.90	12.08	-	-	-	-	-	-	-
NDP-6	12.21	12.17	11.95	6.45	6.59	5.72	-	-	17.66
NDP - 7	11.10	11.20	-	-	-	-	-	-	-
NDP - 8	11.74	11.70	-	-	-	-	-	-	-
NDP - 9	11.75	11.56	-	-	-	-	-	-	-
NDP -10	11.76	11.61	-	-	-	-	-	-	-

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INTRODUCTION

Ultrasonics is one of the fast developing areas, which deals with sound waves having frequencies above 20 KHz. Ultrasound is far above the range of human hearing. However, some mammals such as bats and whales can hear these sound waves.

Ultrasonic technology was first used by U. S. Navy during World War II to detect enemy submarines. Nowadays, this technology is employed in a wide range of applications in agriculture, engineering, research, industry and medicine(1-8). The ultrasonic waves are used for cleaning. This includes the removal of dirt, grease, rust or paint from metal, ceramic, glass and crystal surfaces of parts used in the electronics, automotive, aircraft and precision instruments industries. It can also be used for joining materials. In agriculture, it is used to kill insects (pest control)(9) and in oceanography, it is used for mapping the contours of the sea bottom, searching for schools of fish etc. In medicine, it is widely used for imaging the human body and to sterilize surgical instruments.

Ultrasonics is particularly attractive for non-destructive testing so it can be used with most types of materials. Further, it is one of the best techniques to give valuable information on the structure of solids such as micro structure characterization, elastic constants, discontinuity, mechanical properties and phase change(10-12). The structural changes in the material are well reflected in the density/modulus and hence these changes are well reflected in the variation of ultrasonic velocity. In synthetic chemistry, it is useful to increase the reactivity of metals, to increase yield of product, to reduce the reaction time, to decrease the reaction temperature etc(13). Various workers have used ultrasound waves for chemical reactions(14-17). Further, Knowledge of acoustical and thermodynamic properties of any solution gives information about physicochemical behavior of these solutions. Literature survey shows that a lot of work has been done in pure liquids(18,19), in liquid mixtures(20-24) and in solutions of inorganic salts, complexes, proteins, amino acids, polymers etc.(25-35) but very little work has been done for solid organic compounds(36-40) solutions. Thus, in the present chapter, various acoustical and thermodynamic properties of some Schiff bases of α-naphthalamine in dimethyl formamide (DMF) and tetrahydrofuran (THF) were studied at 313.15 K.

EXPERIMENTAL

For the present study, dimethyl formamide (DMF) and tetrahydrofuran (THF) are used after purification by standard method(41). All the Schiff bases were recrystallized from methanol.

A series of solutions of different concentrations were prepared in each solvent for each Schiff bases. For the pure solvents and for the solutions, the densities (ρ), viscosities (η) and sound velocities (U) were measured by a Pyknometer, an Ubbelohde suspended level viscometer and single frequency ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) operating at 2 MHz respectively. All the measurements were done at 313.15 K. The uncertainty of temperature is ± 0.1 K and that of concentration is 0.0001 mole.

Density measurements

The densities of pure solvents and solutions were measured by means of Pyknometer by taking the weights of distilled water, pure solvents and solutions. The densities were evaluated by using following equation:

$$\rho\ (\mathrm{g/cc}) = [(\text{wt. of solvent or solution})/(\text{wt.of water})] \times [\text{density of water}] \quad \text{--(3.5.1)}$$

***Viscosity Measurements*:**

The viscosity of solvent / solutions was measured by Ubbelohde viscometer(42), which obeys Stoke's law(43). The measured quantity of the distilled water / solvent / solution was placed in the viscometer, which was suspended in a thermostat at 313.15 K. The digital stopwatch with an accuracy of ± 0.01 sec was used to determine flow time of solutions. Using the flow times(t) and known viscosity of standard water sample the viscosity of solvent and solution were determined according to equation:

$$\eta_1 / \eta_2 = t_1\rho_1 / t_2\rho_2 \qquad \text{-----(3.5.2)}$$

***Sound velocity measurement*:**

Ultrasonic interferometer (Model No. F-81, Mittal Enterprise, New Delhi), working at frequency of 2 MHz was used to determine sound velocity.

The solvent/solution was filled in the measuring cell with quartz crystal and then micrometer was fixed. The circulation of water from the thermostat at 313.15 K was started and test solvent/solution in the cell was allowed to thermally equilibrate. The micrometer was rotated very slowly so as to obtain a maximum or minimum of anode current (n). A number of maximum reading of anode current were counted. The total distance (d) traveled by the micrometer for n=10, was read. The wave length (λ) was determined according to the equation (3.5.3).

$$\lambda = 2d / n \qquad \text{----- (3.5.3)}$$

The sound velocity (U) of solvent and solutions were calculated from the wavelength and frequency (F) according to equation (3.5.4).

$$U = \lambda F \qquad \text{----- (3.5.4)}$$

RESULTS AND DISCUSSION

The density (ρ), viscosity (η) and sound velocity (U) of pure solvents and different Schiff bases solutions in tetrahydrofuran (THF) and dimethylformamide (DMF) were calculated at 313.15 K from equations (3.5.1) to (3.5.4) and are reported in Table 3.5.1.

From these measurements, various acoustical parameters like specific acoustical impendence (Z), isentropic compressibility (κ_s), intermolecular free length (L_f), Rao's molar sound function (R_m), molar compressibility (W), Vander Waals constant (b), relaxation strength (r), internal pressure (π), free volume (V_f), solvation number (S_n) etc., were evaluated using the following equations:

1. Specific acoustical impedance:

Specific acoustical impedance (Z) can be calculated as:

$$Z = U\rho \qquad \text{----- (3.5.5)}$$

2. Isentropic compressibility:

Isentropic compressibility (κ_s) can be evaluated by the equation (44):

$$\kappa_s = 1/U^2\rho \qquad \text{----- (3.5.6)}$$

3. Intermolecular free path length:

Jacobson (45) proposed an equation for calculating the intermolecular free path length (L_f), which is given below:

$$L_f = K_J \kappa_s^{1/2} \qquad \text{----- (3.5.7)}$$

where K_J is Jacobson constant (=6.0816×10^4)

Table 3.5.1 : The density (ρ), ultrasonic velocity (U) and viscosity (η) of Schiff bases in DMF and THF 313 K.

Conc. (M)	Density ρ. (gm/cm^3)	Velocity $U . 10^{-5}$ (cm/s)	Viscosity $\eta \times 10^3$ (poise)	Density ρ . (gm/cm^3)	Velocity $U . 10^{-5}$ (cm/s)	Viscosity $\eta . 10^3$ (poise)
		DMF			**THF**	
		NDP-1			**NDP-1**	
0.00	0.9289	1.4172	7.4727	0.8714	1.2340	4.2980
0.01	0.9333	1.4092	7.5987	0.8677	1.2297	4.3543
0.02	0.9341	1.4108	7.6461	0.8696	1.2290	4.3791
0.04	0.9344	1.4196	7.7257	0.8738	1.2285	4.4418
0.06	0.9345	1.4200	7.7422	0.8746	1.2254	4.4586
0.08	0.9366	1.4232	7.6611	0.8751	1.2245	4.5295
0.10	0.9343	1.4244	7.7414	0.8762	1.2229	4.5493
		NDP-2			**NDP-2**	
0.01	0.9343	1.4024	7.5736	0.8702	1.2252	4.2980
0.02	0.9356	1.4068	7.5860	0.8704	1.2262	4.3495
0.04	0.9364	1.4084	7.6358	0.8716	1.2274	4.3945
0.06	0.9386	1.4108	7.6735	0.8731	1.2292	4.4460
0.08	0.9391	1.4156	7.7037	0.8744	1.2312	4.5145
0.10	0.9400	1.4186	7.7918	0.8757	1.2344	4.5326
		NDP-3			**NDP-3**	
0.01	0.9383	1.4260	7.4548	0.8712	1.2324	4.3745
0.02	0.9391	1.4216	7.7693	0.8713	1.2305	4.3229
0.04	0.9394	1.4192	7.8750	0.8716	1.2262	4.3444
0.06	0.9396	1.4166	8.0196	0.8717	1.2242	4.4505
0.08	0.9410	1.4128	8.0799	0.8728	1.2222	4.4935
0.10	0.9412	1.4086	7.6462	0.8741	1.2218	4.6744
		NDP-4			**NDP-4**	
0.01	0.9413	1.4372	8.2897	0.8713	1.2262	4.3590
0.02	0.9440	1.4242	8.3778	0.8715	1.2289	4.4461
0.04	0.9442	1.4174	8.5536	0.8716	1.2304	4.4793
0.06	0.9443	1.4168	8.6173	0.8717	1.2329	4.5126
0.08	0.9450	1.3912	8.6921	0.8724	1.2378	4.5597
0.10	0.9480	1.3865	9.0555	0.8739	1.2386	4.5869
		NDP-5			**NDP-5**	
0.01	0.9390	1.4292	8.0308	0.8713	1.2261	4.3216
0.02	0.9403	1.4163	8.2097	0.8714	1.2262	4.3328
0.04	0.9409	1.4124	8.2703	0.8715	1.2270	4.3540
0.06	0.9419	1.4090	8.4559	0.8722	1.2277	4.4042
0.08	0.9445	1.4077	8.5301	0.8732	1.2285	4.4441
0.10	0.9446	1.4065	8.6129	0.8752	1.2364	4.5012

Table 3.5.1 (Contd.). . . . . .

Conc. (M)	Density ρ. (gm/cm^3)	Velocity U . 10^{-5} (cm/s)	Viscosity η x 10^3 (poise)	Density ρ . (gm/cm^3)	Velocity U . 10^{-5} (cm/s)	Viscosity η . 10^3 (poise)
		DMF			**THF**	
		NDP-6			**NDP-6**	
0.01	0.9357	1.4372	7.9254	0.8855	1.2258	4.3791
0.02	0.9363	1.4352	8.0999	0.8865	1.2269	4.3868
0.04	0.9393	1.4316	8.2926	0.8873	1.2278	4.4043
0.06	0.9410	1.4224	8.3528	0.8904	1.2288	4.4914
0.08	0.9418	1.3940	8.4748	0.8908	1.2298	4.5453
0.10	0.9431	1.3916	8.5270	0.8913	1.2304	4.6004
		NDP-7			**NDP-7**	
0.01	0.9367	1.4508	7.5352	0.8593	1.2256	4.2561
0.02	0.9390	1.4504	8.1549	0.8594	1.2261	4.2645
0.04	0.9418	1.4440	8.2561	0.8606	1.2268	4.2731
0.06	0.9431	1.4392	8.3865	0.8607	1.2269	4.2829
0.08	0.9437	1.4336	8.4379	0.8630	1.2289	4.3009
0.10	0.9441	1.4024	8.6171	0.8643	1.2300	4.3941
		NDP-8			**NDP-8**	
0.01	0.9384	1.4696	8.1291	0.8596	1.2253	4.2510
0.02	0.9393	1.4660	8.2128	0.8605	1.2257	4.2641
0.04	0.9403	1.4661	8.2405	0.8606	1.2260	4.2975
0.06	0.9433	1.4634	8.5026	0.8617	1.2265	4.3354
0.08	0.9440	1.4438	8.5200	0.8626	1.2302	4.3729
0.10	0.9468	1.4328	8.6234	0.8642	1.2360	4.4426
		NDP-9			**NDP-9**	
0.01	0.9372	1.4296	7.9476	0.8584	1.2251	4.2536
0.02	0.9375	1.4236	8.0211	0.8590	1.2254	4.2612
0.04	0.9387	1.4192	8.0741	0.8602	1.2258	4.2685
0.06	0.9393	1.4172	8.1021	0.8605	1.2265	4.2845
0.08	0.9407	1.4148	8.1997	0.8613	1.2276	4.3281
0.10	0.9421	1.4116	8.2983	0.8623	1.2294	4.3556
		NDP-10			**NDP-10**	
0.01	0.9368	1.4284	7.9300	0.8599	1.2249	4.2604
0.02	0.9376	1.4252	8.0133	0.8605	1.2252	4.2766
0.04	0.9418	1.4232	8.2110	0.8607	1.2258	4.3218
0.06	0.9431	1.4196	8.3071	0.8617	1.2264	4.3274
0.08	0.9446	1.4180	8.3522	0.8652	1.2270	4.3596
0.10	0.9453	1.4156	8.4164	0.8653	1.2278	4.3714

4. Rao's molar sound function

Rao's molar sound function (R_m) can be evaluated by an equation given by Bagchi et al (46):

$$R_m = (M/\rho)\, U^{1/3} \qquad \text{----- (3.5.8)}$$

The apparent molecular weight (M) of the solution can be calculated according to equation (3.5.9):

$$M = M_1W_1 + M_2W_2 \qquad \text{------ (3.5.9)}$$

where W_1 and W_2 are weight fractions of solvent and solute, respectively. M_1 and M_2 are the molecular weights of the solvent and compounds, respectively.

5. Molar compressibility

Molar compressibility (W) can be calculated by the equation(47):

$$W = (M/\rho)\, \kappa_s^{-1/7} \qquad \text{-----(3.5.10)}$$

6. Van der Waals Constant

Van der Waals constant (b) can be calculated as follows(48):

$$b = M/\rho\ \{1- (RT/MU^2)\ \sqrt{[1 +(MU^2/ 3RT) - 1]}\} \qquad \text{----- (3.5.11)}$$

where R is the gas constant (=8.3143 JK^{-1} mol^{-1}) and T is the absolute temperature.

7. Relaxation Strength

The relaxation strength (r) can be calculated as follows(49):

$$r = 1- [U/U_\infty]^2 \qquad \text{-----(3.5.12)}$$

where $U_\infty = 1.6 \times 10^5$ cm/sec.

8. Internal Pressure

Suryanarayana and Kuppuswamy(50) gave the following equation for evaluating internal pressure:

$$\pi = bRT\,[K\eta/U]^{1/2}\,\rho^{2/3}/M^{7/6} \qquad \text{-----(3.5.13)}$$

where b is the packing factor (= 2). K is a constant (=4.28 X 10^9). The internal pressure (π) depends on temperature, density, ultrasonic velocity and specific heat at constant pressure.

9. Free volume:

Free volume(51) can be calculated according to equation (3.5.14)

$$V_f = [MU/K\eta]^{3/2} \qquad \text{-------(3.5.14)}$$

10. Solvation Number

The solvation number (S_n) can be evaluated according to assynsky(52) method:

$$S_n = M_2 / \{M_1\,[1-\kappa_s/\kappa_{s\,1}]\,[(100-X)/X]\} \qquad \text{----- (3.5.15)}$$

where X is the number of grams of solute in 100 g. of the solution and M_1 and M_2 are the molecular weights of solvent and solute respectively. κ_{s1} and κ_s are the isentropic compressibility of solvent and solution, respectively.

These acoustical parameters are useful for understanding of molecular interactions in a solution. Some of these parameters are given in Tables 3.5.2 for all the Schiff bases in DMFand THF at 313.15 K.

Further, some of these parameters were also correlated with concentration. The correlation coefficients along with correlation equation for these parameters are given in Tables 3.5.3 and 3.5.4 for all the Schiff bases in both the solvents.

The variation of ultrasound velocity (U) with concentrations of different bases is given in Figure 3.5.1 for both the solvents. It is observed that in DMF solutions, velocity increases with concentration for NDP-1 and NDP-2 only

whereas for other bases, velocity is found to decrease continuously. In THF solutions, velocity increases for all the bases.

Figure 3.5.1 : Variation of ultrasonic velocity (U) against concentration for Schiff bases in DMF and THF at 313.15 K.

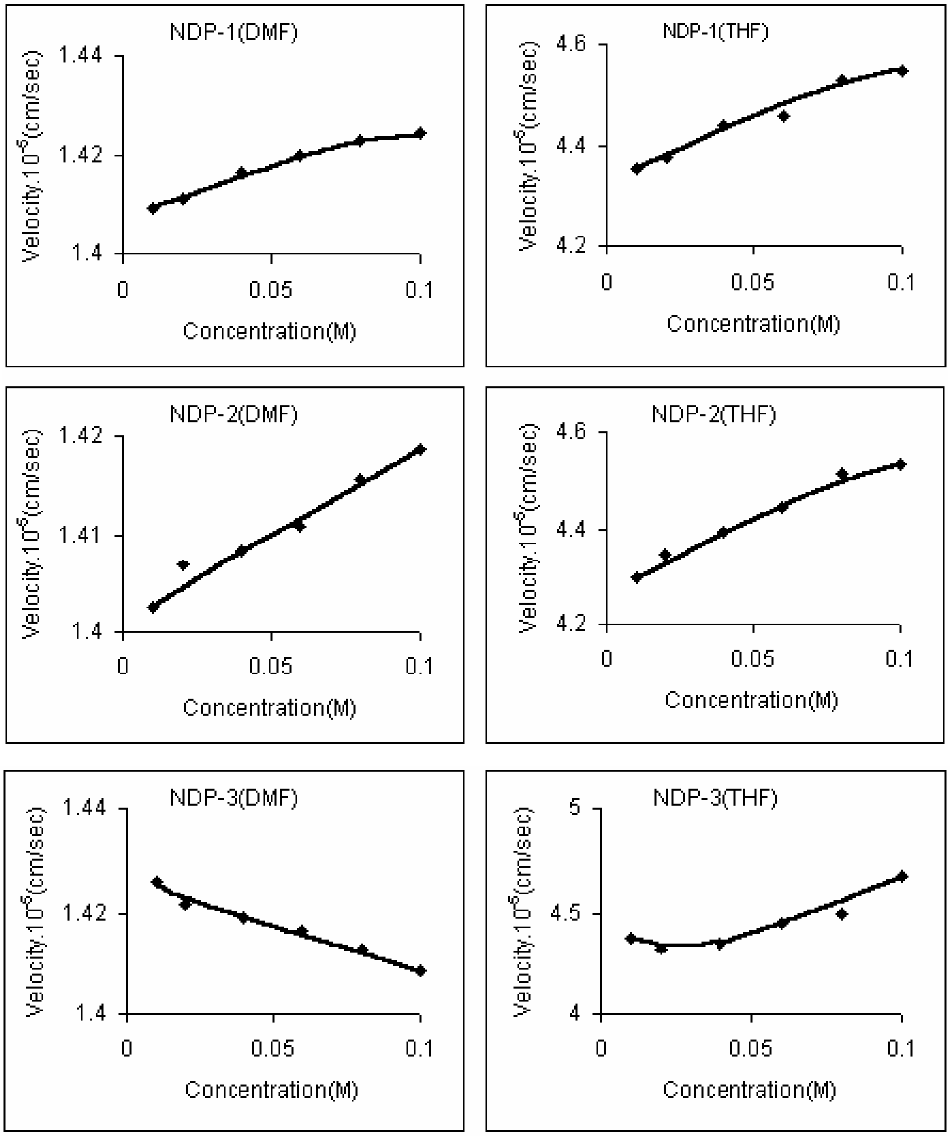


Figure 3.5.1 (contd…)

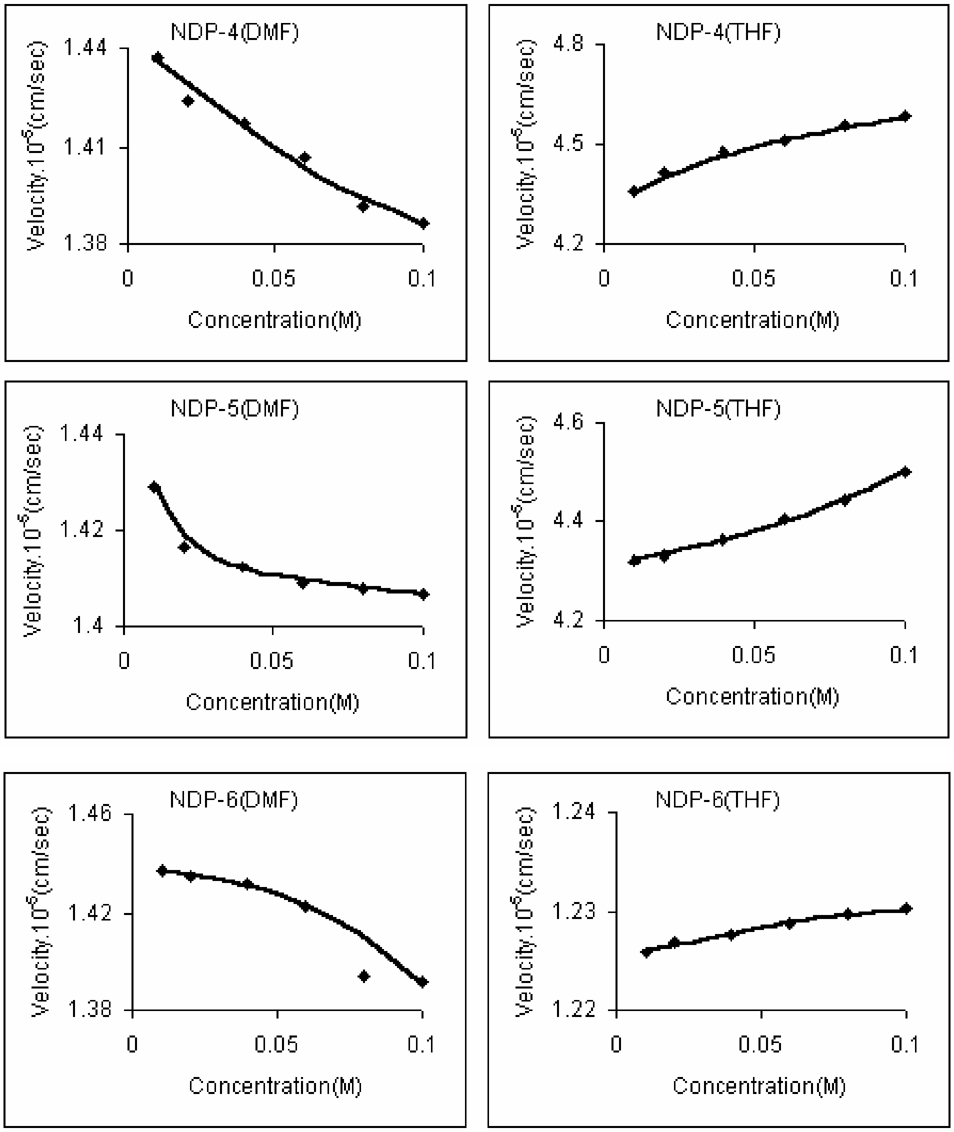
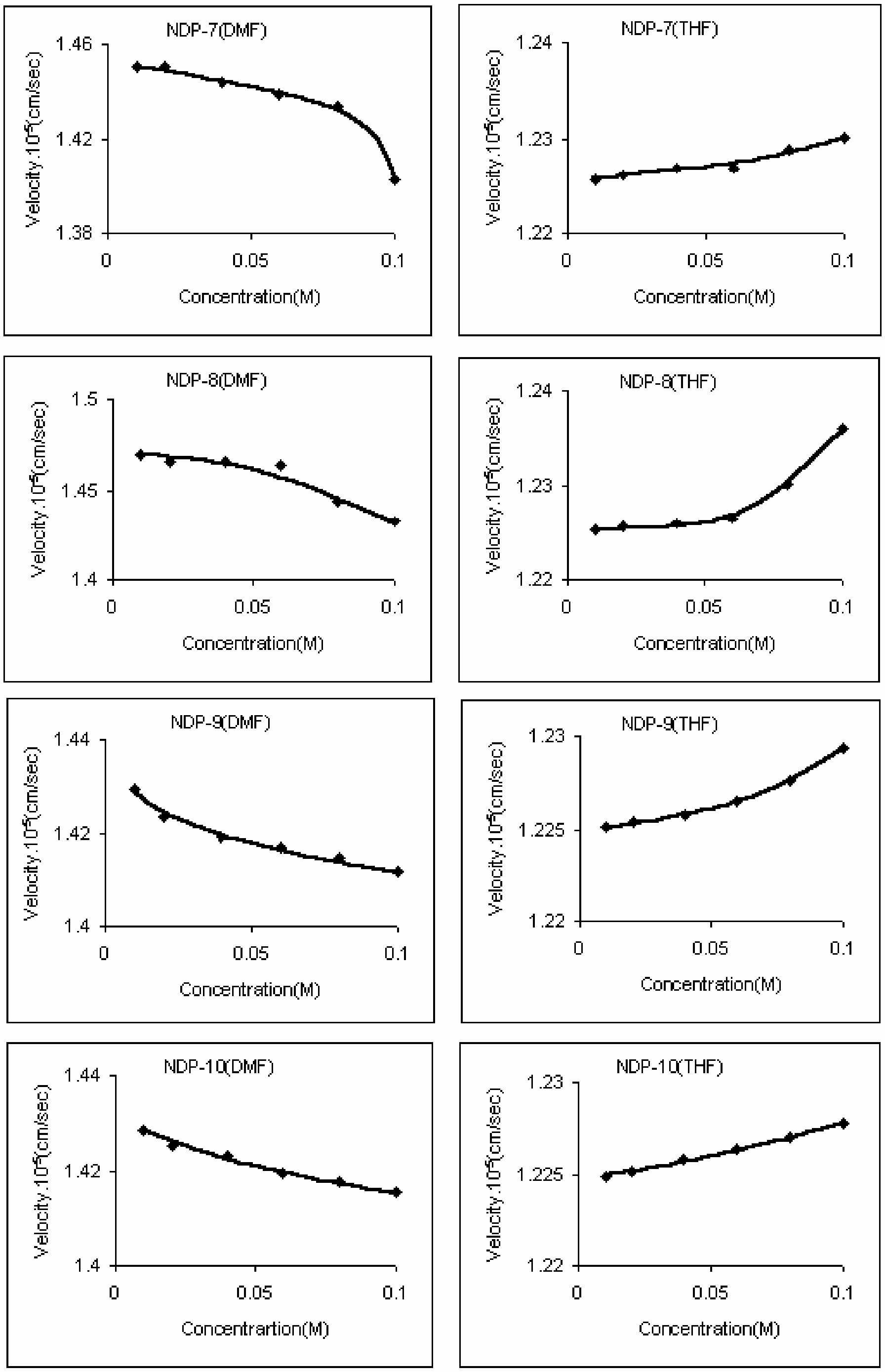


Figure 3.5.1 (contd…)



Ultrasonic velocity is related to intermolecular free length (L_f) inversely. Increase in the L_f causes velocity to decrease or vice versa. It is evident from Table 3.5.2 that when L_f decreases, ultrasonic velocity increases or vice versa. Table 3.5.2 shows that the trend of isentropic compressibility (κ_S) and relaxation strength (r) of the solutions is also similar to that of intermolecular free length. The decrease in L_f means that constituent molecules are close to each other, thereby decreasing the isentropic compressibility due to which velocity increases. This indicates the presence of solute-solvent interaction in the system. This is further confirmed by decrease of relaxation strength (r). Thus, for NDP-1 and NDP-2, in both DMF and THF solutions, predominance of solute-solvent interactions exists. However, for other bases, in DMF solutions, decrease in ultrasonic velocity and increase in intermolecular free length (L_f), isentropic compressibility (κ_S) and relaxation strength (r) suggest the existence of solute-solute interactions. However, in THF solutions, for all the bases velocity increases whereas intermolecular free length (L_f), isentropic compressibility (κ_S) and relaxation strength (r) decreases. This indicates the predominance of solute-solvent interactions in these THF solutions. The absence of complex formation in both DMF and THF solutions is confirmed by linear increase of R_m, W and b (Tables 3.5.2-3.5.4).

The internal pressure (π) is resultant of forces of attraction and repulsion between the molecules in a liquid. It depends upon temperature and concentration. Table 3.5.2 shows that for both DMF and THF solutions, internal pressure decreases. The decrease in internal pressure suggests the decrease of cohesive forces. This suggests that in these solutions, not only solute-solvent but solute-solute interactions also exist. Thus, although some parameters i.e., velocity, intermolecular free length, compressibility, relaxation strength etc., suggest solute-solvent interactions in DMF solutions of NDP-1 and NDP-2, internal pressure suggest the decrease of cohesive forces i.e., existence of solute-solute interactions also.

This is further supported by free volume (V_f), which is an inverse function of internal pressure. The increase in V_f causes π to decrease or vice versa. It is observed that almost for all bases, free volume is found to be inverse of π values as expected. However, in NDP-3 and NDP-6, slight

Table 3.5.2 : Variation of acoustical parameters with concentration of Schiff bases in DMF and THF at 313.15 K.

NDP –1

DMF

Con.	$\kappa_S .10^{11}$ (cm^2/dyn)	L_f (A^O)	r	R_A	R_m. 10^{-3} (cm$^{-8/3}$/ sec$^{1/3}$)	b (cm^3/mol)	W.10^{-3} (cm^{-1} /dyn)	π	V_f (cm^3)	Z .10^{-5} (gm.cm^2)
0.01	5.3955	0.4467	0.2242	1.0066	4.0971	73.9358	2.3068	494.11	0.1796	1.3152
0.02	5.3787	0.4460	0.2225	1.0071	4.1169	74.2788	2.3181	492.60	0.1797	1.3178
0.04	5.3104	0.4432	0.2128	1.0053	4.1677	75.0826	2.3460	487.71	0.1814	1.3265
0.06	5.3069	0.4430	0.2123	1.0054	4.2112	75.8803	2.3706	482.31	0.1838	1.3270
0.08	5.2712	0.4415	0.2088	1.0069	4.2480	76.5147	2.3918	474.27	0.1902	1.3329
0.1	5.2753	0.4417	0.2074	1.0041	4.3037	77.5197	2.4222	470.09	0.1904	1.3308
THF										
0.01	7.6216	0.5109	0.4093	0.9969	4.1568	77.8815	2.3312	393.52	0.3311	1.0670
0.02	7.6234	0.5207	0.4100	0.9993	4.1711	78.1725	2.3400	392.67	0.3309	1.0687
0.04	7.5827	0.5296	0.4104	1.0042	4.1980	78.7110	2.3568	391.58	0.3293	1.0735
0.06	7.6149	0.5307	0.4135	1.0060	4.2382	79.5450	2.3800	387.92	0.3317	1.0717
0.08	7.6210	0.5309	0.4143	1.0068	4.2823	80.4129	2.4051	386.22	0.3291	1.0716
0.1	7.6313	0.5313	0.4158	1.0085	4.3223	81.2174	2.4281	382.70	0.3317	1.0715

Table : 3.5.2 (Contd.). . . . . .

NDP –2 DMF										
Con.	**$\kappa_S .10^{11}$ (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**$R_m. 10^{-3}$ ($cm^{-8/3}/ sec^{1/3}$)**	**b (cm^3/mol)**	**$W.10^{-3}$ (cm^{-1} /dyn)**	**π**	**V_f (cm^3)**	**$Z .10^{-5}$ ($gm.cm^2$)**
0.01	5.4421	0.4486	0.2317	1.0093	4.0899	73.9096	2.3036	494.23	0.1795	1.3103
0.02	5.4006	0.4469	0.2269	1.0097	4.1140	74.2904	2.3173	490.82	0.1816	1.3162
0.04	5.3838	0.4462	0.2252	1.0102	4.1630	75.1738	2.3450	485.40	0.1835	1.3188
0.06	5.3529	0.4450	0.2225	1.0113	4.2061	75.9389	2.3699	480.13	0.1859	1.3242
0.08	5.3138	0.4433	0.2172	1.0114	4.2593	76.8485	2.3997	473.76	0.1891	1.3294
0.1	5.2860	0.4422	0.2139	1.0116	4.308	77.7166	2.4277	469.75	0.1899	1.3335
THF										
0.01	7.6554	0.5321	0.4136	1.0010	4.1440	77.7230	2.3254	394.32	0.3303	1.0662
0.02	7.6406	0.5316	0.4126	1.0010	4.1726	78.2543	2.3414	393.11	0.3290	1.0673
0.04	7.6157	0.5307	0.4115	1.0020	4.2246	79.2378	2.3709	389.42	0.3304	1.0698
0.06	7.5804	0.5295	0.4098	1.0033	4.2756	80.1894	2.4000	386.56	0.3301	1.0732
0.08	7.5445	0.5282	0.4079	1.0042	4.3275	81.1548	2.4295	381.57	0.3354	1.0766
0.1	7.4943	0.5265	0.4048	1.0048	4.3806	82.1188	2.4595	377.27	0.3392	1.0810

Table : 3.5.2 (Contd.). . . . . .

NDP –3 DMF										
Con.	κ_S .10^{11} (cm^2/dyn)	L_f (A^O)	r	R_A	R_m. 10^{-3} (cm$^{-8/3}$/ sec$^{1/3}$)	b (cm^3/mol)	W.10^{-3} (cm^{-1} /dyn)	π	V_f (cm^3)	Z .10^{-5} (gm.cm^2)
0.01	0.9383	0.4426	0.2057	1.0080	4.1432	74.5209	2.3296	489.66	0.1819	1.3237
0.02	0.9391	0.4414	0.2106	1.0099	4.1200	74.1819	2.3208	494.37	0.1784	1.3350
0.04	0.9394	0.4421	0.2132	1.0108	4.1743	75.2223	2.3517	490.18	0.1781	1.3332
0.06	0.9396	0.4429	0.2161	1.0116	4.2288	76.2694	2.3826	487.28	0.1764	1.3310
0.08	0.9410	0.4437	0.2203	1.0141	4.2762	77.2083	2.4101	482.58	0.1773	1.3294
0.1	0.9412	0.4450	0.2249	1.0153	4.3285	78.2465	2.4400	476.53	0.1794	1.3257
THF										
0.01	7.5575	0.5287	0.4067	1.0002	4.1514	77.7349	2.3293	394..15	0.3309	1.0737
0.02	7.5798	0.5295	0.4085	1.0008	4.1811	78.3411	2.3461	388.62	0.3400	1.0722
0.04	7.6306	0.5313	0.4127	1.0023	4.2392	79.5412	2.3793	383.45	0.3439	1.0688
0.06	7.6542	0.5321	0.4145	1.0030	4.3009	80.7674	2.4141	381.66	0.3380	1.0672
0.08	7.6696	0.5326	0.4165	1.0048	4.3571	81.8934	2.4463	377.56	0.3398	1.0668
0.1	7.6632	0.5324	0.4168	1.0064	4.4138	82.9991	2.4787	379.05	0.3272	1.0680

Table : 3.5.2 (Contd.). . . . . .

NDP –4 DMF										
Con.	**κ_S .10^{11} (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**R_m. 10^{-3} ($cm^{-8/3}$/ $sec^{1/3}$)**	**b (cm^3/mol)**	**W.10^{-3} (cm^{-1} /dyn)**	**π**	**V_f (cm^3)**	**Z .10^{-5} (gm.cm^2)**
0.01	5.1432	0.4361	0.1931	1.0086	4.1003	73.5886	2.3092	512.29	0.1631	1.3528
0.02	5.2222	0.4394	0.2076	1.0146	4.1090	73.9485	2.3161	513.52	0.1602	1.3445
0.04	5.2714	0.4415	0.2152	1.0164	4.1671	75.1251	2.3494	510.67	0.1597	1.3383
0.06	5.2756	0.4417	0.2159	1.0167	4.2315	76.3255	2.3858	503.48	0.1598	1.3379
0.08	5.4675	0.4497	0.2440	1.0236	4.2676	77.4050	2.4085	501.50	0.1570	1.3147
0.1	5.4873	0.4505	0.2491	1.0280	4.3129	78.3322	2.4356	504.99	0.1502	1.3143
THF										
0.01	7.6328	0.5313	0.4126	1.0020	4.1485	77.7927	2.3283	393.97	0.3307	1.0684
0.02	7.5978	0.5301	0.4101	1.0015	4.1874	78.4931	2.3499	393.44	0.3264	1.0710
0.04	7.5786	0.5294	0.4086	1.0012	4.2623	79.9075	2.3918	386.75	0.3319	1.0724
0.06	7.5468	0.5283	0.4062	1.0006	4.3384	81.3256	2.4344	380.14	0.3378	1.0747
0.08	7.4809	0.5260	0.4015	1.0001	4.4142	82.6916	2.4767	374.15	0.3431	1.0799
0.1	7.4589	0.5252	0.4007	1.0016	4.4805	83.9555	2.5144	368.46	0.3489	1.0824

Table : 3.5.2 (Contd.). . . .

NDP –5 **DMF**										
Con.	**κ_S .10^{11} (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**R_m. 10^{-3} (cm$^{-8/3}$/ sec$^{1/3}$)**	**b (cm^3/mol)**	**W.10^{-3} (cm^{-1} /dyn)**	**π**	**V_f (cm^3)**	**Z .10^{-5} (gm.cm^2)**
0.01	5.2137	0.4391	0.2021	1.0080	4.1023	73.7394	2.3101	504.88	0.1696	1.3420
0.02	5.3019	0.4428	0.2165	1.0125	4.1166	74.2027	2.3197	508.56	0.1637	1.3317
0.04	5.3277	0.4439	0.2207	1.0141	4.1750	75.3422	2.3531	502.12	0.1651	1.3289
0.06	5.3475	0.4447	0.2244	1.0159	4.2317	76.4462	2.3857	499.66	0.1628	1.3272
0.08	5.3427	0.4445	0.2260	1.0191	4.2823	77.4116	2.4153	494.29	0.1641	1.3296
0.1	5.3513	0.4449	0.2272	1.0195	4.3448	78.5888	2.4507	488.38	0.1652	1.3286
THF										
0.01	7.6342	0.5314	0.4127	1.0020	4.1477	77.7802	2.3278	392.36	0.3349	1.0683
0.02	7.6319	0.5313	0.4126	1.0021	4.1836	78.4688	2.3480	388.92	0.3380	1.0685
0.04	7.6216	0.5309	0.4119	1.0020	4.2564	79.8568	2.3888	382.05	0.3446	1.0693
0.06	7.6065	0.5304	4.4112	1.0026	4.3259	81.1859	2.4281	376.88	0.3477	1.0708
0.08	7.5879	0.5298	0.4104	1.0036	4.3938	82.4811	2.4665	371.52	0.3519	1.0727
0.1	7.4744	0.5258	0.4029	1.0037	4.4644	83.6928	2.5062	366.33	0.3571	1.0821

Table : 3.5.2 (Contd.). . . . .

NDP –6 DMF										
Con.	**$\kappa_S .10^{11}$ (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**$R_m . 10^{-3}$ ($cm^{-8/3}/sec^{1/3}$)**	**b (cm^3/mol)**	**W.10^{-3} (cm^{-1}/dyn)**	**π**	**V_f (cm^3)**	**Z .10^{-5} ($gm.cm^2$)**
0.01	5.1740	0.4374	0.1931	1.0026	4.1173	73.8891	2.3168	499.99	0.1739	1.3448
0.02	5.1851	0.4379	0.1954	1.0037	4.1384	74.3084	2.3290	502.38	0.1696	1.3477
0.04	5.1946	0.4383	0.1994	1.0078	4.1725	74.9970	2.3496	502.82	0.1661	1.3447
0.06	5.2525	0.4407	0.2097	1.0118	4.2065	75.7689	2.3700	499.79	0.1657	1.3385
0.08	5.4641	0.4495	0.2409	1.0195	4.2248	76.5587	2.3830	501.78	0.1602	1.3129
0.1	5.4754	0.4500	0.2435	1.0215	4.2663	77.3718	2.4071	497.37	0.1611	1.3124
THF										
0.01	7.5153	0.5272	0.4130	1.0184	4.0727	76.3730	2.2910	400.23	0.3272	1.0855
0.02	7.4936	0.5265	0.4120	1.0193	4.0966	76.8160	2.3047	397.60	0.3300	1.0877
0.04	7.4756	0.5258	0.4111	1.0199	4.1484	77.7994	2.3341	392.38	0.3350	1.0895
0.06	7.4379	0.5245	0.4102	1.0232	4.1888	78.5680	2.3579	391.06	0.3321	1.0941
0.08	7.4220	0.5239	0.4092	1.0234	4.2422	79.5777	2.3880	387.51	0.3330	1.0955
0.1	7.4111	0.5235	0.4086	1.0238	4.2944	80.5747	2.4176	384.20	0.3335	1.0967

Table : 3.5.2 (Contd.). . . . . .

NDP –7										
DMF										
Con.	**κ_S .10^{11} (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**R_m. 10^{-3} (cm$^{-8/3}$/ sec$^{1/3}$)**	**b (cm^3/mol)**	**W.10^{-3} (cm^{-1} /dyn)**	**π**	**V_f (cm^3)**	**Z .10^{-5} (gm.cm^2)**
0.01	5.0721	0.4331	0.1778	1.0005	4.1299	74.0627	2.2476	509.89	0.1906	1.3590
0.02	5.0624	0.4327	0.1782	1.0031	4.1505	74.3085	2.3357	501.05	0.1711	1.3619
0.04	5.0922	0.4340	0.1855	1.0076	4.1923	75.1783	2.3607	497.79	0.1705	1.3600
0.06	5.1192	0.4351	0.1909	1.0109	4.2419	76.1666	2.3895	494.71	0.1693	1.3573
0.08	5.1560	0.4367	0.1972	1.0120	4.2937	77.2075	2.4193	489.32	0.1704	1.3529
0.1	5.3856	0.4463	0.2317	1.0199	4.3199	78.1935	2.4368	492.07	0.1631	1.3240
THF										
0.01	7.7474	0.5353	0.4132	0.9884	4.2029	78.8229	2.3542	386.11	0.3421	1.0532
0.02	7.7400	0.5350	0.4127	0.9883	4.2376	79.4809	2.3736	382.77	0.3456	1.0537
0.04	7.7206	0.5344	0.4121	0.9895	4.3012	80.6979	2.4097	376.26	0.3532	1.0558
0.06	7.7182	0.5343	0.4120	0.9896	4.3697	82.0161	2.4481	369.78	0.3606	1.0560
0.08	7.6726	0.5327	0.4101	0.9917	4.4285	83.1151	2.4817	364.28	0.3676	1.0606
0.1	7.6476	0.5318	0.4090	0.9929	4.4910	84.3034	2.5172	361.92	0.3647	1.0631

Table : 3.5.2 (Contd.). . . . . .

NDP –8 DMF										
Con.	**$\kappa_S .10^{11}$ (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**$R_m. 10^{-3}$ ($cm^{-8/3}/sec^{1/3}$)**	**b (cm^3/mol)**	**W.10^{-3} (cm^{-1}/dyn)**	π	**V_f (cm^3)**	**Z .10^{-5} ($gm.cm^2$)**
0.01	4.9342	0.4272	0.1564	0.9981	4.1298	73.6440	2.3224	502.61	0.1728	1.3791
0.02	4.9537	0.4280	0.1605	0.9998	4.1420	73.9215	2.3298	503.35	0.1707	1.3770
0.04	4.9476	0.4278	0.1603	1.0009	4.1767	74.5554	2.3496	499.06	0.1723	1.3786
0.06	4.9499	0.4279	0.1634	1.0047	4.1993	75.0156	2.3637	503.04	0.1662	1.3805
0.08	5.0817	0.4335	0.1857	1.0099	4.2157	75.6158	2.3747	501.83	0.1646	1.3629
0.1	5.1448	0.4362	0.1981	1.0155	4.2303	76.0584	2.3848	502.52	0.1620	1.3566
THF										
0.01	7.7483	0.5353	0.4135	0.9888	4.1887	78.5554	2.3464	387.35	0.3411	1.0533
0.02	7.7351	0.5349	0.4131	0.9897	4.2068	78.8995	2.3568	385.77	0.3424	1.0547
0.04	7.7307	0.5347	0.4129	0.9897	4.2508	79.7416	2.3815	382.58	0.3439	1.0551
0.06	7.7143	0.5342	0.4124	0.9809	4.2899	80.4880	2.4038	379.92	0.3449	1.0569
0.08	7.6597	0.5323	0.4088	0.9909	4.3336	81.2615	2.4283	376.75	0.3473	1.0612
0.1	7.5744	0.5229	0.4032	0.9912	4.3759	81.9694	2.4521	374.92	0.3467	1.0681

Table 3.5.2 contd…..

NDP –9 DMF										
Con.	**$\kappa_S .10^{11}$ (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**$R_m. 10^{-3}$ ($cm^{-8/3}/sec^{1/3}$)**	**b (cm^3/mol)**	**W.10^{-3} (cm^{-1}/dyn)**	**π**	**V_f (cm^3)**	**Z .10^{-5} ($gm.cm^2$)**
0.01	5.2208	0.4394	0.2016	1.0060	4.1036	73.7552	2.3102	502.53	0.1719	1.3398
0.02	5.2632	0.4412	0.2083	1.0077	4.1223	74.1913	2.3213	502.33	0.1700	1.3346
0.04	5.2891	0.4423	0.2132	1.0101	4.1641	75.0321	2.3456	497.95	0.1707	1.3322
0.06	5.3007	0.4428	0.2154	1.0112	4.2107	75.9250	2.3723	492.30	0.1726	1.3312
0.08	5.3108	0.4432	0.2181	1.0132	4.2539	76.7460	2.3967	489.25	0.1722	1.3309
0.1	5.3270	0.4439	0.2216	1.0155	4.2940	77.5597	2.4207	486.46	0.1716	1.3298
THF										
0.01	7.7621	0.5358	0.4137	0.9875	4.2016	78.8041	2.3531	386.36	0.3416	1.0516
0.02	7.7522	0.5355	0.4134	0.9881	4.2284	79.3157	2.3683	383.70	0.3444	1.0527
0.04	7.7363	0.5349	0.4130	0.9893	4.2814	80.3335	2.3985	378.20	0.3509	1.0545
0.06	7.7250	0.5345	0.4124	0.9895	4.3392	81.4352	2.4309	372.94	0.3564	1.0554
0.08	7.7043	0.5338	0.4113	0.9901	4.3947	82.4867	2.4623	369.11	0.3586	1.0573
0.1	7.6723	0.5327	0.4096	0.9908	4.4499	83.5166	2.4934	364.65	0.3631	1.0601

Table : 3.5.2 (Contd.). . . . .

NDP –10 DMF										
Con.	**$\kappa_S .10^{11}$ (cm^2/dyn)**	**L_f (A^O)**	**r**	**R_A**	**$R_m. 10^{-3}$ ($cm^{-8/3}/ sec^{1/3}$)**	**b (cm^3/mol)**	**$W.10^{-3}$ (cm^{-1} /dyn)**	**π**	**V_f (cm^3)**	**$Z .10^{-5}$ ($gm.cm^2$)**
0.01	5.2318	0.4399	0.2030	1.0059	4.1118	73.9224	2.3148	500.97	0.1727	1.3381
0.02	5.2509	0.4407	0.2066	1.0074	4.1384	74.4641	2.3303	499.72	0.1715	1.3363
0.04	5.2421	0.4403	0.2088	1.0125	4.1837	75.3380	2.3574	498.43	0.1690	1.3404
0.06	5.2615	0.4411	0.2128	1.0147	4.2399	76.4347	2.3899	493.39	0.1693	1.3388
0.08	5.2650	0.4413	0.2146	1.0167	4.2967	77.5132	2.4226	486.78	0.1715	1.3394
0.1	5.2790	0.4419	0.2172	1.0180	4.3563	78.6541	2.4566	480.78	0.1730	1.3382
THF										
0.01	7.7506	0.5354	0.4139	0.9892	4.2025	78.8289	2.3542	386.24	0.3417	1.0533
0.02	7.7417	0.5351	0.4136	0.9898	4.2376	79.5017	2.3741	383.09	0.3445	1.0543
0.04	7.7318	0.5347	0.4130	0.9899	4.3128	80.9396	2.4163	377.22	0.3485	1.0551
0.06	7.7158	0.5342	0.4125	0.9909	4.3836	82.2959	2.4562	370.13	0.3572	1.0568
0.08	7.6765	0.5328	0.4119	0.9948	4.4404	83.3882	2.4895	365.20	0.3625	1.0616
0.1	7.6657	0.5324	0.4111	0.9947	4.5155	84.8214	2.5316	358.56	0.3706	1.0624

Table 3.5.3 : The correlation coefficient (γ) and correlation equations between some acoustical parameters and concentrations (C) of schiff bases in DMF at 313.15 K

Parameters	**γ**	**Correlation equation**
	NDP-1	
U($cm \cdot sec^{-1}$)	0.9816	U - 7789.6C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9944	B + 37.493C = 73.521
W($cm^{-1} . dyn^{-1}$)	0.9990	W + 1222.1C = 2294.9
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9987	R_m + 2170.7C = 4076
	NDP-2	
U($cm \cdot sec^{-1}$)	0.9816	U -7789.6C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9997	b + 42.309C = 73.46
W($cm^{-1} . dyn^{-1}$)	0.9997	W + 1373.5C= 2289.6
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9995	R_m + 2429.2C = 4072
	NDP-3	
U($cm \cdot sec^{-1}$)	0.9816	U -7789.6 C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9861	b + 45.857C = 73.543
W($cm^{-1} . dyn^{-1}$)	0.9912	W + 1496.6C= 2295.5
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9878	R_m + 2617.5C = 4077.2
	NDP-4	
U($cm \cdot sec^{-1}$)	0.9816	U-7789.6C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9991	b + 56.296C = 72.865
W($cm^{-1} . dyn^{-1}$)	0.9991	W + 1802.8C = 2277.3
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9988	R_m + 3186.8C = 4039.6
	NDP-5	
U($cm \cdot sec^{-1}$)	0.9816	U-7789.6C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9970	b + 54.861C = 73.102
W($cm^{-1} . dyn^{-1}$)	0.9996	W + 1761.2C = 2283.7
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9995	R_m + 3108.4C = 4052.8

Table 3.5.3 contd….

	NDP-6	
$U(cm \cdot sec^{-1})$	0.9816	U- 7789.6C = 123069
$b(cm^{3} \cdot mol^{-1})$	0.9996	r + 40.324C = 73.368
$W(cm^{-1} . dyn^{-1})$	0.9999	W + 1323C= 2290.8
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9998	R_m + 2318.8C = 4067.5
	NDP-7	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6C= 123069
$b(cm^{3} \cdot mol^{-1})$	0.9989	b + 49.473C + 73.196
$W(cm^{-1} . dyn^{-1})$	0.9996	W + 1600.9C = 2286.2
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9994	R_m + 2815.1C = 4058
	NDP-8	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6C = 123069
$b(cm^{3} \cdot mol^{-1})$	0.9988	b + 28.484C = 73.2
$W(cm^{-1} . dyn^{-1})$	0.9982	W + 963.37C= 2286.3
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9975	R_m + 1675.9C = 4058.2
	NDP-9	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6C = 123069
$b(cm^{3} \cdot mol^{-1})$	0.9799	b + 46.427C = 73.25
$W(cm^{-1} . dyn^{-1})$	0.9821	W + 1348C= 2295.4
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9757	R_m + 2364.1C + 4077.2
	NDP-10	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6C = 123069
$b(cm^{3} \cdot mol^{-1})$	0.9992	b + 52.209C = 73.326
$W(cm^{-1} . dyn^{-1})$	0.9993	W + 1569.5C = 2297.5
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9990	R_m + 2702.7C = 4081.5

Table 3.5.4 : The correlation coefficient (γ) and correlation equations between some acoustical parameters and concentrations (C) of schiff bases in THF at 313.15 K.

Parameters	γ	Correlation equation
	NDP-1	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6 C= 123069
$b(cm^{3} \cdot mol^{-1})$	0.9964	b + 37.468 C = 77.388
$W(cm^{-1} \,.\, dyn^{-1})$	0.9974	W + 1084.7 C = 2317.5
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9961	R_m + 1857.3 C = 4132.2
	NDP-2	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6 C =123069
$b(cm^{3} \cdot mol^{-1})$	0.9999	b + 48.617 C = 77.268
$W(cm^{-1} \,.\, dyn^{-1})$	0.9999	W + 1481.2 C = 2311.3
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9999	R_m + 2610.6 C = 4119.3
	NDP-3	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6 C = 123069
$b(cm^{3} \cdot mol^{-1})$	0.9998	b + 58.728 C = 77.179
$W(cm^{-1} \,.\, dyn^{-1})$	0.9999	W + 1664.9 C = 23129
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9999	Rm + 2925 C = 4122.8
	NDP-4	
$U(cm \cdot sec^{-1})$	0.9816	U - 7789.6 C =123069
$b(cm^{3} \cdot mol^{-1})$	0.9998	b + 68.92 C = 77.133
$W(cm^{-1} \,.\, dyn^{-1})$	0.9998	W + 2081.3 C = 2308.4
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9997	Rm + 3714.5 C = 4113.3
	NDP-5	
$U(cm \cdot sec^{-1})$	0.9816	U -7789.6 C = 123069
$b(cm^{3} \cdot mol^{-1})$	0.9997	b + 65.97 C = 77.169
$W(cm^{-1} \,.\, dyn^{-1})$	0.9999	W + 1978 C = 2308.7
$R_m(cm^{-8/3} \cdot sec^{-1/3})$	0.9999	Rm + 3511.2 C = 4113.9

Table 3.5.4 contd…

	NDP-6	
U($cm \cdot sec^{-1}$)	0.9816	U -7789.6 C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9993	b + 46.275 C = 75.894
W($cm^{-1} . dyn^{-1}$)	0.9995	W + 1395.1 C = 2276.8
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9993	Rm + 2440.9 C = 4047.7
	NDP-7	
U($cm \cdot sec^{-1}$)	0.9816	U - 7789.6 C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9996	b + 60.888 C = 78.26
W($cm^{-1} . dyn^{-1}$)	0.9998	W + 1810.7 C = 2337.2
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9997	Rm + 3199.3 C = 4173.2
	NDP-8	
U($cm \cdot sec^{-1}$)	0.9816	U - 7789.6 C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9997	b + 38.31 C = 78.173
W($cm^{-1} . dyn^{-1}$)	0.9999	W + 1178.2 C = 2333.9
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9998	Rm + 2087.2c = 4166.5
	NDP-9	
U($cm \cdot sec^{-1}$)	0.9816	U -7789.6 C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9999	b + 52.602 C = 78.264
W($cm^{-1} . dyn^{-1}$)	0.9999	W + 1563.3 C = 2337
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9999	Rm + 2768.8 C = 4172.8
	NDP-10	
U($cm \cdot sec^{-1}$)	0.9816	U -7789.6 C = 123069
b($cm^3 \cdot mol^{-1}$)	0.9993	b + 66.046 C = 78.217
W($cm^{-1} . dyn^{-1}$)	0.9995	W + 1956.4 C = 2335.9
R_m($cm^{-8/3} \cdot sec^{-1/3}$)	0.9993	Rm + 3449.2 C = 4170.5

discrepancies are observed. All these observation suggest the existence of different types of interactions occurring in the solution. The predominance of one is reflected in some properties whereas other is reflected in other parameters.

The solvation number (S_n) is a measure of structure forming or structure breaking tendency of solute in a solution. The positive S_n values are due to structure forming tendency of solute or vice versa.

Figures 3.5.3 show the variation of S_n with concentration of solutions in both the solvents. It is clear from Figure 3.5.3, in DMF solutions of NDP-1, S_n value increases with increase in concentration whereas for other bases, S_n is found to decrease. The increase of S_n values with concentration indicates the increase in structure forming tendency of solute with concentration whereas the decrease of S_n values with concentration indicates the structure breaking tendency of solute with concentration. For other bases in DMF, the decrease in salvation number indicates the structure breaking tendency of these solutes.

In THF solutions, the S_n values are found to increase with concentration (Figure 3.5.3) and are positive, indicating thereby predominance of solute-solvent interactions in these solutions.

Thus, in DMF, except NDP-1 and NDP-2, other bases shows structure breaking tendency. NDP-1 and NDP-2 in DMF and all studied bases in THF exhibit structure forming tendency. Further, both solute-solute and solute-solvent interactions exist in solutions, however some are predominated in some parameters.

Figure 3.5.3 : Variation of S_n against concentration for Schiff bases in DMF and THF at 313.15 K.

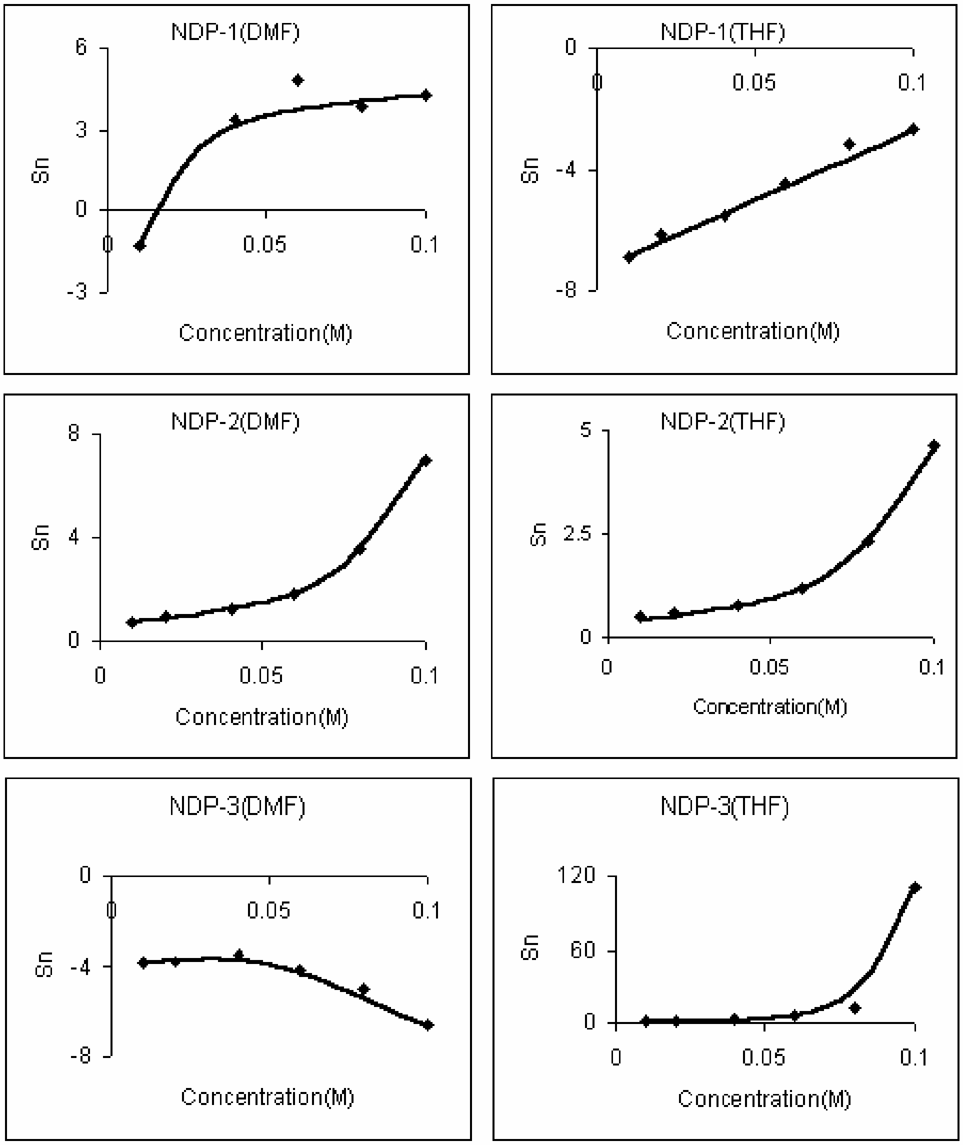


Figure 3.5.3 (Contd.)……

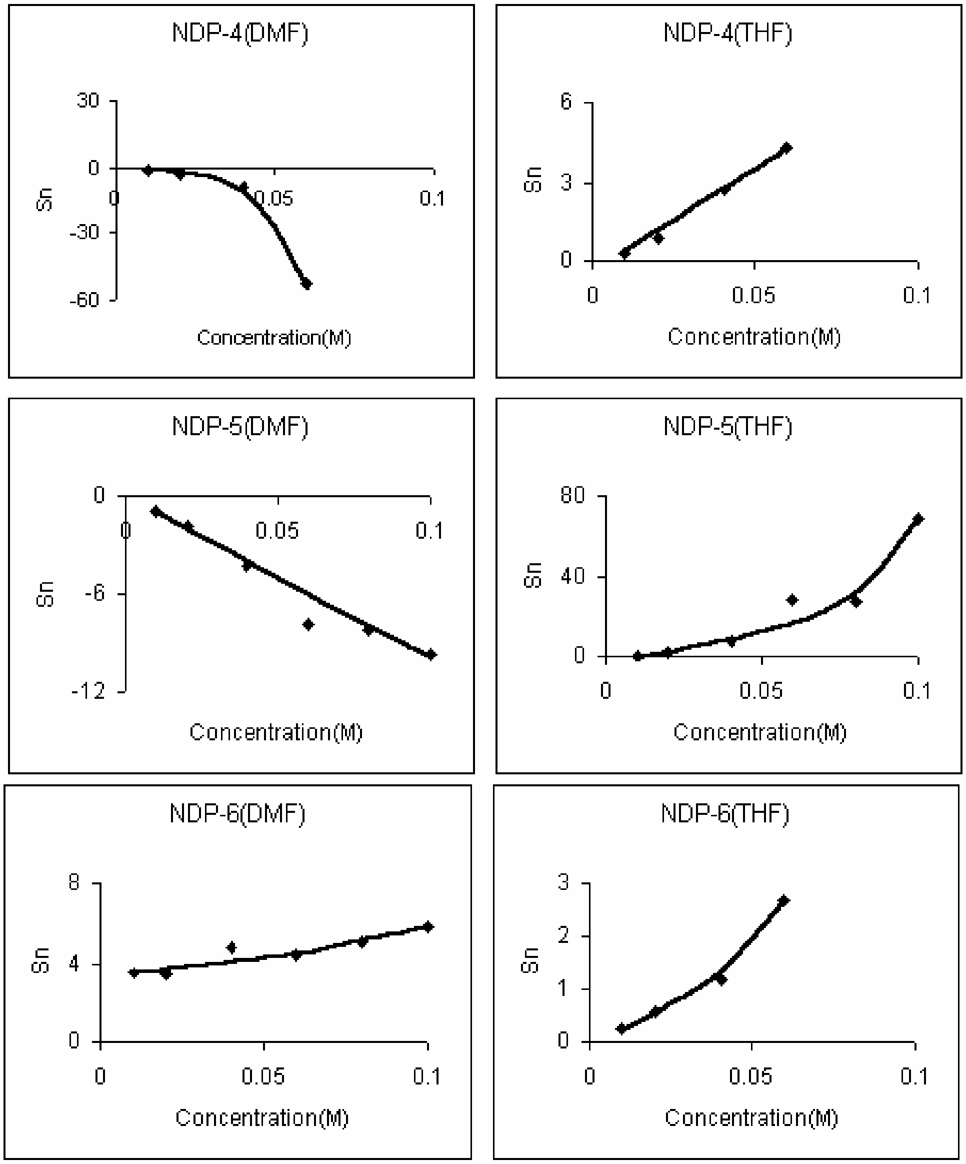
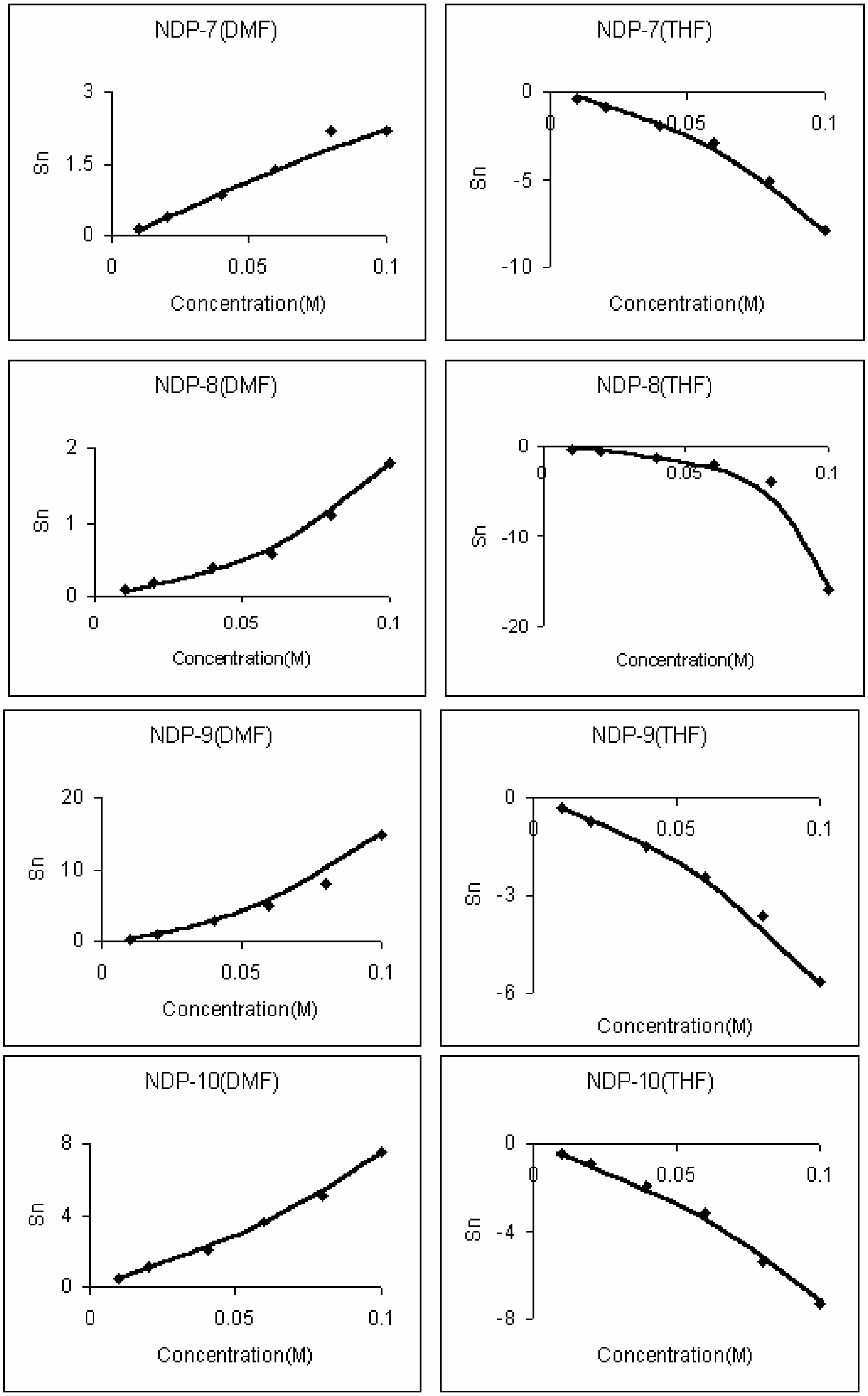


Figure 3.5.3 (Contd.)……



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INTRODUCTION

Thermal techniques are among the most powerful experimental tools developed during the last century. Thermal analysis has become an established method in the study of thermal behavior of materials and finds wide applications in diverse industrial and research fields. Among the thermal methods, the most widely used techniques are thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) which find extensive use in chemistry, biochemistry, metallurgy, materials science and various other areas. Further, this analysis has been used to determine physical and chemical properties of polymers, composites, geological material, ceramics and coal(1-5). It could also play an important role in pharmaceutical field(6-8). Information on thermal stability of diverse materials is of paramount importance in material science, both for qualitative and quantitative analysis of various components as well as for evaluating the influence of various factors on the reactivity of the materials, catalysts, ceramics, explosives, food stuffs, metals and alloys, pharmaceuticals and many others. Similarly, the range of applications of thermal methods is also wide. For example, phase changes and phase equilibria, thermal stability, kinetic studies, thermodynamic studies, characterization of materials, quality control and so on. Thermal production of new high technology materials and the resulting requirement for a more precise characterization of these substances have increased the demand for thermal analysis technique. Thermal analysis is useful in both quantitative and qualitative analysis.

Thermo Gravimetric Analysis (TGA) is a thermal analysis technique in which the mass of a sample is monitered as a function of temperature or time, when it is subjected to a programmed temperature change in a specified atmosphere. The plot of a mass change versus temperature is termed as a thermo gravimetric or TG curve.

Differential Thermal Analysis (DTA) is one of the simplest and oldest thermal techniques employed to study the physical and chemical transformations in the materials, associated with the energy changes. The technique involves the measurement of temperature difference between the sample and the thermally inert reference material when both are heated simultaneously at the predetermined constant heating rate in controlled atmosphere. The sensitivity of DTA instrument depends only depends on the type of thermocouple used, type and shape of sample container and the material from which it is fabricated(9,10).

Differential Scanning Calorimetry (DSC) is a versatile thermal analysis technique used to measure heat flows associated with transitions in materials as a function of temperature or time. It is widely used to provide quantitative and qualitative information about physical and chemical changes involving endothermic or exothermic processes or heat capacity changes. In DSC, the sample and reference are both maintained at a programmed temperature and the amount of energy which has to be supplied to or withdrawn from the sample to maintain zero temperature difference between a sample and a reference is the experimental parameter displayed as the ordinate of thermal analysis curve of crystallites, glass transition temperature, kinetic parameters etc.

Thermal properties of many organic and inorganic compounds have also been studied by different workers(11-15). Tanaka and Koga(16) have studied kinetics of dehydration of the salt and its admixture with KCl($CuCl_2$ $2H_2O$) in connection with their main investigation. Thermal properties of some compounds of cobalt, nickel and copper with cinnamic acid were also reported(17). Naik and Ramappa(18) reported thermal stability data of some cobalt imipramine complexes. Apelblat and Manzurola(19) reported thermal properties of some salts. Different methods of thermal analysis were used for a comparative characterization of the thermal oxidative stabilities and low-temperature behavior of vegetable and mineral oil-based hydralic fluids(20). Thermal properties of some Schiff bases have also been studied(21-23).

From TG curves, various kinetic parameters can be evaluated by several methods. It is assumed that thermal and diffusion barriers are negligible because small quantity of material, the shape of any TG curve depends on the nature of apparatus and the way in which it is used. Further, in all these method, Arrhenius equation is valid.

The kinetic treatments are generally based on the relationship of the type:

$dC/dt = K\,f(C)$ ……(3.6.1)

where C is the degree of conversion, t is time and K is rate constant. f(C) is a temperature independent function of C.

The constant K is assumed to have the Arrhenius form:

$K = A\,e^{-E/RT}$ ……(3.6.2)

C is defined as the conversion with respect to initial material and is given as:

$C = 1-(W/W_0)$ ……(3.6.3)

where W_0 and W are the initial weight at t=0 and weight at any time t of the material.

Equation (3.6.3) can be written as:

$(W/W_0) = (1-C)$ …...(3.6.4)

W/W_0 is known as residual weight fraction.

Thus, the rate of conversion is,

$dC/dt = -\,(1/W_0)\,(dW/dt)$ ....(3.6.5)

For homogeneous kinetics, the conversion is assumed to be of the form:

$f(C) = (1-C)^n$ ......(3.6.6)

where n is order of the reaction.

Substituting the values from equation (3.6.2) and (3.6.6) in equation (3.6.1) gives:

$dC/dt = A\,e^{-E/RT}\,(1-C)^n$

or $dC/dt = (A/\beta)\,e^{-E/RT}\,(1-C)^n$ ......(3.6.7) where A is the frequency factor, β is the rate of heating and E is the energy of activation.

Various methods for single and multiple heating rates have been reported [24-28]. The methods of single heating rate are as follows:

1. Freeman-Carroll[24] and Anderson-Freeman method[25]:

To analyze TG data at a single heating rate, Freeman and Carroll gave the following equation:

$\ln(dC/dt)/\ln(1-C) = n - E/R\,[(1/T)/(\Delta\ln(1-C)]$ ......(3.6.8)

A plot of left hand side against $\Delta(1/T)/[\Delta\ln(1-C)]$ gives a straight line with a slope equal to -E/R and the intercept is equal to n.

Anderson and Freeman used the following equation (3.6.8):

$[\Delta\ln(dC/dt)] = n\,[\Delta\ln(1-C)] - E/R\,\Delta(1/T)$ ......(3.6.9)

The plot of $[\Delta\ln(dC/dt)]$ against $[\Delta\ln(1-C)]$ for equal intervals of $\Delta(1/T)$ gives a straight line with slope equal to n and intercept $-E/R\,\Delta(1/T)$.

2. Sharp-Wentworth method[26]:

Sharp and Wentworth derived the following relation for first order kinetics (n=1) to analyse the TG data:

$\log[(dC/dt)/(1-C)] = \log(A/\beta) - (E/2.303R).(1/T)$ ....(3.6.10)

The plot of $\log[(dC/dt)/(1-C)]$ against 1/T would be a straight line with slope equal to - (E/2.303R) and intercept equal to $\log(A/\beta)$.

3. Chatterjee Method [27]:

Chatterjee used the equation (3.6.11):

$n = [\log(dW/dt)_1 - \log(dW/dt)_2]/(\log W_1 - \log W_2)$ ...... (3.6.11) where W_1 and W_2 are the sample weights.

4. Horowitz and Metzger method [28]:

The energy of activation E can be determined from a single TG curve by the relation:

$$\ln [\ln(1-C)^{-1}] = (E/RT_s^2)\theta \qquad \text{...... (3.6.12)}$$

where $\theta = T-T_s$. T_s is the temperature at which the rate of decomposition is maximum.

Using the following equations (3.6.13) and (3.6.14) the frequency factor A and entropy change ΔS can be determined.

$$\ln E - \ln (RT_s^2) = \ln A - \ln\beta - E/RT_s^2 \qquad \text{...... (3.6.13)}$$

$$A = (k_bT / h)\, e^{\Delta S/R} \qquad \text{...... (3.6.14)}$$

where k_b is Boltzmann constant and h is Planck's constant.

EXPERIMENTAL

The differential scanning calorimetric (DSC), Thermogravimetric analysis (TG) and Differential thermal analysis (DTA) measurements were made on the instrument “Universal V 2.6D TA Instrument” at the heating rate of 10^0C per minute in nitrogen atmosphere for some Schiff bases derived from α-naphthalamine and benzidine.

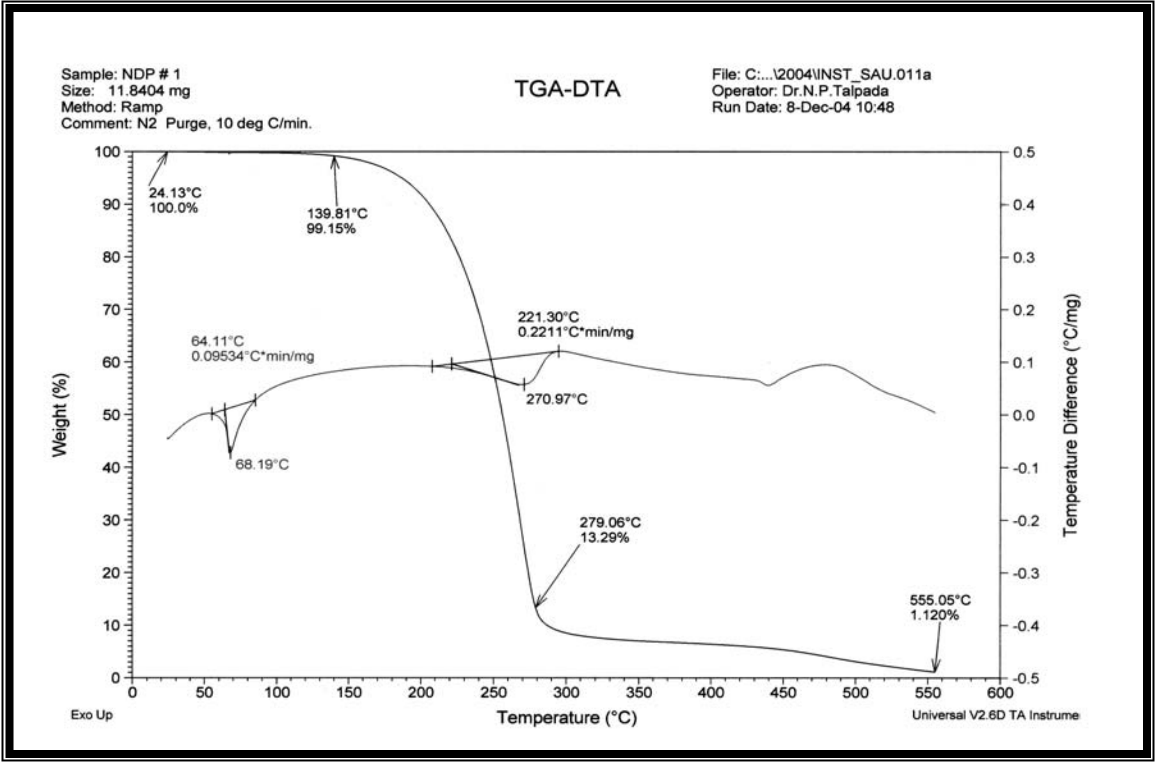
RESULTS AND DISCUSSION

The TG/DTA and DSC thermograms of Schiff bases derived from α-naphthalamine and benzidine are given in Figures 3.6.1 to 3.6.14. The thermal properties of only four Schiff bases of benzidine were studied. Various thermal properties such as initial decomposition temperature (IDT), the decomposition temperature range and the maximum degradation along with the percentage weight loss and Exo/Endo transitions of Schiff bases are reported in Tables 3.6.1 and 3.6.2. Further, the experimental melting points are also given for comparison.

It is observed from the Table 3.6.1 that the initial decomposition temperature is minimum for NDP-1 and maximum for NDP-8. However, % weight loss is minimum for NDP-3 and NDP-7. Maximum weight loss is observed for NDP-8. The weight loss decreases in the order: NDP-8 > NDP-6 > NDP-10 > NDP-1 > NDP-5 > NDP-9 > NDP-2 > NDP-4 > NDP-3, NDP-7. Thus, NDP-8, which appears to be thermally stable losses maximum weight upon decomposition. The temperature of maximum degradation is maximum for NDP-5 followed by NDP-8. NDP-7 and NDP-9 has minimum temperature of maximum degradation. Overall, all NDP Schiff bases show maximum degradation between 274.7 and 342.2^{0}C. The thermal stability of a compound depends upon type of groups and structure. In the studied NDP Schiff bases, central moiety is same but side chains are different. In NDP-8, side chain is furfurlaldehyde whereas, it is benzaldehyde in NDP-1. So, presence of benzaldehyde decreases the stability. The experimental melting points are also compared with those observed by DSC and DTA analysis. It is observed that for some Schiff bases, values are in good agreement with those observed by DSC and DTA analysis.

Among benzidine Schiff bases, initial decomposition temperature is minimum for DVA-3 whereas maximum is observed for DVA-2. However, minimum weight loss is observed to be for DVA-4 followed by DVA-3. DVA-1 shows minimum weight loss. In these Schiff bases, central moiety is benzidine with different side chains. DVA-1 has benzaldehyde side chain, DVA-2, which is **Figure 3.6.1 :** The

TGA/DTA and DSC graph of NDP-1



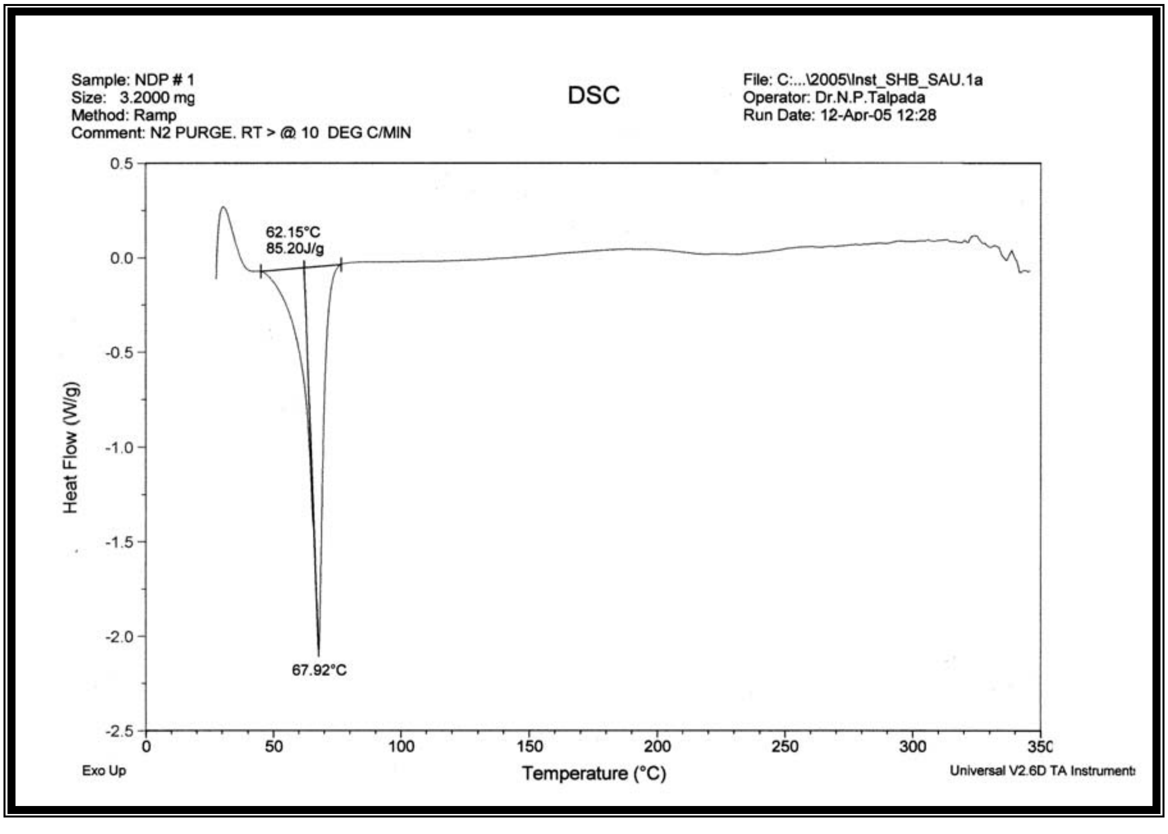
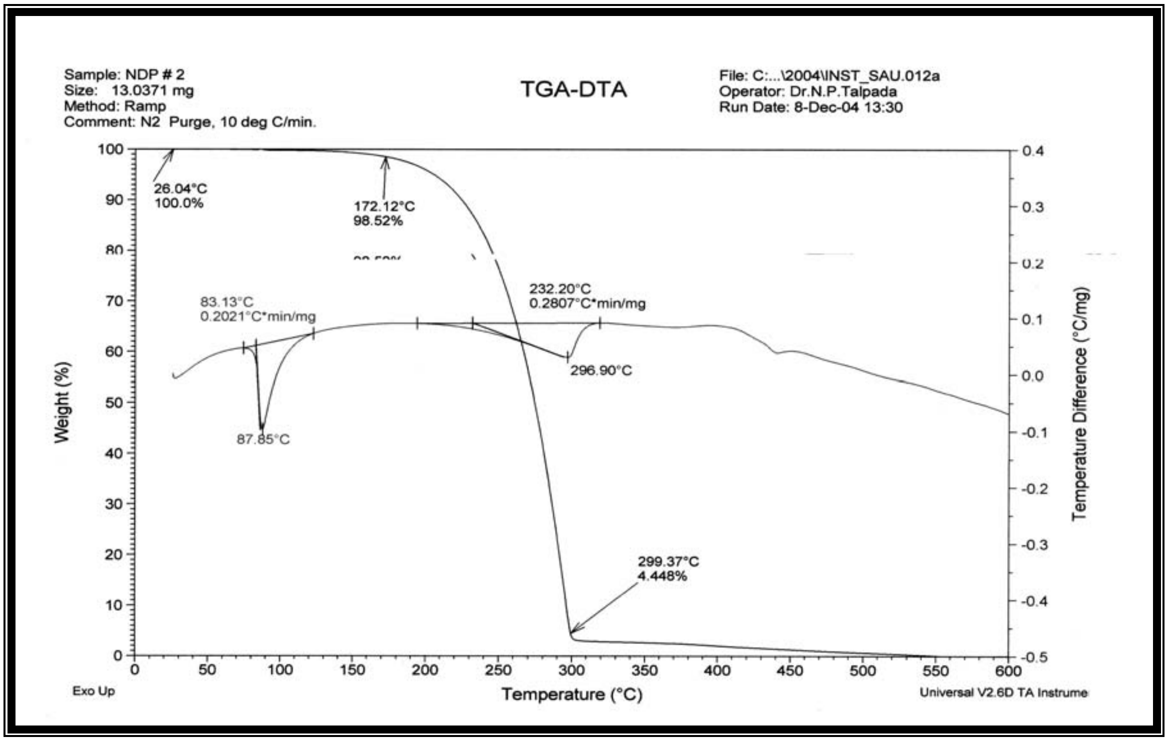


Figure 3.6.2 : The TGA/DTA and DSC graph of NDP-2



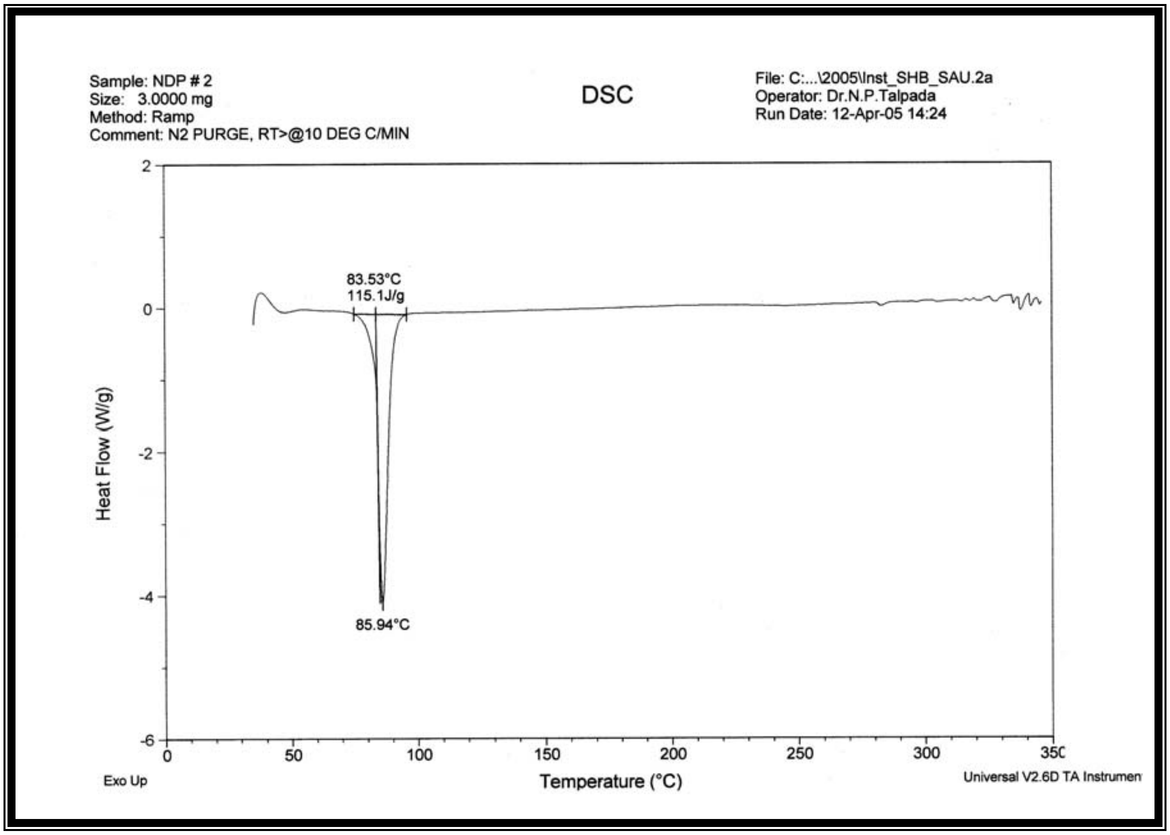
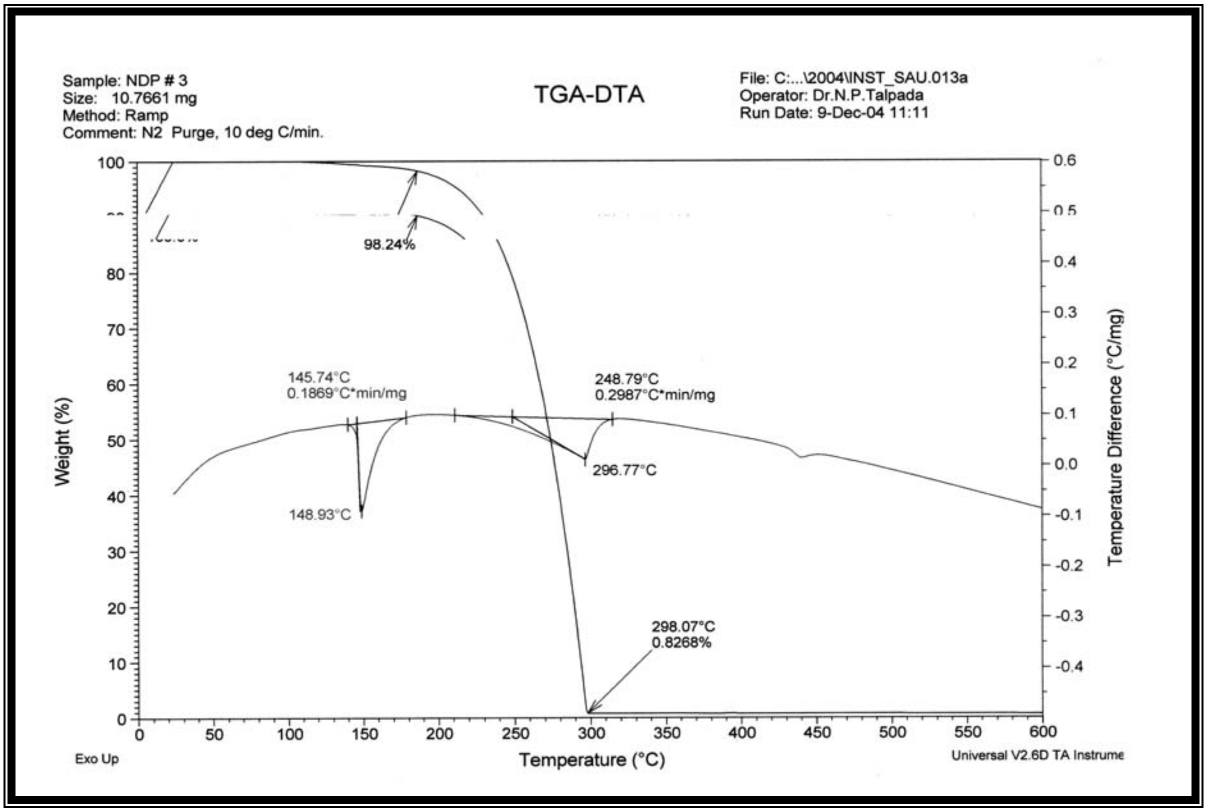


Figure 3.6.3 : The TGA/DTA and DSC graph of NDP-3



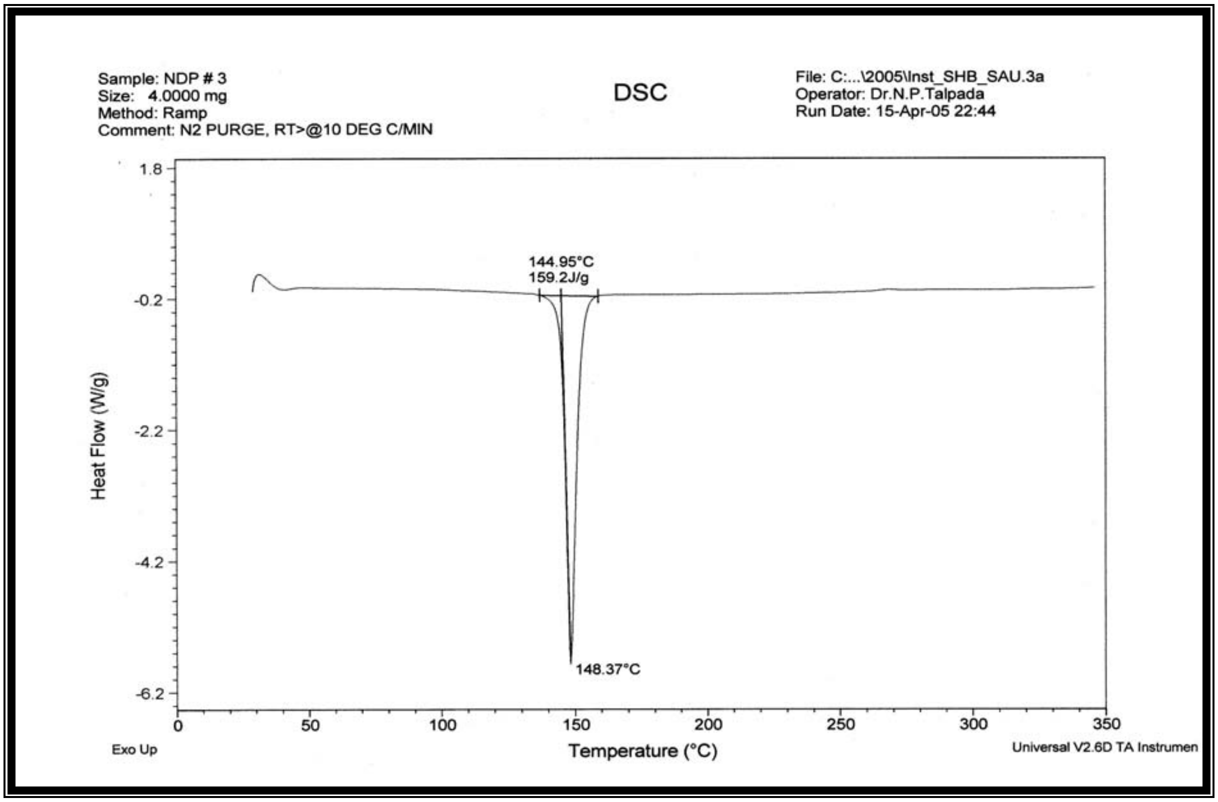
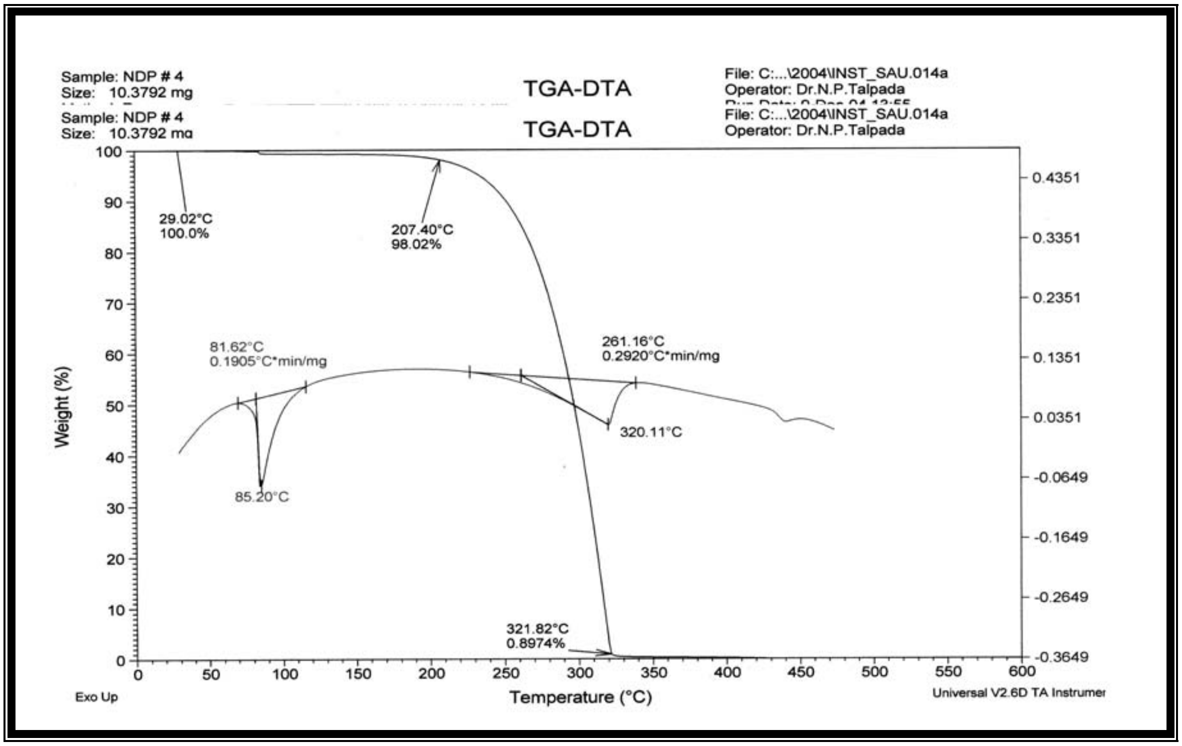


Figure 3.6.4 : The TGA/DTA and DSC graph of NDP-4



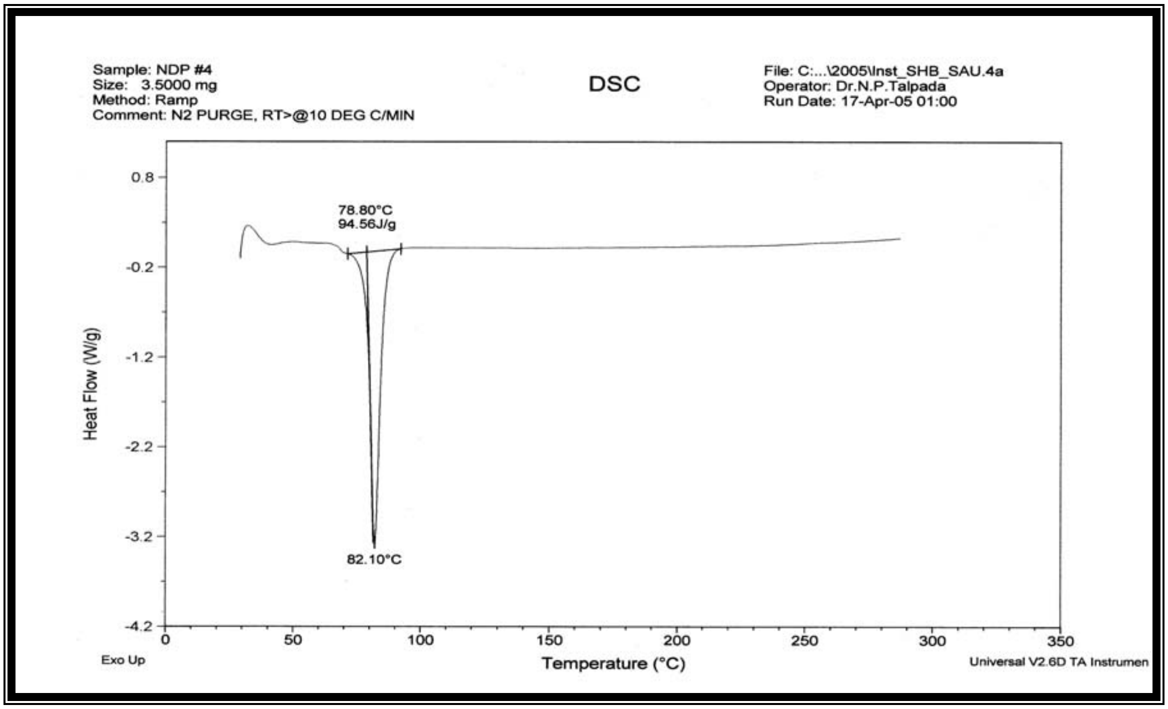
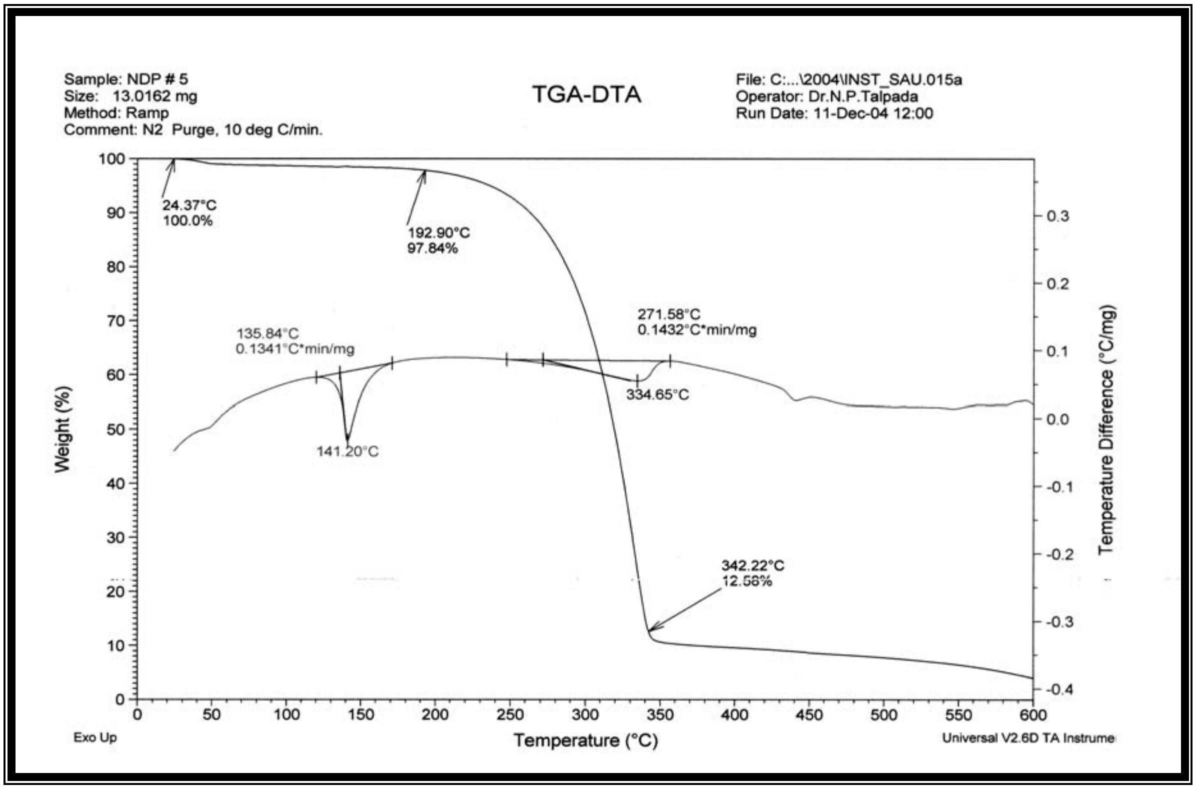


Figure 3.6.5 : The TGA/DTA and DSC graph of NDP-5



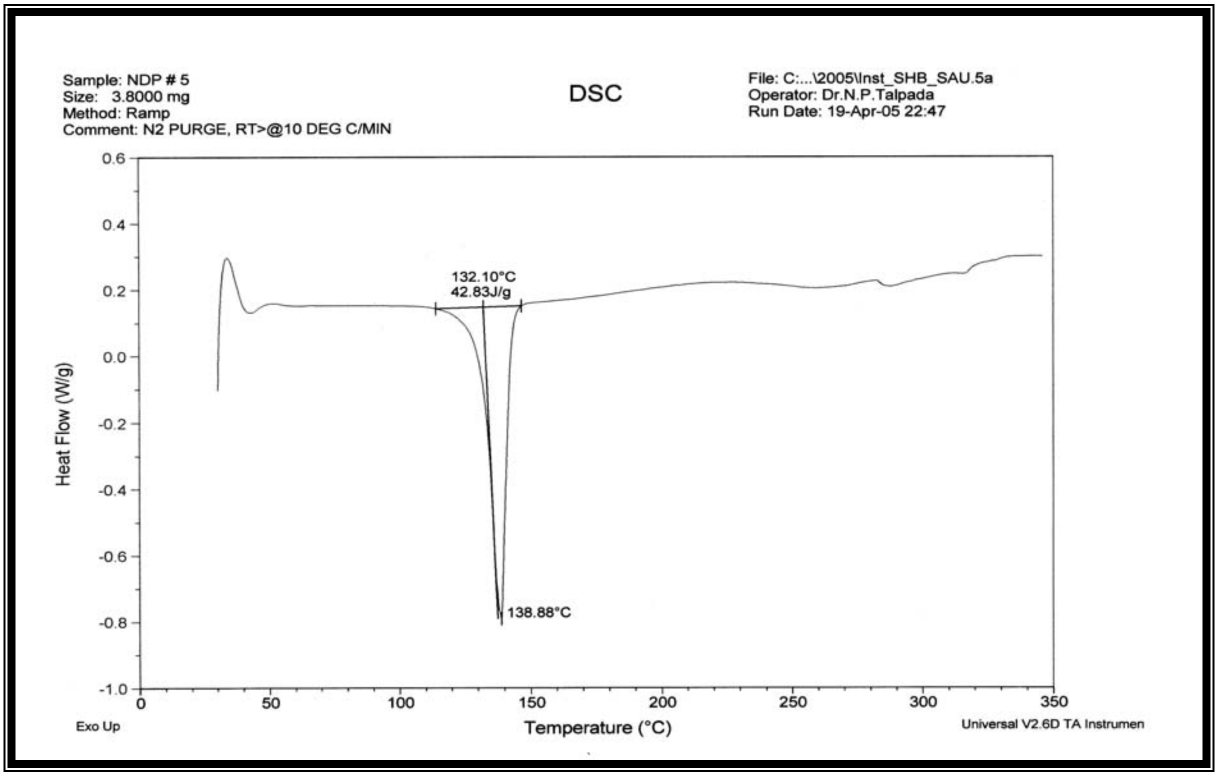
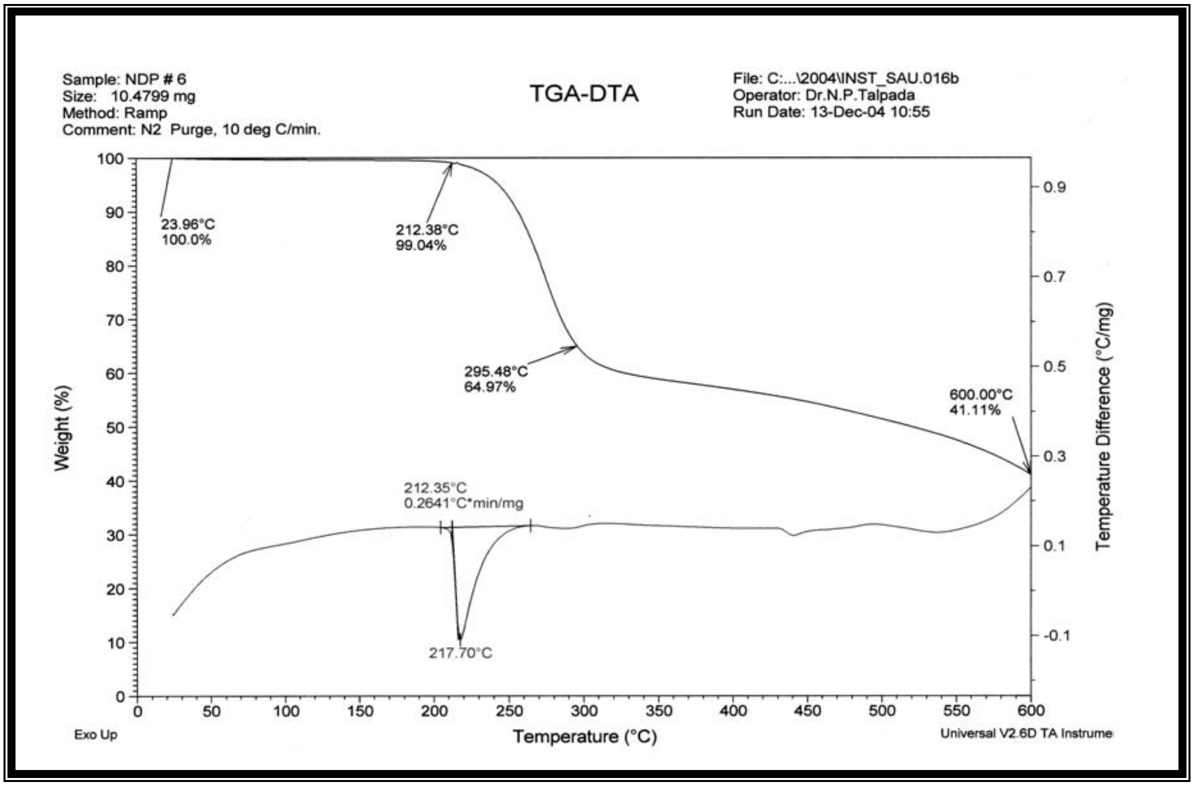


Figure 3.6.6 : The TGA/DTA and DSC graph of NDP-6



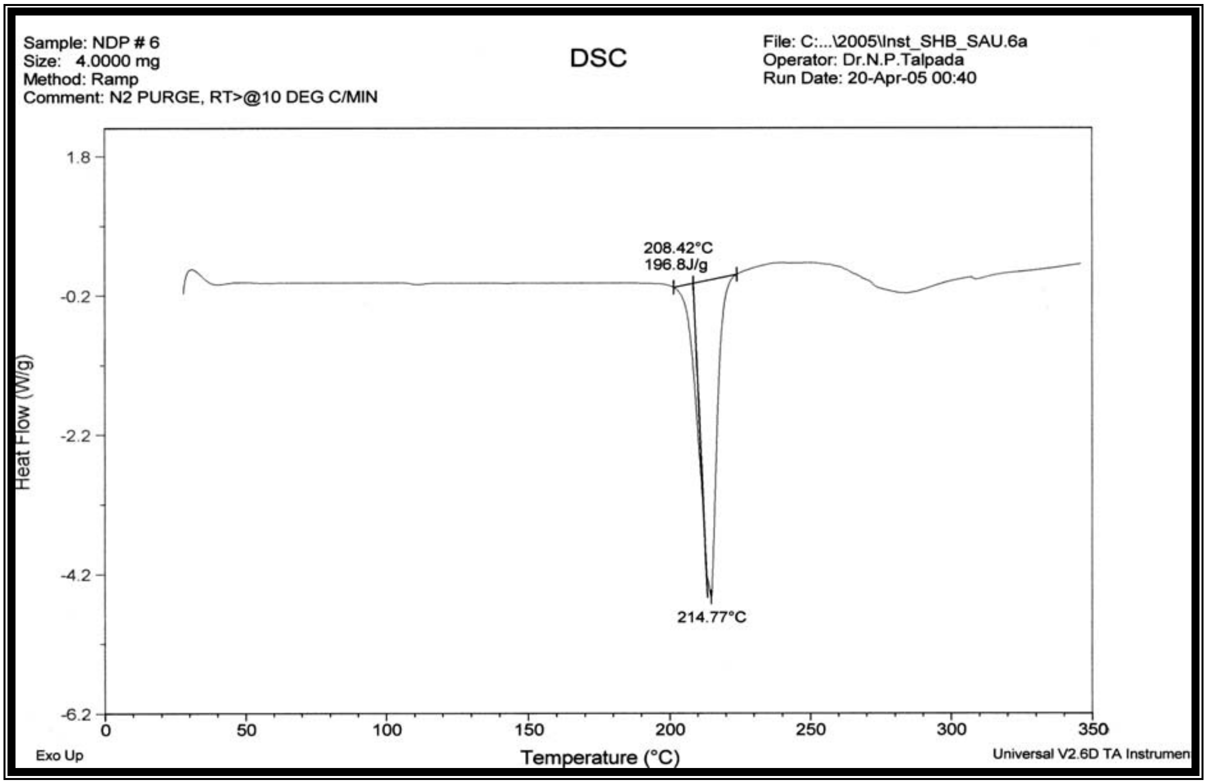
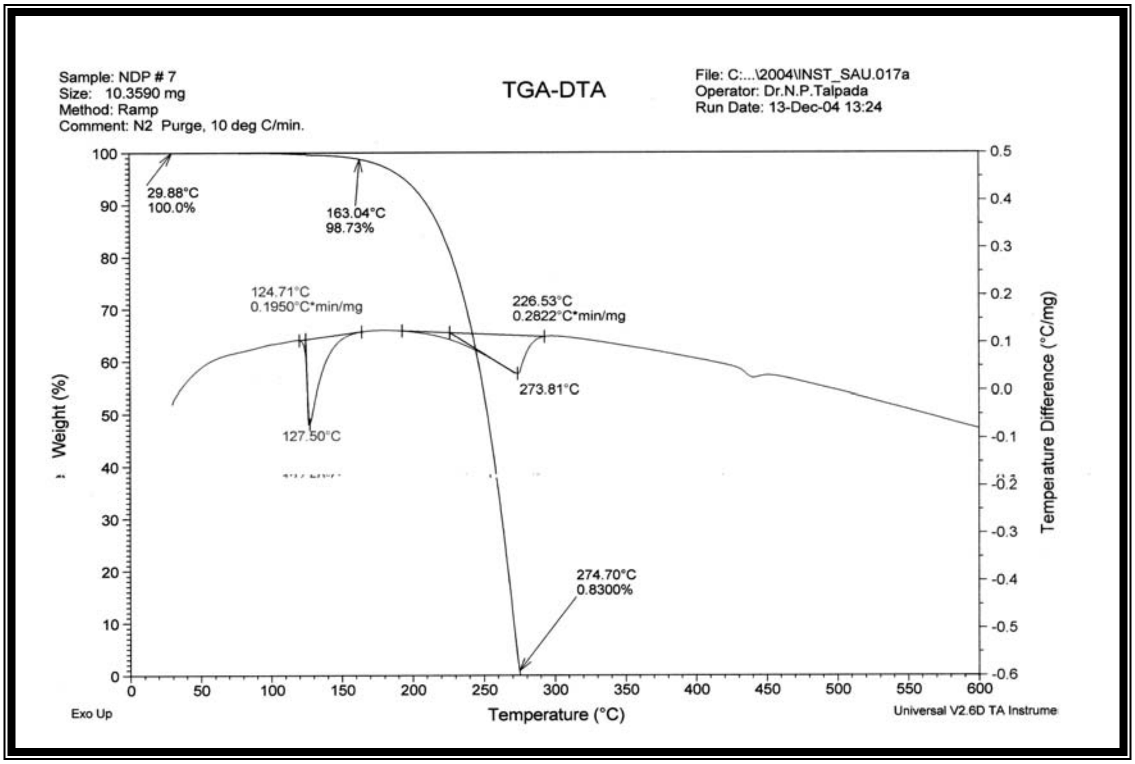


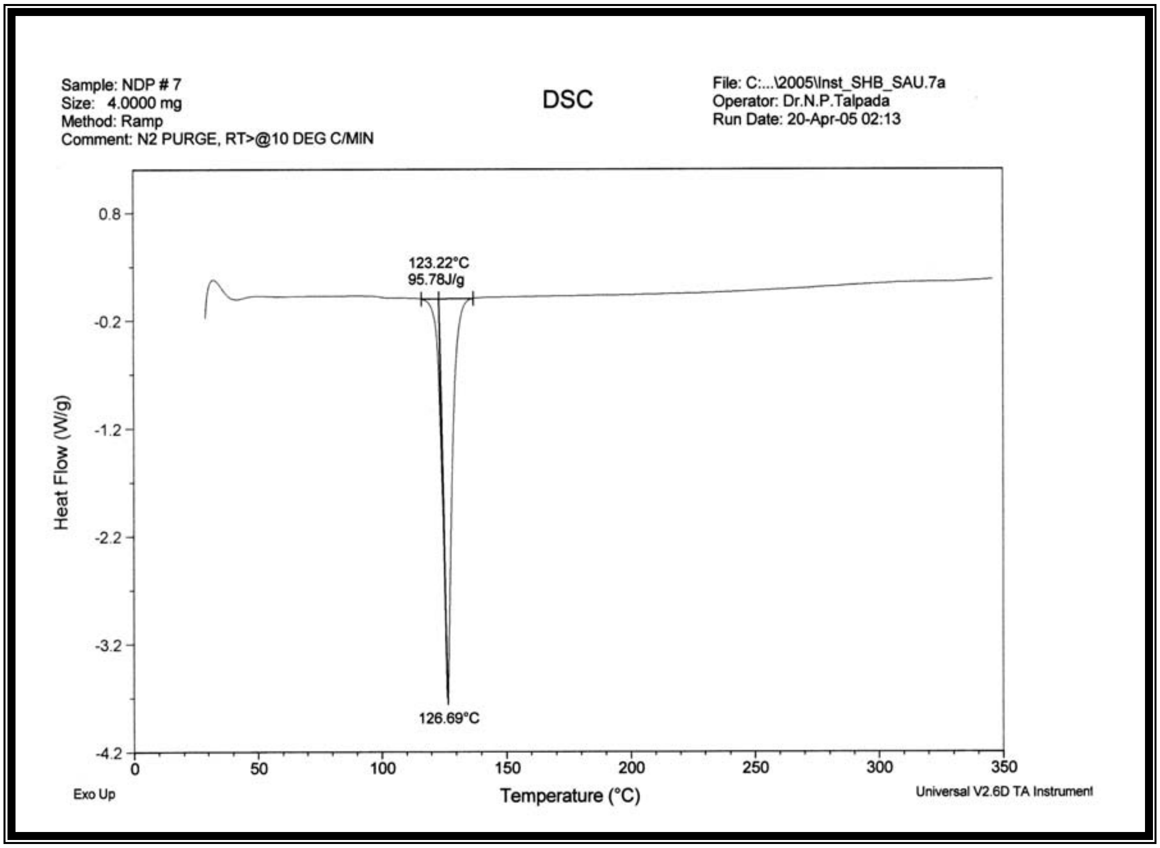
Figure 3.6.7 : The TGA/DTA and DSC graph of NDP-7



Sample: NDP # 7
Size: 10.3590 mg
Method: Ramp
Comment: N2 Purge, 10 deg C/min.

TGA-DTA

File: C:...\2004\INST_SAU.017a
Operator: Dr.N.P.Talpada
Run Date: 13-Dec-04 13:24

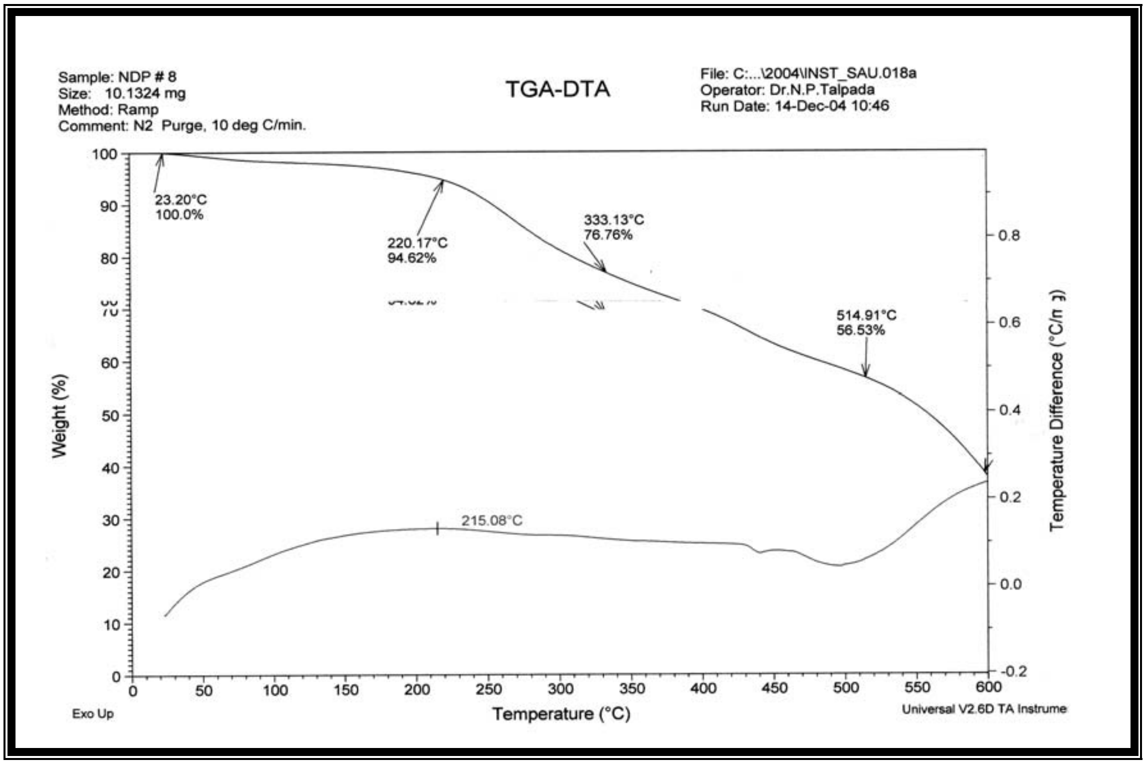


Sample: NDP # 7
Size: 4.0000 mg
Method: Ramp
Comment: N2 PURGE, RT>@10 DEG C/MIN

DSC

File: C:...\2005\Inst_SHB_SAU.7a
Operator: Dr.N.P.Talpada
Run Date: 20-Apr-05 02:13

Figure 3.6.8 : The TGA/DTA and DSC graph of NDP-8



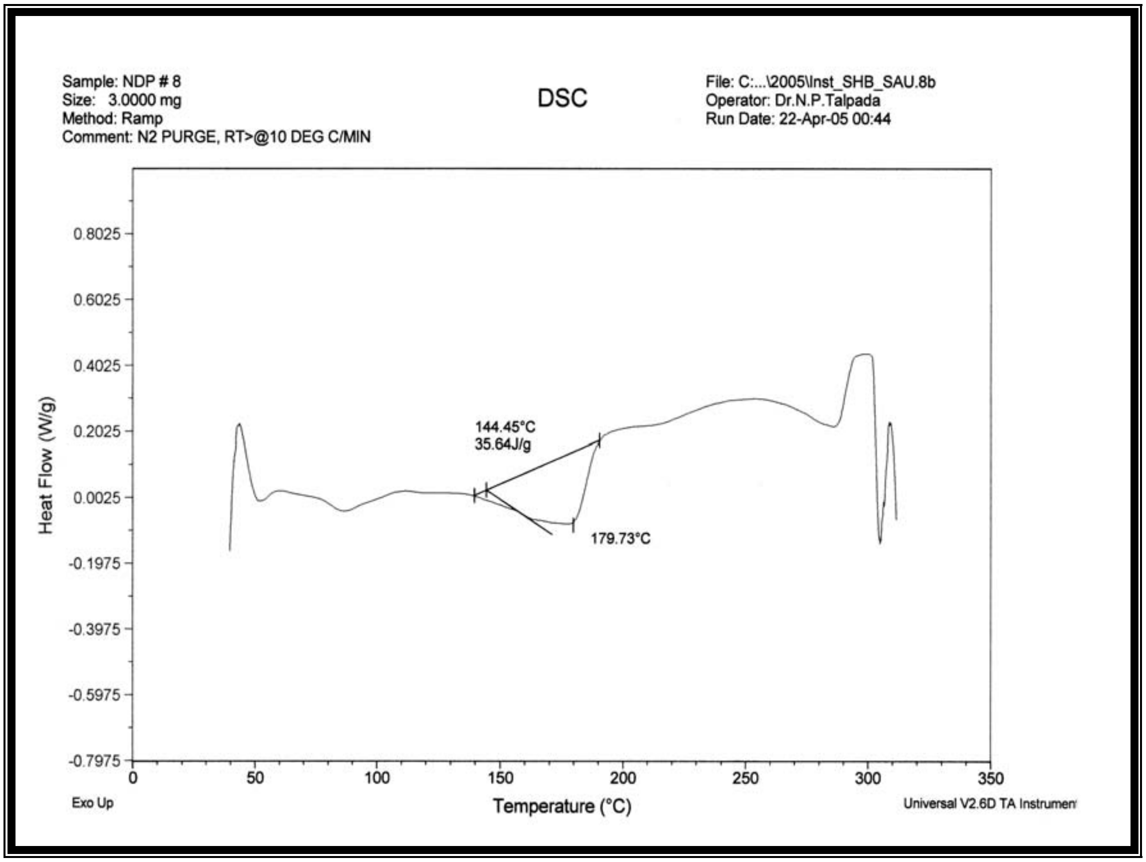
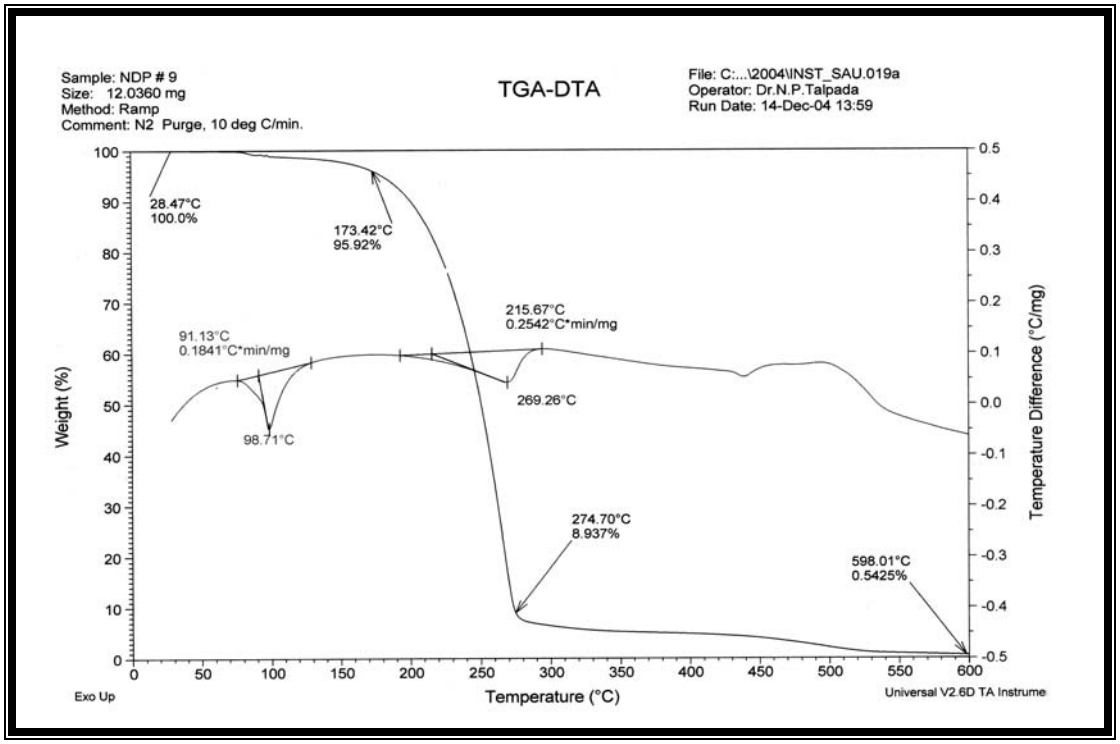


Figure 3.6.9 : The TGA/DTA and DSC graph of NDP-9



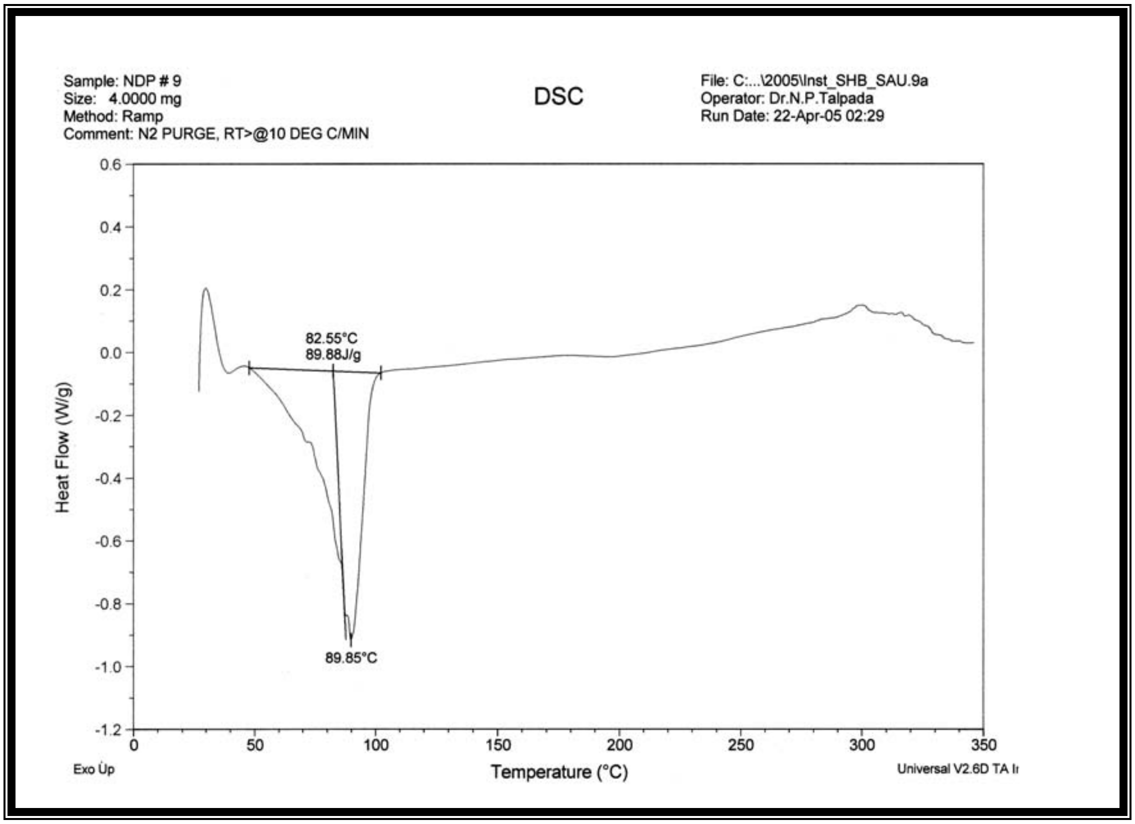
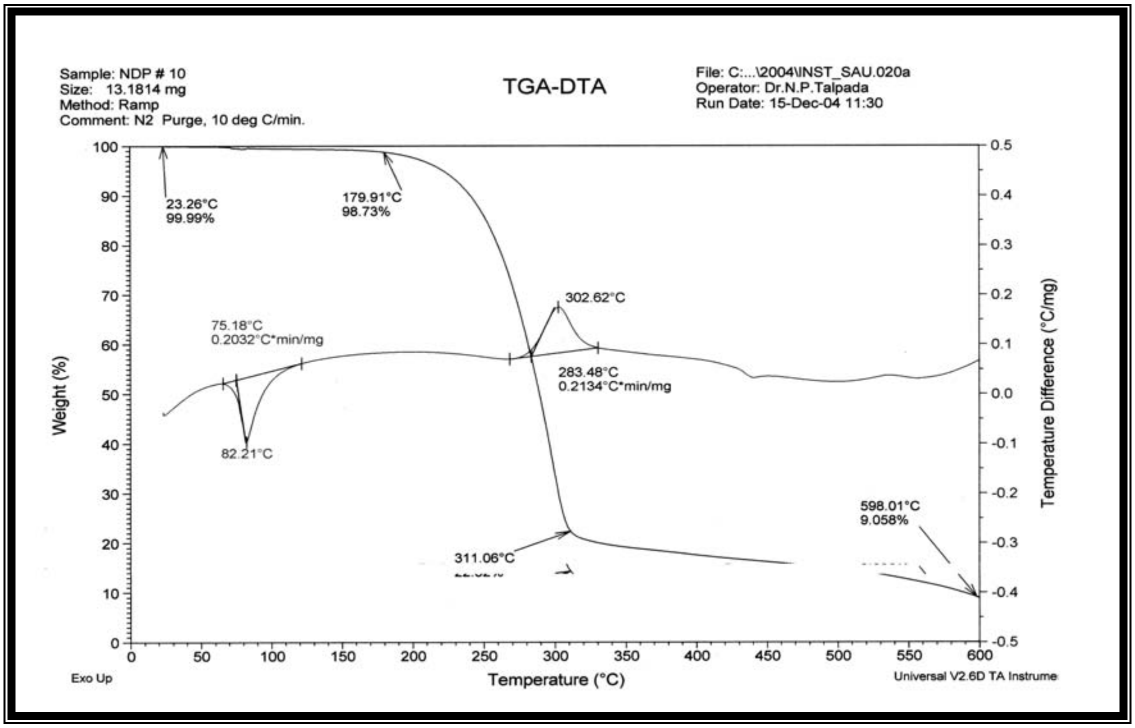


Figure 3.6.10 : The TGA/DTA and DSC graph of NDP-10



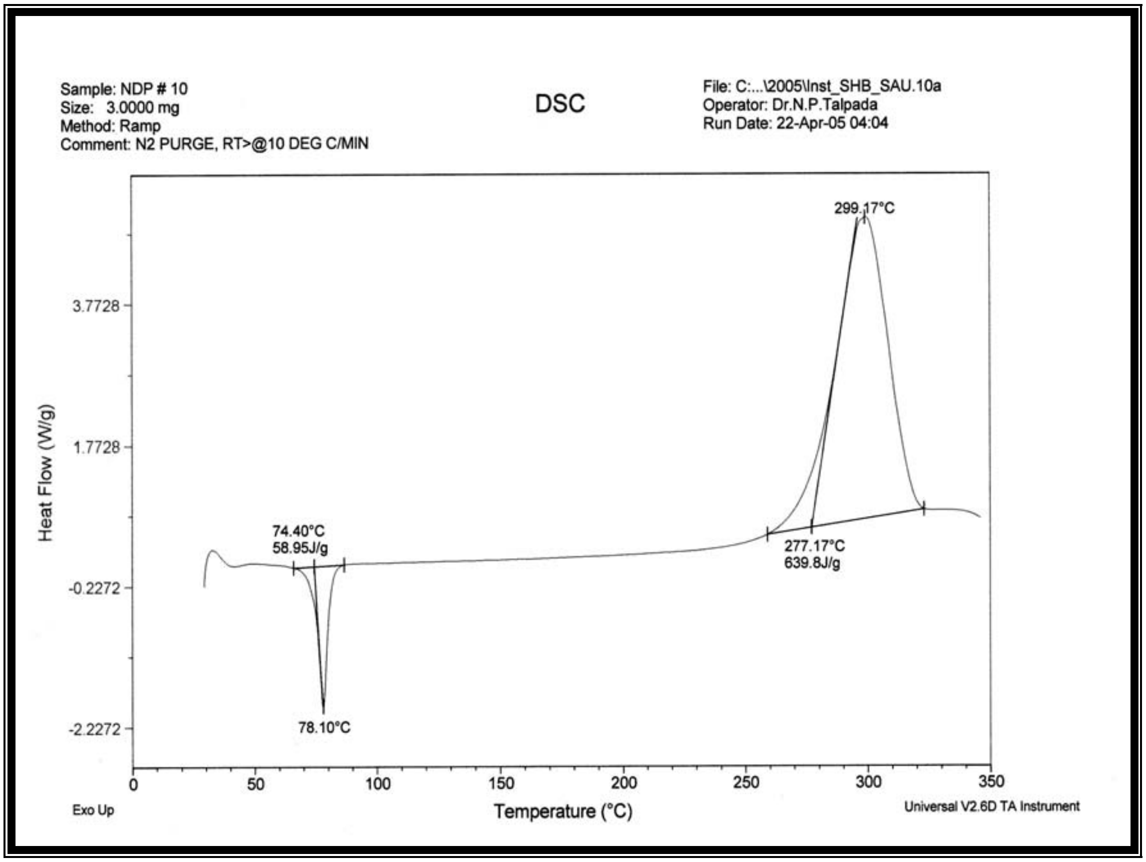


Figure 3.6.11 : The TGA/DTA and DSC graph of DVA-1

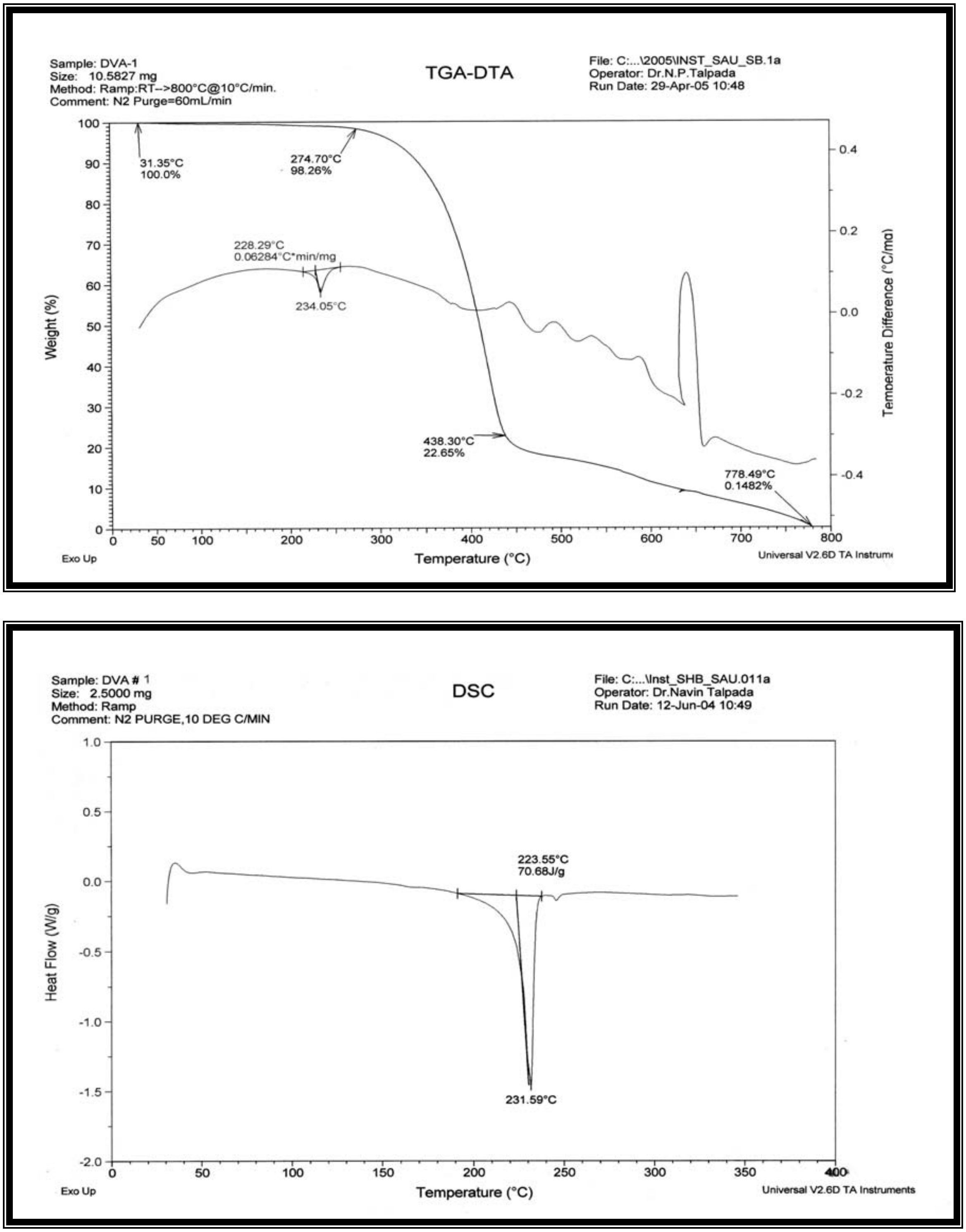


Figure 3.6.12 : The TGA/DTA and DSC graph of DVA-2

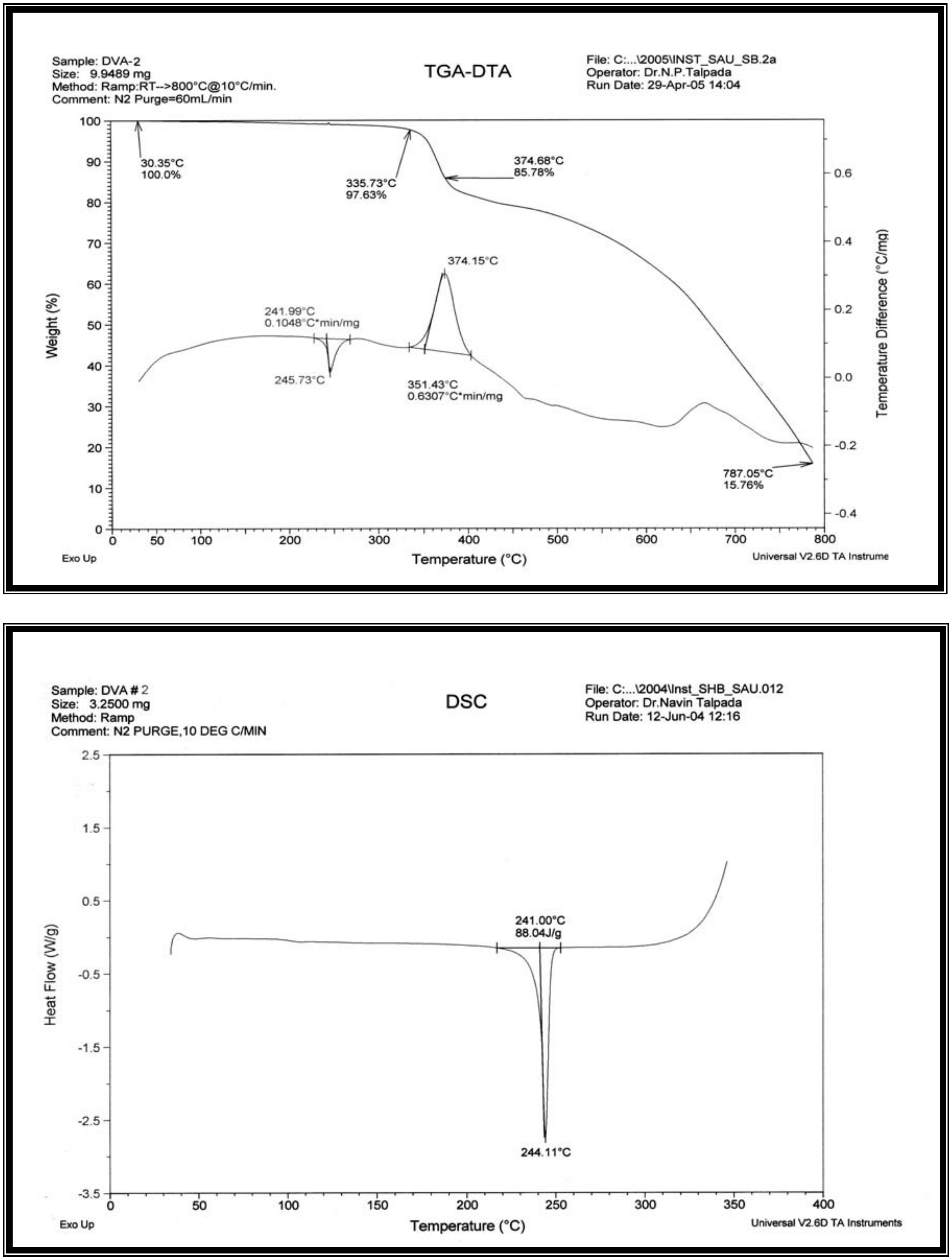
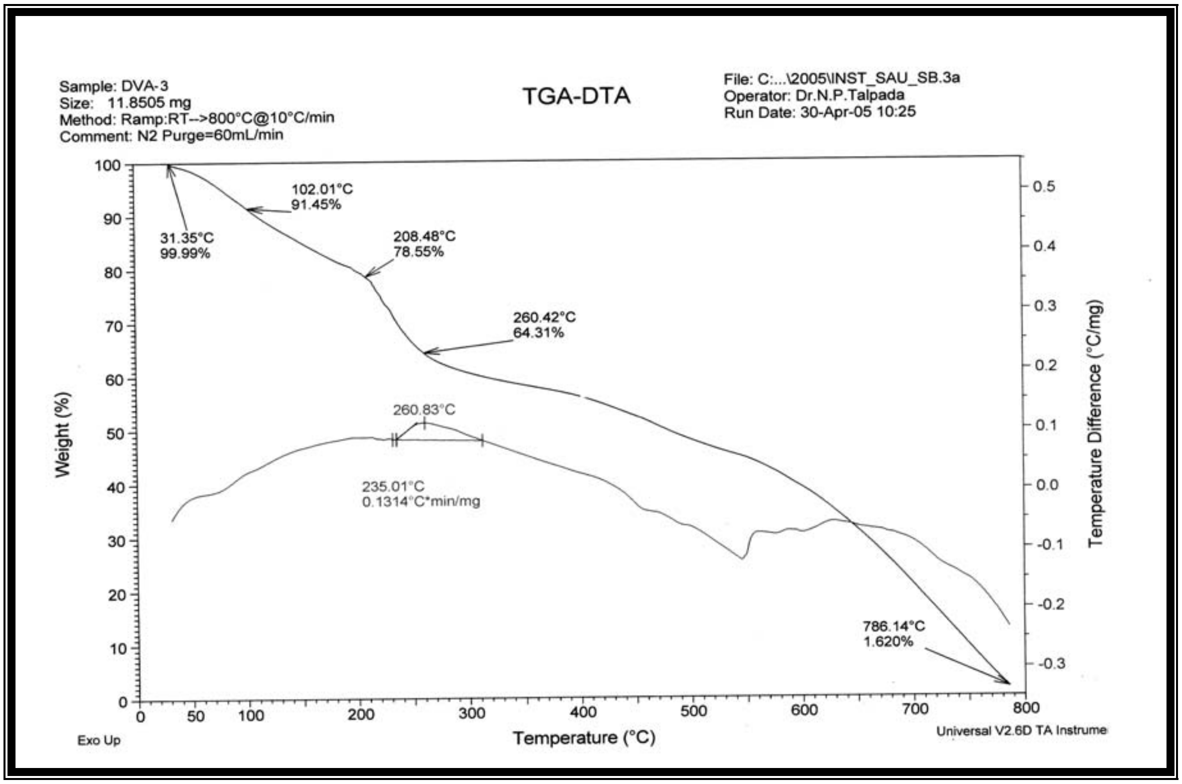


Figure 3.6.13 : The TGA/DTA and DSC graph of DVA-3



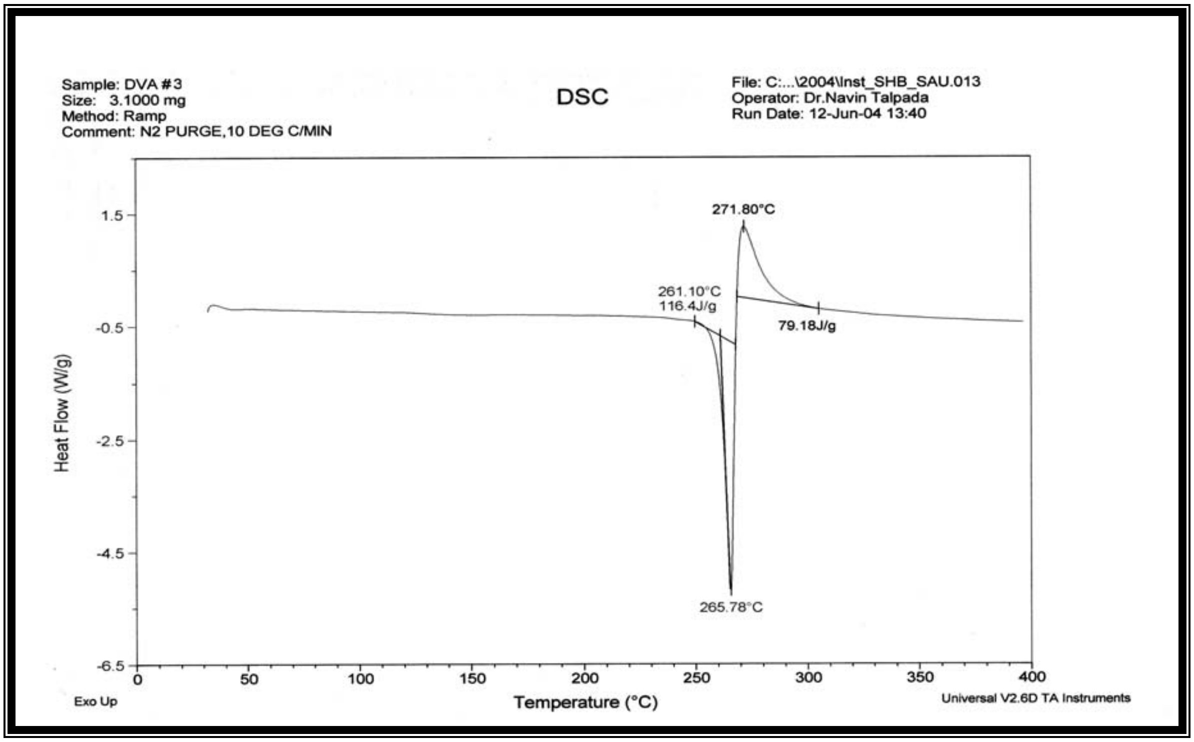
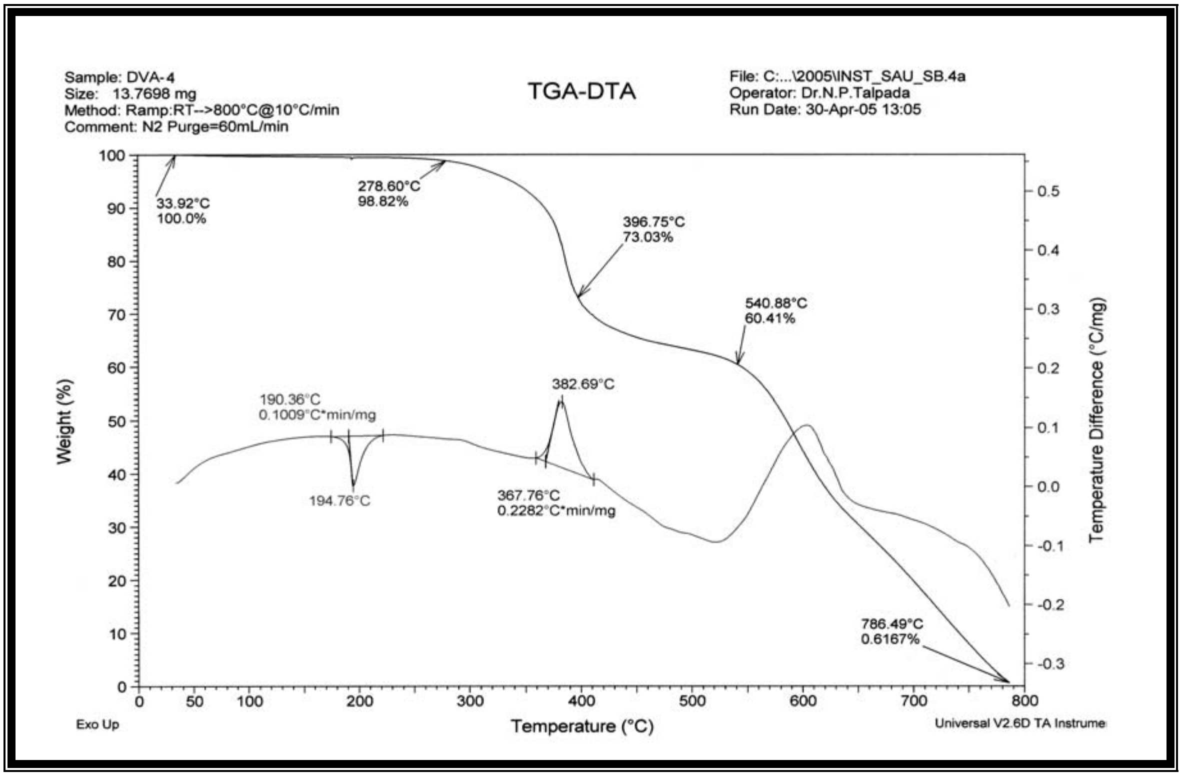


Figure 3.6.14 : The TGA/DTA and DSC graph of DVA-4



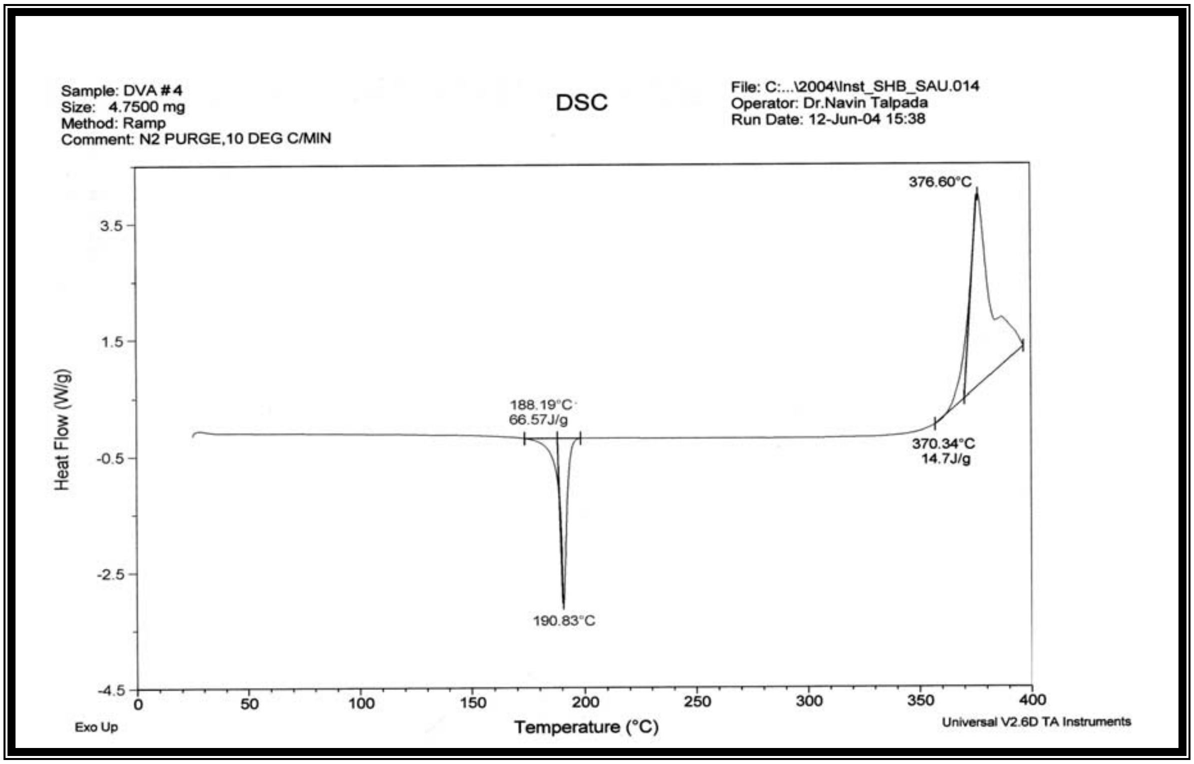


Table 3.6.1 : TG, DTA and DSC data for the Schiff bases of α-naphthyl amine.

Comp. code	Amt. mg	IDT ^{0}C	Decomp. Range ^{0}C	% Wt. Loss	Residual Wt. Loss Mg.	Temp. of maximum degrada -tion	Transition	DSC Temp. ^{0}C	DTA Temp. ^{0}C	Expl. M.P ^{0}C
NDP-1	11.84	139.81	139.81-279.06	13.29	1.5736	279.06	Endo Endo	67.92	68.19 270.97	85
NDP-2	13.04	172.12	172.12-299.37	4.45	0.5799	299.37	Endo Endo	85.94	87.85 296.90	89
NDP-3	10.77	186.41	186.41-298.07	0.83	0.0890	298.07	Endo Endo	148.37	148.93 296.77	144
NDP-4	10.38	207.40	207.40-321.82	0.90	0.0931	321.82	Endo Endo	82.10	85.20 320.11	80
NDP-5	13.02	192.90	192.90-342.22	12.58	1.6374	342.22	Endo Endo	138.88	141.20 334.65	130
NDP-6	10.48	212.38	212.38-295.48	64.94	6.8088	295.48	Endo	214.77	217.70	204
NDP-7	10.36	163.04	163.04-274.70	0.83	0.0860	274.70	Endo Endo	126.69	127.50 273.81	122
NDP-8	10.13	220.17	220.17-333.13	76.76	7.7776	333.13	Endo	179.73	215.08	193
NDP-9	12.04	173.42	173.42-274.70	8.94	1.0757	274.70	Endo Endo	89.85	98.71 269.26	85
NDP-10	13.18	179.91	179.91-311.06	22.32	2.9421	311.06	Exo. Endo	78.10	83.48 82.21	104

Table 3.6.2 : TG, DTA and DSC data for the Schiff bases of benzidine.

Comp. code	**Amt. mg**	**IDT ^{0}C**	**Decomp. Range ^{0}C**	**% Wt. Loss**	**Residual Wt. Loss Mg.**	**Temp of maximum degrada -tion**	**Transition**	**DSC Temp. ^{0}C**	**DTA Temp. ^{0}C**	**Expl. M.P ^{0}C**
DVA-1	10.58	274.70	274.70-438.30	22.65	2.3970	438.30	Exo Endo	231.59	- 234.05	220
DVA-2	9.95	335.73	335.73-787.05	15.76	1.5679	787.05	Exo Endo	244.11	374.15 245.73	208
DVA-3	11.85	102.01	102.01-786.14	1.620	0.1920	786.14	Exo Endo	265.78	260.83 -	260
DVA-4	13.77	278.60	278.60-786.49	0.6167	0.0849	786.49	Exo Endo	190.83	194.76 382.69	175

most thermally stable contains 2-nitro benzaldehyde, DVA-3 has 4-hydroxy benzaldehyde and DVA-4 contains 2-chloro benzaldehyde. Thus, 2-nitro benzaldehyde increases the stability whereas 4-hydroxy benzaldehyde decreases the stability.

Both NDP-1 and DVA-1 contain benzaldehyde as side chain. Comparison of these two Schiff bases suggests that benzidine increases the stability whereas α-naphthalamine decreases the stability although same side chain is present. Similarly, it is observed that presence of 4-hydroxy benzaldehyde increases the stability when attached to α-naphthalamine but with benzidine, it decreases the stability. This again confirms that thermal stability of a compound depends upon type of groups present.

The kinetic parameters, such as order of the degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) are reported in Tables 3.6.3 and 3.6.4 along with correlation coefficient (γ). The Freeman Carroll plots for NDP-1 and NDP-2 and DVA-1 and DVA-2 are given in Figures 3.6.15 and 3.6.16.

Table 3.6.3 shows that, order of reaction (n) is maximum for NDP-2. For all the Schiff bases, the order of reaction is greater than one. For NDP-9, its value is 1.25 which is close to one. For all the Schiff bases, energy of activation decreases in the following order: NDP-3 > NDP-7 > NDP-9 > NDP-10 > NDP-2 > NDP-5 > NDP-8 (first step) > NDP-6 > NDP-4 > NDP-1. The frequency factor A is also observed to be maximum for NDP-3 and NDP-7 and minimum for NDP-1. Overall, wide range of A is observed. It follows the same order as energy of activation. The change in entropy (ΔS) for all the Schiff bases is positive, which indicates that the transition state is in less ordered state. The entropy of Schiff bases decreases in the following order: NDP-7 > NDP-3 > NDP-9 > NDP-10 > NDP-2 > NDP-5 > NDP-8 (first step) > NDP-6 > NDP-4 > NDP-1.

For DVA Schiff bases, order of reaction is maximum for DVA-2 (3.91) and minimum for DVA-1(1.17) which is close to unity. The frequency factor is maximum for DVA-1 and minimum for DVA-3. Energy of activation and entropy

Figure 3.6.15 : The Freeman and Carroll plots for (A)NDP-1 and (B)NDP-2

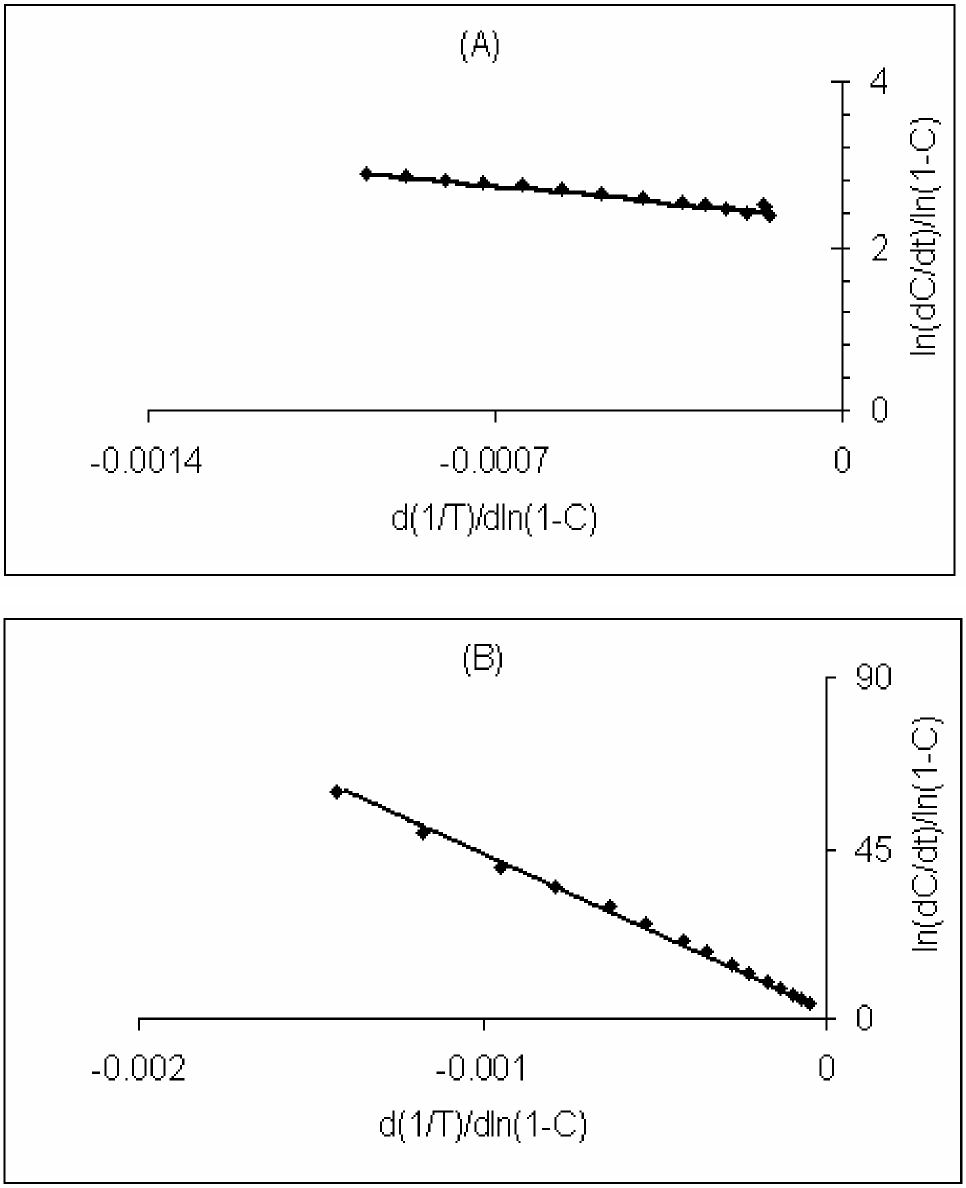
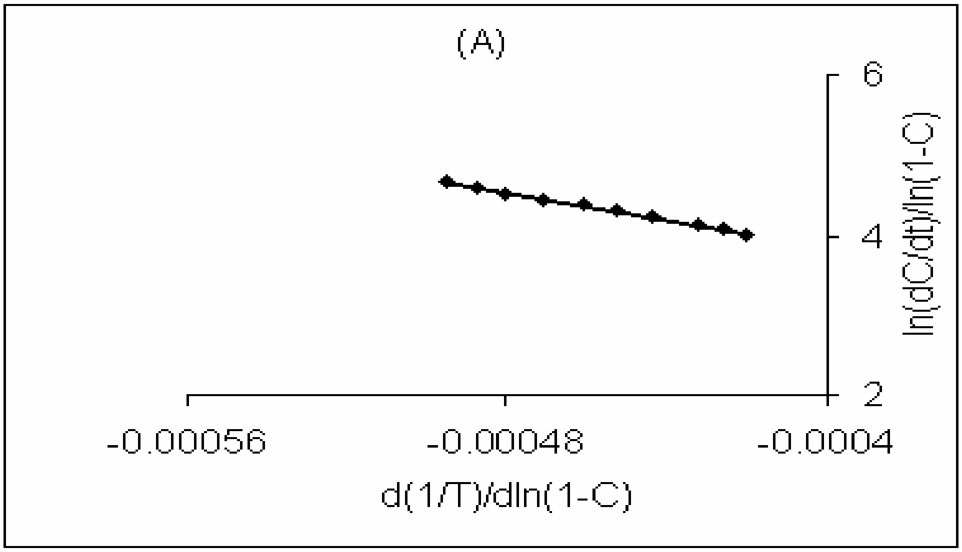


Figure 3.6.16 : The Freeman and Carroll plots for NDP-8 (A) First Step (B) Second Step.



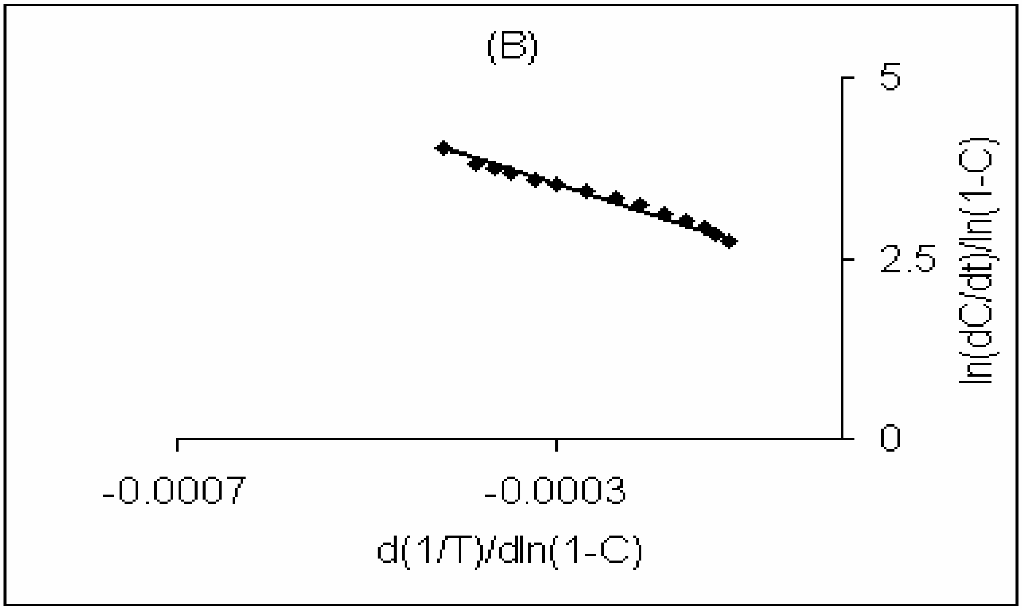
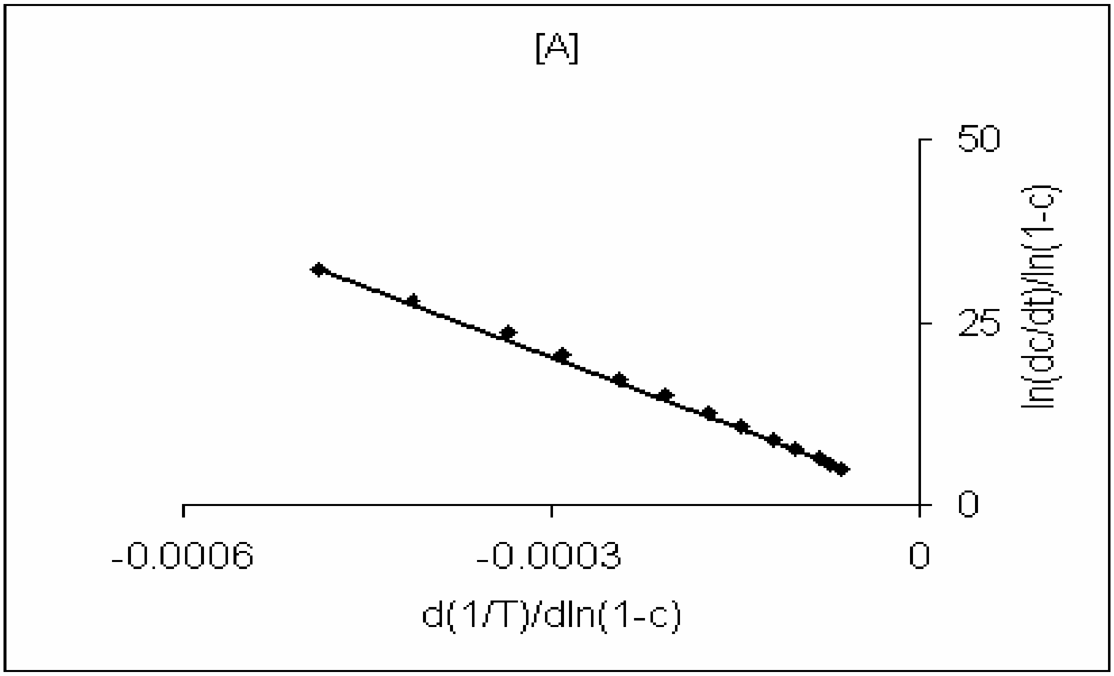


Figure 3.6.17 : The Freeman and Carroll plots for (A)DVA-1 and (B)DVA-2



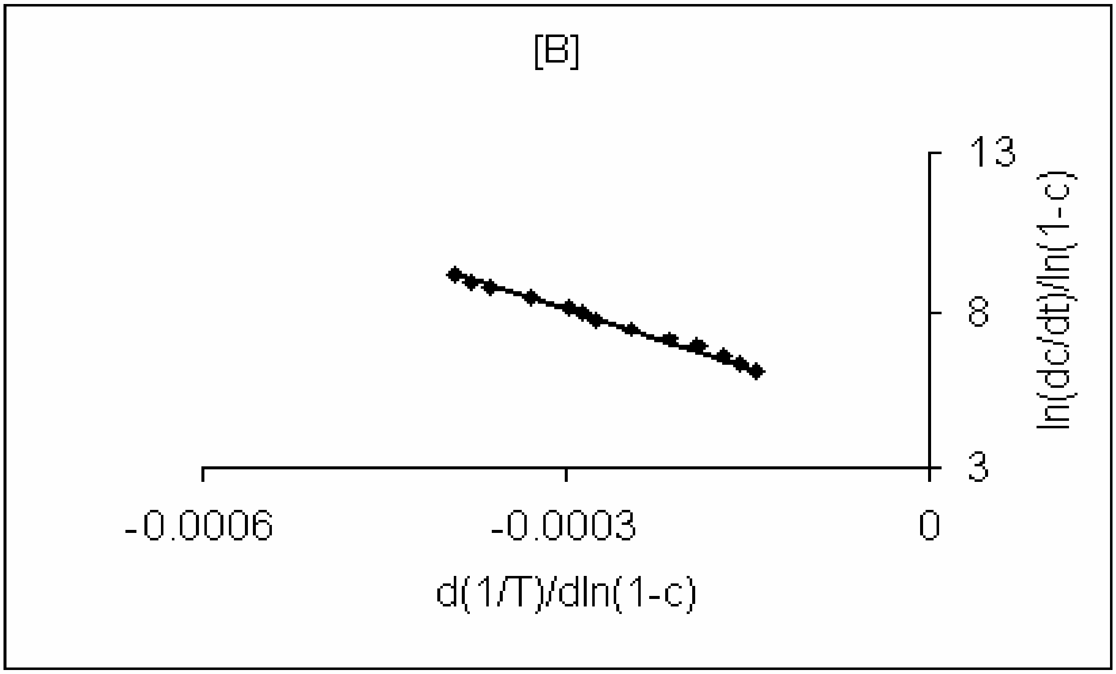


Table 3.6.3 : The Kinetic parameters calculated for the Schiff bases of α-naphthylamine

Compd. code	**n**	**E (KJ)**	**A(sec^{-1})**	**∆S**	**γ**
NDP-1	2.44	8.85	0.11	231.92	0.95
NDP-2	5.57	266.26	9.07×10^{23}	708.97	0.98
NDP-3	3.64	494.78	1.52×10^{45}	1115.26	1.00
NDP-4	3.41	14.23	0.40	243.15	0.97
NDP-5	3.25	233.30	2.23×10^{19}	621.32	0.98
NDP-6	3.11	36.09	131.05	290.82	0.99
NDP-7	1.56	486.83	2.41×10^{46}	1137.90	1.00
NDP-8	Step-I 3.72 Step-II 2.31	105.24 33.471	1.9×10^{8} 5.06	409.29 266.48	0.99 0.98
NDP-9	1.25	423.32	1.85×10^{40}	1020.82	1.00
NDP-10	3.16	288.66	3.1×10^{25}	738.51	0.99

Table 3.6.4 : The Kinetic parameters calculated for the Schiff bases of benzidine.

Compd. code	**n**	**E (KJ)**	**A(sec^{-1})**	**ΔS**	**γ**
DVA-1	1.17	538.50	2.08×10^{39}	1004.85	1.00
DVA-2	3.91	114.12	2.42×10^{4}	339.37	0.98
DVA-3	3.02	93.32	1.89×10^{3}	318.17	0.97
DVA-4	1.84	174.29	3.44×10^{7}	339.74	0.99

also follow the same order. DVA-2 and DVA-4 are having almost the same entropy. All entropy values are positive which indicates that the transition state in these bases also, is in less ordered state.

Thus, the thermal properties suggest that thermal stability depends upon the type of substituents present. The presence of benzaldehyde as side chain increases the stability, when bonded with benzidine whereas with α-naphthalamine, it decreases the stability. Similarly, presence of 4-hydroxy benzaldehyde increases the stability when attached to α-naphthalamine but with benzidine, it decreases the stability.

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INTRODUCTION

A literature survey shows that many Schiff bases have been known to be medicinally important(1-3) and are used to design medicinal compounds. Various Schiff bases have been found to posses pharmacological activities such as antitubercular(4), anticancer(5-7), antitumer(8), antibacterial(9-13), fungicidal(14-19), antipyretics(20-21), physiological activity(22-24) and anti HIV(25-27) etc.

Considering these properties of Schiff bases, in the present chapter, biological activities of all Schiff bases derived from α-naphthalamine were studied using strains of Gram positive and Gram negative bacteria.

EXPERIMENT

The antibacterial activities of all the Schiff bases were studied in polar solvents DMF and DMSO.

Preparation of test compound solution

The studied Schiff bases are soluble in 1,4-dioxane, DMF and DMSO. Only DMF and DMSO were selected for the present study.

Three different concentrations i.e., 2mg/0.1ml, 0.2 mg / 0.1 ml and 0.02 mg / 0.1 ml were prepared for all the Schiff bases in both DMF and DMSO.

Preparation of the plates and microbiological assays

A loop full of the given test strain was inoculated in 20ml of N-broth (Nutrient Broth). To activate the given bacterial strain, it was incubated for 24 hours in an incubator at 37^0C. The Agar well diffusion method (28) is used for antibacterial assay. 28-30 ml of molten agar (Mueller Hinton Agar No. 2) was added into the 100 mm diameter Petri plate. To maintain sterile condition, all these procedures were done in the laminar air flow. The media was allowed to solidify. After solidification of the media, a well was made in the plates with the help of cup-borer (0.85 cm) and then it was filled with the synthesized Schiff bases solution (dissolved in DMF/DMSO).

The antibacterial activity of these synthesized bases was determined by the inhibition zone formed by these compounds against the particular test bacterial strain.

Test microorganisms

The bacterial strains studied are identified strains and were obtained from National Chemical Laboratory (NCL), Pune, India. The investigated microorganisms are *E. coli* ATCC 25922, *S. aureus* ATCC 25923, *P. vulgaris* NCTC 8313, *K. pneumoniae* NCIM 2719. and *P. aeruginosa* ATCC 27853.

RESULTS AND DISCUSSION

The antibacterial activity of all the Schiff bases in DMF and DMSO against Gram positive and Gram negative bacteria is shown in Figure 1-3. Out of the three concentration evaluated, the lowered concentration had little effect while the compounds were slightly effective at a concentration of 0.2 mg/0.1ml (data is not shown). The third concentration (i.e.,2 mg/0.1ml) was effective and only this data will be presented.

From Figure 4.1, it is obvious that against *E. coli*, NDP-5 showed maximum inhibition in both DMF and DMSO. NDP-2, NDP-7, NDP-8 and NDP-9 showed no inhibition in DMF as well as in DMSO. Against *S. aureus*, NDP-9 showed maximum inhibition in DMF whereas in DMSO, NDP-4 showed maximum inhibition followed by NDP-9. All other bases showed no inhibition in DMSO against *S. aureus*. In DMF, NDP-2 and NDP-6 showed no activity at all whereas other bases showed negligible activity against *S. aureus.*

This suggests that inhibition depends upon three main factors: solvent, structure and strain. All Schiff bases have α-naphthylamine as central moiety to which different groups are attached. These different side chains affect differently in different solvents against different bacteria. Thus, dimethyl benzaldehyde is effective against *E. coli* in both DMF and DMSO whereas against *S. aureus, o*-nitro benzaldehyde exhibited more inhibition in DMF and m-nitro benzaldehyde showed more inhibition in DMSO.

In Figure 4.2, inhibition against *P. valgaris* and *K. pneumoniae* are shown in both the solvents. For both these bacteria, overall inhibition is less in DMSO. In DMF, NDP-9 showed rather more inhibition than other bases. Against *P. valgaris,* NDP-2, NDP-3, NDP-4 shows no activity at all whereas against *K. pneumoniae,* all Schiff bases showed activity in DMF. In DMSO, against both *P. valgaris* and *K. pneumoniae,* NDP-1 showed maximum inhibition. NDP-3, NDP-7, NDP-8 and NDP-9 could not affect *P. vulgaris,* whereas *K. pneumoniae* was not affected by NDP-3, NDP-4 and NDP-9 in DMSO. Again, o-nitro benzaldehyde is found to be more effective against *P. vulgaris* and *K. pneumoniae* in DMF solution whereas benzaldehyde is proved

Fig.4.1 : Comparative study of Schiff bases in (A) DMF and (B) DMSO.

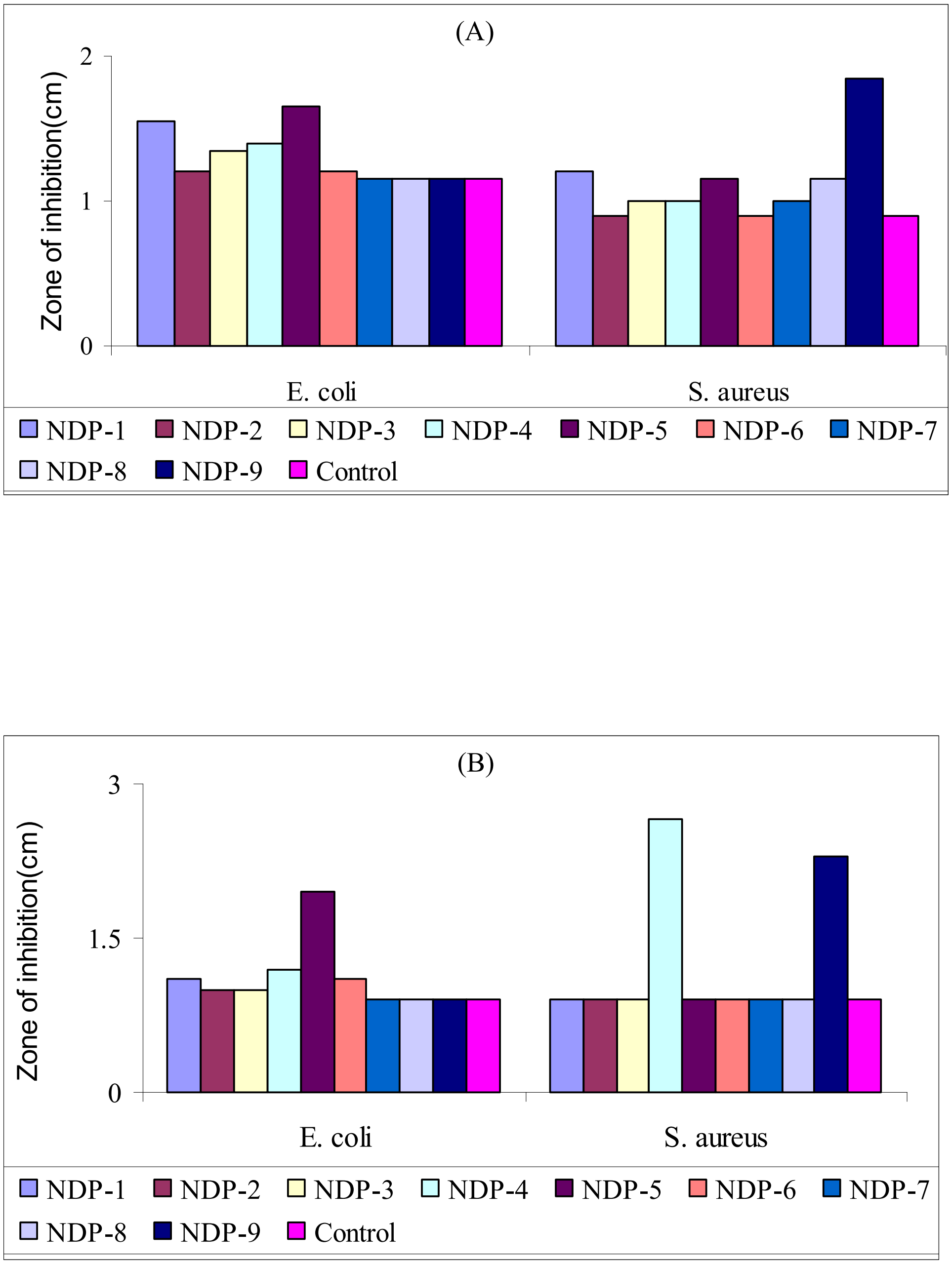
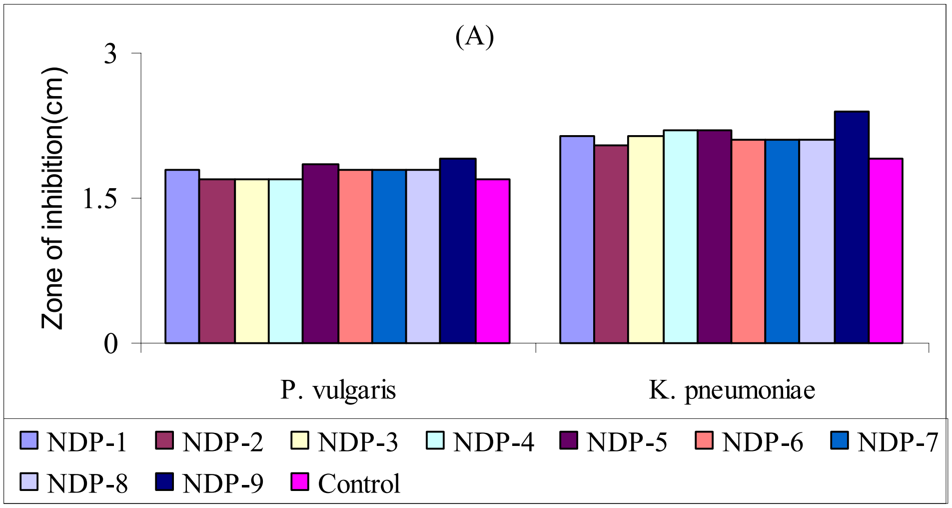


Fig. 4.2 : Comparative study of Schiff bases in (A) DMF and (B) DMSO.



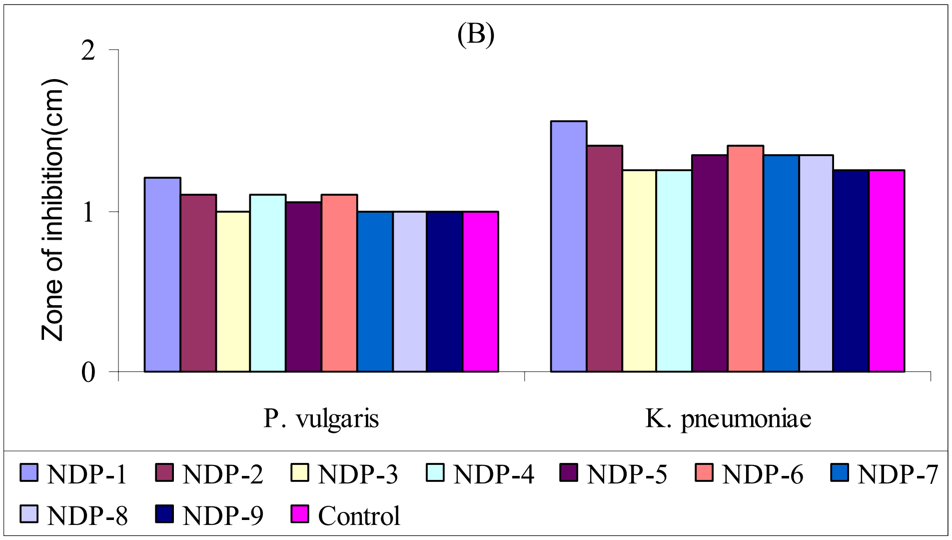
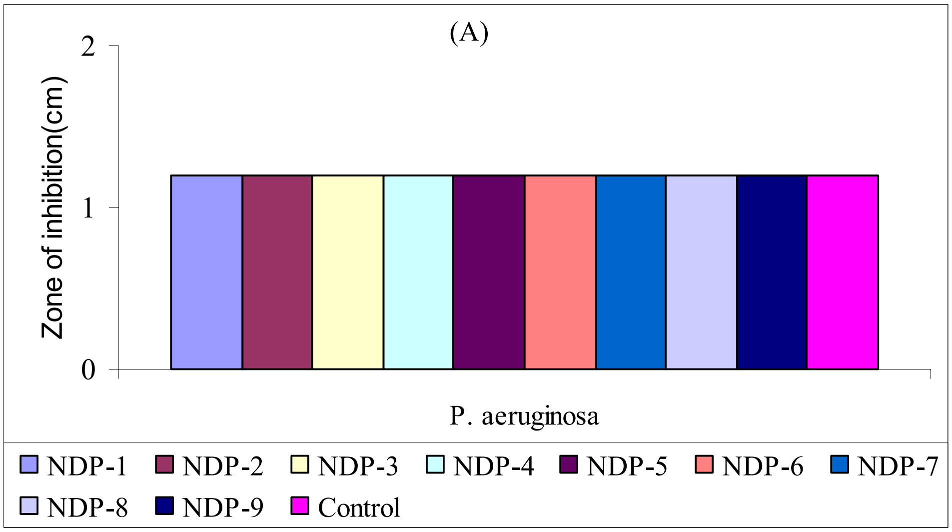
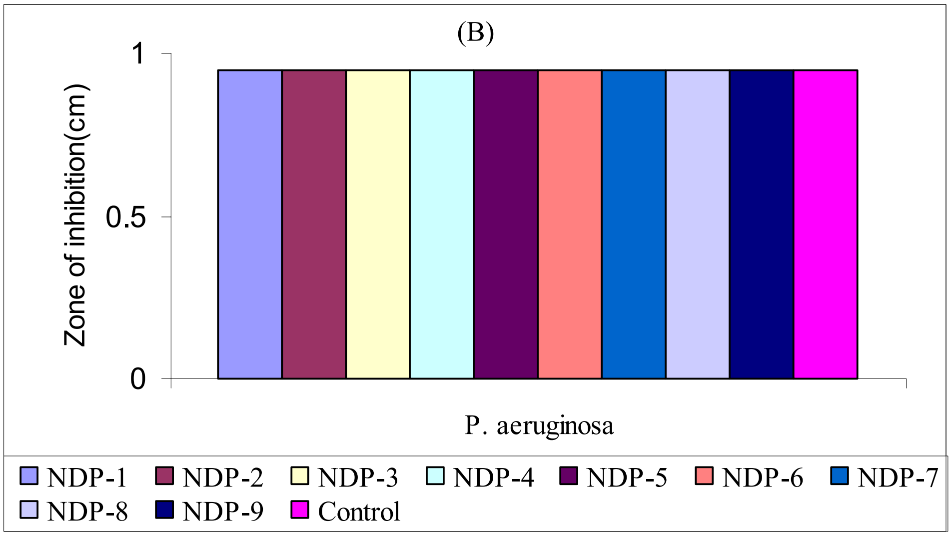


Fig. 4.3 : Comparative study of Schiff bases in (A) DMF and (B) DMSO.





to be effective in DMSO against these two bacteria. As shown in Figure-4.3, *P. aeroginosa* was not affected by any Schiff base neither in DMF nor in DMSO.

Thus, it is concluded that *P. aeruginosa* is most resistant bacteria. Overall, NDP-1 and NDP-9 are effective in inhibiting other four bacteria in both DMF and DMSO. NDP-1 contain benzaldehyde group whereas in NDP-9, o-nitro-benzaldehyde group is present. These two groups along with α-naphthyl amine are found to have significant activity in comparison to other bases.

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A COMPREHENSIVE CONCLUSION OF THE WORK

CHAPTER-1 :	This chapter describes the literature survey on Schiff bases.
CHAPTER-2 :	In this chapter, synthesis of Schiff bases is given along with their characterization viz. IR, ^{1}H NMR and Mass spectral data.
CHAPTER-3 :	Physicochemical studies of some Schiff bases derived from α-naphthalamine are described in different sections.
Section-I :	This section density and refractive index of Schiff bases are determined at 313.15K. Further the density of Schiff bases werecalculated theoretically. It dimethylformamide and tetrahydrofuran at 313.15K. t is observed that, there is deviation between experimental and calculated values of densities, which suggest the presence of termolecular interactions between solute and solvent molecules.
Section-II :	In this section, heats of solution of Schiff bases are determined in dimethylformamide and tetrahydrofuran at different Temperature (303.15-323.15 K). It is observed that solubility of Schiff bases increases with temperature. The solubility is greater in THFthan in 1, 4-dioxane. The melting temperature of Schiff bases are also calculated using solubility data. In most of the cases, good agreement is observed between the value of m.p. calculated from solubility data and those observed experimentally, Scand DTA data. Further, heats of solution are observed to be positive for all the Schiff bases in both the solvents indicating there by exothermic behavior of these bases.
Section-III :	This section describes the conductance of Schiff bases in dimethylformamide and dimethylsulfoxide at 313.15 K. The equivalent conductance is found to increases with dilution. It is observed that all the studies bases are of weak electrolytic nature.

	The equivalent conductance is observed to depend on solvent and on the nature of solute rather than on its molecular weight.
Section-IV :	In this Section, the dissociation constants of some Schiff bases in water-dioxane mixture are studied at 313.15 K. NDP-2 and NDP-6 are of H_2L type. NDP-2 is more acidic than NDP-6. Out of other bases (of HL type), NDP-1, NDP-4 and NDP-5 are acidic. The presence of $–NO_2$ group is found to increase the acidic character whereas methoxy group decreases the acidity.
Section-V :	To understand the interactions occurring in different solutions, the acoustical properties of Schiff bases are measured in dimethylformamide and tetrahydrofuran at 313.15K. It is observed that solute-solute and solute-solvent interactions exist in all the solutions.
Section-VI :	In this chapter, thermal properties of Schiff bases are studied .Thermal stability is found to be affected by the substituent groups. NDP-8 is observed to be more stable. Various kinetic parameters such as order of reaction, energy of activation, frequency factor and entropy change were calculated. Further, the value of entropy change is observed to be positive which suggest the less ordered transition state.
CHAPTER-4 :	This chapter describes biological activity of some Schiff bases by using some gram positive and gram negative bacteria. It is observed that substituent attached to the central moiety and solvent polarity play an important role in inhibiting the bacteria. It is observed that o-nitro benzaldehyde and benzaldehyde substitution are effective in inhibition the studied bacterial. *P.aeruginosa* is most resistant bacteria.

List of Papers Published

(1) "Thermodynamic and acoustical studies of binary mixtures of diethyl malonate at 308.15K",

-Shipra Baluja, Nirmal Pandya, Nikunj Kachhadia, Asif Solanki and Pranav Inamdar.

-Physics and Chemistry of Liquids, 43(3), 301-310(2005).

(2) Theoretical evaluation in binary liquid mixture.

-Shipra Baluja, Nirmal Pandya, Nikunj Kachhadia and Asif Solanki

-J. Ultra Scientist of Physical Sciences. (In Press)

Papers presented in different conferences/symposia

(1) Synthesis of some Schiff bases derived from benzidine"

-Shipra Baluja and N. D. Pandya

XVIII Gujarat Science Congress" held at Saurashtra University Rajkot, 2004.

(2) Synthesis of some Schiff bases derived from Benzidine.

-N. D. Pandya and Shipra Baluja

9th National Conference on " Bio-active heterocycles and drug discovery Paradigm- held at Saurashtra University Rajkot, 2005.

(3) Synthesis and Thermodynamics studies of some α-naphthyl amine derivatives in DMF, and THF solution at 313.15 K.

-Shipra Baluja, N. D. Pandya and N. Kachhadia.

20th International Conference on Solution Chemistry, held at Portroz, Slovenija, August 21st – 25th, 2005.

Papers Communicated

(1) “Theoretical evaluation of refractive Index in binary liquid mixtures”
-Shipra Baluja, Nirmal Pandya, Nikunj Kachhadia, Asif Solanki.
-E-Journal of Chemistry.

(2) Acoustical studies of binary mixtures of acetone at 308.15K
-Shipra Baluja, Nirmal Pandya, Nikunj Kachhadia, Asif Solanki.
-Journal of Indian Chemical Society.

(3) Physico chemical properties of some derivatives of α-naphthyl amine.
-S. Baluja, N. Kachhadia and N. Pandya.
-Journal of Indian Chemical Society.

(6) Studies of some physicochemical properties of some benzidine derivatives.
-N. Pandya, A. Solanki and S. Baluja.
-Russian Journal of Physical Chemistry.

(7) Thermal analysis of some Schiff bases.
-N. Pandya and S. Baluja.
-Journal of Thermal Analysis.

(8) Dissociation constants of some derivatives of benzidine and α-naphthyl amine.
-S. Baluja and N. Pandya.
- Institution of Chemists.

(9) “Thermodynamic and acoustical studies of binary mixtures of diethyl malonate at 308.15K”,
-Shipra Baluja, Nirmal Pandya, Nikunj Kachhadia, Asif Solanki and Pranav Inamdar.
-Physics and Chemistry of Liquids.

(10) “Synthesis and Thermodynamic Studies of Some α-naphthyl amine Derivatives in DMF and THF Solutions at 313.15 K ”
-Shipra Baluja, N. D. Pandya and N. Kachhadia
Journal of Molecular Liquids.