EXPERIMENTAL.

EXPERIMENTAL

1. Preparation of Compounds

1.1 LOW MELTING SMECTOGENIC ESTERS WITH BROKEN ALKOXY CHAINS.

1.1.1 n - Alkyl Halides

All the alkyl halides (Bromides or Iodides) used were of Fluka, B.D.H. or equivalent quality.

1.1.2 Ethoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates : **series - I**

1.1.2a 4-n-Alkoxy benzoic acids.

Commercially available 4-methoxy benzoic acid (4 - anisic acid B.D.H) was used. Number of methods (221, 222) are known for alkylation of p-hydroxy benzoic acid. However, in the present study, the method developed by Dave and Vora (223) was followed. 4-Hydroxybenzoic acid (0.1 mole), appropriate n-alkyl halide (0.12 mole) and potassium hydroxide (0.25 mole) were dissolved in 100 ml ethanol and refluxed for seven to eight hours. Ten percent aqueous potassium hydroxide solution (25ml) was added and reflux was continued for two hours to hydrolyse any ester formed. The solution was cooled and acidified with 1:1 cold hydrochloric acid to precipitate the acid. The alkoxy acids were crystallized several times from ethanol or acetic acid until constant transition temperatures were obtained. The transition temperatures are in good accordance with the literature (221).

1.1.2b 4-n-Alkoxybenzoyl chlorides.

4-n-Alkoxybenzoyl chlorides were prepared by reacting the corresponding 4-n-alkoxy benzoic acid with excess of thionyl chloride and heating on a water-bath till the evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using water pump and the acid chloride left behind as a residue was used in next reaction without further purification.

1.1 2c Ethoxyethyl 4-hydroxybenzoate.

Ethoxyethyl 4-hydroxybenzoate was synthesized by using conventional method of esterification (224). 4-Hydroxybenzoic acid (0.125 mole), ethoxyethanol (0.25 mole) and concentrated sulphuric acid (0.018 mole) were taken in a round bottom flask. Mixture was refluxed on a sand bath for five - six hours. The whole mass was allowed to cool and poured into about 250 ml of saturated sodium hydrogen carbonate. The organic compounds were extracted by ether. The ether extract was dried on anhydrous magnesium sulphate and evaporated on a rotary evaporator. The residue was distilled under reduced pressure. Boiling point is 128 °C. The IR (KBr) spectra (Fig.6) of the compound showed broad peak for intermolecularly hydrogen bonded phenolic -OH at 3600 - 3200 cm^{-1}. The -COO- stretching vibrations were obtained at 1720 cm^{-1}. Other signals observed were at 1605, 1510, 1450, 1380, 1250, 1210, 1180, 1100, 1020, 860 cm^{-1}.

		C(%)	H(%)
Analytical data :-	Required	62.86	6.67
	Found	62.44	6.78

1.1.2d Preparation of ethoxyethyl 4 (4'-n-alkoxybenzoyloxy) benzoates :

Ethoxyethyl 4 (4'-n-alkoxybenzoyloxy) benzoates were synthesized by condensing appropriate 4- n- alkoxybenzoyl chloride with ethoxyethyl 4 - hydroxybenzoate. Ethoxyethyl 4-hydroxybenzoate (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxybenzoyl chloride (0.01 mole). The mixture was heated on water bath for an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid, and the precipitates obtained were filtered and washed with water followed by cold dilute sodium hydroxide solution and cold water. The esters were crystallised several times from methanol until constant transition temperatures were obtained (Table 1). The elemental analyses are recorded in Table 2. The IR (KBr) spectra (Fig. 7) of the compounds showed -COO- stretching vibration at 1725 cm^{-1}. Other signals observed were at 2900, 1600, 1510, 1415, 1390, 1270, 1210, 1160, 1065, 830 cm^{-1}.

NMR spectra (Fig. 8) (90 MHz, solvent $CDCl_3$ standard TMS of compound No. 9. Table 1. δ 8.1 (d, J=9Hz, 4H at C-2, C-6, C-2' and C-6') 7.2 (d, J=9Hz, 2H at C-3 and C-5) 6.9 (d, J=9Hz, 2H at C-3' and C-5') 4.4 (t, 2H at -COO- CH_2-) 4.0 (t, 2H at - $PhOCH_2$-) 1.0 - 1.9 (m, 19H for 8 X -CH_2 at C-4' and 3H of CH_3 at C-1) 0.9 (t, 3H of C-CH_3 at C-4').

1.1.3. Methoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates : **Series - II.**

1.1.3a 4-n-alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides were prepared by the method described in sections 1.1.2a and 1.1.2b, respectively.

1.1.3b Methoxyethyl 4-hydroxybenzoate.

Methoxyethyl 4-hydroxybenzoate was synthesized by using conventional method of esterification as described in section 1.1.2.c. The ester was crystallised several times from methanol until constant melting point was obtained, m.p. 87 ^{o}C The IR (KBr) spectra (Fig. 6) of the compound showed broad peak for intermolecularly hydrogen bonded phenolic -OH at 3600 - 3200 cm^{-1}. The -COO- stretching vibrations were obtained at 1715 cm^{-1}. Other signals observed were at 1610, 1520, 1320, 1290, 1250, 1185, 1100, 1035, 860 cm^{-1}.

	C(%)	H(%)
Analytical data : Required	61.22	6.12
Found	61.36	6.43

1.1.3c Preparation of Methoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates.

Methoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates were synthesized by condensing appropriate 4-n-alkoxybenzoyl chloride with methoxyethyl 4-hydroxybenzoate. Methoxyethyl 4-hydroxybenzoate (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxybenzoyl chloride (0.01 mole) as described in section 1.1.2.d. The esters were crystallised several times from methanol until constant transition temperatures were obtained (Table 3). The elemental analyses are recorded in Table 4. the IR (KBr) spectra (Fig 9) of the compounds showed -COO-stretching vibrations at 1730 cm^{-1}. Other signals observed were at 2900, 1600, 1500, 1420, 1275, 1210, 1160, 1065, 840 cm^{-1}.

NMR spectra (Fig. 10) (200 MHz, solvent $CDCl_3$ standard TMS) of compound No. 11 Table 3. δ 8.1 (d, J=8.5Hz, 4H at C-2, C-6, C-2' and C-6') 7.2 (d, J=8.7Hz, 2H at C-3 and C-5) 6.9 (d, J=8.9Hz, 2H at C-3' and C-5') 4.45(t, 2H at -$COOCH_2$-) 4 1 (t, 2H at -$PhOCH_2$-) 3.7 (t, 2H at -COO-C-CH_2 - O-) 3.4 (S, 3H at - OCH_3) 1.9 (qunt., 2H, -Ph-O-C-CH_2 -C-) 1.25-1.65 (m, 22 H for 11 x -CH_2 at C-4') 0.9(t, 3H of -C-CH_3 at C-4').

1.1.4 Methoxyethyl *trans*-4-(4'-n-alkoxy-benzoyloxy) - ∝ - methyl cinnamates:

Series III.

1.1.4a 4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides were prepared by the method described in sections 1.1.2a and 1.1.2b respectively.

1.1.4b *trans* - 4 - Hydroxy -∝- methyl cinnamic acid.

trans -4-Hydroxy-∝- methyl cinnamic acid was syntheized by the process reported in the literature (225). A mixture of 0.2 mole of pure 4-hydroxy benzaldehyde, 0.25 mole of propionic anhydride and 0.2 mole of fused sodium propionate is heated with occasional shaking for thirty hours in an oil bath at 130 - 135 °C. The warm mixture is poured into about 500 ml of water, stirred thoroughly and neutralized by the addition of solid sodium carbonate. The unreacted 4-hydroxy benzaldehyde is removed by washing with organic solvent and the solution is warmed with 3-4g of animal charcoal and filtered hot. The warm filtrate is poured slowly with stirring into an excess of concentrated hydrochloric acid mixed with chopped ice. The crude product p-propionoxy -∝- methyl cinnamic acid is crystallised from dilute alcohol. Melting point 185°C. The hydrolysis of p-propionoxy -∝- methyl cinnamic acid with 10% KOH

solution gave *trans*-4-hdyroxy- ∝-methyl cinnamic acid which was crystallised several times from dilute alcohol. Melting point 206 °C.

1.1.4c Methoxyethyl *trans* - 4- hydroxy -∝- methyl cinnamate.

Methoxyethyl *trans*-4 hydroxy-∝-methyl cinnamate was synthesized by using conventional method of esterification as described in section 1.1.2 c.

The ester was crystallised several times from aqueous methanol. Melting point 95 °C. The IR (KBr) spectra (Fig. 6) of the compund showed broad peak for intermolecularly hydrogen bonded phenolic -OH at 3500 - 3100 cm^{-1}. The -COO- stretching vibrations were obtained at 1705 cm^{-1}. Other signals observed were at 1620 (-CH = C (CH_3)), 1600, 1520, 1450, 1385, 1320, 1285, 1260, 1190, 1100, 1035, 990, 850. cm^{-1}.

		C (%)	H(%)
Analytical data : -	Required	66.10	6.78
	Found	66.42	6.45

1.1.4d Preparation of Methoxyethyl *trans*-4-(4'-n-alkoxybenzoyloxy) -∝-methyl cinnamates :

Methoxyethyl *trans* -4(4'-n-alkoxybenzoyloxy) -∝-methyl cinnamates were synthesized by condensing appropriate 4-n-alkoxybenzoyl chloride with methoxyethyl *trans*-4-hydroxy-∝-methyl cinnamate.

Methoxyethyl *trans* -4-hydroxy-∝-methyl cinnamate (0.01mole) was dissolved in dry pyridine (10ml) and was added slowly with constant stirring to cold 4-n-alkoxybenzoyl chloride (0.01 mole) as described in section 1.1.2d.

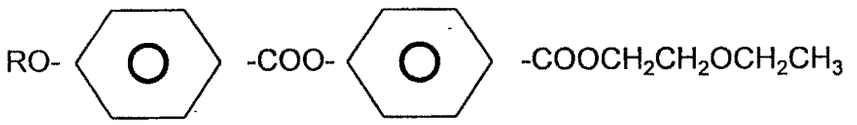
The esters were crystallised several times from methanol until constant transition temperatures were obtained (Table 5). The elemental analyses are recorded in Table 6. The IR (KBr) spectra (Fig. 11) of the compounds showed -COO- stretching vibrations at 1725 cm^{-1}. Other signals observed were at 2900, 1635, (-HC=C-(CH_3)), 1600, 1450, 1270,1215, 1160, 1070, 1020, 840 cm^{-1}.

NMR spectra (Fig. 12) (90 MHz, solvent $CDCl_3$, standard TMS) of compound No. 7 (Table 5). δ8.0 (d, J=9Hz, 2H at C-2' and C-6') 7.6 (s,1H at -Ph-CH=C-) 7.35 (d, J=9Hz, 2H at C-2 and C-6) 7.15(d, J=9Hz, 2H at C-3 and C-5) 6.85(d, J=9Hz, 2H at C-3' and C-5') 4.3(t,2H at -COO-CH_2-) 4.0(t, 2H at -PhOCH_2-) 3.65(t,2H at -COO-CH_2CH_2) 3.35 (s, 3H at -OCH_3) 1.1 - 1.7 (brs, 23H for 10 x C-CH_2- and C=C-CH_3) 0.9 (t, 3H of C-CH_3 at C-4').

The fluorescence pattern (Fig. 13) of the n-dodecyl derivative showed the excitation peak at 345 nm and the emission peak at 402 nm.

Table - 1

Ethoxyethyl 4 (4'- n- alkoxybenzoyloxy) benzoates.



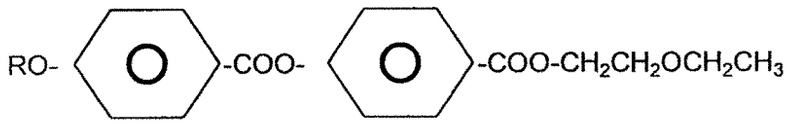
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C S_A	I
1	Methyl	-	60.0
2	Ethyl	-	57.0
3	Propyl	-	79.0
4	Butyl	-	76.0
5	Pentyl	(39.0)*	42.0
6	Hexyl	43.0	54.0
7	Heptyl	(43.0)	49.0
8	Octyl	47.0	58.0
9	Decyl	(61.0)	67.0
10	Dodecyl	(62.0)	70.0
11	Tetradecyl	(61.0)	71.0
12	Hexadecyl	(53.0)	75.0

( )* Monotropic value.

Table - 2

Ethoxyethyl 4 (4'-n- alkoxybenzoyloxy) benzoates

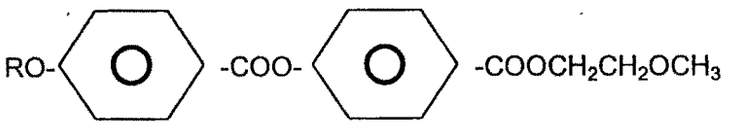


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)		Found (%)	
		C	H	C	H
1	Methyl	66.28	5.81	66.14	5.98
2	Ethyl	67.04	6.15	67.26	6.34
3	Propyl	67.74	6.45	67.48	6.67
4	Butyl	68.39	6.73	68.82	6.31
5	Pentyl	69.00	7.00	68.55	6.93
6	Hexyl	69.57	7.25	70.00	7.17
7	Heptyl	79.09	7.48	70.56	7.31
8	Octyl	70.59	7.69	70.96	7.42
9	Decyl	71.49	8.09	71.94	7.79
10	Dodecyl	72.29	8.43	71.91	8.01
11	Tetradecyl	73.00	8.75	72.97	8.35
12	Hexadecyl	73.65	9.03	73.20	8.56

Table - 3

Methoxyethyl 4 (4'- n- alkoxybenzoyloxy) benzoates.



Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C	
		S_A	I
1	Methyl	-	65.0
2	Ethyl	-	67.0
3	Propyl	-	81.0
4	Butyl	-	63.0
5	Pentyl	(40.0)*	62.0
6	Hexyl	(43.0)	49.0
7	Heptyl	38.0	51.0
8	Octyl	37.0	64.0
9	Decyl	40.0	73.0
10	Dodecyl	42.0	71.0
11	Tetradecyl	58.0	70.0
12	Hexadecyl	59.0	69.0

( )* Monotropic value.

Table - 4

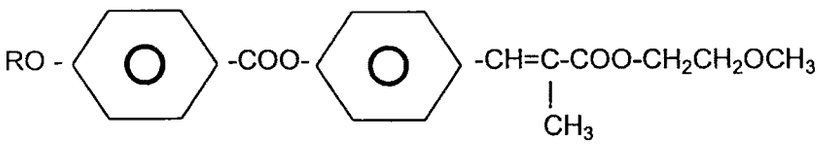
Methoxyethyl 4 (4'-n- alkoxybenzoyloxy) benzoates

Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)		Found (%)	
		C	H	C	H
1	Methyl	65.45	5.45	65.16	5.64
2	Ethyl	66.28	5.81	65.85	6.02
3	Propyl	67.04	6.15	67.45	6.34
4	Butyl	67.74	6.45	68.11	6.83
5	Pentyl	68.39	6.74	68.48	6.78
6	Hexyl	69.00	7.00	69.45	7.18
7	Heptyl	69.57	7.25	69.55	7.37
8	Octyl	70.09	7.48	70.48	7.65
9	Decyl	71.05	7.89	70.61	7.76
10	Dodecyl	71.90	8.26	71.44	7.88
11	Tetradecyl	72.66	8.59	73.02	8.36
12	Hexadecyl	73.33	8.89	73.64	8.47

Table - 5

Methoxyethyl trans- 4 (4'- n- alkoxybenzoyloxy)- α-methyl cinnamates.



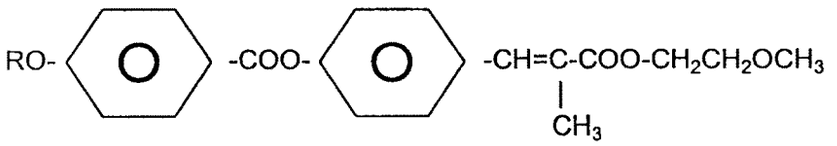
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperature °C S_A	I
1	Butyl	-	73.0
2	Pentyl	-	41.0
3	Hexyl	-	38.0
4	Heptyl	(33.0)*	38.0
5	Octyl	38.0	43.0
6	Decyl	33.0	54.0
7	Dodecyl	40.0	61.0
8	Tetradecyl	51.0	64.0
9	Hexadecyl	59.0	66.0

( )* Monotropic value.

Table - 6

Methoxyethyl *trans*- 4 (4'- n- alkoxybenzoyloxy)- α-methyl cinnamates.



Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)		Found (%)	
		C	H	C	H
1	Butyl	69.90	6.80	69.63	7.08
2	Pentyl	70.42	7.04	70.05	7.14
3	Hexyl	70.91	7.27	70.48	7.08
4	Heptyl	71.37	7.49	71.14	7.43
5	Octyl	71.79	7.69	71.37	7.26
6	Decyl	72.58	8.07	73.00	8.31
7	Dodecyl	73.28	8.40	73.41	7.96
8	Tetradecyl	73.91	8.69	73.48	8.85
9	Hexadecyl	74.48	8.96	74.96	8.56

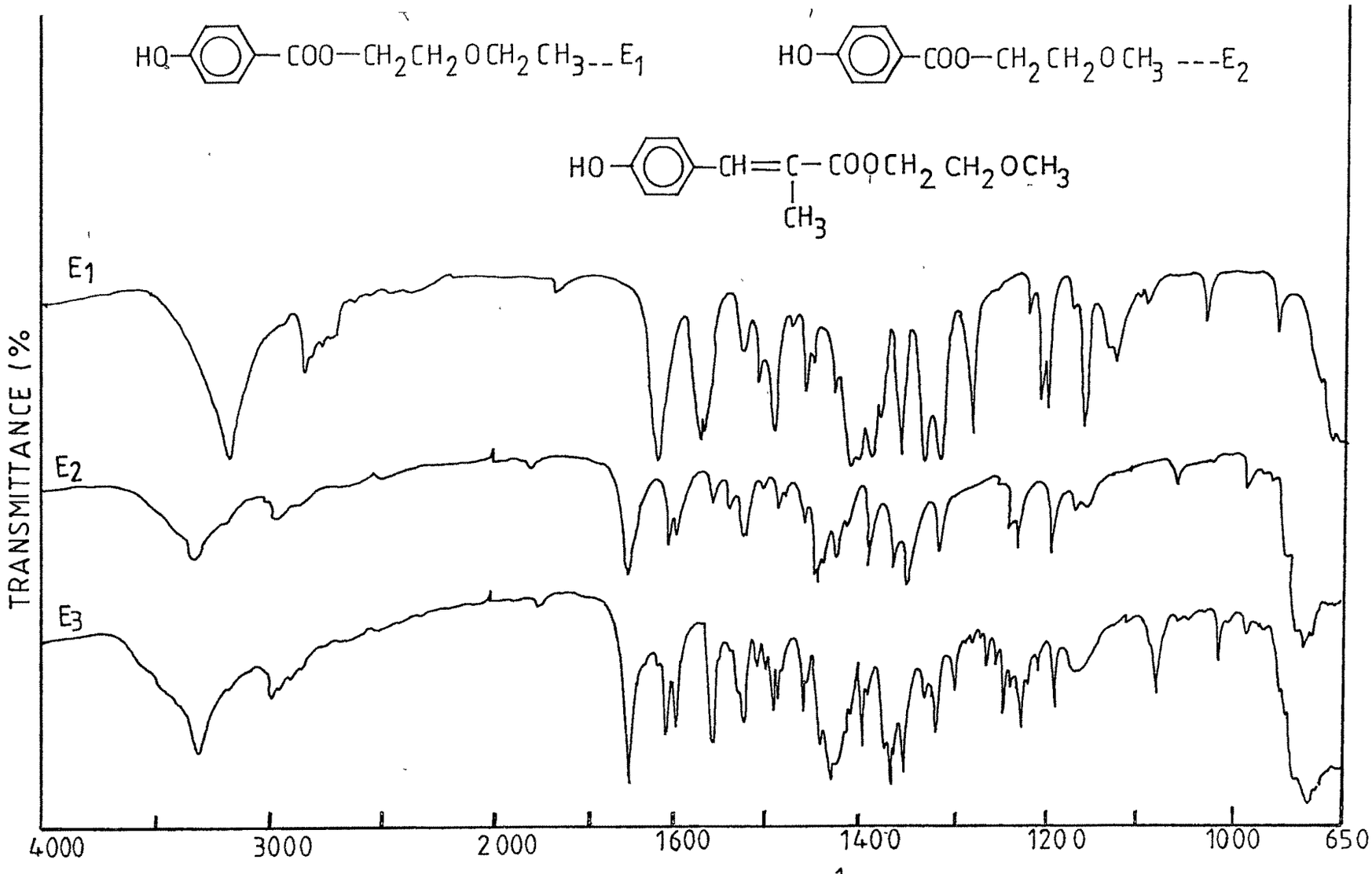


Fig.6. I. R. SPECTRA

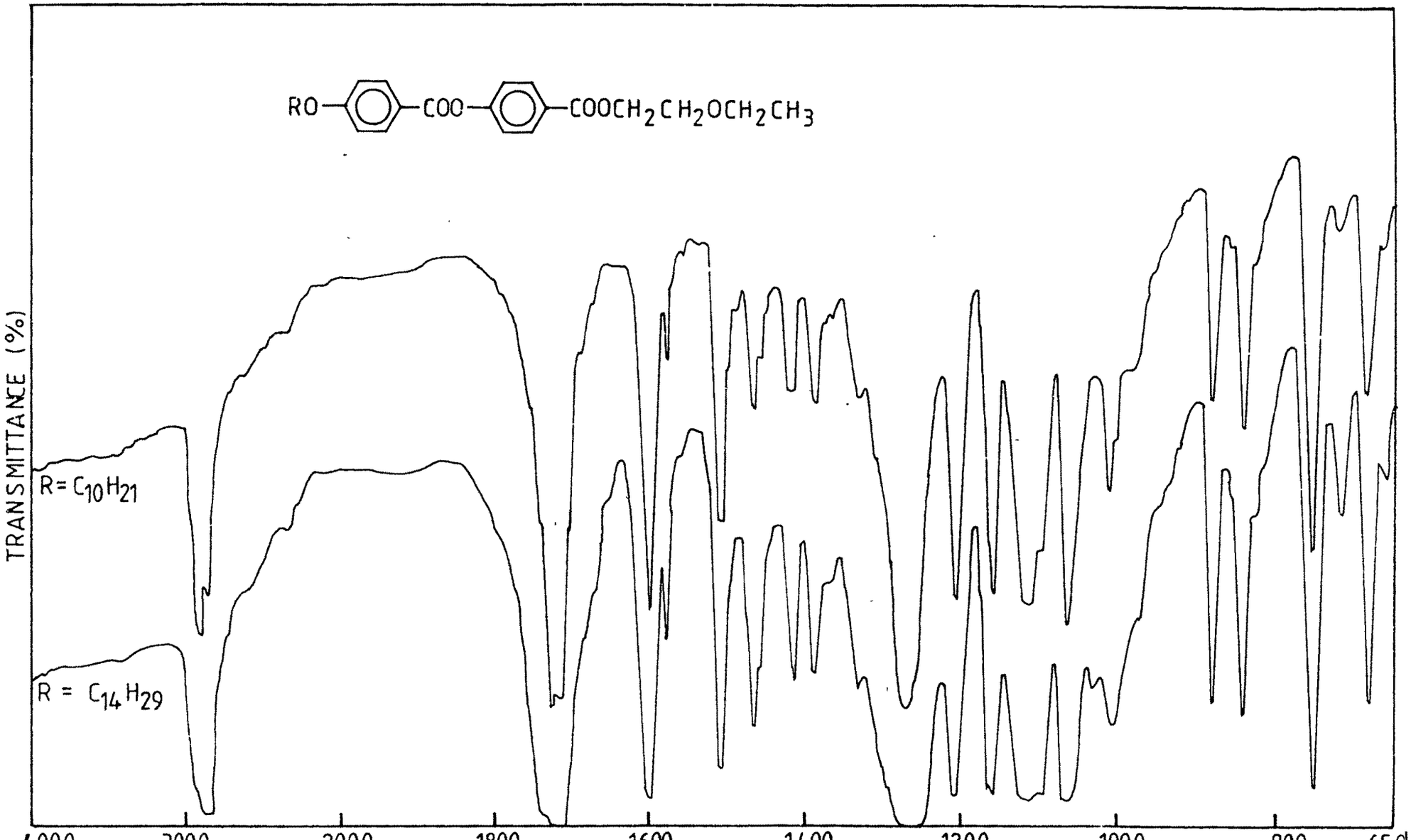


Fig.7 I. R. SPECTRA

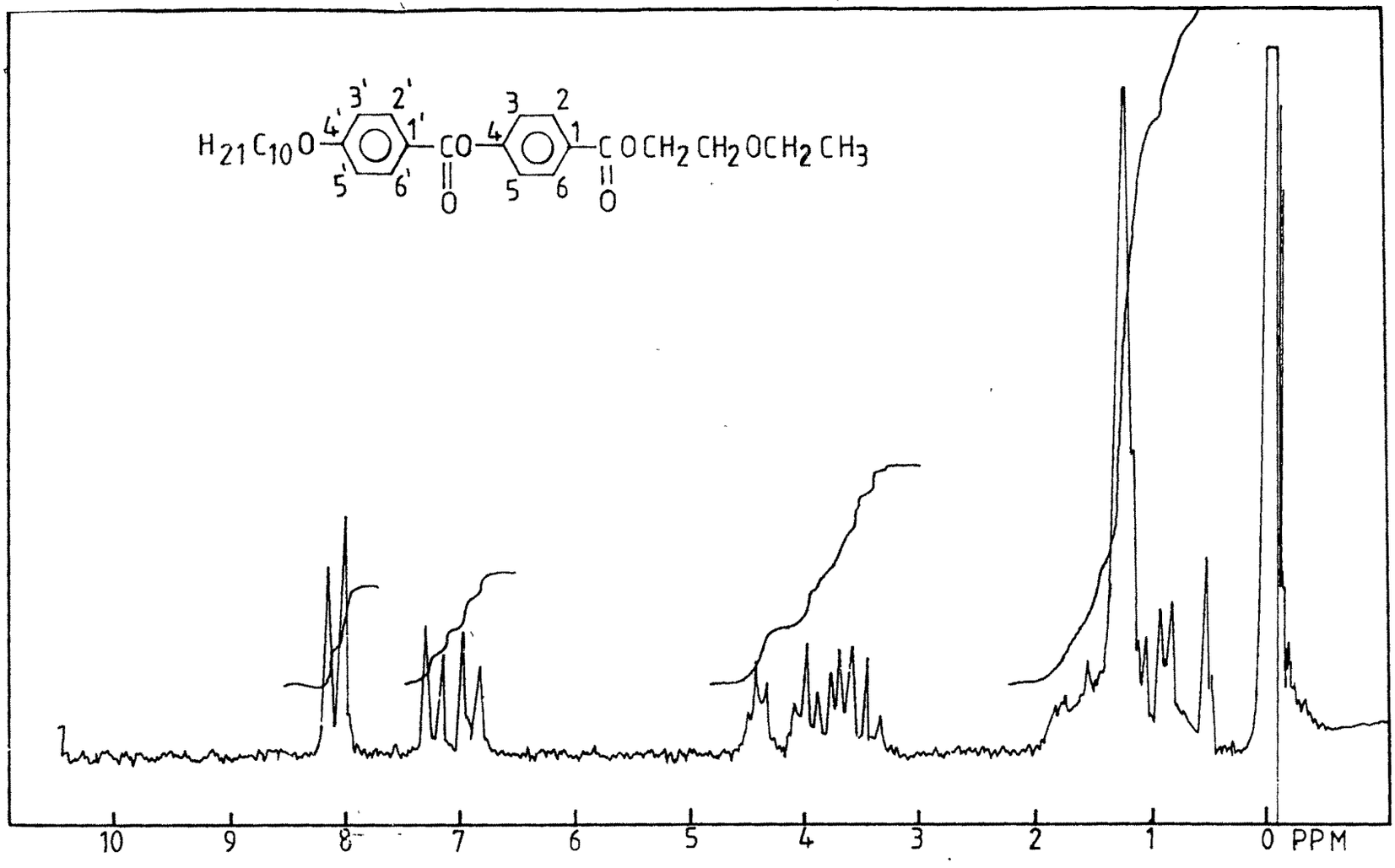


Fig. 8 NMR SPECTRA

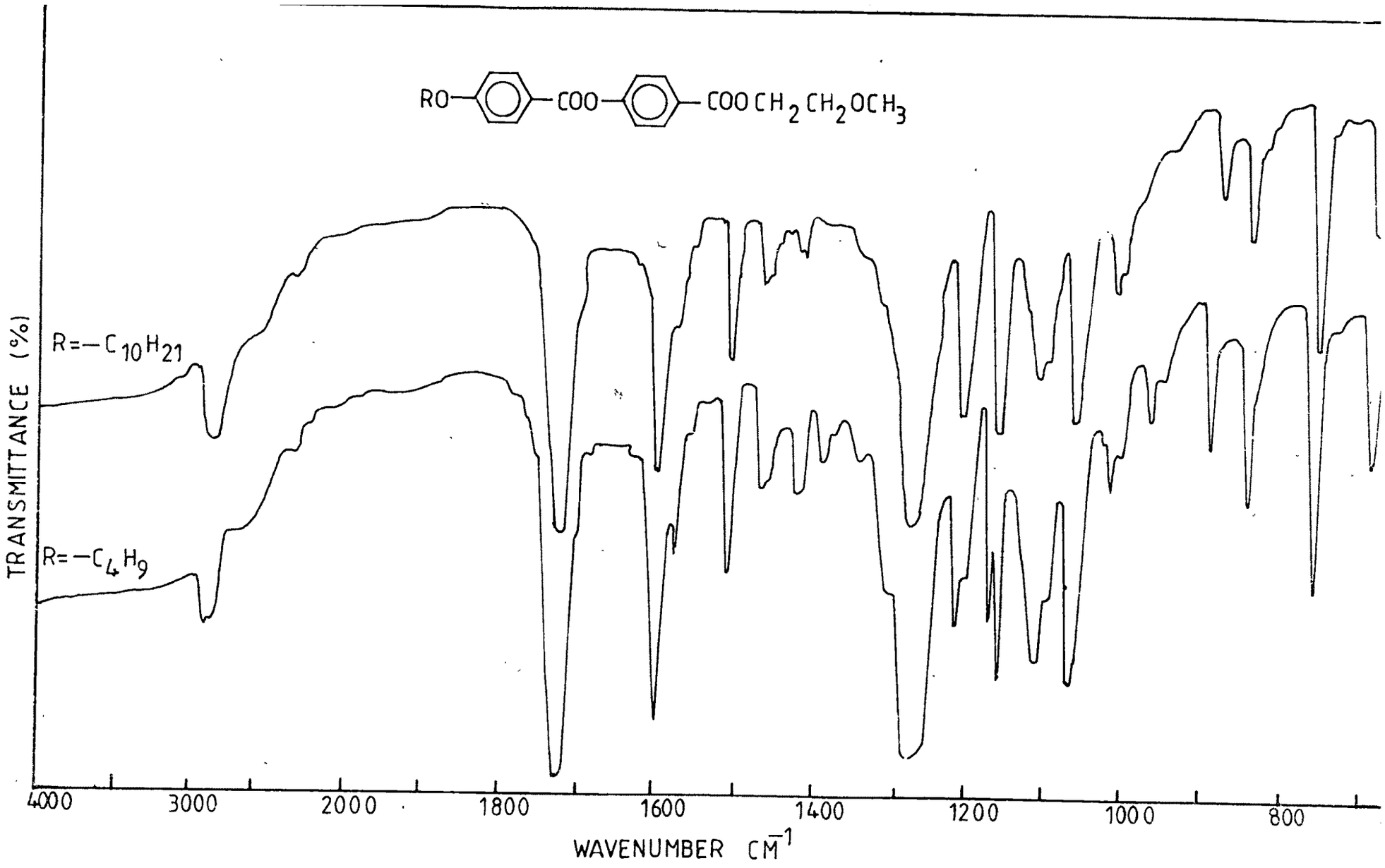


Fig. 9 I. R. SPECTRA

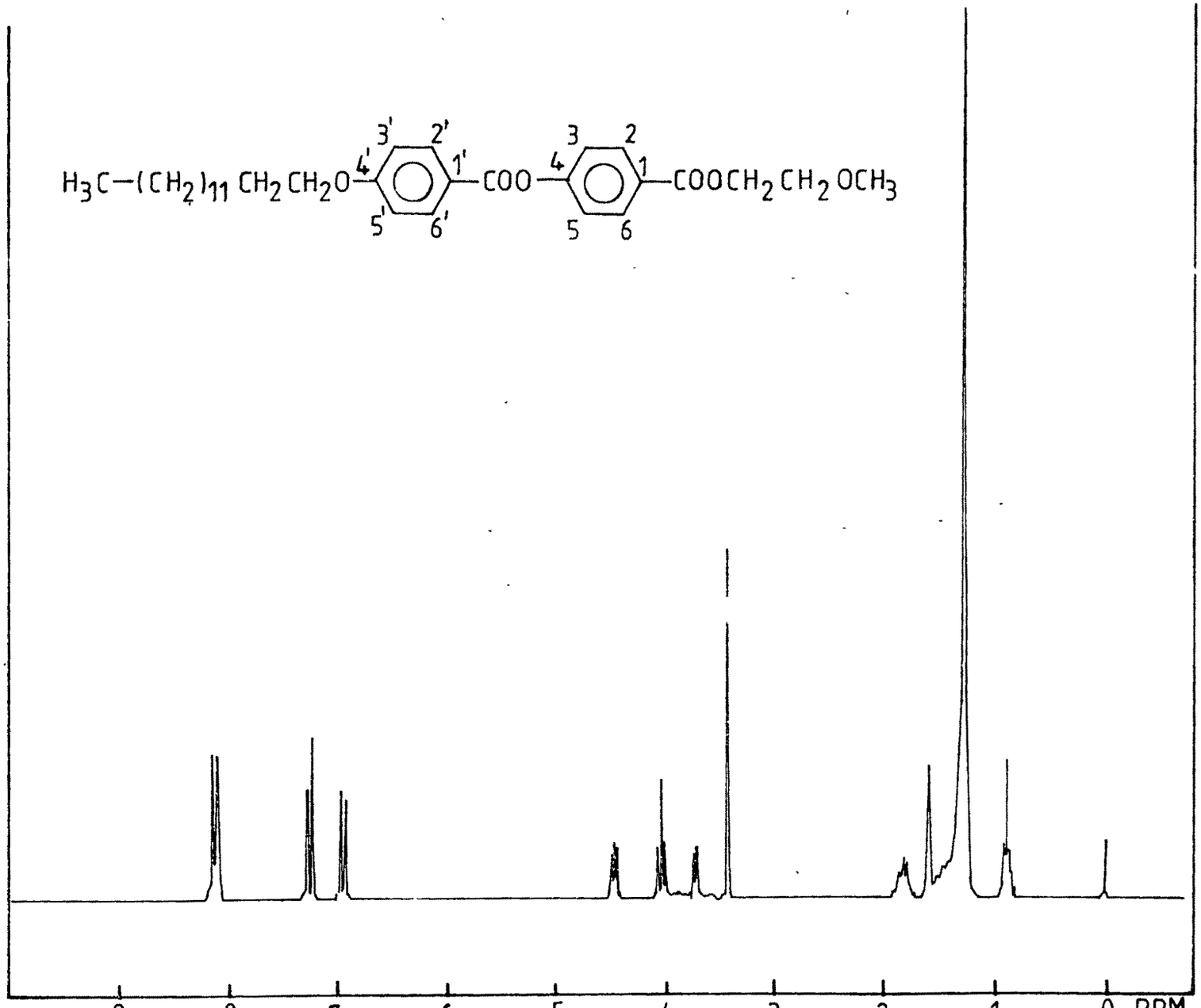


Fig.10 NMR SPECTRA

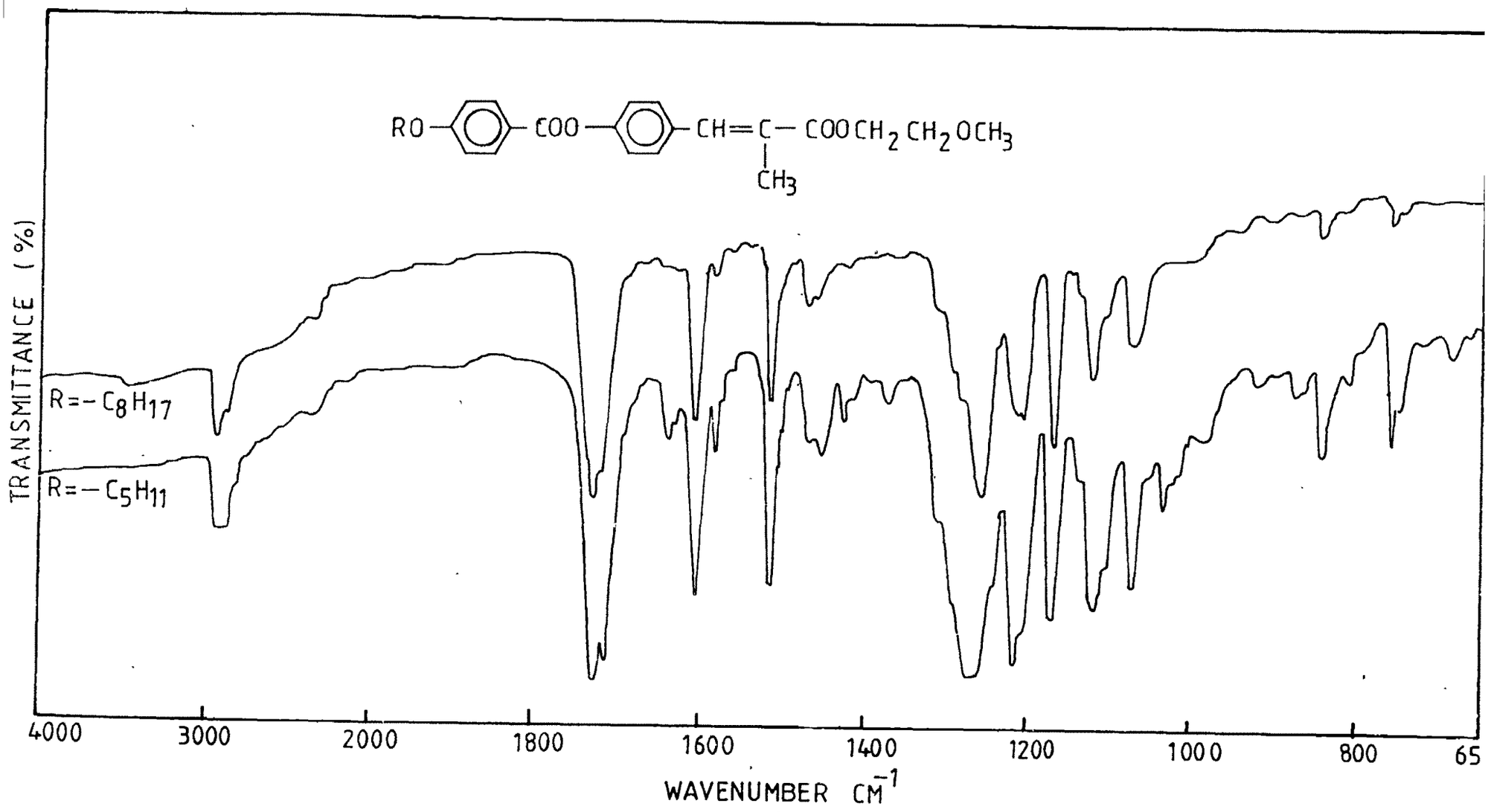


Fig.11 I. R. SPECTRA

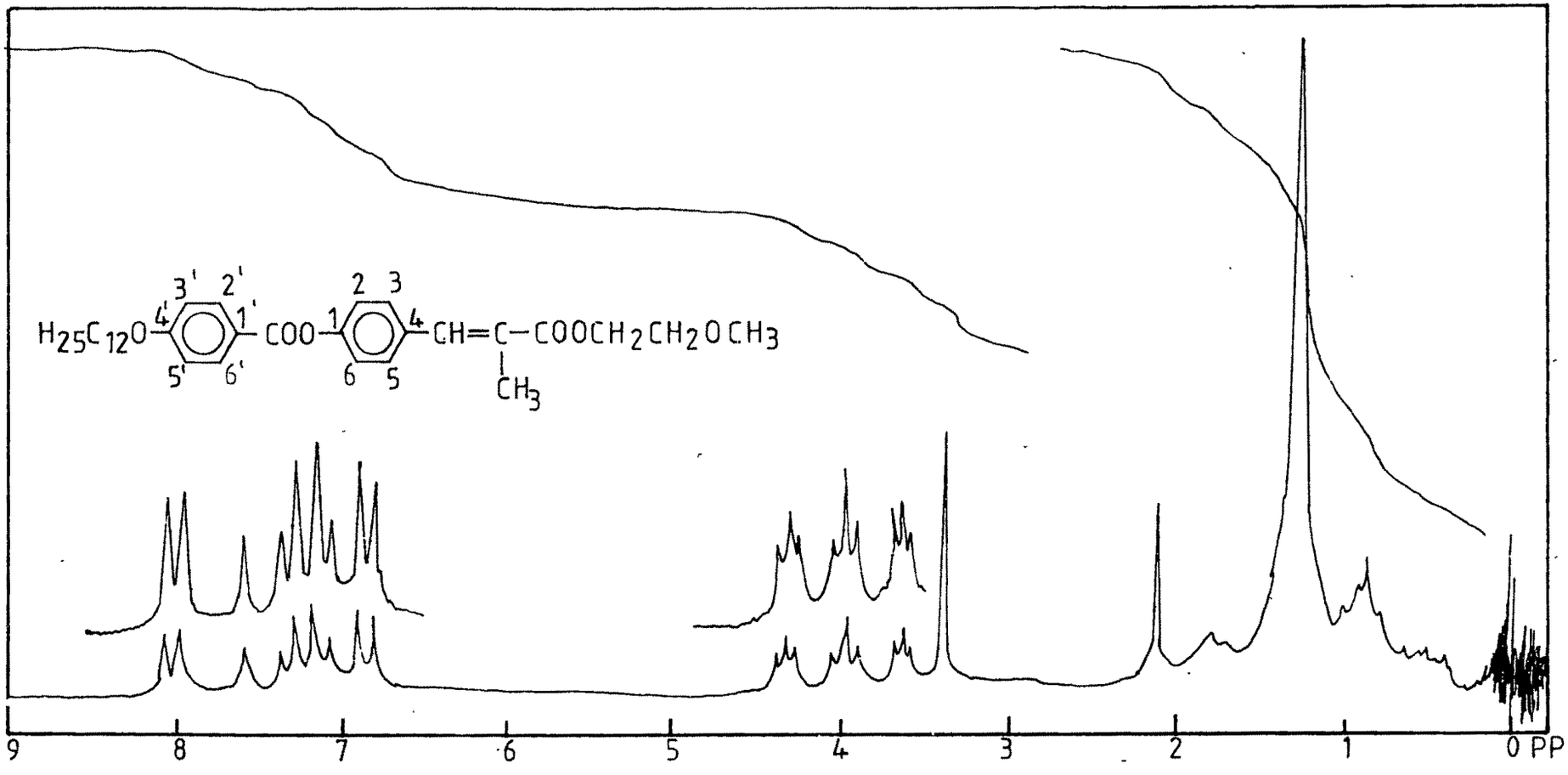
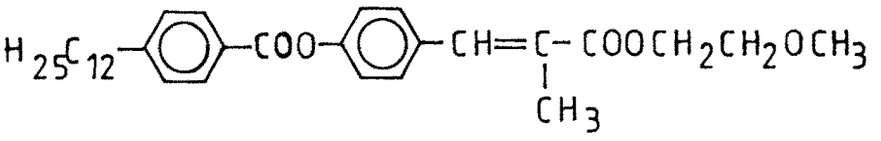


Fig.12 NMR SPECTRA



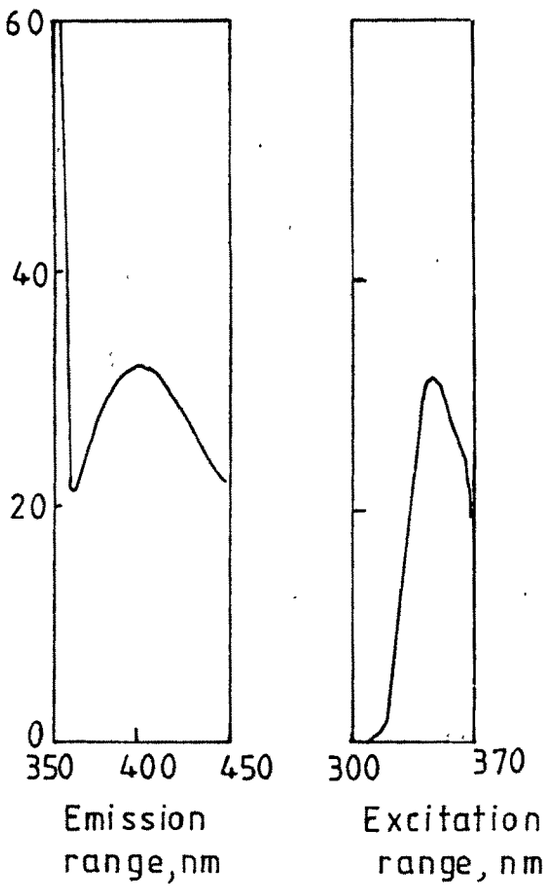


Fig. 13 FLUORESCENCE SPECTRA

2.0 LIQUID CRYSTALLINE SCHIFF BASES WITH NAPHTHALENE NUCLEUS AND AZOMESOGENS.

2.1. 4-n-Alkoxybenzylidene - 2'-aminonaphthalenes.

2.1a 4-n-Alkoxybenzaldehydes.

Commercially available 4-methoxybenzaldehyde (4-anisaldehyde, B.D.H) was used. Preparation of 4-n-alkoxybenzaldehydes, where alkoxy group varies from -OC_2H_5 to -$OC_{18}H_{37}$ has been variously described by Hildescheimer (226), Steermer and Wodarg (227), Weygard and Gabler (228), Gray and Jones (221). In this investigation, however, the modified method of Vyas and Shah (229) was followed.

4-Hydroxybenzaldehyde (0.1 mole), appropriate n-alkylhalide (0.15 mole) and anhydrous K_2CO_3 (0.15 mole) were added to dry acetone (60 ml). The mixture was refluxed using water bath for four to six hours. The whole mass was then added to the water and the aldehyde thus separated was extracted with ether. Ether extract was washed with dilute sodium hydroxide to remove unreacted 4-hydroxy benzaldehyde followed by water. On evaporation of dry ether extract yellow liquid was obtained for lower members and waxy solid for the higher members. They were directly used for next step.

2.1b Preparation of 4-n-alkoxybenzylidene -2'-amino naphthalenes :

4-n-Alkoxybenzylidene-2'-amino naphthalenes were synthesized by condensing appropriate 4-n- alkoxybenzaldehyde (0.01 mole) and 2-aminonaphthalene (0 01 mole) in ethanol at reflux temperature. The compounds were crystallised several times from ethanol till constant transition temperatures were obtained (Table 7). The elemental analyses are recorded in Table 8. The IR (KBr) spectra (Fig. 14) of the

compounds showed -C=N-stretching vibrations for azomethine central linkage at 1615 cm^{-1}. Other signals observed were at 2920, 1600, 1470, 1430, 1315, 1260, 1180, 850, 835, 750 cm^{-1}.

NMR spectra (Fig. 15) (90 MHz, solvent $CDCl_3$, standard TMS) of compound No. 10. Table 7. δ 8.35 (s, 1H, for -CH=N-) 7.55 - 7.8 (m, 7H of naphthalene ring system) 7.2 - 7.45 (m, 2H at C-2 and C-6) 6.8 - 7.0(d, J=9Hz, 2H at C-3 and C-5) 3.95 (t, 2H at $-PhOCH_2-$) 1.0 - 1.8 (brs, 2OH, 10 x $-CH_2-$) 0.90 (t, 3H, CH_3).

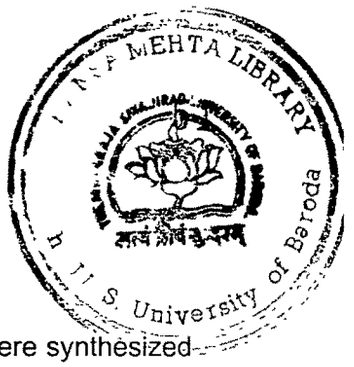
2.2 4(4'-n-Alkoxybenzoyloxy benzylidene) 2"-aminonaphthalenes : **series V**.

2.2a 4-n-Alkoxybenzoic acids and 4-n-Alkoxybenzoyl chlorides were prepared by the method described in sections 1.1.2a and 1.1.2b, respectively.

2.2b 4-n-Alkoxybenzoyloxy -4'-benzaldehydes.

4-n-Alkoxybenzoyloxy -4'-benzaldehydes were synthesized by the process reported in the literature (230). 4-n-Alkoxybenzaldehyde (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-Alkoxybenzoyl chloride (0.01 mole) as described in section 1.1.2d.

The compounds were crystallized several times from ethanol until constant transition temperatures were obtained. The transition temperatures are in good accordance with the literature value (230).



2.2c Preparation of 4(4'-n-Alkoxybenzoyloxy benzylidene) 2" - amino naphthalenes :

4(4'-n-Alkoxybenzoyloxybenzylidene) 2"-amino naphthalenes were synthesized by condensing appropriate 4-n-Alkoxybenzoyloxy-4'-benzaldehyde (0.01 mole) and 2-amino naphthalene (0.01 mole) in ethanol at reflux temperature. The compounds were crystallised several times from ethanol or benzene-ethanol mixture till constant transition temperatures were obtained (Table 9). The elemental analyses are recorded in Table 10. The IR (KBr) spectra (Fig. 16) of the compounds showed -COO- stretching vibrations at 1730 cm^{-1} and -CH=N- stretching vibrations at 1605 cm^{-1}. Other signals observed were at 2900, 1510, 1470, 1420, 1275, 1205, 1160, 1070, 1010, 840, 755 cm^{-1}.

NMR spectra (Fig. 17) (200 MHz, solvent $CDCl_3$, standard TMS) of compound no.11 Table. 9. δ 8.60 (s,1H for -CH=N-) 8.20 (d, J=8.8 Hz, 2H at C-2' and C-4') 8 05 (d, J=9Hz, 2H at C-2 and C-6) 7.85 (m, 3H of naphthalene ring at C-3', C-5' and C-8") 7.65 (s, 1H of naphthalene ring at C-1") 7.50 (m, 3H of naphthalene ring at C-4",C-6" and C-8") 785 (s,lH of naphalene ring at C-4", C-6" and C-7") 7.30 (d, J=8.5 Hz, 2H at C-3 and C-5) 7.00 (d J=8.9 Hz, 2H at C-3' and C-5') 4.05 (t, 2H at -$PhOCH_2$-) 1.85 (qunt., 2H of -Ph-O-C-CH_2-) 1.25-1.55 (m, 22H for 11X -CH_2-) 0.9 (t, 3H, -C-CH_3).

2.3 4(4'-n-Alkoxybenzoyloxybenzylidene) 2"-aminonaphthalene -1"-thiols :**Series VI.**

2.3a 4-n-Alkoxybenzoloxy - 4'- benzaldehydes.

4-n-alkoxybenzoyloxy-4'-benzaldehydes were synthesized by the method described in section 2.2b.

2.3 b 2-Aminonapthalene-1-thiol.

2-Aminonaphthalene-1-thiol can be synthesized by different routes (231-237). In the present study the following route was followed as it is more convenient with shorter reaction time and offering better yield (237).

(i) 2-Amino -1- thiocyanatonaphthalene.

A cold (-5 °C) solution of Br_2 (6ml, 10.04g, 0.063 mole) in MeOH (15ml) was added dropwise to a well-stirred solution of 2-aminonaphthalene (14.3g, 0.1 mole)and NH_4SCN (15.2g, 0.2 mole) in MeOH (140 ml) cooled at -5 °C. After the addition was complete the mixture was allowed to stand for ten minutes at 0 °C and then twenty minutes at room temperature. The product was collected by filteration, was washed with water and crystallised from ethanol, Melting point 153 °C (Reported m.p. 153-155°C).

(ii) 2-Aminonaphthalene-1-thiol :

To a warm and stirred solution $Na_2S.9H_2O$(48.0g,0.2 mole) in water (130ml) was added protionwise a suspension of 2-amino-1-thiocyanato -naphthalene (20g,0.1 mole in EtOH(50ml). The mixture was heated on a steam-bath for 40 min., until a clear solution was obtained. After cooling it was filtered and then filtrate was neutralized with 5N AcOH. The product was extracted with $CHCl_3$. The organic layer washed with water and dried (Na_2SO_4). Evaporation of solvent gave the required 2-aminonaphthalene -1-thiol as a yellow oil (17g) in quantitative yield. Compound 2-aminonaphthalene-1-thiol was used immediately in the next step without further purification because it is sensitive to air.

2.3c Preparation of 4(4'-n-alkoxybenzoyloxybenzylidene) 2"-amino - naphthalene-1"- thiols :

4(4'-n-Alkoxybenzoyloxybenzylidene) 2"-aminonaphthalene-1"-thiols were synthesized by condensing appropriate 4-n-alkoxybenzoyloxy-4'-benzaldehyde (0.01 mole) and 2-aminonaphthalene-1-thiol (0.01 mole) in boiling ethanol. The compounds were crystallized several times from ethanol or benzene - ethanol mixture till constant transition temperatures were obtained (Table-11). The elemental analyses are recorded in Table-12. The IR (KBr) spectra (Fig. 18) of the compounds showed weak band for - SH stretching vibration at 2345 cm^{-1} . The -COO- and -CH=N- stretching vibrations were obtained at 1730 and 1610 cm^{-1} , respectively. Other signals observed were at 2900, 1510, 1470, 1410 1275, 1210, 1170, 1075, 1010, 845 760 cm^{-1}.

NMR spectra (Fig 19) (60 MHZ, solvent $CDCl_3$, standard TMS) of compound No.10 Table 11. 7 - 6 - 8.3 (m, 9H, 6H of naphthalene ring system ; 2H at C-2' and C-6'; 1H of -CH=N-) 7.1-7.6 (m,4H at C-3,C-5,C-2 and C-6) 6.7-7.1 (m,2H at C-3' and C-5') 3.7-4.2 (m, 3H, 2H of $-PhOCH_2-$ and 1H of -PhSH) 1.1-1.6 (brs, 20H, $10x-CH_2-$) 0.90 (t, 3H, $-CH_3$ at C-4).

2.4 4-n-Alkoxybenzylidene- 4' - isopropyl anilinines : **Series VII.**

2.4a 4-n-Alkoxybenzaldehydes.

4-n-Alkoxybenzaldehydes were prepared by the method described in section 2.1a.

2.4b Preparation of 4-n-alkoxybenzylidine -4'-isopropyl anilines :

4-n-Alkoxybenzylidene -4'-n-isopropyl- anilines were synthesized by condensing appropriate 4-n-alkoxybenzaldehyde (0.01 mole) in boiling ethanol. The compounds

were crystallised several times from ethanol till constant transistion temperatures were obtained (Table .13). The elemental analyses are recorded in Table 14. IR(KBr) spectra (fig. 20) showed -CH=N- streching vibrations at 1615 cm^{-1} and gemdimethyl -CH $(CH_3)_2$ stretching vibrations were obtained at 1385 and 1370 cm^{-1}. Other signals observed were at 2900, 1600,1470, 1430,1315, 1250, 1150, 830 cm^{-1}

NMR spectra (Fig 21) (60MHZ, solvent $CDCl_3$, standard TMS) of compound No.10 Table.13. δ 8.3 (s, IH for -CH=N-) 7.8 (d, J=9Hz, 2H at C-2 and C-6), 7.2 (d,J=9Hz, 4H at C-2', C-6', C-3 and C-5) 6.9 (d, J = 9Hz, 2H at C-3' and C-5') 3 9 (t, 2H at -$PhOCH_2$-) 2.4-3.1 (m, 7H at - CH $(CH_3)_2$) 1.1-1.9 (m, 20H, 10x-CH_2-) 0 9 (t, 3H-CH_3 at C-4').

2.5 4-n-Alkoxy phenylazo -2'-naphthalenes : **Series VIII.**

2.5a 4-Hydroxyphenylazo-2'- naphthalene

4-Hydroxyphenylazo-2'- naphthalene was synthesized by using conventional method of diazotization and coupling (238)

2-Amino naphthalene (0.1 mole) was dissolved in 1:1 hydrochloric acid (100ml) and solution was cooled to 0 °C. This was diazotized by adding saturated sodium nitrite solution (0.1 mole) with constant stirring, maintaining faint positive test on starch-iodide paper. After the completion of diazotization, small quantity of urea was added to decompose excess of nitrous acid. The cold solution of diazonium cholride was coupled with phenol (0.1 mole) in alkaline (NaOH) condition (0-5 °C). After the addition of diazotized solution, the material was stirred for about fifteen minutes and then acidified with concentrated hydrochloric acid. The precipitates obtained were filtered and washed with water. It was then dried and crystallised from ethanol till constant melting point was obtained. Melting point is 147 °C. The IR (KBr) spectra

(Fig.22) of the compound showed broad peak for intermolecularly hydrogen bonded phenolic -OH at 3600-3200 cm^{-1}. The -N=N- stretching vibrations were obtained at 1615 cm^{-1}. Other signals observed were at 1600, 1505, 1470, 1260, 1220, 875, 850, 750 cm^{-1}.

2 5b Prepartion of 4-n-Alkoxyphenylazo -2'-naphthalenes.

4-n-Alkoxyphenylazo - 2'-naphthalenes were synthesized by the alkylation of 4-hydroxyphenylazo -2'-napththalene using known method described in section 2 1a : The compounds were crystallized from alcohol till constant melting points were obtained. (Table-15). The elemental analyses were recorded in Table-16. The IR(KBr) spectra (Fig.22) of the compounds showed -N=N- stretching vibrations at 1610 cm^{-1}. Other signals observed were at 2950, 2835, 1590, 1505, 1470, 1415, 1270, 1150, 875, 830, 755 cm^{-1}.

2.6 4(4'-n-alkoxybenzoyloxy) phenylazo-2"-naphthalenes : **Series IX.**

2.6a 4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides were prepared by the method described in section 1.1.2a and 1.1.2b, respectively.

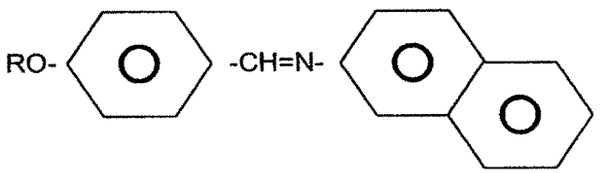
2.6b 4-Hydroxyphenylazo-2'- naphthalene was synthesized by the method described in section 2.5a.

2.6c Preparation of 4(4'-n-alkoxybenzoyloxy) phenylazo-2"-naphthalenes :

4(4'-n-alkoxybenzoyloxy) phenylazo-2"-naphthalenes were synthesized by condensing appropriate 4-n-alkoxybenzoyl chloride with 4-hydroxyphenylazo-2'-napththalene.

Table - 7

4-n-Alkoxybenzylidene-2'-aminonaphthalenes



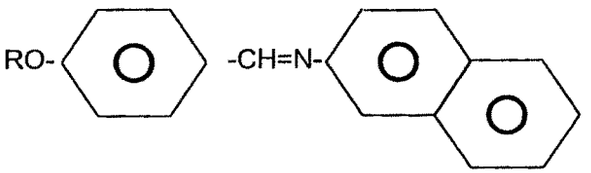
Transition Temperatures °C

Sr. No.	R = n - alkyl group	S_A	N	I
1	Methyl	-	-	104.0
2	Ethyl	-	-	117.0
3	Propyl	-	-	122.0
4	Butyl	-	-	90.0
5	Pentyl	-	-	79.0
6	Hexyl	-	(70.0)*	81.0
7	Heptyl	-	(70.0)	88.5
8	Octyl	-	(76.0)	85.0
9	Decyl	-	(78.0)	88.0
10	Dodecyl	(76.0)	(79.0)	92.0
11	Tetradecyl	-	-	97.0
12	Hexadecyl	-	-	100.0

( )* Monotropic value.

Table - 8

4-n-Alkoxybenzylidene-2'-aminonaphthalenes

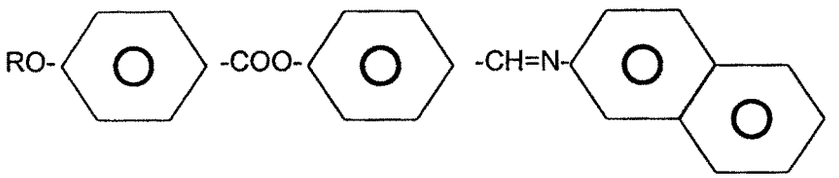


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	82.76	5.75	5.36	82.77	5.87	4.93
2	Ethyl	82.91	6.18	5.09	82.81	6.36	5.39
3	Propyl	83.04	6.57	4.84	82.76	6.61	5.09
4	Butyl	83.17	6.93	4.62	83.10	6.75	4.40
5	Pentyl	83.28	7.26	4.42	83.37	7.13	4.84
6	Hexyl	82.63	7.49	4.19	83.00	7.98	4.51
7	Heptyl	83.48	7.83	4.06	83.91	8.22	4.40
8	Octyl	83.57	8.08	3.90	83.66	8.53	4.22
9	Decyl	83.72	8.53	3.62	83.85	8.86	3.96
10	Dodecyl	83.85	8.92	3.37	83.50	9.16	3.71
11	Tetradecyl	83.97	9.26	3.16	84.41	9.53	3.45
12	Hexadecyl	84.08	9.55	2.97	83.64	9.84	3.12

Table - 9

4 (4'- n- Alkoxybenzoyloxybenzylidene)-2"-aminonaphthalenes.



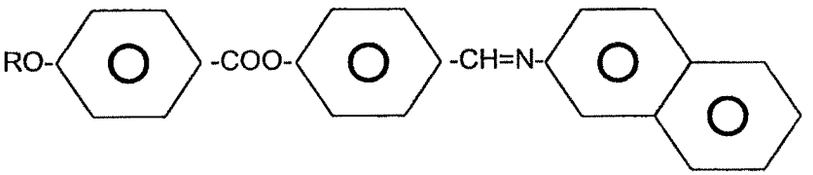
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperature °C Sc	N	I
1	Methyl	---	142.0	270.
2	Ethyl	---	137.0	267.0
3	Propyl	---	129.0	254.0
4	Butyl	---	133.0	249.0
5	Pentyl	---	128.0	239.0
6	Hexyl	---	116.0	235.0
7	Heptyl	(85.0)*	120.0	225.0
8	Octyl	(94.0)	115.0	220.0
9	Decyl	109.0	141.0	209.0
10	Dodecyl	106.0	157.0	198.0
11	Tetradecyl	101.0	162.0	194.0
12	Hexadecyl	95.0	155.0	187.0

( )* Monotropic value.

Table - 10

4(4'-n-Alkoxybenzoyloxybenzylidene)-2'-aminonaphthalenes

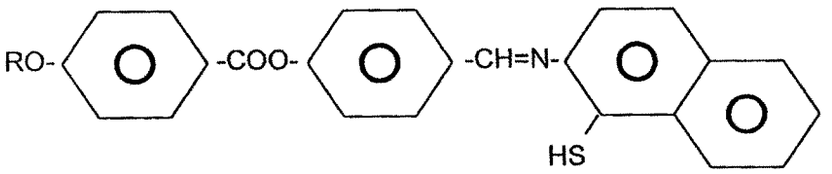


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	78.74	4.97	3.67	78.41	5.32	4.09
2	Ethyl	78.99	5.32	3.54	78.62	5.59	3.78
3	Propyl	79.22	5.62	3.42	78.92	5.80	3.66
4	Butyl	79.43	5.91	3.31	79.03	5.96	3.47
5	Pentyl	79.63	6.18	3.20	79.18	6.42	3.22
6	Hexyl	79.82	6.43	3.10	79.84	6.83	3.42
7	Heptyl	80.00	6.66	3.01	79.61	6.24	3.37
8	Octyl	80.17	6.89	2.92	79.79	6.52	3.34
9	Decyl	80.47	7.30	2.76	80.04	6.88	3.16
10	Dodecyl	80.75	7.66	2.62	80.56	7.37	3.01
11	Tetradecyl	80.99	7.99	2.49	80.54	7.51	2.94
12	Hexadecyl	81.22	8.29	2.37	80.87	8.10	2.70

Table - 11

4 (4'- n- alkoxybenzoyloxybenzylidene)-2"-aminoaphthalene-1"-thiols.



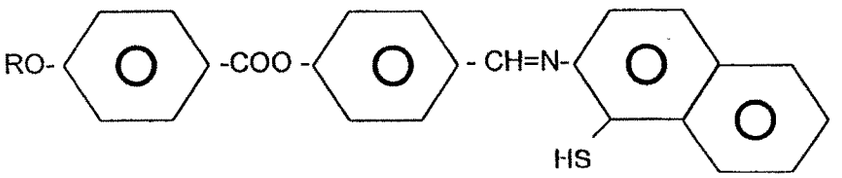
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C Sc	N	I
1	Methyl	---	188.0	284.0
2	Ethyl	---	187.0	281.0
3	Propyl	---	191.0	264.0
4	Butyl	---	184.0	263.0
5	Pentyl	---	170.0	248.0
6	Hexyl	---	163.0	249.0
7	Heptyl	---	150.0	235.0
8	Octyl	---	145.0	236.0
9	Decyl	---	136.0	225.0
10	Dodecyl	(125.0)*	142.0	215.0
11	Tetradecyl	134.0	143.0	204.0
12	Hexadecyl	129.0	148.0	196.0

( )* Monotropic value.

Table - 12

4(4'-n-Alkoxybenzoyloxybenzylidene)-2"-aminonaphthalene-1"thiols

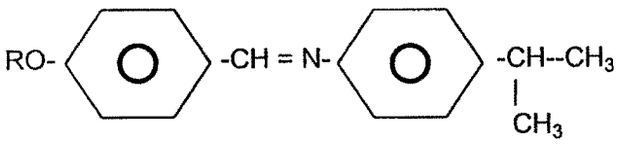


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	72.64	4.60	3.39	72.40	4.53	3.63
2	Ethyl	73.07	4.92	3.28	72.80	4.93	3.19
3	Propyl	73.47	5.21	3.17	73.15	5.44	3.36
4.	Butyl	73.85	5.49	3.08	73.40	5.08	3.47
5	Pentyl	74.20	5.76	2.98	73.81	5.66	3.40
6	Hexyl	74.53	6.00	2.90	74.26	5.74	3.28
7	Heptyl	74.85	6.24	2.82	74.68	5.86	3.26
8	Octyl	75.15	6.46	2.74	75.60	6.19	3.20
9	Decyl	75.70	6.86	2.60	75.60	6.42	2.87
10	Dodecyl	76.19	7.23	2.47	76.46	7.08	2.81
11	Tetradecyl	76.64	7.56	2.35	76.22	7.26	2.80
12	Hexadecyl	77.05	7.87	2.25	76.74	7.55	2.68

Table - 13

4 - n- Alkoxybenzylidene -4'-isopropylanilines.



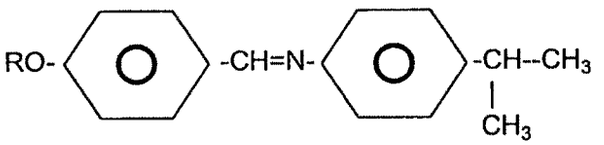
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C S_A	I
1	Methyl	---	71.0
2	Ethyl	---	73.0
3	Propyl	---	61.0
4	Butyl	---	66.0
5	Pentyl	---	60.0
6	Hexyl	---	64.0
7	Heptyl	---	58.0
8	Octyl	56.5	59.0
9	Decyl	(60.0)*	64.0
10	Dodecyl	54.5	60.0
11	Tetradecyl	(64.0)	74.0
12	Hexadecyl	---	80.0

( )* Monotropic value.

Table - 14

4-n-Alkoxybenzylidene-4'-isopropylanilines

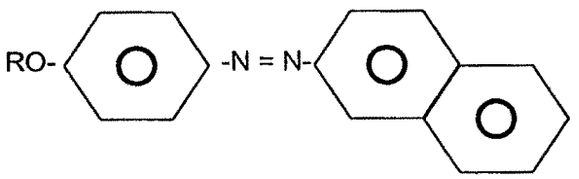


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	80.63	7.51	5.53	80.53	7.13	5.89
2	Ethyl	80.90	7.87	5.24	80.47	7.40	5.57
3	Propyl	81.14	8.18	4.98	80.68	7.73	5.36
4	Butyl	81.36	8.47	4.75	80.95	8.00	5.15
5	Pentyl	81.55	8.74	4.53	81.08	8.29	4.91
6	Hexyl	81.73	8.98	4.33	81.85	9.35	4.38
7	Heptyl	81.90	9.20	4.15	81.48	8.80	3.96
8	Octyl	82.05	9.40	3.99	81.75	9.79	4.02
9	Decyl	82.32	9.76	3.69	82.51	10.13	3.83
10	Dodecyl	82.55	10.07	3.44	82.31	9.64	3.82
11	Tetradecyl	82.76	10.34	3.23	82.37	10.68	3.68
12	Hexadecyl	82.94	10.58	3.02	83.00	11.02	3.11

Table - 15

4'- n- Alkoxyphenylazo -2'- naphthalenes.

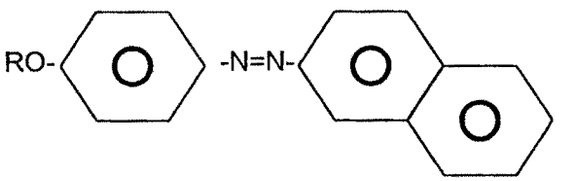


Melting Points °C

Sr. No.	R = n - alkyl group	Melting Points °C
1	Hexyl	93.5
2	Heptyl	99.5
3	Octyl	109.0
4	Decyl	100.0
5	Dodecyl	94.0
6	Tetradecyl	91.0
7	Hexadecyl	95.0

Table - 16

4'- n- Alkoxyphenylazo -2'- napthalenes.

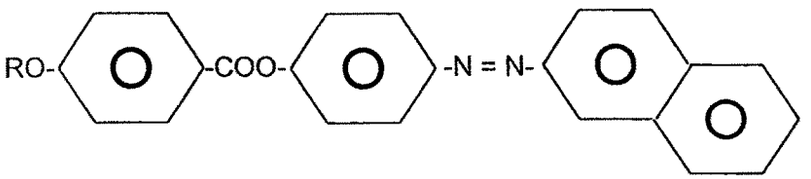


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Hexyl	79.52	7.23	8.43	79.26	7.43	8.28
2	Heptyl	79.77	7.51	8.09	79.47	7.62	8.32
3	Octyl	80.0	7.78	7.78	79.92	7.56	7.84
4	Decyl	80.41	8.25	7.22	80.64	8.32	7.04
5	Dodecyl	80.77	8.65	6.73	80.83	8.27	6.92
6	Tetradecyl	81.08	9.01	6.31	80.78	8.86	6.63
7	Hexadecyl	81.36	9.32	5.93	81.65	8.91	5.78

Table - 17

4 (4'- n- Alkoxybenzoyloxy) phenylazo-2"-naphthalenes.



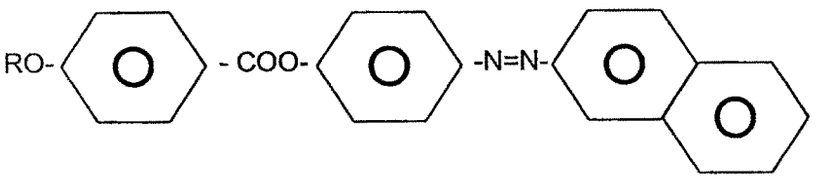
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C		
		Sc	N	I
1	Methyl	---	173.0	284.0
2	Ethyl	---	158.0	274.0
3	Propyl	---	144.0	230.0
4	Butyl	---	158.0	262.0
5	Pentyl	---	119.0	220.0
6	Hexyl	---	138.0	226.0
7	Heptyl	---	135.0	218.0
8	Octyl	---	138.0	213.0
9	Decyl	(90.0)*	123.0	210.0
10	Dodecyl	(112.0)	133.0	201.0
11	Tetradecyl	(121.0)	125.0	183.0
12	Hexadecyl	127.0	134.0	177.0

( )* Monotropic value.

Table - 18

4 (4'- n- Alkoxybenzoyloxy) phenylazo-2"-naphthalenes.



Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	75.20	4.96	7.31	75.48	4.66	7.45
2	Ethyl	75.57	5.29	7.05	75.23	4.91	7.17
3	Propyl	75.91	5.59	6.81	75.72	5.83	7.21
4	Butyl	76.23	5.88	6.59	75.87	5.58	6.16
5	Pentyl	76.53	6.15	6.38	77.06	6.38	6.28
6	Hexyl	76.82	6.40	6.18	76.83	6.19	6.04
7	Heptyl	76.09	6.64	5.99	75.87	6.39	5.59
8	Octyl	77.34	6.86	5.82	77.71	6.56	5.80
9	Decyl	77.80	7.27	5.50	78.09	7.21	5.84
10	Dodecyl	78.21	7.63	5.21	78.43	7.74	5.48
11	Tetradecyl	78.58	7.96	4.96	78.36	7.67	5.23
12	Hexadecyl	78.92	8.26	4.72	78.76	7.88	4.64

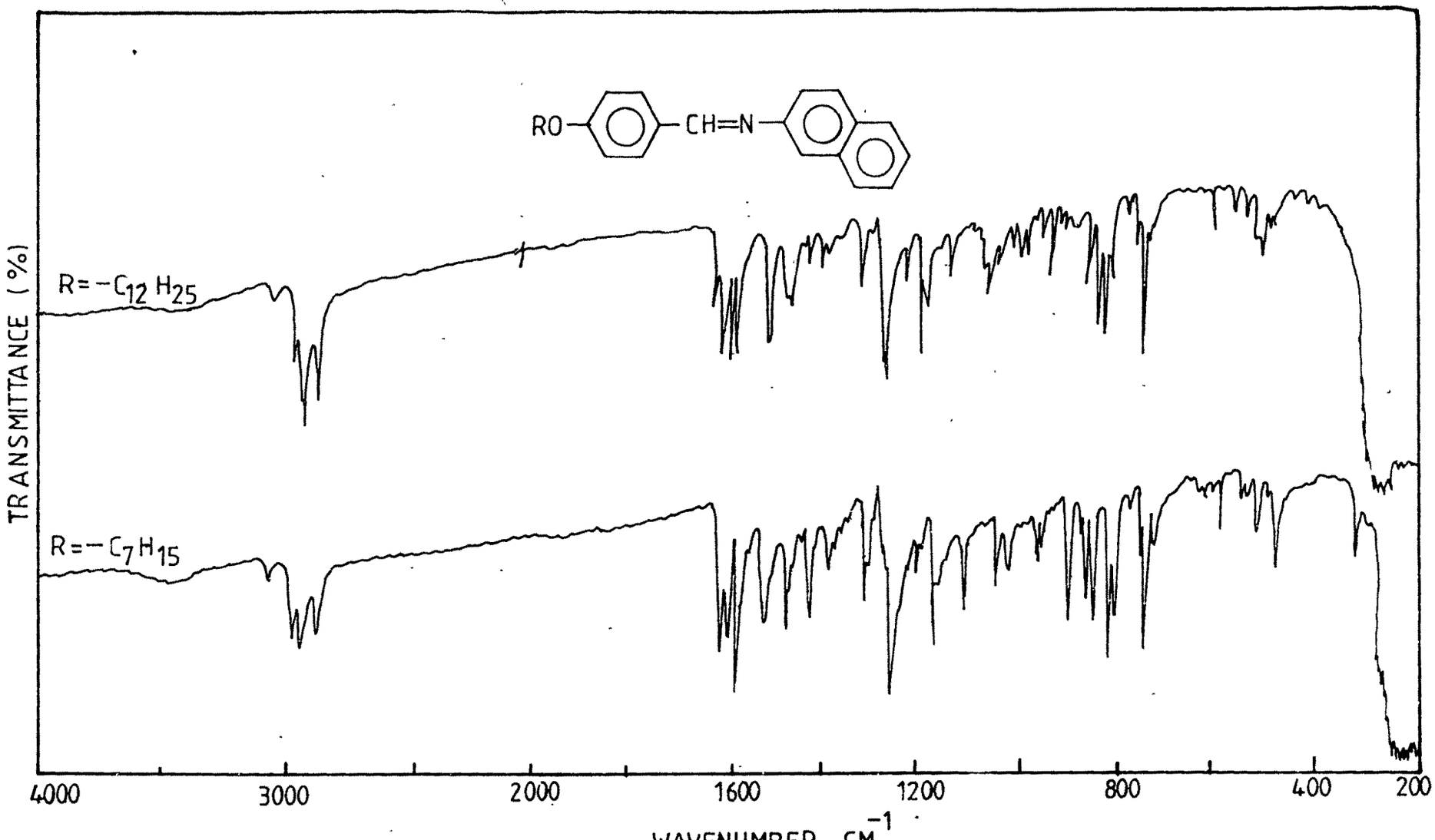


Fig.14 I. R. SPECTRA

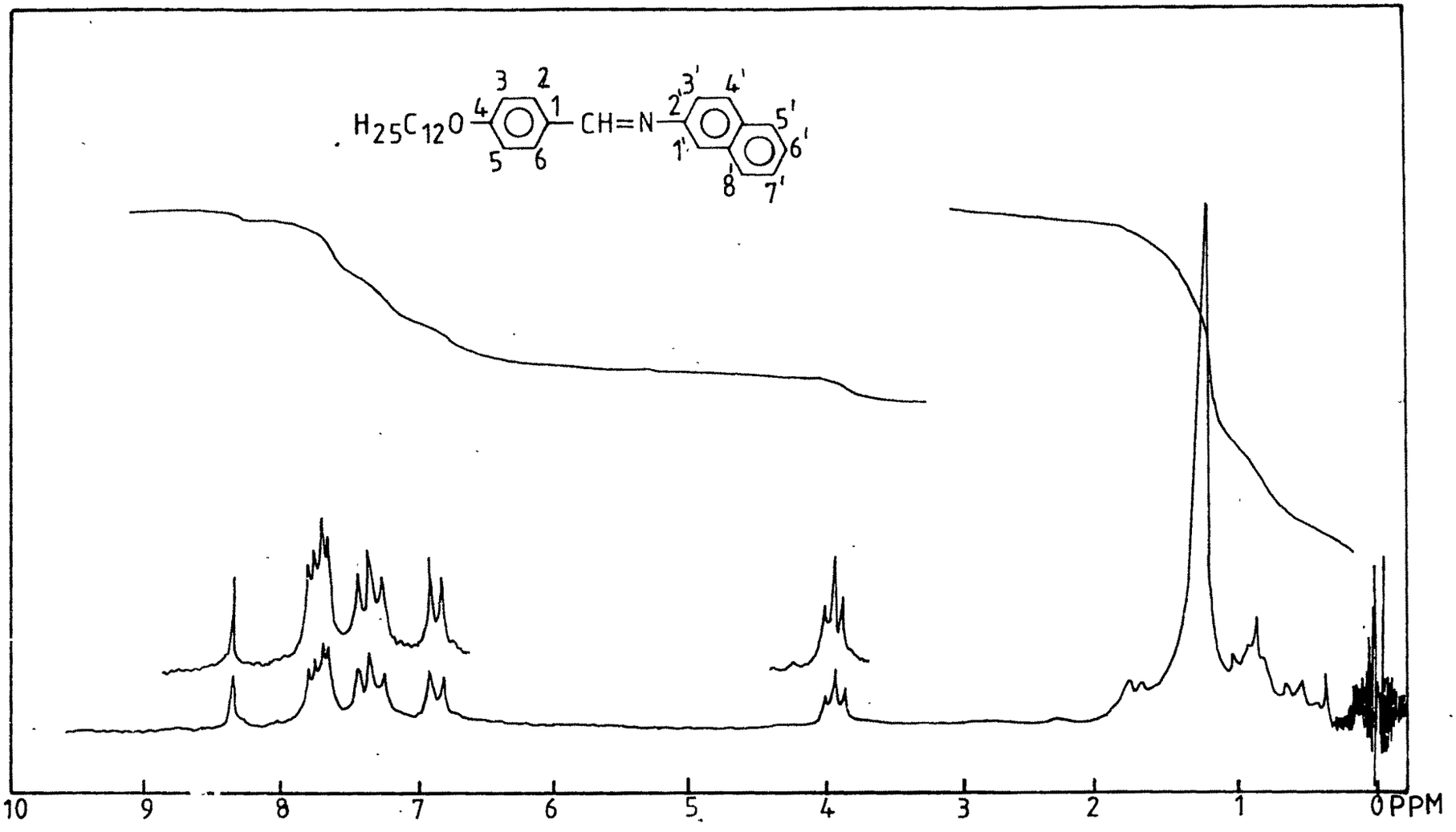


Fig. 15 NMR SPECTRA

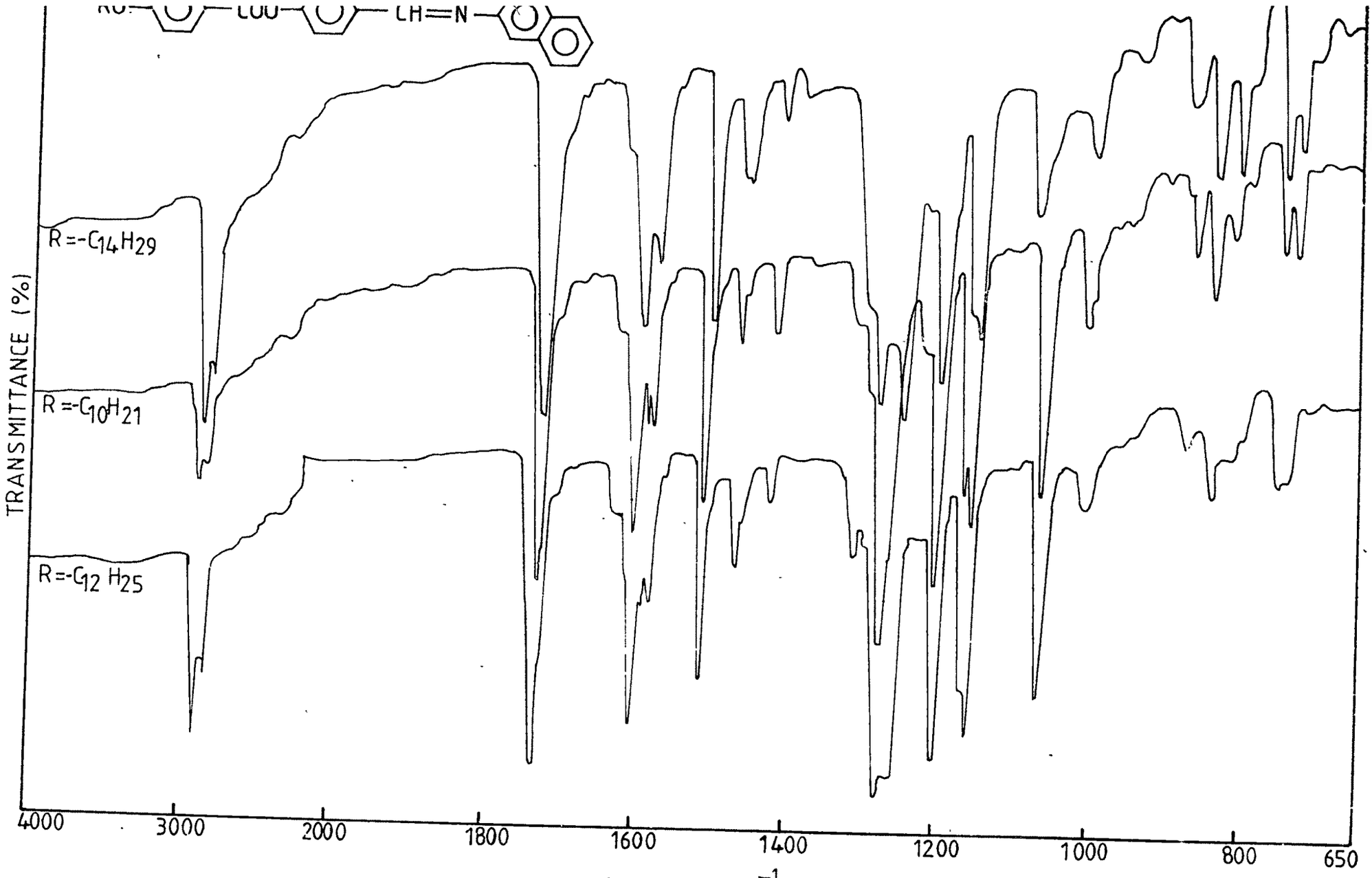


Fig.16 I.R. SPECTRA

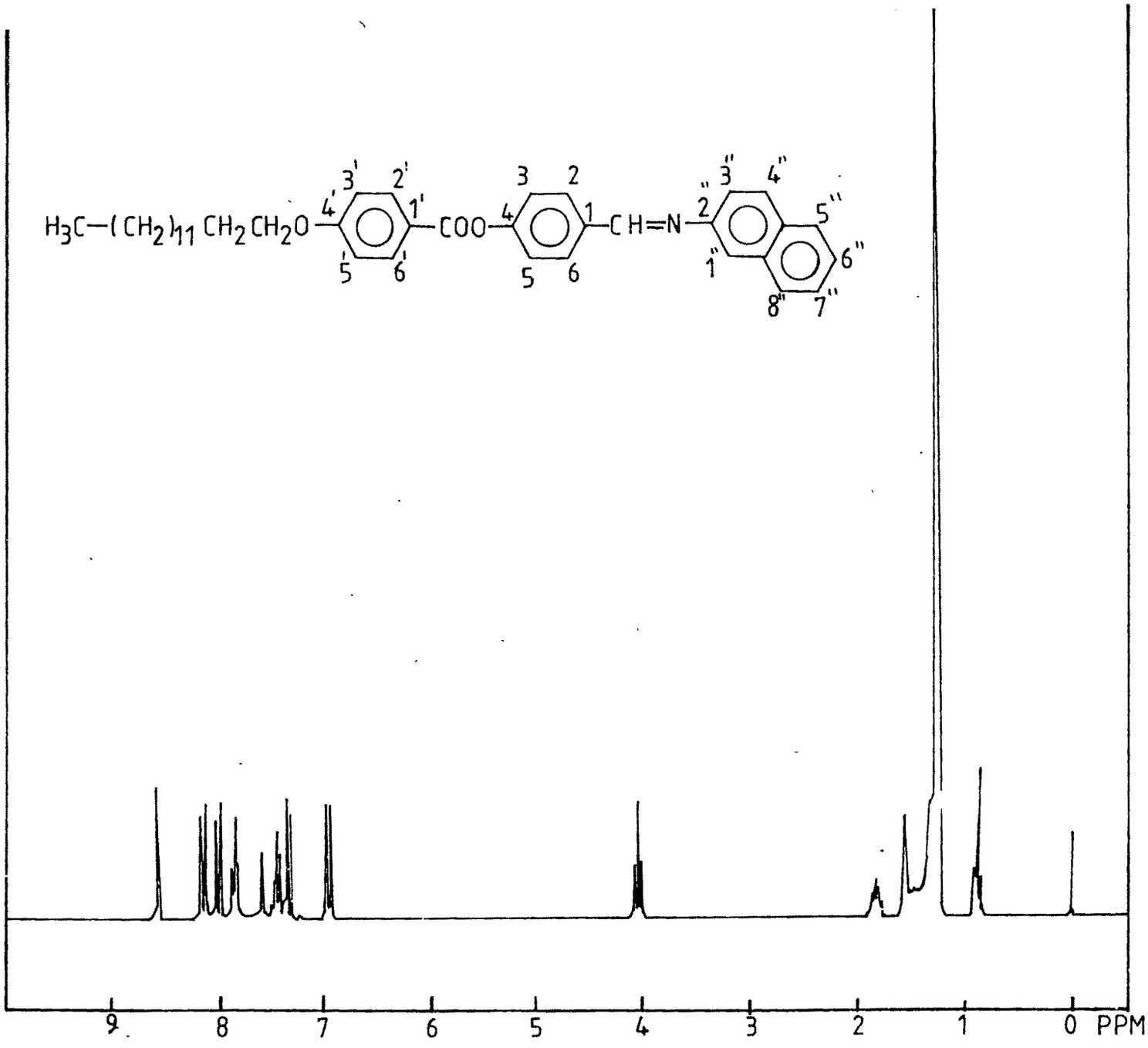


Fig.17 NMR SPECTRA

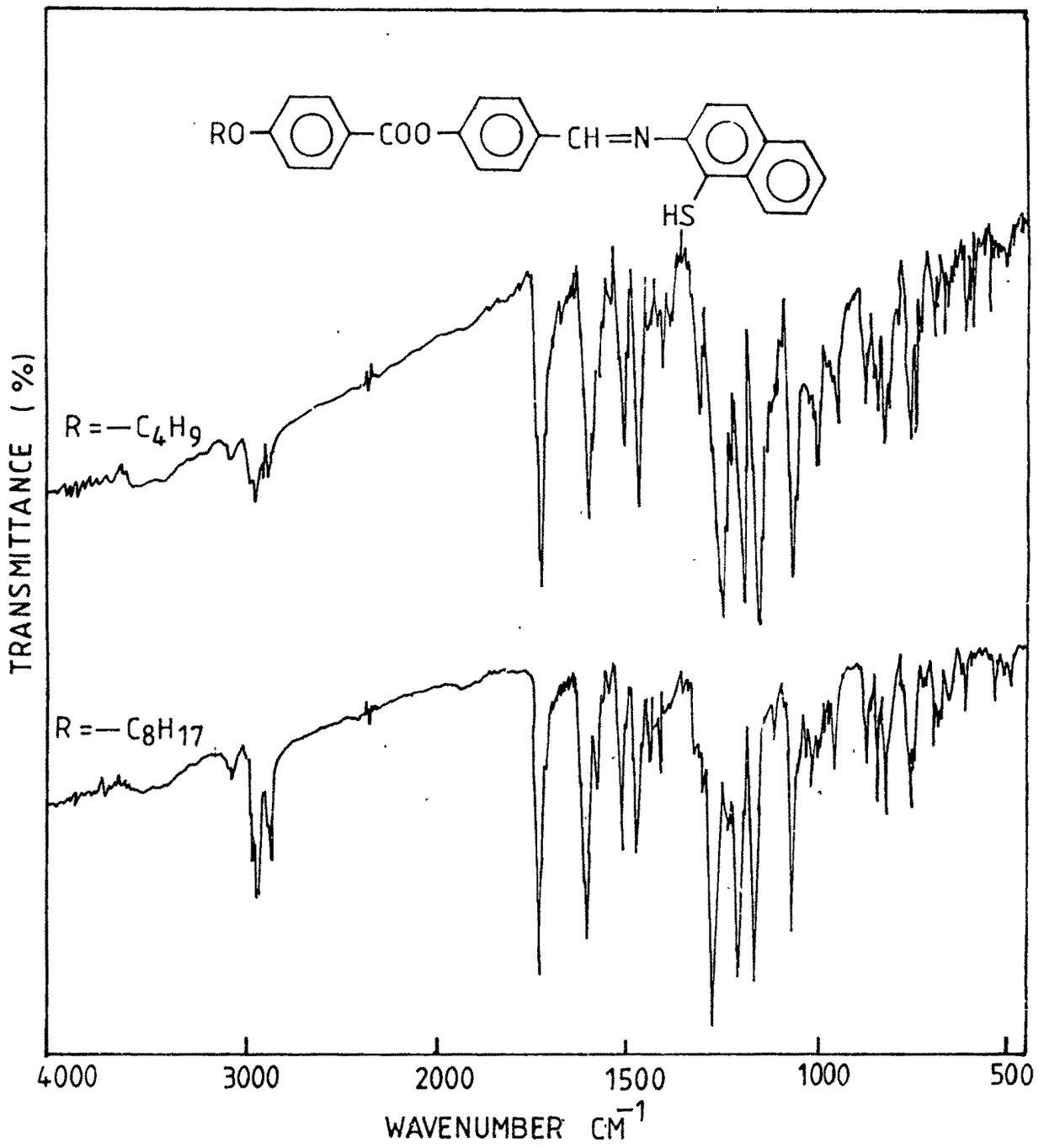


Fig. 18 I.R. SPECTRA

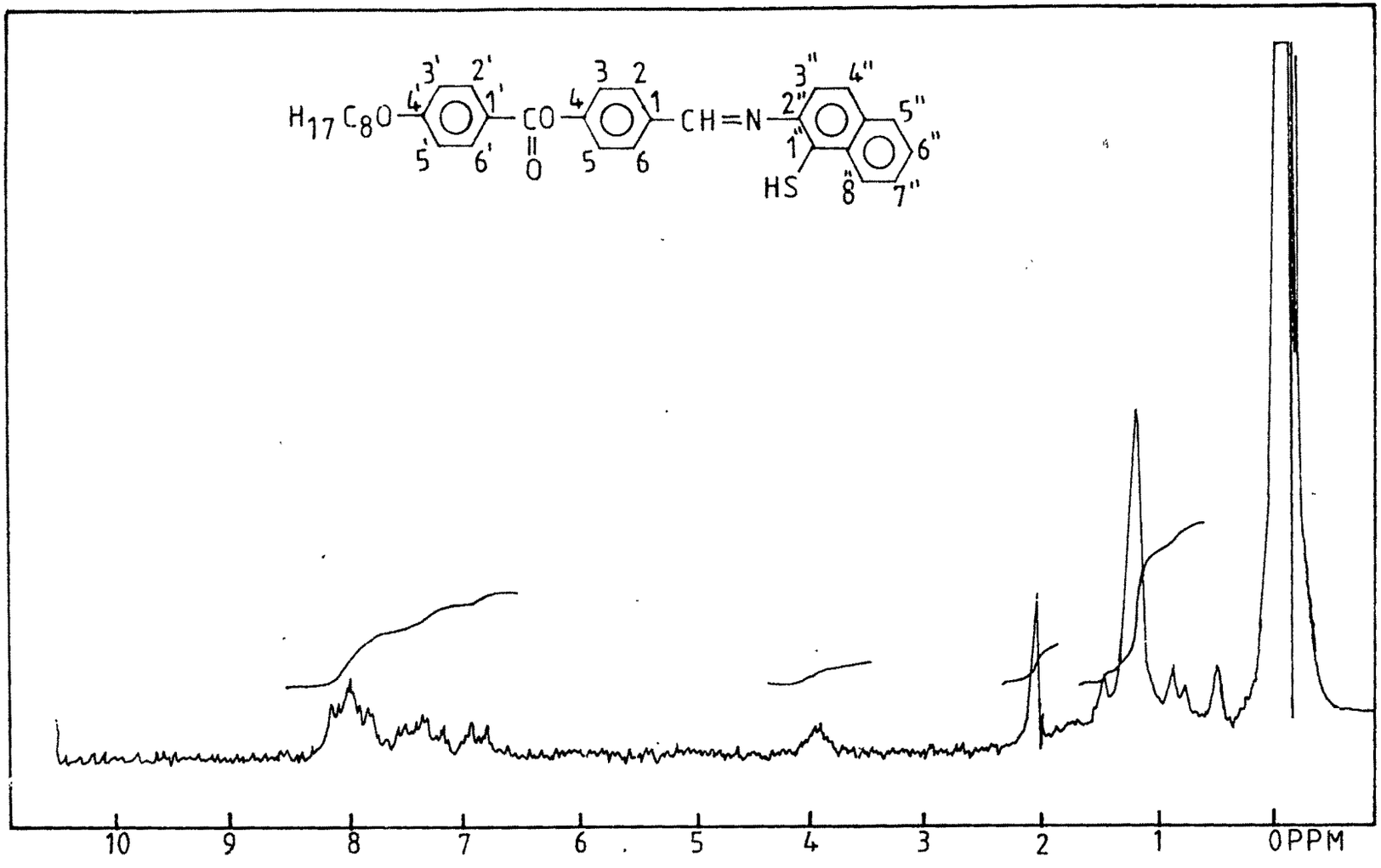


Fig.19 NMR SPECTRA

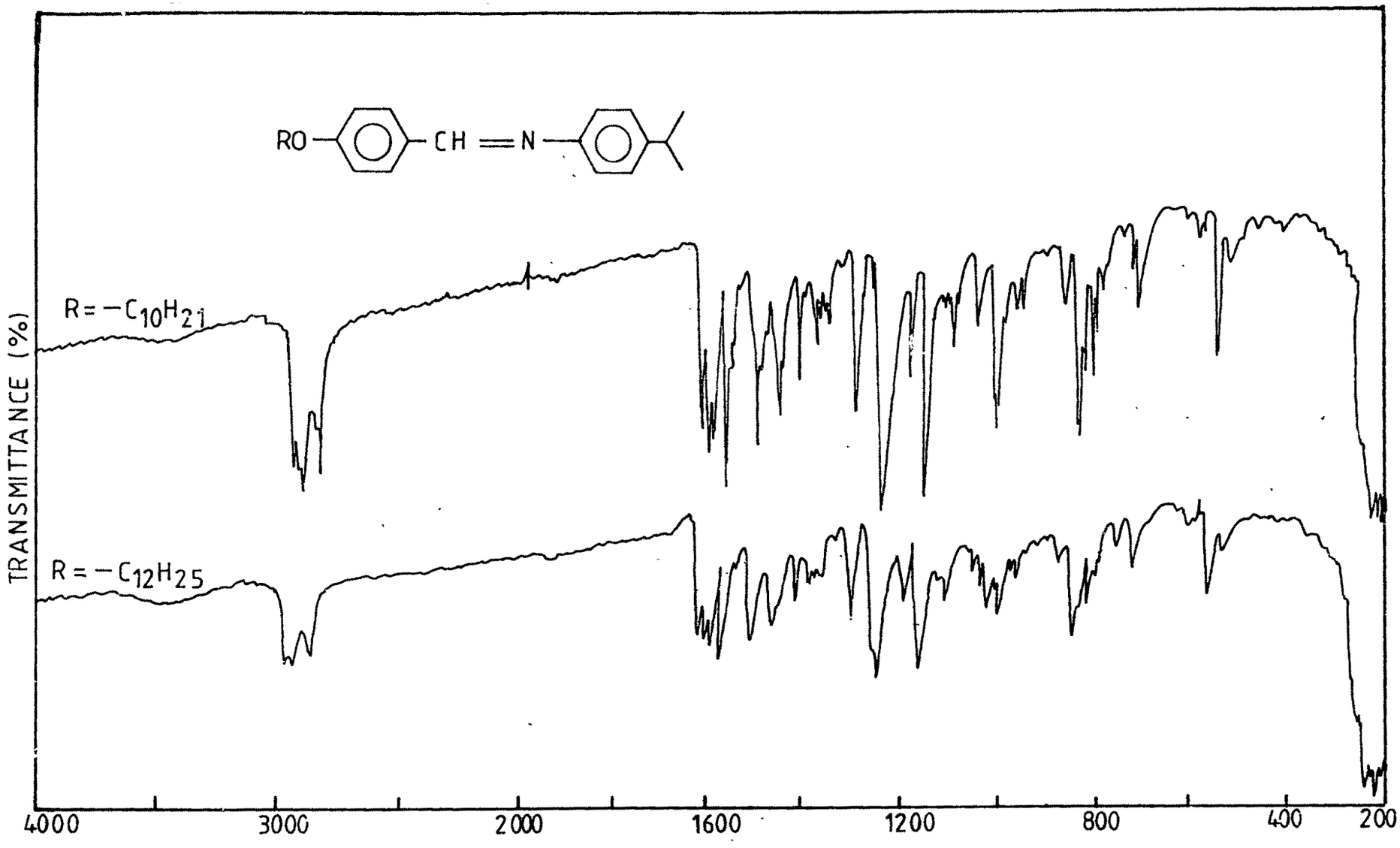


Fig.20 I. R. SPECTRA

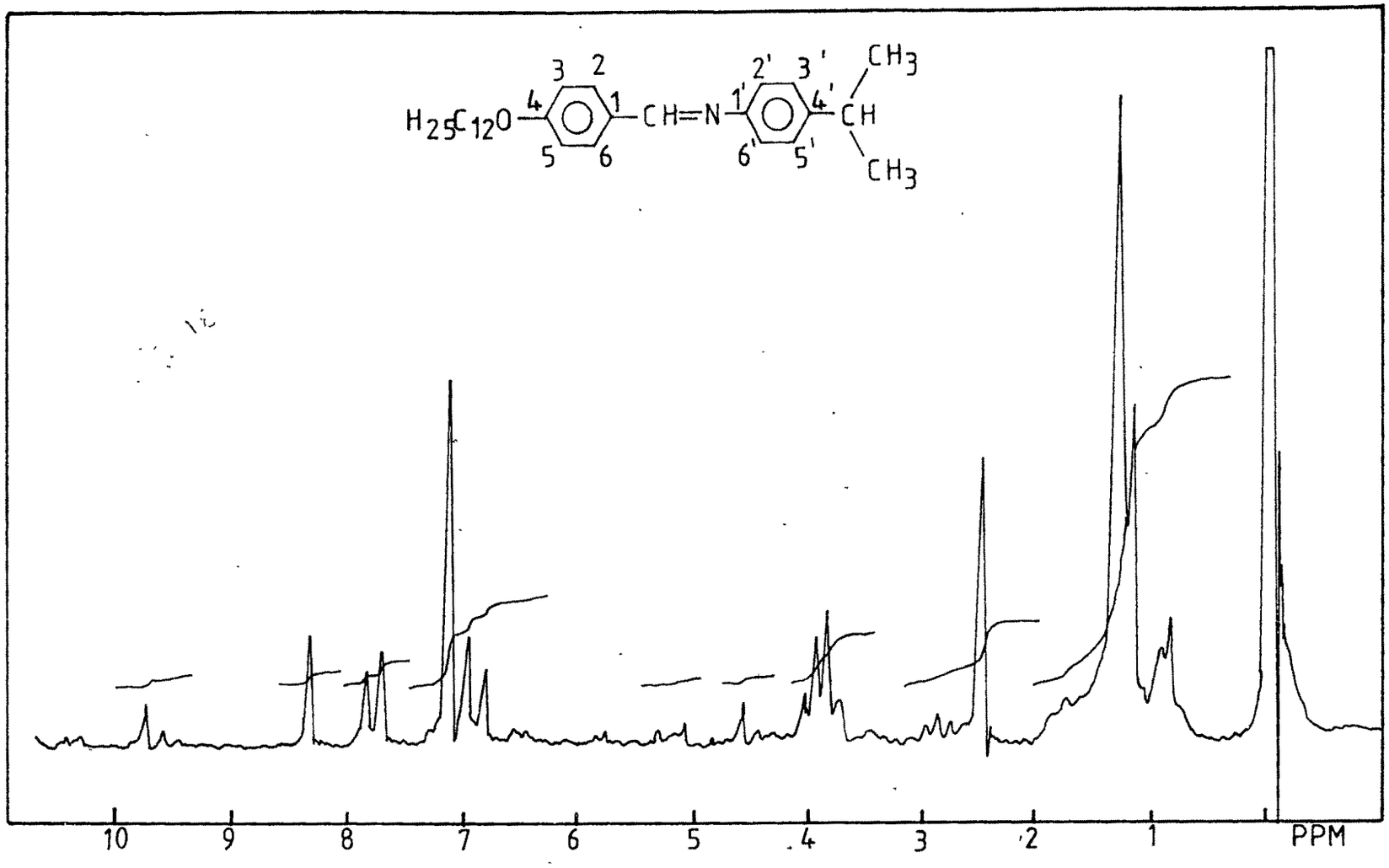


Fig. 21 NMR SPECTRA

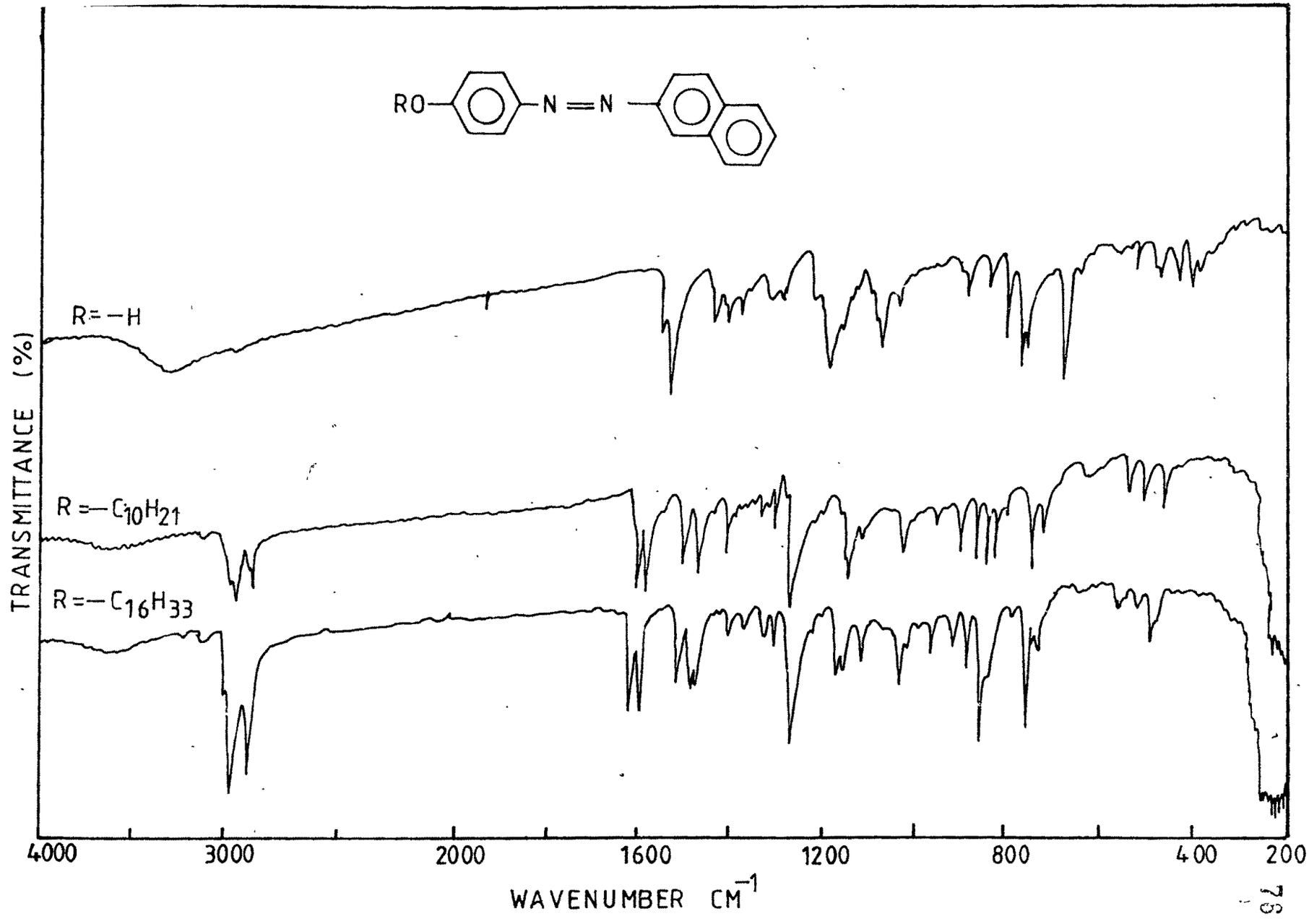


Fig.22. I. R. SPECTRA

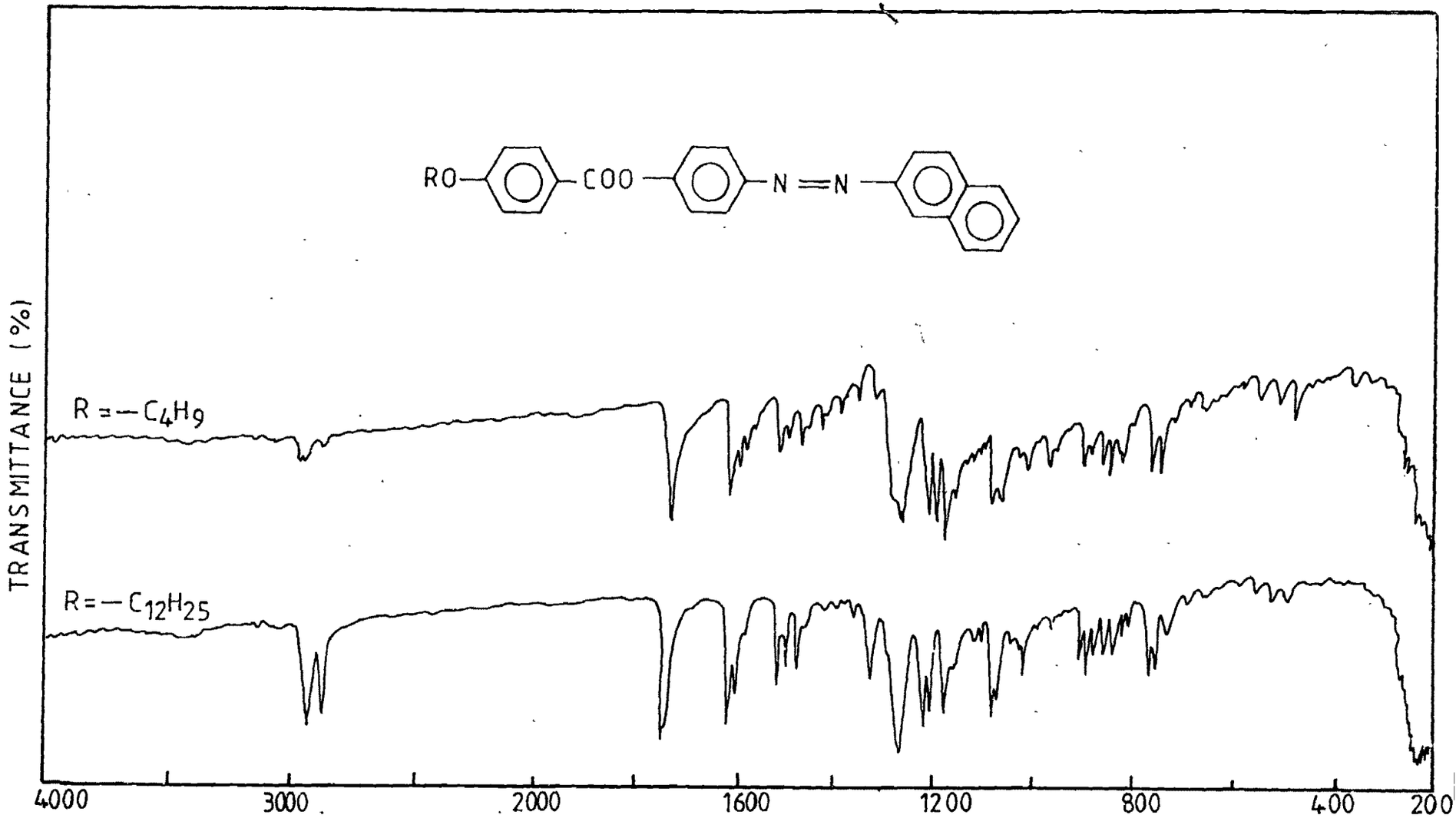


Fig. 23. I. R. SPECTRA

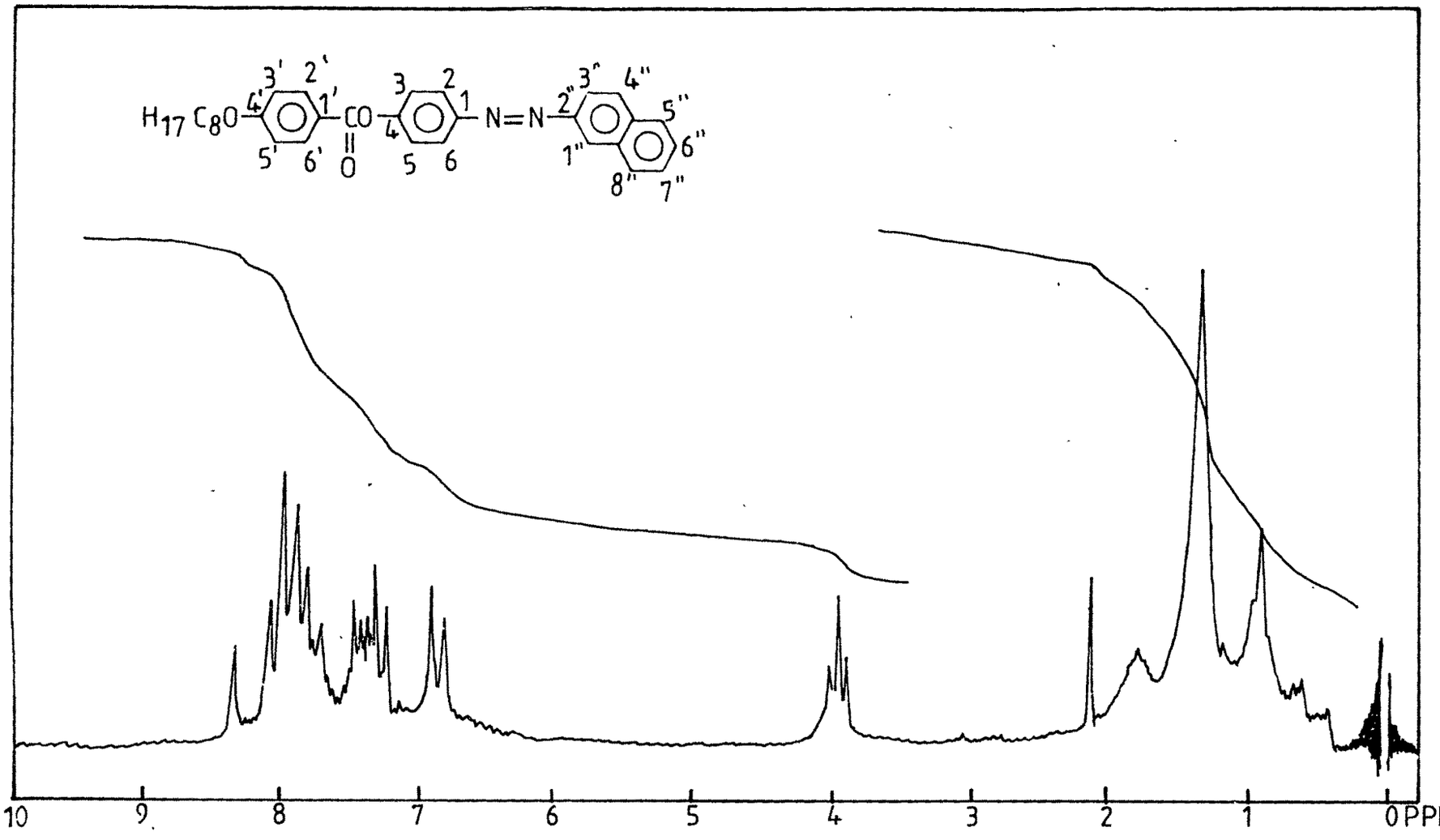


Fig. 24 NMR SPECTRA

4-hydroxyphenylazo-2'-napththalene (0.01 mole) was dissolved in dry pyridine (10ml) and was added slowly with constant stirring to cold 4-n-alkoxybenzoyl chloride (0.01 mole) as described in section 1.1.2. The compounds were crystallised from acetic acid till constant transition temperatures were obtained (Table 17). The elemental analyses are recorded in Table 18. The IR (KBr) spectra (Fig-23) of the compounds showed -COO- stretching vibrations at 1745 cm^{-1} and -N=N- stretching vibrations at 1620 cm^{-1}. Other signals observed were at 2900, 1600, 1510, 1470, 1260, 1210, 1170, 1080, 1010, 845, 760 cm^{-1}.

NMR spectra (Fig 24) (90MHz, solvent $CDCl_3$, standard TMS) of compound No.8 Table-17. δ 8.00 (d, J=9Hz, 2H at C-2' and C-6') 7.20-8.30 (m, 9H, 7H of naphthalene ring system and 2H at C-2 and C-6) 7.15 (d, J=9Hz, sH at C-3 and C-5) 6.85 (d, J=9Hz, 2H at C-3' and C-5') 3.95 (t, 2H of -$PhOCH_2$-) 1.20 - 1.90 (brs, 12 H for 6 x -CH_2-) 0.95 (t, 3H, -CH_3).

3.0 LIQUID CRYSTALLINE HOMOLOGOUS SERIES WITH BIPHENYL NUCLEUS

3.1 4 (4'-Methoxy phenyl) 4"-n-alkoxy benzanilides. **Series X.**

3.1a 4-n-Alkoxy anilines.

4-n-Alkoxy anilines can be synthesized by different routes. (229, 239). In the present study the following route was followed as it gives over all better yields of 4-n-alkoxy anilines (239).

(i) 4-n-Alkoxy acetanilides.

Paracetamol (0.1 mole) anhydrous potassium carbonate (0.15 mole), n-alkylbromides (0.15 mole) and dry acetone (60ml) were taken in round bottom flask The reaction mixture was refluxed on water bath for eight to ten hours. The whole mass was then added to water and extracted with ether. The ether was evaporated and the residual solids, alkoxy acetanilides were directly used for hydrolysis.

(ii) 4-n-Alkoxy anilines :

A mixture of 4-n-alkoxy acetanilide (0.146 mole) water and concentrated hydrochloric acid (45 ml) were stirred for ten to twelve hours at 90 - 95 °C and then cooled to room temperature. The mixture was made alkaline with 50 % sodium hydroxide solution at 20 °C. The oily product (for the lower members) was extracted with ether. The ether extract was dried and concentrated at reduced pressure to give an oil which was purified by distillation.

The higher members separated as solids and were filtered directly without ether extraction, Melting points and boiling points agree well with the reported values (229, 239)

3.1b 4-Methoxybiphenyl-4'-carboxylic acid.

4-Methoxybiphenyl- 4'- carboxylic acid was synthesized by three step method reported in the literature. (240,241).

(i) 4-Methoxybiphenyl

In a 500 ml three-necked flask fitted with a pressure equalising separatory funnel, a mechanical stirrer and a reflux condensor was placed 4-hydroxybiphenyl (40g, 0.23 mole), a solution of sodium hydroxide (9.6g, 0.24 mole) in water (96 ml) and ethylalcohol (275 ml). The reaction flask was cooled in an ice-bath and while stirring, dimethylsulphate (28.98g, 0.23 mole) was added dropwise to it over a period of forty

minutes. After the addition, the reaction mixture was refluxed for one hour, When a clear solution was obtained. The reaction flask was cooled to room temperature which resulted in the precipitation of the product. It was filtered, washed with water and air dried. This was crystallised from ethyl alcohol. Melting point 80 °C (Reported mp 80.5 °C) (241).

(ii) 4-Methoxy-4'- acetylbiphenyl.

In a 500ml three-necked flask equipped with a mechanical stirrer, a pressure equalising funnel and a reflux condenser carrying an anhydrous calcium chloride guard tube, a mixture of 4-methoxybiphenyl (36g, 0.19 mole) anhydrous aluminium chloride (35.5g, 0.26 mole) and dry carbon disulphide (200 ml) was placed. This was stirred, cooled in an ice-bath and acetyl chloride (14.8g, 0.19 mole) was added dropwise during thirty minutes. After the completion of addition, the reaction mixture was stirred at room temperature for five hours and then refluxed for one hour. Carbon disulphide was removed by distillation and the sticky residue was added slowly to a mixture of ice-water (500 ml) and hydrochloric acid (10 ml). The solid formed was filtered and boiled with diethyl ether (50 ml) for fifteen to twenty minutes and the ethereal solution was decanted off. This operation was repeated thrice and then the ether insoluble portion was crystallised from isopropanol. Melting point 156 °C (Reported m.p. 156.5 °C) (241).

(iii) 4-Methoxybiphenyl-4'- carboxylic acid

This was prepared following the procedure of Jhonson et al., (240). A solution of sodium hypobromite was prepared by the addition of bromine (66.4 g, 0.41 mole) in small portions to an aqueous solution of sodiumhydroxide (58g , 1.45 mole in 290 ml water) maintained at 0 °C. This was added to vigorously stirred solution of 4-methoxy 4'-acetylbiphenyl (18.0g, 0.08 mole) in 1,4 dioxane (400ml). The addition was carried

out at room temperature, during one hour. The temperature of the reaction mixture was slowly raised to 55 °C to ensure completion of the reaction and stirring was continued for a further two hours. Enough quantity of sodium metabisulphite solution was added to remove the excess of hypobromite and the mixture was diluted with water (1200 ml). About 500ml of the liquid was distilled, the reaction mixture was cooled and acidified with hydrochloric acid. The crude product so obtained was filtered and washed with water and air dried. The product was crystallised from acetic acid Transition temperatures K 259.0 N 300.0 I. (Reported transition temperatures K 258.0 N 300.0 I) (241).

3.1c 4-Methoxy-4' biphenyl carboxyl chloride.

4-Methoxy-4' biphenyl carboxyl chloride was prepared by reacting 4-methoxybiphenyl-4'-carboxylic acid with excess of thionylchloride and heating on a water bath till the evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using water pump and the acid chloride left behind as a residue was used in next reaction without further purification.

3.1d Preparation of 4 (4'-Methoxy phenyl) 4"-n-alkoxy benzanilides.

4 (4'-Methoxy phenyl) 4"-n-alkoxy benzanilides were synthesized by condensing 4-methoxy-4'-biphenyl carboxyl chloride with appropriate 4-n-alkoxyanilines.

Appropriate 4-n-alkoxyaniline (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-methoxy-4'-biphenyl carboxyl chloride (0.01 mole) as described in section 1.1 2d.

The benzanilides were crystallised several times from DMF until constant transition temperatures were obtained(Table-19). The elemental analyses are recorded in Table-20. The IR (KBr) spectra (Fig. 25) of the compound showed -NH- stretching vibration for secondary amide linkage at 300 cm^{-1} and -C=0 stretching vibrations for

secondary amide linkage at 1640 cm^{-1}. Other signals observed were at 2900, 1600, 1530, 1490, 1410, 1240, 820 cm^{-1}.

NMR spectra (Fig. 26) (200 MHz, solvent $CDCl_3$ + DMSO-d6, standard TMS) of compound No-2 Table 19. δ 9.9 (S, 1H for - CONH-) 8.0-8.1 (m, 2H at C-2"and C-6") 7.5-7.7 (m,6H at C-2, C-6, C-2,' C-6', C3 and C-5') 6.95-7.15 (m, 2H at C-3" and C-5") 6.85 (d, 2H at C-3 and C-5) 3.8-4.0 (m, 5H for 3H at -$PhOCH_3$ and 2H at -$PhOCH_2$-) 1.4 (t, 3H of -C-CH_3 at C-4").

3.2 4'-Methoxy- ∝ -methyl biphenylidene -4"-n- alkoxy anilines. **Series XI.**

3.2a 4-n-Alkoxy anilines.

4-n-Alkoxyanilines were prepared by the method described in section 3.1a

3.2b 4-Methoxy-4'-acetyl biphenyl.

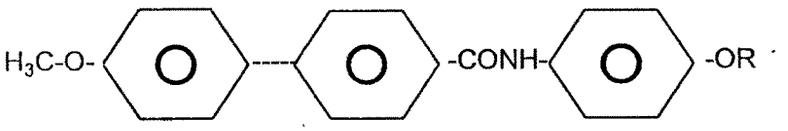
4-Methoxy-4'-acetylbiphenyl was prepared by the method described in section 3.1b (ii).

3.3c Preparation of 4'-methoxy -∝- methylbiphenylidene-4"-n-alkoxy anilines.

4'-Methoxy -∝- methylbiphenylidene-4"-n- alkoxy anilines were synthesized by condensing appropriate 4-n-alkoxyaniline (0.01 mole) and 4-Methoxy-4'- acetyl-biphenyl (0.01 mole) in boiling DMF. The compounds were crystallised several times from DMF till constant transition temperatures were obtained. (Table-21). The elemental analyses are recorded in Table-22. IR (KBr) spectra (Fig.27) of the compounds showed -C=N- stretching vibrations for azomethine central linkage at 1600 cm^{-1}. Other signals observed were at 2900, 1500, 1470, 1390, 1245, 1200, 1180, 1030, 820, 750, cm^{-1}.

Table - 19

4(4'-Methoxy phenyl) -4"-n-alkoxy benzanilides

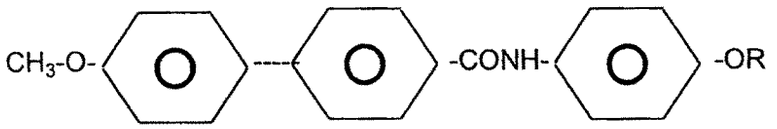


Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C		
		S_A	N	I
1	Methyl	---	254.0	288.0
2	Ethyl	242.0	247.0	277.0
3	Propyl	237.0	248.0	270.0
4	Butyl	227.0	255.0	268.0
5	Pentyl	219.0	---	264.0
6	Hexyl	215.0	---	270.0
7	Heptyl	210.0	---	271.0
8	Octyl	208.0	---	272.0
9	Decyl	204.0	---	270.0
10	Dodecyl	200.0	---	263.0
11	Tetradecyl	200.0	---	258.0
12	Hexadecyl	189.0	---	248.0

Table - 20

4(4'-Methoxy phenyl) -4"-n-alkoxy benzanilides

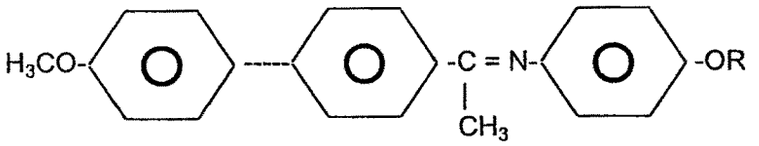


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	75.68	5.71	4.20	75.25	5.26	4.59
2	Ethyl	76.08	6.05	4.03	76.20	6.25	4.25
3	Propyl	76.45	6.37	3.88	76.48	6.55	4.29
4	Butyl	76.80	6.67	3.73	76.40	6.95	3.98
5	Pentyl	77.12	6.94	3.60	76.66	6.97	3.74
6	Hexyl	77.42	7.20	3.47	77.00	6.75	3.79
7	Heptyl	77.70	7.43	3.36	77.33	7.05	3.71
8	Octyl	77.96	7.66	3.25	77.68	7.47	3.48
9	Decyl	78.43	8.06	3.05	78.91	7.67	3.44
10	Dodecyl	78.85	8.42	2.87	78.93	8.17	3.30
11	Tetradecyl	79.22	8.74	2.72	79.62	8.32	3.11
12	Hexadecyl	79.56	9.02	2.58	79.82	9.01	2.95

Table - 21

4'-Methoxy-α-biphenylidene) -4"-n-alkoxy anilines

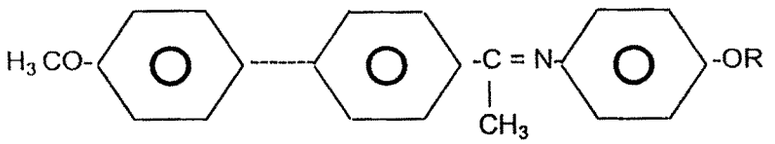


Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C N	I
1	Methyl	216.0	257.0
2	Ethyl	189.0	252.0
3	Propyl	208.0	245.0
4	Butyl	204.0	248.0
5	Pentyl	193.0	235.0
6	Hexyl	183.0	220.0
7	Heptyl	181.0	210.0
8	Octyl	178.0	207.0
9	Decyl	175.0	205.0

Table - 22

4'-Methoxy-α-biphenylidene) -4"-n-alkoxy anilines



Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	79.76	6.34	4.23	80.11	6.47	4.25
2	Ethyl	80.00	6.66	4.06	79.98	6.91	4.42
3	Propyl	80.22	6.96	3.90	80.53	7.40	4.27
4	Butyl	80.43	7.24	3.75	80.03	6.83	3.93
5	Pentyl	80.62	7.49	3.62	80.21	7.90	3.96
6	Hexyl	80.79	7.73	3.49	81.13	8.14	3.33
7	Heptyl	80.96	7.95	3.37	80.87	7.58	3.70
8	Octyl	81.12	8.16	3.26	80.83	8.40	3.55
9	Decyl	81.40	8.53	3.06	81.83	8.92	3.31

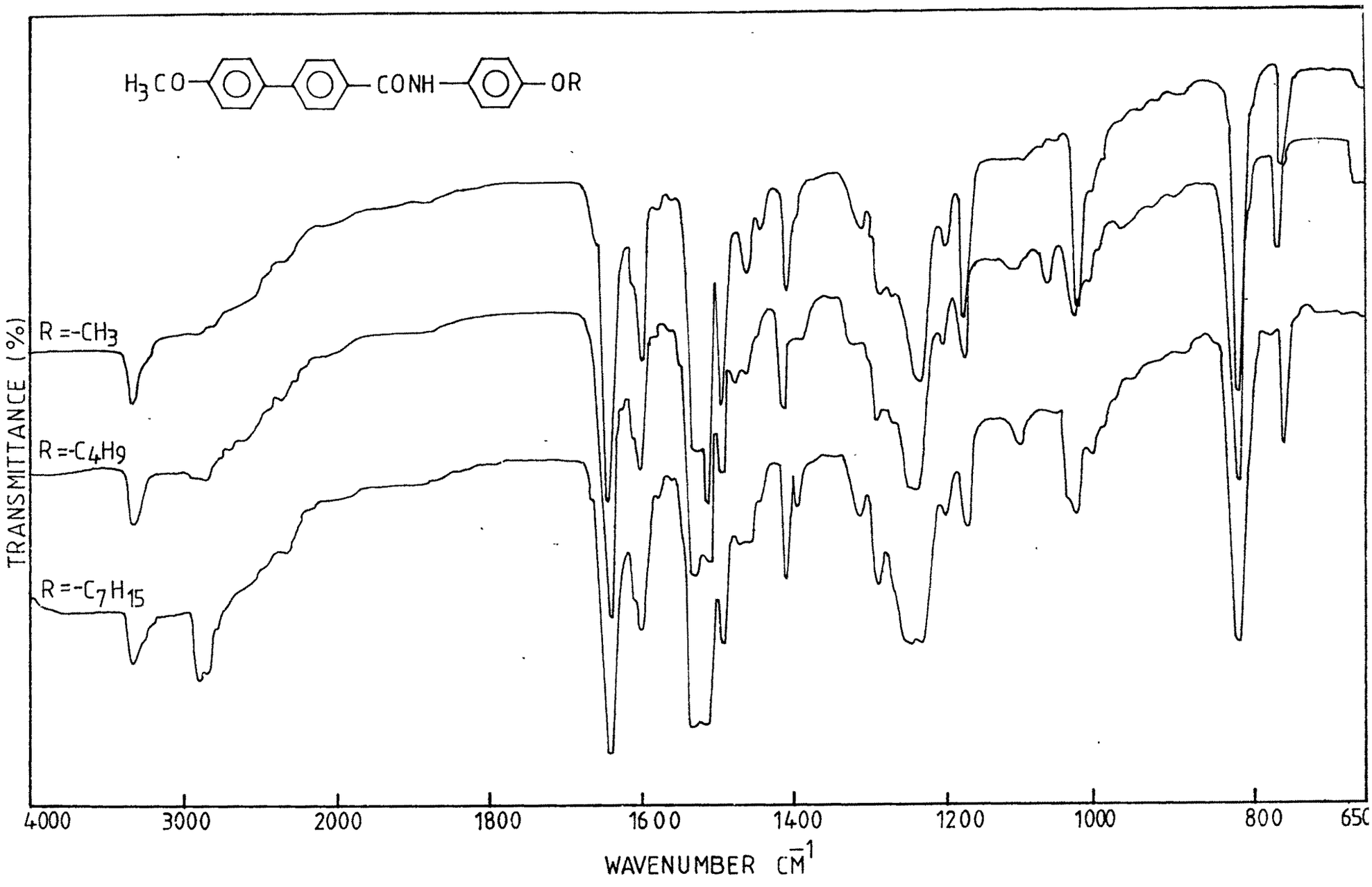


Fig. 25. I.R. SPECTRA

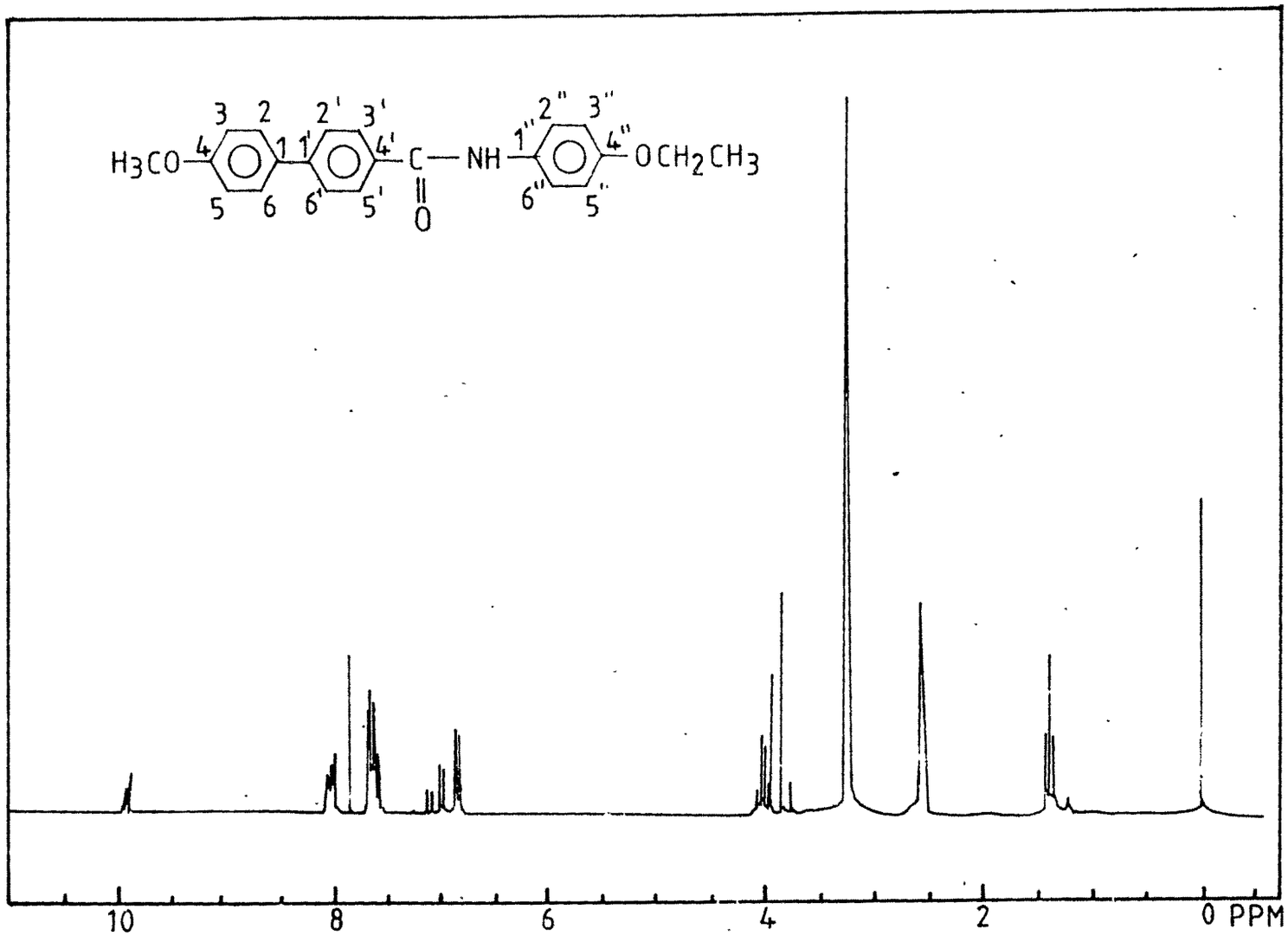


Fig. 26 NMR SPECTRA

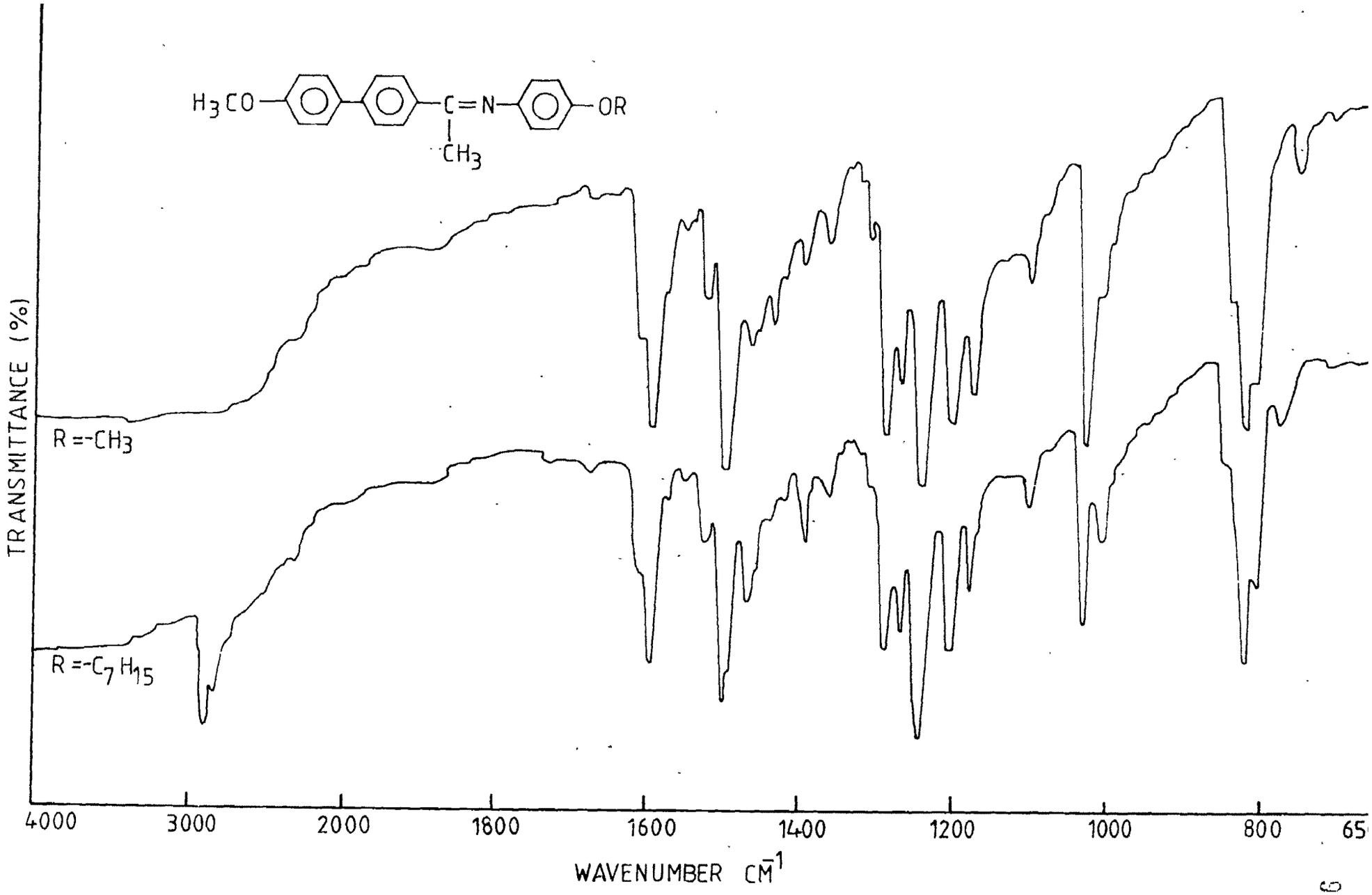


Fig. 27. I. R. SPECTRA

Higher members could not be synthesised by this method hence the respective, 4-n-alkoxy anilines and 4-methoxy 4'-acetyl biphenyl were fused together at 175 °C in an oil bath for one hour. Subseqently they were crystallised from DMF till constant transition temperatures were obtained However, it is difficult to get n-dodecyloxy onwards derivative fused 4-methoxy 4'-acetyl biphenyl to get pure Schiff base. Hence, higher members could not be synthesised.

4.0 DESIGNING MESOGENIC MATERIALS FOR NLO PROPERTIES.

4.1 4-methyl-2', 4'-bis(4"-n-alkoxybenzoloxy) azobenzenes : **Series XII .**

4.1a 4-n-Alkoxybenzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the methods described in section 1.1.2a and 1.1.2b, respectively.

4.1b 4-methyl-2',4'-dihydroxy azobenzene.

4-methyl-2', 4'-dihdroxy azobenzene was synthesized by coupling a diazonium salt of 4-methyl aniline (p-toluidine) with resorcinol by the method described in section 2.5a. The dye was crystallised from aqueous ethanol till constant melting point was obtained. Melting point is 198 °C.

The FTIR (KBr) spectra (Fig. 28) of the compounds showed broad peak for intra- as well as intermolecularly hydrogen bonded phenolic -OH at 3500-3100 cm^{-1}. The -N = N - stretching vibrations were obtained at 1620 cm^{-1}. Other signals observed were at 1510, 1480, 1415, 1240, 1200, 1080, 830, 720 cm^{-1}.

		C(%)	H(%)	N(%)
Analytical data :	Required	68.42.	5.26	12.28
	Found	68.00	5.67	12.44.

4.1c Preparation of 4-methyl-2', 4' bis (4"-n-alkoxybenzoyloxy) azobenzenes :

4-methyl-2', 4'-bis-(4"-n-alkoxybenzoyloxy) azobenzenes were synthesized by condensing appropriate two moles of 4-n-alkoxybenzoyl chloride with 4-methyl-2', 4'-dihydroxy azobenzene.

4-methyl-2', 4'-dihydroxy azobenzene (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxybenzoyl chloride (0.02 mole) as described in section 1.1.2d. The diesters were crystallised several times from ethanol till constant transition temperatures were obtained (Table- 23). The elemental analyses are recorded in Table 24. The IR (KBr) spectra (Fig. 29) of the compounds showed the absence of intramolecularly hydrogen bonded phenolic -OH stretching vibrations. The -COO- stretching vibrations were obtained at 1730 cm^{-1} and -N=N- stretching vibrations were obtained at 1610 cm^{-1}. Other signals observed were at 1510, 1480, 1420, 1300, 1250, 1170, 1130, 830, 750 cm^{-1}.

NMR spectra (Fig. 30) (90 MHz solvent $CDCl_3$ standard TMS) compound No 4 Table 23. δ 7.9-8.3 (m, 4H at C-2" and C-6") 7.4-7.9 (dd, 4H at C-3" and C-5") 6.75-7.3 (m, 7H at C-3, C-5, C-3', C-5', C-2, C-6 and C-6') 4.0 (t, 4H, 2 X -OCH_2-) 2.3 (s, 3H at -$PhCH_3$) 1.4-1.9 (m, 8H, for 4X-CH_2-) 0.95 (t, 6H, 2 X C-CH_3).

4.2 4-methyl-2'-hydroxy-4'-(4"-n-alkoxybenzoyloxy) azobenzenes : **Series XIII.**

4.2a Preparation of 4-methyl-2'-hydroxy-4'-(4"-n-alkoxybenzoyloxy) azobenzenes :

4-methyl-2'-hydroxy-4'-(4"-n-alkoxybenxoyloxy) azobenzenes were synthesized by condensing appropriate 4-n-alkoxybenzoyl chloride with 4-methyl-2', 4'-dihydroxy azobenzene in equimolar proportion.

4-mehtyl-2',4'-dihydroxy azobenzene (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxybenzoyl chloride (0.01 mole) as described in section 1.1.2d. The monoesters obtained were filtered and washed with water followed by saturated sodium hydrogen carbonate and cold water. The monoesters were crystallised several times from acetic acid till constant transition temperatures were obtained (Table-25) The elemental analyses are recorded in Table-26. The IR (KBr) spectra (Fig. 31) of the compound showed broad peak for intramolecularly hydrogen bonded -OH at 3600-3200 cm^{-1}. The -COO- stretching vibrations were obtained at 1740 cm^{-1}. Other signals observed were at 1605, 1510, 1480, 1415, 1310, 1250, 1180, 1150, 1120, 1080, 830, 750 cm^{-1}.

NMR spectra (Fig. 32) (90 MHz, solvent $CDCl_3$, standard TMS) of compound No.4 Table-25. δ7.95 (d, 9Hz, 2H at C-2" and C-6") 7.4-7.8 (m, 5H at C-2, C-6, C-6', C-3"and C-5") 7.1 (d, 9Hz, 2H at C-3 and C-5) 6.75 (d, 9Hz, 2H at C-3' and C-5') 3.9 (t, 2H,-OCH_2-) 2.3 (s,3H, -$PhCH_3$) 1.3-1.9 (m, 4H, 2X-CH_2-) 0.95 (t, 3H,-CH_3).

4.3 4-Methyl-2' hydroxy- 4'- n-alkoxy azobenzenes : **Series XIV**.

4.3a Preparation of 4-Methyl-2' hydroxy -4'- n-alkoxy azobenzenes.

The monoalkylation of 4-methyl 2', 4'-dihydroxy azobenzene was carried out by the process described in section 2.1a. The monoethers were crystallised several times from alcohol till constant transition temperatures were obtained (Table-28). The purity of the homologues was checked by GC as there is a possibility of the presence of an impurity of the dialkylated product. The percentage purity found to be 99.93%. The elemental analyses are recorded in Table-28. The FTIR (KBr) spectra (Fig. 33) of the compound showed broad peak for intramolecularly hydrogen bonded phenolic -

OH at 3600-3200 cm^{-1}. Other signals observed were at 1610, 1500, 1400, 1380, 1320, 1280, 1230, 1200, 1090, 1030, 815, 720 cm^{-1}.

NMR spectra (Fig. 34) (90MHz, solvent $CDCl_3$, standard TMS) of compound No.4 Table-27. δ 7.45-7.8 (m, 3H at C-2, C-6 and C-6') 7.1-7.3 (d, J=9Hz at C-3 and C-5) 6.3-6.55 (m, 2H at C-3'and C-5') 3.9 (t, 2H, $-OCH_2-$) 2.4 (s, 2H, $-PhCH_3$). 1.4-1 9 (m, 4H, $2X-CH_2-$) 1.1 (t, 3H, $-CH_3$).

4.4 4-Methyl 2',4' di-n-alkoxy azobenzenes : **Series XV.**

The common alkylation method described in section 2.1a failed in dialkylation of 4-methyl 2',4'-dihydroxy azobenzene. A modified method described here was used for dialkylation.

4.4a Dipotassium salt of 4-methyl 2', 4'- dihydroxyazobenznene.

Dipotassium salt of 4-methyl 2', 4'- dihydroxyazobenznene was synthesized by treating 4-methyl 2', 4'-dihydroxyazobenzene (22.8g, 0.1 mole) with alcoholic potassium hydroxide solution (11.2g in 20ml alcohol, 0.2 mole). After that alcohol was evaporated and resulting dry solid powder of dipotassium salt of 4-methyl 2', 4'-dihydroxyazobenzene was used.

4.4b Preparation of 4-methyl 2', 4' di-n-alkoxy azobenzenes.

The dipotassium salt of 4-methyl 2', 4'-dihydroxy azobenzene (0.01 mole) was dissolved in 30 ml of dry DMF. To this solution (0.24 mole) respective n-alkylbromide was added. The whole mass was then refluxed for ten to twelve hours on sand-bath The mixture was cooled upto room temperature then poured into cold water. It was then extracted with solvent ether. Ether layer was washed with dilute NaOH and water. Ether extract was dried over anhydrous calcium chloride and finally ether was

evaporated. Solid obtained was further purified by crystallization from methanol several times till constant melting point was obtained (Table-29). The elemental analyses are recorded in Table-30. The FTIR (KBr) spectra (Fig. 35) of the compounds showed the absence of intramolecularly hydrogen bonded phenolic -OH stretching vibrations. The signals observed were at 1605, 1500, 1400, 1380, 1320, 1280, 1240, 1190, 1100, 1050, 810, 710 cm^{-1}.

NMR spectra (Fig. 36) (90 MHz, solvent $CDCl_3$, standard TMS) of compound No.4 Table-29. δ7.4-7.8 (d, 2H at C-2 and C-6) 7.0-7.2 (m, 3H at C-3', C-5' and C-6') 6.3-6.5 (m, 2H at C-3' and C-5') 3.8-4.2 (m, 4H, 2X-OCH_2-) 2.35 (s, 3H, -PhCH_3) 1 3-1 8 (m, 8H, 4X-CH_2-) 9.5 (t, 6H, 2X-CH_3).

4.5 4-Methyl -2'- acetyloxy -4' (4"-n-alkoxybenzoyloxy) azobenzenes : **Series XVI.**

4.5a 4-Methyl-2'- hydroxy-4' (4"-n-alkoxybenzoyloxy) azobenzenes:

4-Methyl-2'-hydroxy-4- (4"-n-alkoxybenzoyloxy) azobenzenes were synthesized by the method described in section 4.2 c.

4.5b Preparation of 4-methyl-2'-acetyloxy -4'-(4"-n-alkoxybenzoyoloxy) azobenzenes.

4-methyl-2'-acetyloxy-4'-(4"-n-alkoxybenzoyloxy)azobenzenes were synthesized by condensing acetylchloride with appropriate 4-methyl-2'- hydroxy-4' (4"-n-alkoxy-benzoyloxy) azobenzenes.

Respective 4-methyl -2'- hydroxy-4' (4"-n-alkoxybenzoyloxy) azobenzene (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold acetyl chloride (0.01 mole) as described in section 1.1.2d. The unsymmetrical diesters obtained were filtered and washed with water followed by dilute sodium hydroxide solution and cold water. All the members were crystallized several times from alcohol till constant transition temperatures were obtained (Table 31). The

elemental analyses are recorded in Table 32. The IR (KBr) spectra (Fig. 37) of the compounds showed the absence of intramolecularly hydrogen bonded phenolic -OH The - COO- stretching vibrations were obtained at 1760 (CH_3COO-) and 1720 (Ph - COO-) cm^{-1}. The other signals observed were at 1600, 1505, 1465, 1420, 1365, 1250, 1230, 1200, 1165, 1130, 835, 755 cm^{-1}.

NMR spectra (Fig. 38) (60 MHz, solvent $CDCl_3$, standard TMS) of compound no 4. Table 31. δ 8.0-8.2 (d, 9Hz, 2H at C-2" and C-6") 7.6 - 8.0 (m, 4H at C-3" C-5", C-2 and C-6) 6.8 - 7.2(m, 5H at C-3', C-5', C-3, C-5 and C-6') 4.0 (t, 2H at -OCH_2-) 2.4(s, 3H, -$OCOCH_3$) 2.3(s,3H, -$PhCH_3$) 1.4 - 1.7(m, 4H, 2 X -CH_2-) 0.90 (t, 3H, -CH_3).

4.6 Bis [5-(4'-n octyloxy benzoyloxy) 2-(4"-methylphenylazo) phenyl] adipate.

4.6a Adipoyl chloride was synthesized by the method described in section 1.1 2b.

4.6b 4-methyl-2'-hydroxy-4'-(4"-n-octyloxy benzoyloxy) azobenzene was synthesized by the method described in section 4.2c.

4.6c Preparation of bis [5-(4'-n-octyloxybenzoyloxy) 2-(4"-n methylphenylazo) phenyl] adipate.

The above diester was synthesized by condensing one mole of adipoyl chloride with two moles of 4-methyl-2'-hydroxy-(4"-n-octyloxybenzoyloxy) azobenzene.

4-Methyl-2-hydroxy-4'-(4"-n-octyloxy benzoyloxy) azobenzene (0.005 mole)was dissoled in dry pyridine (20 ml) and was added slowly with constant stirring to cold adipoyl chloride (0.0025 mole) in dry toluene as described in section 1.1 2d. The organic layer obtained on adding to cold 1:1 hydrochloric acid was extracted with ether. Ether extract was washed with saturated sodium hydrogen carbonate followed by water to remove unreacted adipic acid and with dilute NaOH followed by water to remove unreacted 4-methyl-2'-hydroxy 4'-(4"-n- octyloxy benzoyloxy)

azobenzene. The organic layer was separated and distilled under reduced pressure. The solid diester of adipic acid was crystallised several times from alcohol till constant transition temperatures were obtained K(87.0) Sc101.0 I.

		C(%)	H(%)	N(%)
Analytical data :	Required	72.23	6.80	6.44
	Found	72.47	6.64	6.14

The IR(KBr) spectra (Fig. 39) of the compound showed the absence of intra - as well as intermolecularly hydrogen bonded -OH stretching vibrations. The -COO- stretching vibrations were obtained at 1760 (-CH_2COO -Ph) and 1730 (-Ph COO - Ph) cm^{-1}. The other signals observed were at 1640, 1580, 1510, 1470, 1325, 1270, 1230, 1180, 1150, 1050, 860, 825 cm^{-1}.

NMR spectra (Fig. 40) (200 MHz, solvent $CDCl_3$, standard TMS) δ 8 1 (d, J=9Hz, 4H at C-2' and C-6') 7.85 (d, J= 9Hz, 2H at C-3) 7.7(d,J=9Hz, 4H at C-3', and C-5') 7.15-7.35 (m, 8H at C-2", C-6", C-3" and C-5") 6.95 (d,J=9HZ, 4H at C-4 and C-6) 4.05 (t, 4H for 2 X -Ph-O-CH_2-) 2.7 (t,4H for 2 X -PhOC-CH_2-) 2.4 (s, 6H for 2 X -Ph-CH_3) 1.75-1.95 (m, 8H, 4H for 2 X -PhO-C-CH_2- and 4H for 2 X -PhOCO-CH_2-) 1.25-1.5 (m, 2OH, for 10 X -PhO-C-C-$(CH_2)_5$ -) 0.90 (t, 6H for 2 X -CH_3).

4.7. [5-(4'-n- Octyloxybenzoyloxy) 2-(4"-methylphenylazo) phenyl] hydrogen adipate.

4.7a Adipoyl chloride was synthesized by the method described in section 1:1.2b.

4.7b 4-Methyl-2'-hydroxy-4'(4"-n-octyloxybenzoyloxy) azobenzene was synthesized by the method described in section 4.2c.

4.7c Preparation of [5-(4'-n-octyloxybenzoyloxy)-2-(4"-methylphenylazo) phenyl] hydrogen adipate.

The above monoester of adipic acid was synthesized by condesing adipoyl chloride with 4-methyl-2'-hydroxy - 4' (4"-n- octyloxybenzoyloxy) azobenzene

4-methyl-2'-hydroxy -4'(4"-n-octyloxybenzoyloxy) azobenzene (0 005 mole) was dissolved in dry pyridine (20ml) and was added slowly with constant stirring to cold adipoyl chloride (0.005 mole) in dry toluene as described in section 4.6c.

The monoester of adipic acid was crystallised several times from acetic acid till constant melting point was obtained. M.P. 154 °C.

		C(%)	H(%)	N(%)
Analytical data :	Required	69.39	6.80	4.76
	Found	69.68	6.42	4.81

The IR(KBr) spectra (Fig. 41) of the compound showed broad peak for intermolecularly hydrogen bonded -OH stretching vibrations at 3120 - 2280 cm^{-1}. The -COO- stretching vibrations were obtained at 1650, 1590, 1520, 1500, 1410, 1380, 1260, 1180, 1150, 1060, 935, 870, 830 cm^{-1}.

NMR spectra (Fig. 42) (200MHz solvent $CDCl_3$ standard TMS) δ 8.15 (d, J=9Hz 2H at C-2' and C-6') 7.85 (d, J=9Hz , 1H at C-3) 7.7 (d, J=9Hz 2H at C-3' and C-5') 7.15-7.30 (m, 4H at C-2", C-6", C-3" and C-5") 6.95 (d, J=9Hz, 2H at C-4 and C-6) 4.05 (t, 2H for -PhO-CH_2-) 2.7 (t, 2H for -PhO CO-CH_2-) 2.35 (s,3H -Ph CH_3) 1.80 - 1.95 (m,4H, 2H for -PhO-C-CH_2- and 2H for -CH_2-COOH) 1.30-1.55 (14H, 10H for -PhO-C-C-$(CH_2)_5$- and 4H for -PhO-CO-C-CH_2-CH_2-C) 0 90 (t, 3H for -CH_3).

4.8 Cu(II) and Ni(II) complexes of 4-methyl-2'-hydroxy-4'-(4"-n-hexadecyloxy-benzoyloxy) azobenzene

4.8a 4-methyl-2'-hydroxy-4'-(4"-n-hexadecyloxybenzoyloxy)azobenzene was synthe - sized by the method described in section 4.2c.

4.8b Preparation of Cu(II) and Ni(II) complexes of 4-Methyl-2'-hydroxy-4'-(4"-n-hexadecyloxybenzoyloxy) azobenzene.

4-Methyl-2'-hydroxy-4'-(4"-n-hexadecyloxybenzoyloxy)azobenzene (0.002 mole) was dissolved in dry acetone and was added slowly with constant stirring to a solution of copper(II) acetate (0.001 mole) and nickel(II) acetate (0.001 mole), respectively, in acetone. The reaction mixture was refluxed on water bath for three hours Both the metal complexes were crystallised several times from DMF. M.P of Cu(II) complex is 185 ^{o}C. The transition temperatures of Ni(II) complex is K182N203I.

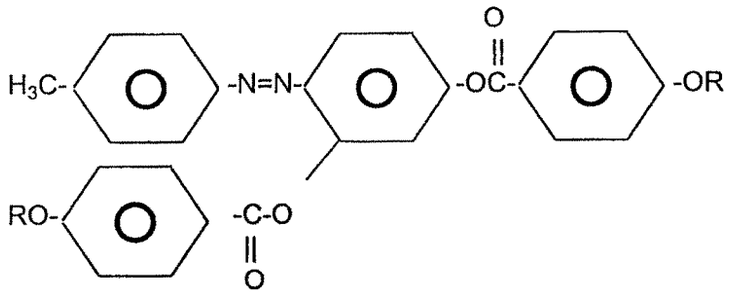
Analytical data :		C(%)	H(%)	N(%)
Cu(II) complex	Required	71.67	7.80	4.64
	Found	71.28	7.95	4.36
Ni(II) complex	Required	72.00	7.83	4.67
	Found	71.61	8.10	4.88

IR (KBr) spectra of Ni(II) and Cu(II) complexes (Fig. 43)

IR (KBr) spectra of the ligand showed a strong band at 1605 cm^{-1}. This is shifted in both the metal complexes to a lower frequency region and appears at 1595 cm^{-1} which indicated coordination of the nitrogen atoms with the metal ions. The braod peak observed inthe region 3300-3600 cm^{-1} indicates the presence of coordinated water molecule, which is further confirmed by the presence of a band at 800 cm^{-1} due to rocking mode of water molecules. The new bands observed in I.R. spectra of metal chelate at 495 cm^{-1} and 420 cm^{-1} are due to νM-O and νM-N frequencies, respectively.

Table - 23

4-Methyl-2', 4'-bis(4"-n-alkoxybenzoyloxy) azobenzenes.



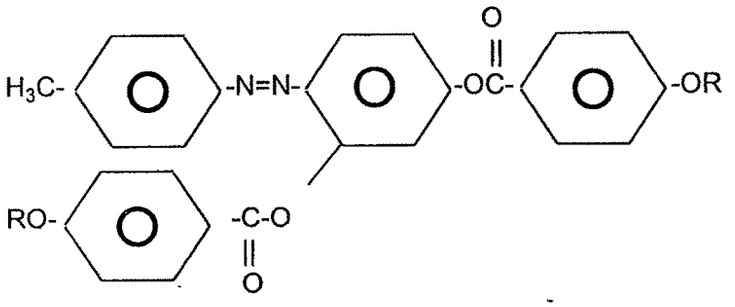
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C	
		S_C	I
1	Methyl	---	155.0
2	Ethyl	---	104.0
3	Propyl	---	123.0
4	Butyl	(34.0)*	110.0
5	Pentyl	(26.0)	85.0
6	Hexyl	(44.0)	88.0
7	Heptyl	(42.0)	64.0
8	Octyl	(50.0)	69.0
9	Decyl	(52.0)	89.0
10	Dodecyl	(58.0)	76.0
11	Tetradecyl	(65.0)	83.0
12	Hexadecyl	(57.0)	90.0

( )* Monotropic Value

Table - 24

4-Methyl-2', 4'-bis(4"-n-alkoxybenzoyloxy) azobenzenes.

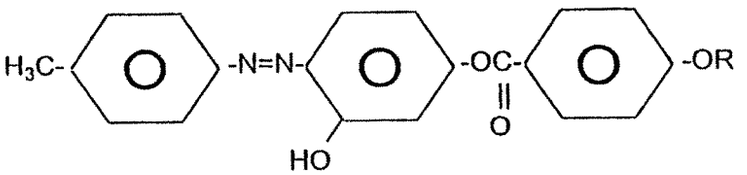


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	70.16	4.84	5.64	70.56	4.81	6.09
2	Ethyl	70.99	5.34	5.34	70.67	5.13	5.68
3	Propyl	71.74	5.80	5.07	71.72	5.65	5.41
4	Butyl	72.41	6.21	4.83	72.00	6.22	4.35
5	Pentyl	73.03	6.58	4.61	73.40	6.16	4.97
6	Hexyl	73.59	6.92	4.40	73.89	6.50	4.79
7	Heptyl	74.10	7.23	4.22	74.36	7.48	3.99
8	Octyl	74.57	7.51	4.05	74.21	7.10	4.49
9	Decyl	75.40	8.02	3.74	75.06	7.60	4.11
10	Dodecyl	76.12	8.46	3.48	76.48	8.25	3.79
11	Tetradecyl	76.77	8.84	3.26	77.01	8.42	3.57
12	Hexadecyl	77.29	9.17	3.06	76.83	8.80	3.26

Table - 25

4-Methyl-2' hydroxy -4'-(4"-n-alkoxybenzoyloxy) azobenzenes.

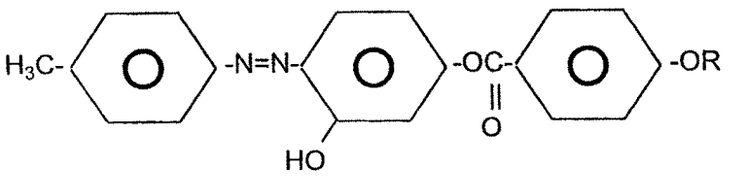


Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C	
		N	I
1	Methyl	173.0	254.0
2	Ethyl	134.0	257.0
3	Propyl	144.0	248.0
4	Butyl	132.0	248.0
5	Pentyl	120.0	240.0
6	Hexyl	119.0	238.0
7	Heptyl	117.0	225.0
8	Octyl	118.0	214.0
9	Decyl	111.0	196.0
10	Dodecyl	104.0	182.0
11	Tetradecyl	104.0	178.0
12	Hexadecyl	103.0	172.0

Table - 26

4-Methyl-2' hydroxy -4'-(4"-n-alkoxybenzoyloxy) azobenzenes.

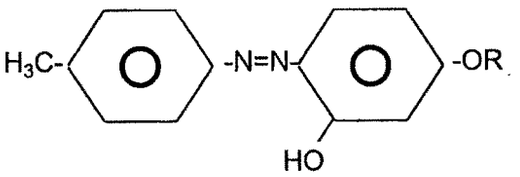


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	69.61	4.97	7.73	69.48	5.34	7.36
2	Ethyl	70.21	5.32	7.45	70.18	5.64	7.76
3	Propyl	70.77	5.64	7.18	70.68	5.81	7.03
4	Butyl	71.29	5.94	6.93	71.50	5.48	6.52
5	Pentyl	71.77	6.22	6.70	71.68	6.14	6.93
6	Hexyl	72.22	6.48	6.48	72.65	6.15	6.04
7	Heptyl	72.65	6.73	6.28	73.08	6.37	6.61
8	Octyl	73.04	6.96	6.09	73.11	6.84	6.30
9	Decyl	73.77	7.38	5.74	73.63	6.91	5.38
10	Dodecyl	74.42	7.75	5.43	74.03	7.36	5.09
11	Tetradecyl	75.00	8.09	5.15	75.11	7.68	5.39
12	Hexadecyl	75.52	8.39	4.89	75.14	8.67	4.48

Table - 27

4-Methyl-2' hydroxy-4'-n-alkoxy azobenzenes.



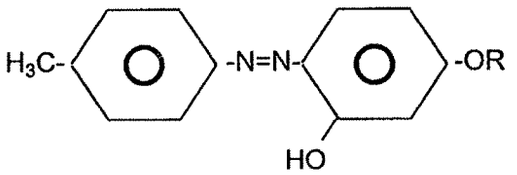
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C	
		N	I
1	Ethyl	---	143.0
2	Propyl	(70.0)*	100.0
3	Butyl	86.0	90.0
4	Pentyl	66.0	75.0
5	Hexyl	85.0	89.0
6	Heptyl	64.0	89.0
7	Octyl	71.0	88.0
8	Decyl	70.0	86.0
9	Dodecyl	65.0	84.0
10	Tetradecyl	64.0	81.0
11	Hexadecyl	72.0	80.0

( )* Monotropic Value

Table - 28

4-Methyl-2' hydroxy-4'-n-alkoxy azobenzenes.

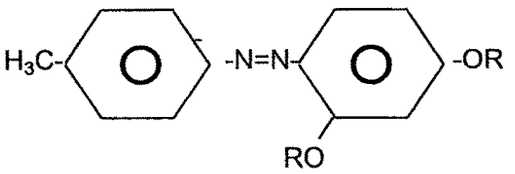


Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Ethyl	70.31	6.25	10.94	70.72	6.10	11.37
2	Propyl	71.11	6.67	10.37	70.85	6.36	10.64
3	Butyl	71.83	7.04	9.86	71.42	7.32	9.48
4	Pentyl	72.42	7.38	9.40	72.57	7.49	9.28
5	Hexyl	73.08	7.69	8.97	73.24	7.27	9.57
6	Heptyl	73.62	7.97	8.59	73.43	7.64	8.73
7	Octyl	74.12	8.23	8.23	74.58	8.27	8.45
8	Decyl	75.00	8.70	7.61	75.21	8.63	8.15
9	Dodecyl	75.76	9.09	7.07	75.75	9.23	7.41
10	Tetradecyl	76.41	9.43	6.60	76.27	9.34	7.02
11	Hexadecyl	76.99	9.73	6.19	76.76	9.88	6.1

Table - 29

4-Methyl-2',4'-di-n-alkoxy azobenzenes.

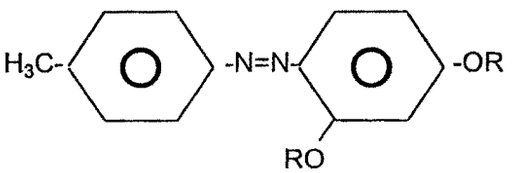


Melting Point °C

Sr. No.	R= n-alkyl group	Melting Point °C
1.	Butyl	53.0
2	Pentyl	49.0
3.	Hexyl	45.0
4.	Heptyl	56.0
5.	Octyl	59.5
6	Decyl	43.5
7.	Dodecyl	47.5
8.	Tetradecyl	54.0
9.	Hexadecyl	49.0

Table - 30

4-Methyl-2',4'-di-n-alkoxy azobenzenes.

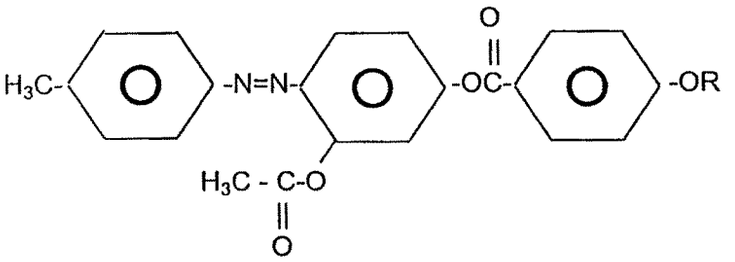


Melting Point °C

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Butyl	74.12	8.23	8.23	74.24	8.15	8.55
2	Pentyl	75.00	8.70	7.61	74.87	8.93	7.94
3	Hexyl	75.76	9.09	7.07	76.20	8.80	7.44
4	Heptyl	76.41	9.43	6.60	76.55	9.39	6.44
5	Octyl	76.99	9.73	6.19	76.55	9.91	6.33
6	Decyl	77.95	10.24	5.51	78.07	10.03	5.99
7	Dodecyl	78.72	10.64	4.96	78.35	10.79	4.92
8	Tetradecyl	79.35	10.97	4.52	78.95	10.65	4.64
9	Hexadecyl	79.88	11.24	4.14	79.45	10.84	4.27

Table - 31

4-Methyl-2' -acetyloxy-4'- (4"-n-alkoxybenzoyloxy) azobenzenes.



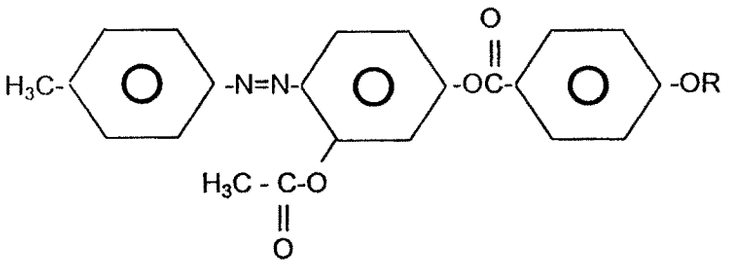
Transition Temperatures °C

Sr. No.	R = n - alkyl group	Transition Temperatures °C	
		N	I
1	Methyl	(125.0)*	156.0
2	Ethyl	(129.0)	148.0
3	Propyl	(104.0)	134.0
4	Butyl	(119.0)	128.0
5	Pentyl	(93.0)	121.0
6	Hexyl	(103.0)	148.0
7	Heptyl	(97.0)	125.0
8	Octyl	(94.0)	102.0
9	Decyl	(92.5)	101.0
10	Dodecyl	87.5	91.0
11	Tetradecyl	78.0	90.0
12	Hexadecyl	(87.0)	104.0

( )* Monotropic Value

Table - 32

4-Methyl-2' -acetyloxy-4'- (4"-n-alkoxybenzoyloxy) azobenzenes.



Elemental Analysis

Sr.No.	R = n - alkyl group	Calculated(%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	68.32	4.95	6.93	68.14	5.06	6.45
2.	Ethyl	68.90	5.26	6.70	68.66	5.49	6.91
3	Propyl	69.44	5.55	6.48	69.83	5.78	6.27
1	Butyl	69.95	5.83	6.28	70.03	5.84	5.97
2	Pentyl	70.43	6.09	6.09	70.14	6.38	6.24
3	Hexyl	70.89	6.33	5.91	70.88	6.55	5.55
4	Heptyl	71.31	6.56	5.74	71.70	6.89	5.37
5	Octyl	71.71	6.77	5.58	71.64	6.94	5.26
6	Decyl	72.45	7.17	5.28	72.00	7.09	5.61
7	Dodecyl	73.12	7.53	5.02	73.27	7.93	4.85
8	Tetradecyl	73.72	7.85	4.78	73.64	7.71	4.86
9	Hexadecyl	74.27	8.14	4.56	74.56	7.88	4.14

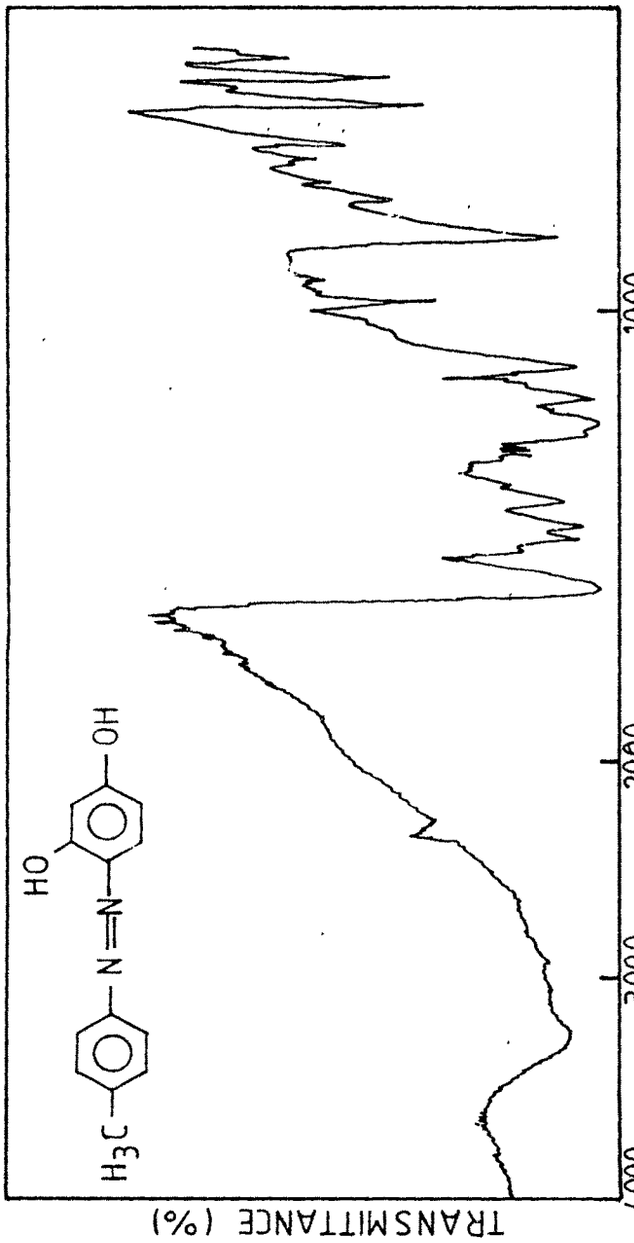


Fig. 28 I. R. SPECTRA

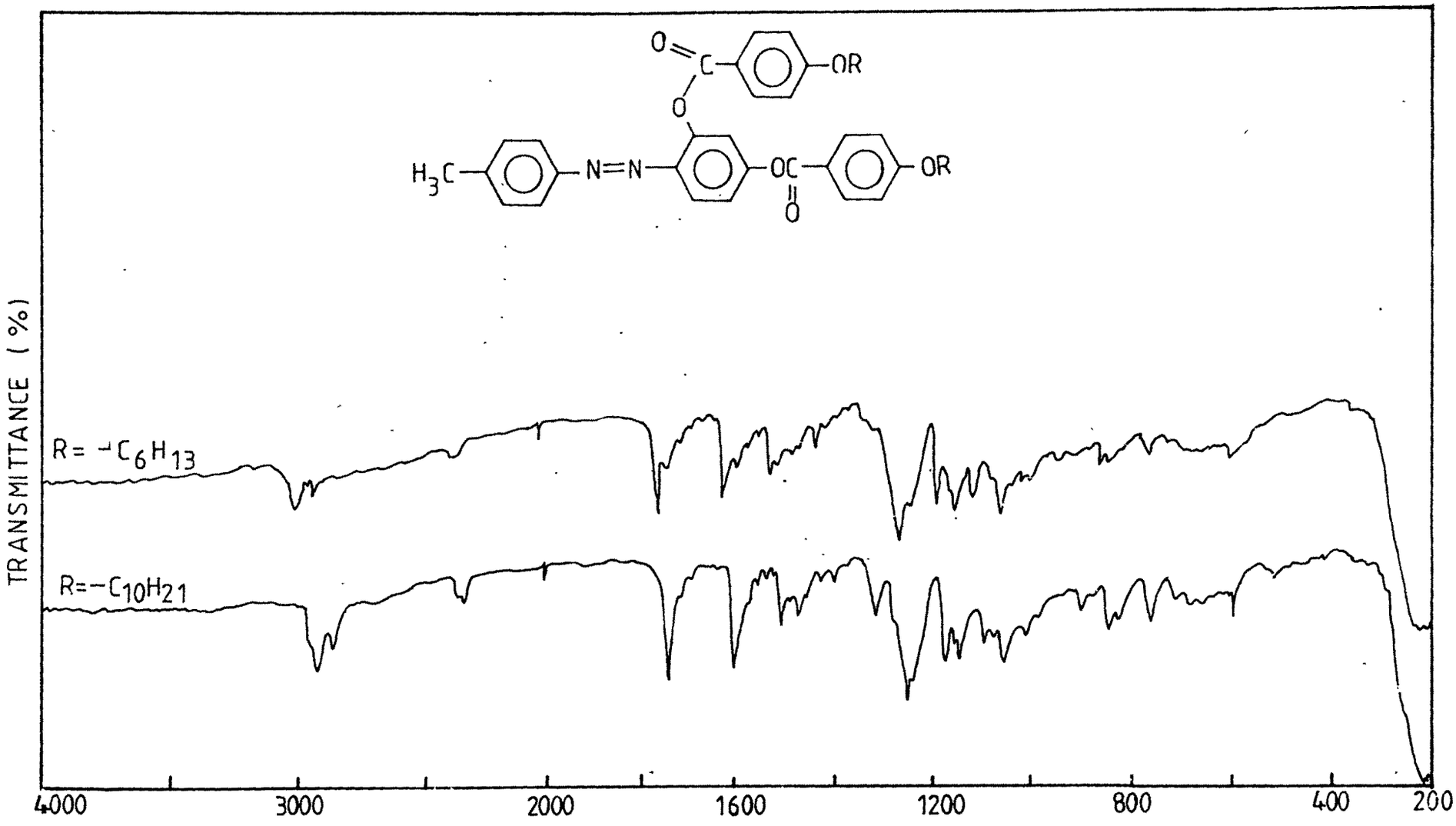


Fig. 29 I. R. SPECTRA

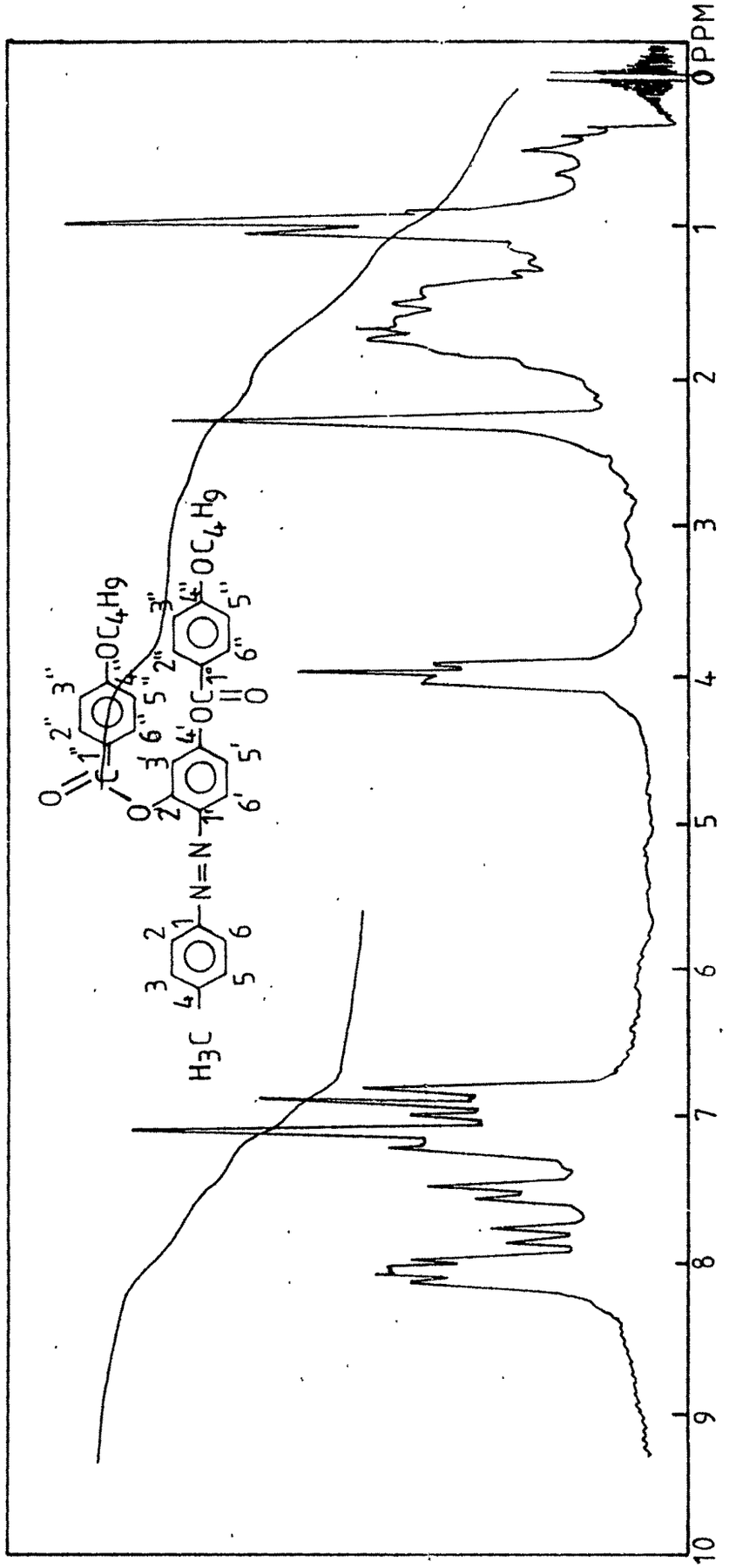


Fig.30 NMR SPECTRA

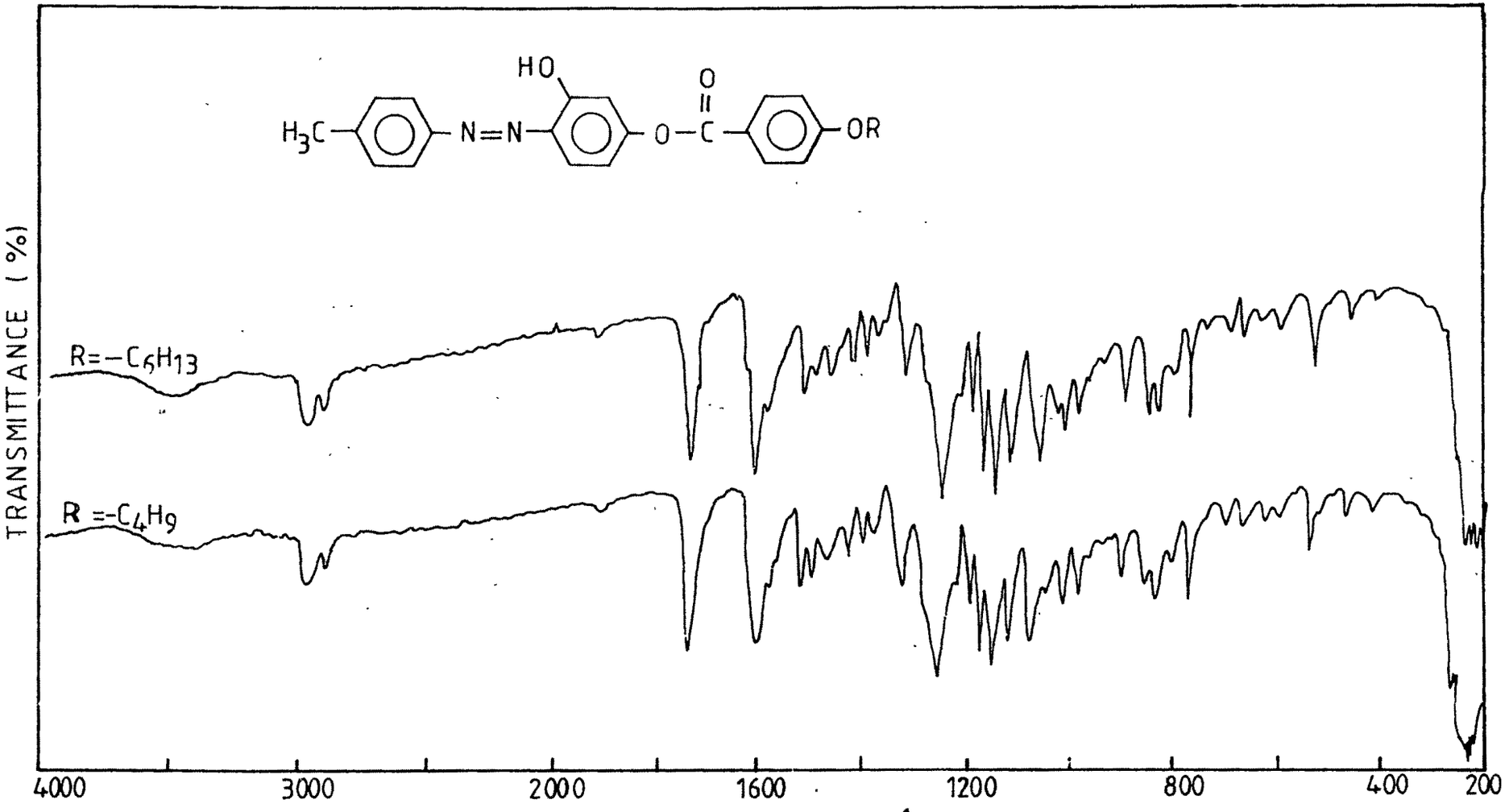


Fig. 31 I. R. SPECTRA

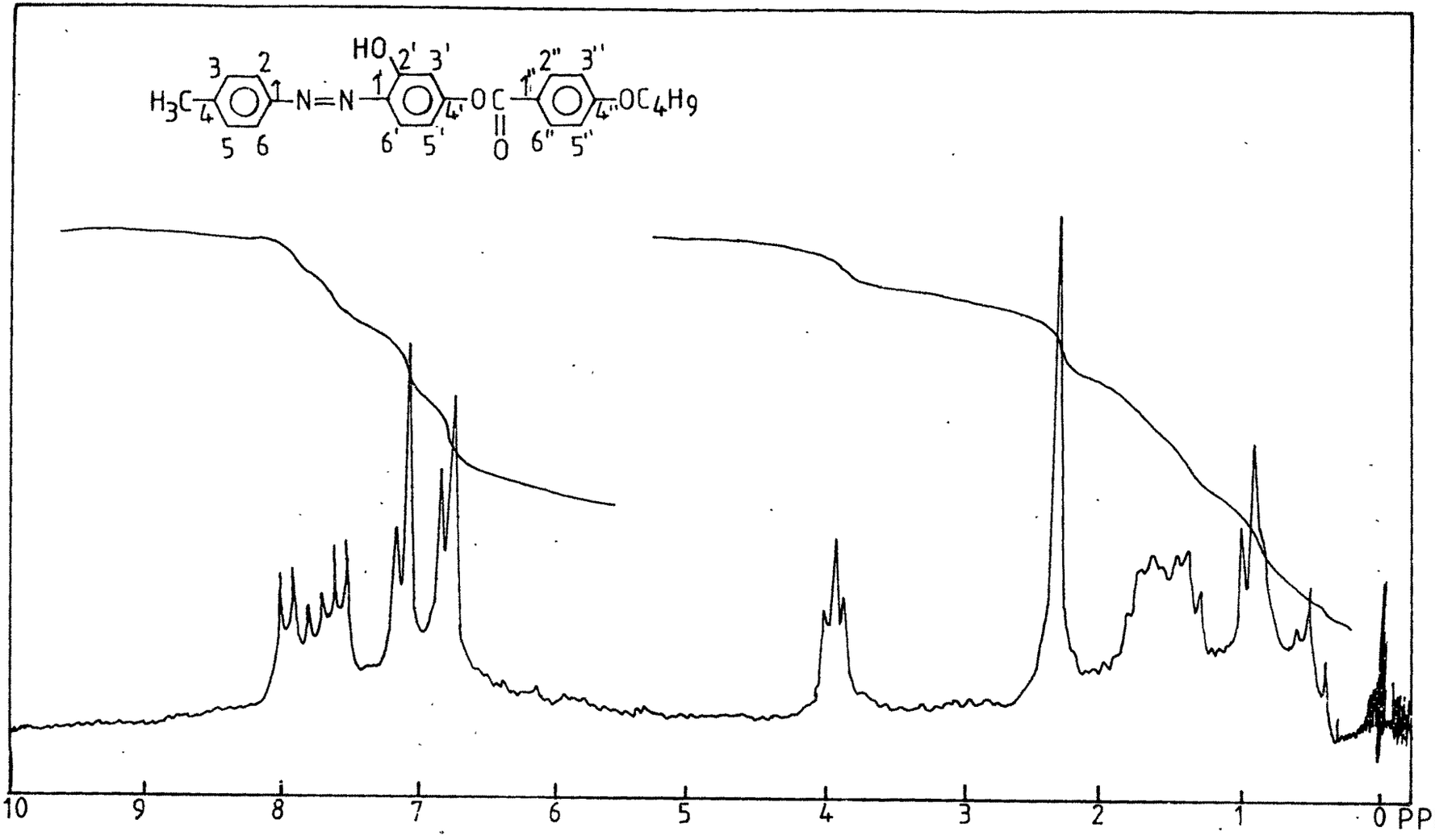


Fig .32 NMR SPECTRA

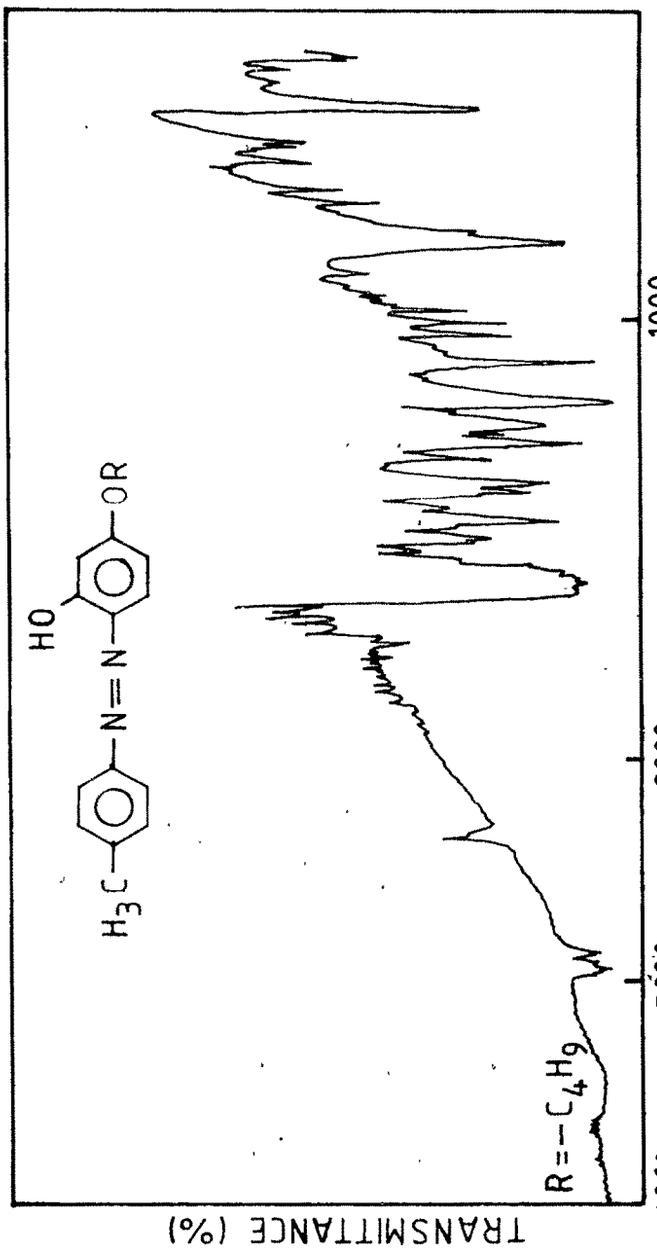


Fig.33 I.R. SPECTRA

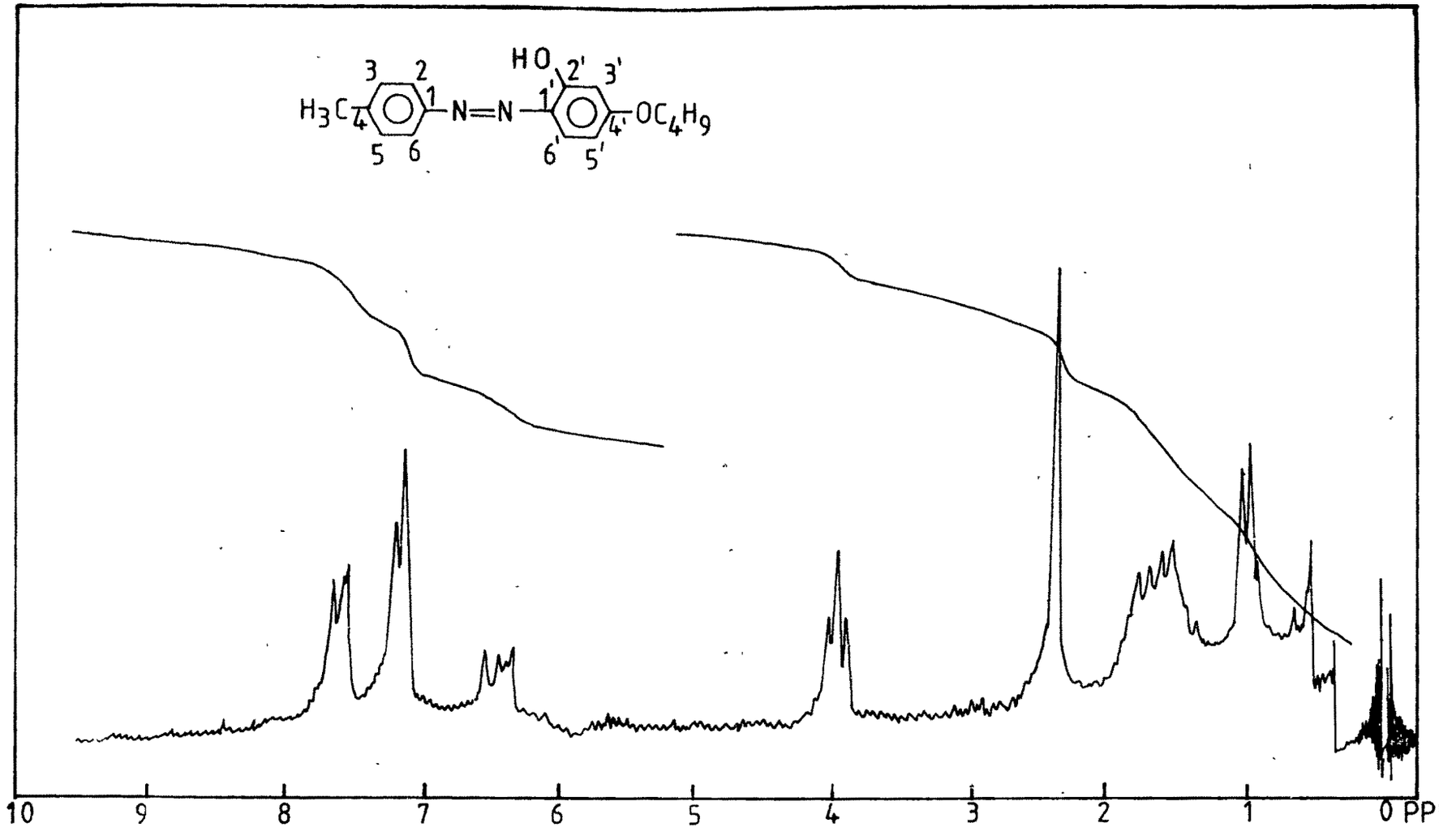


Fig. 34 NMR SPECTRA

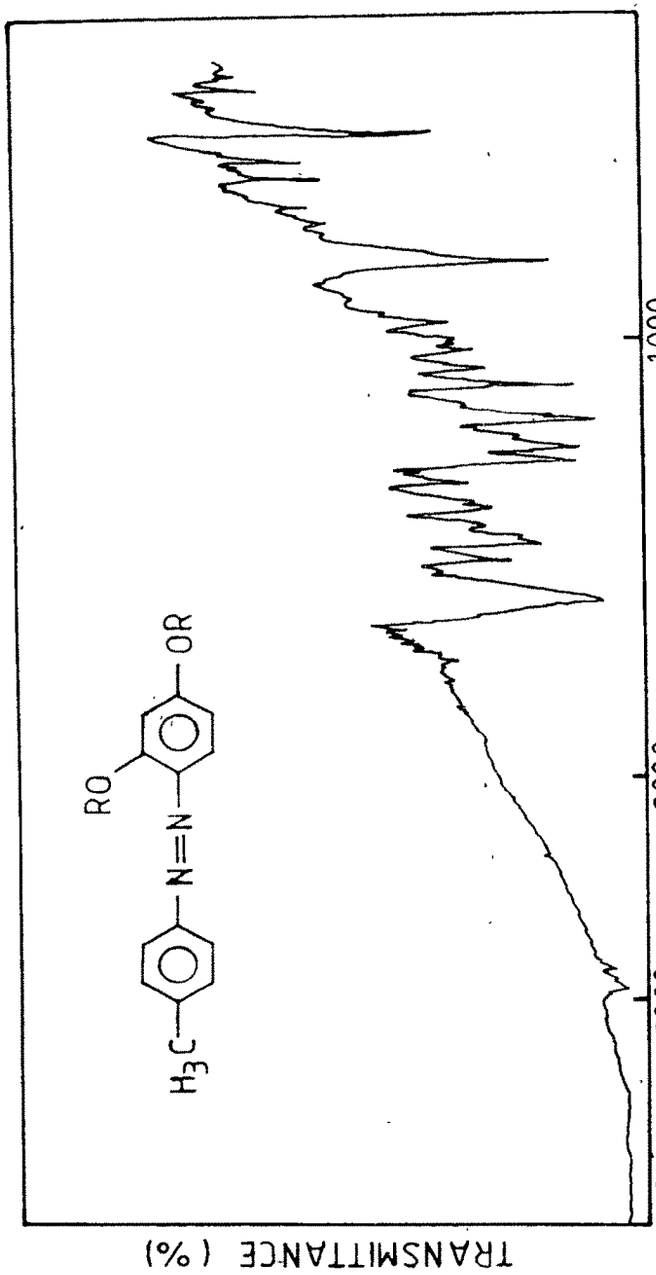


Fig.35 I. R. SPECTRA

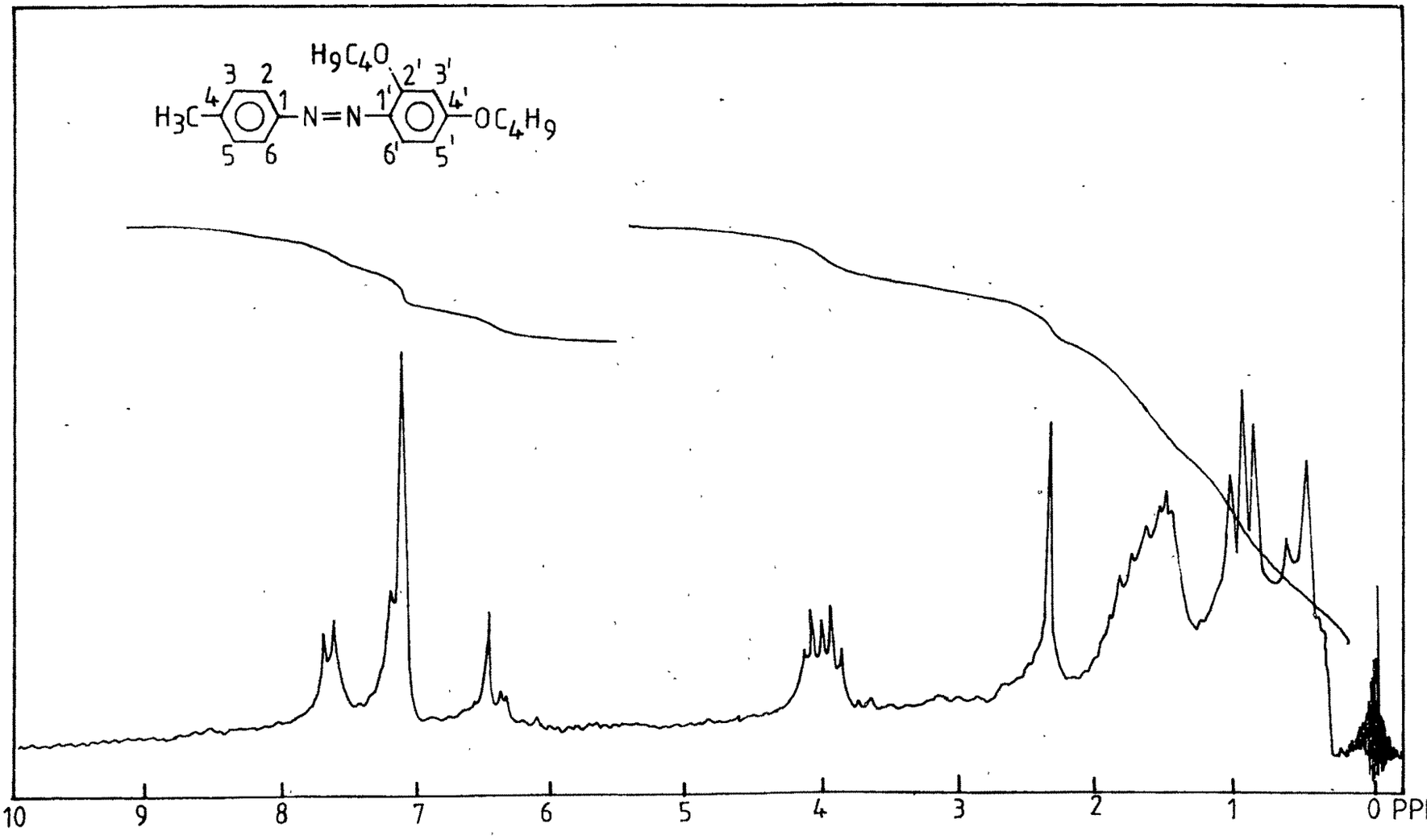


Fig. 36 NMR SPECTRA

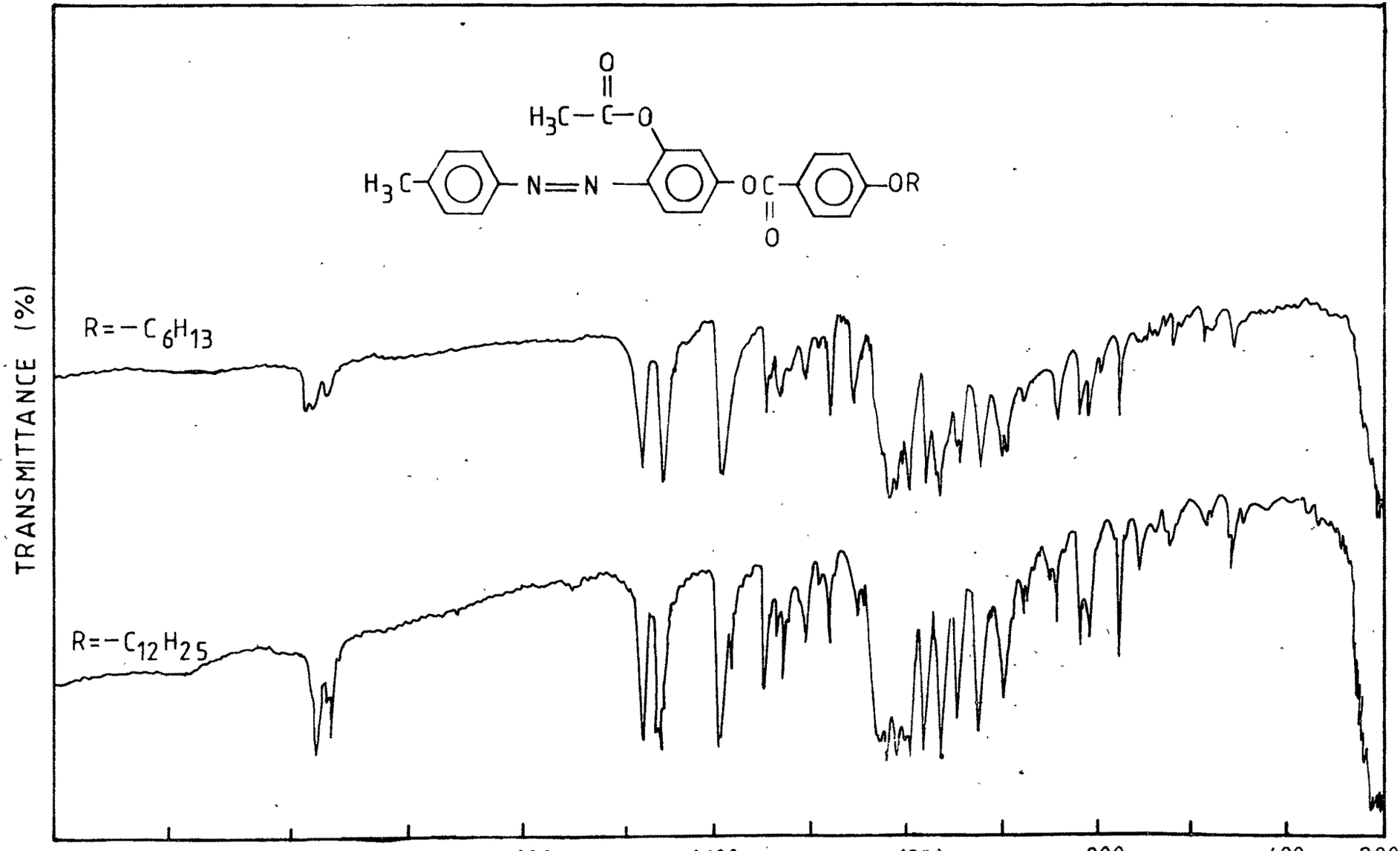


Fig. 37 I. R. SPECTRA

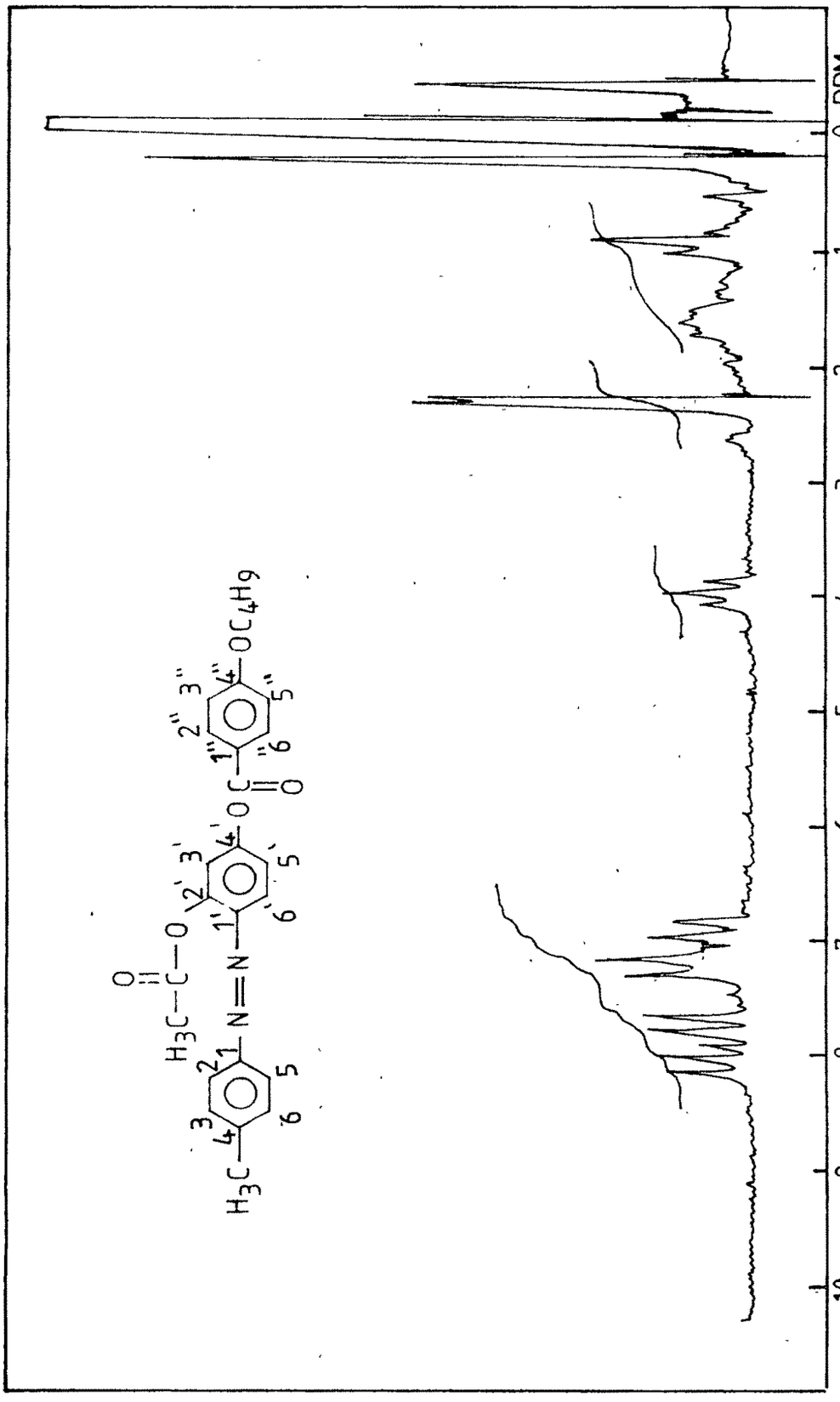


Fig.38 NMR SPECTRA

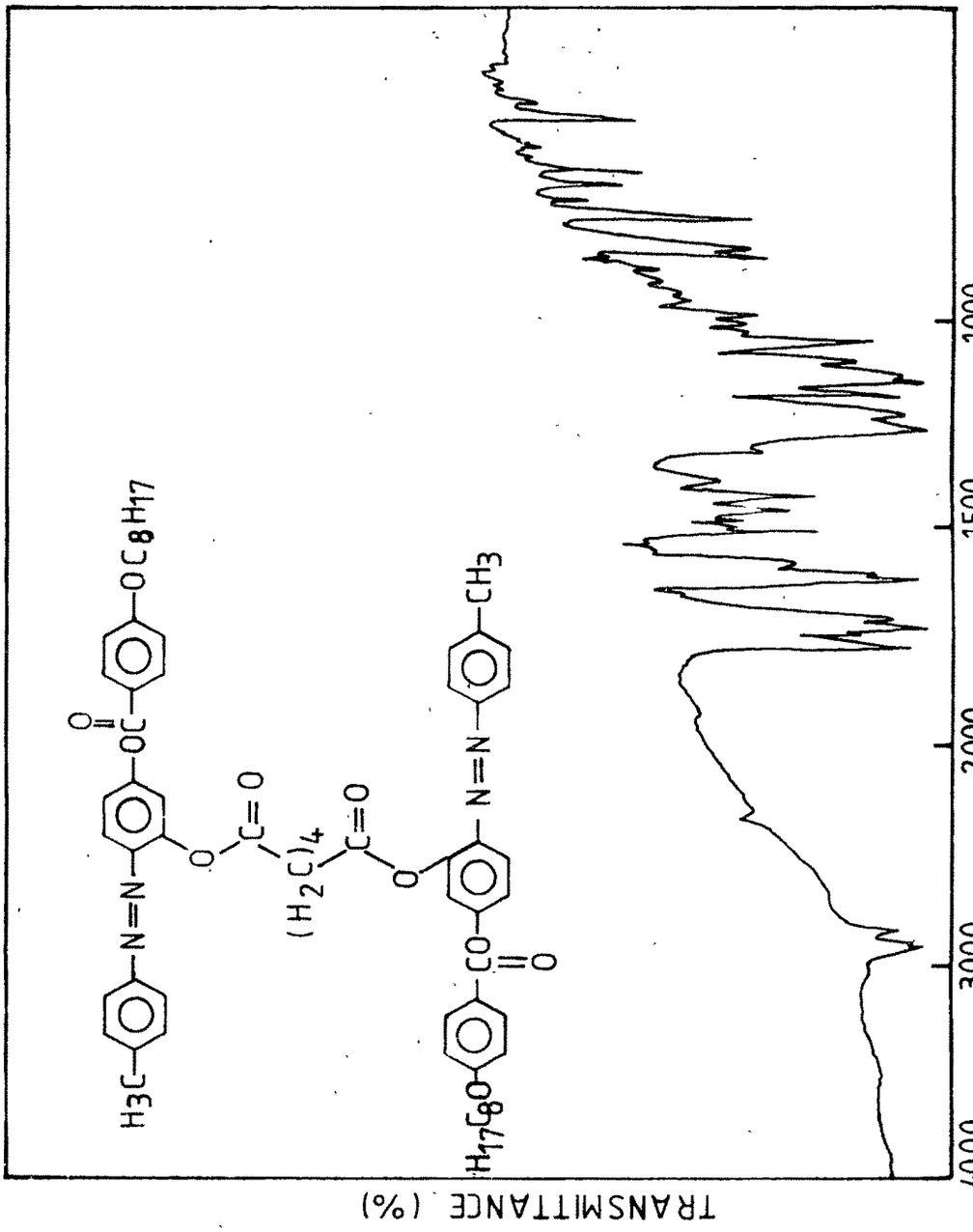


Fig.39 I.R. SPECTRA

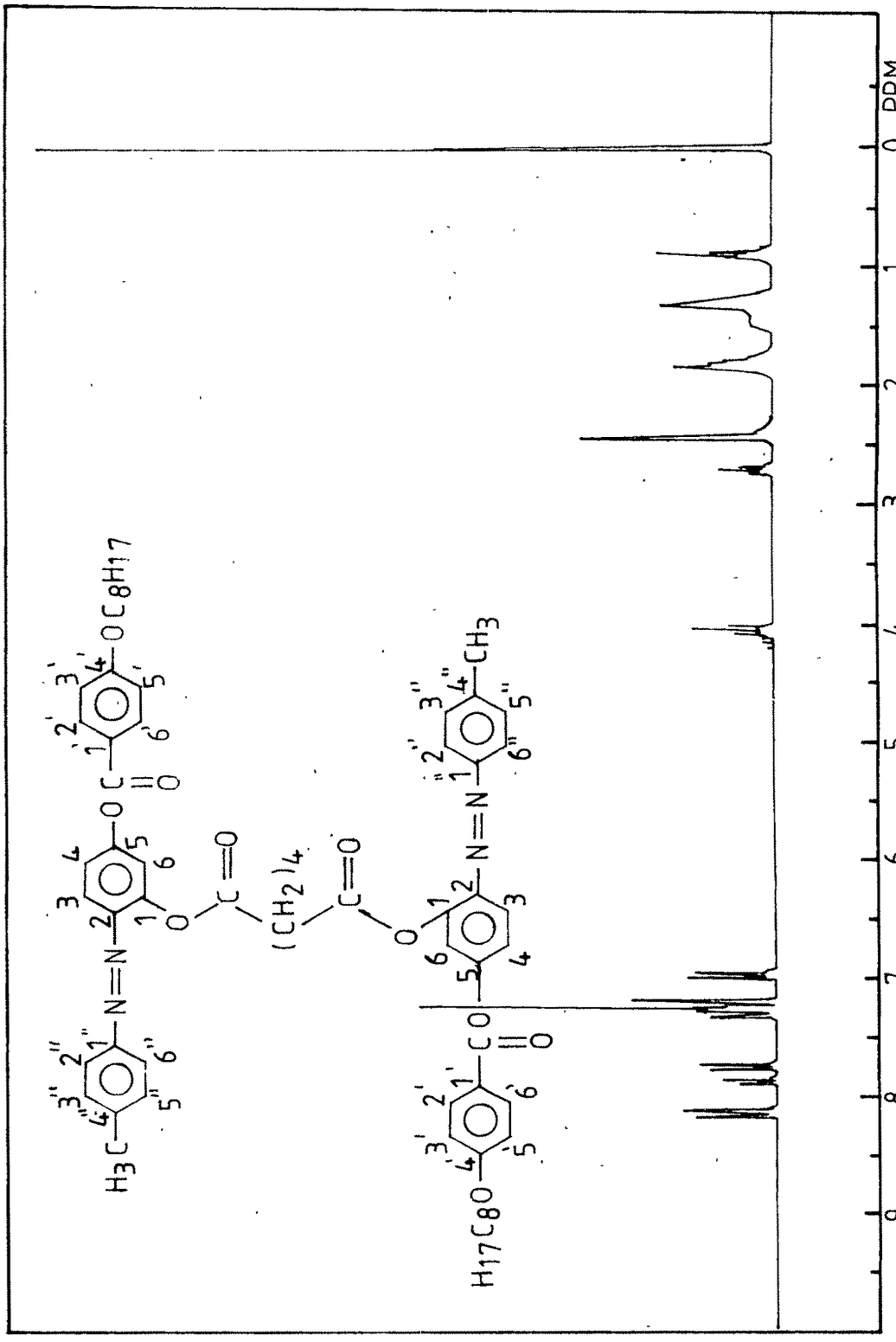


Fig.40 NMR SPECTRA

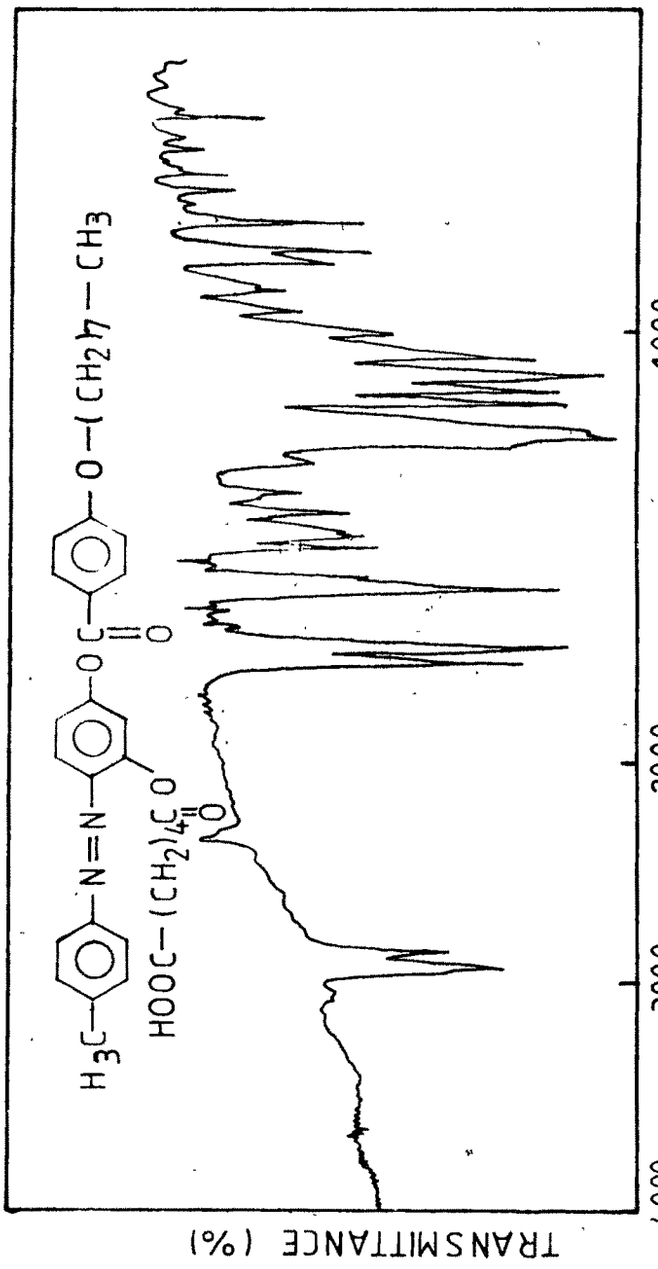


Fig.41 I.R. SPECTRA

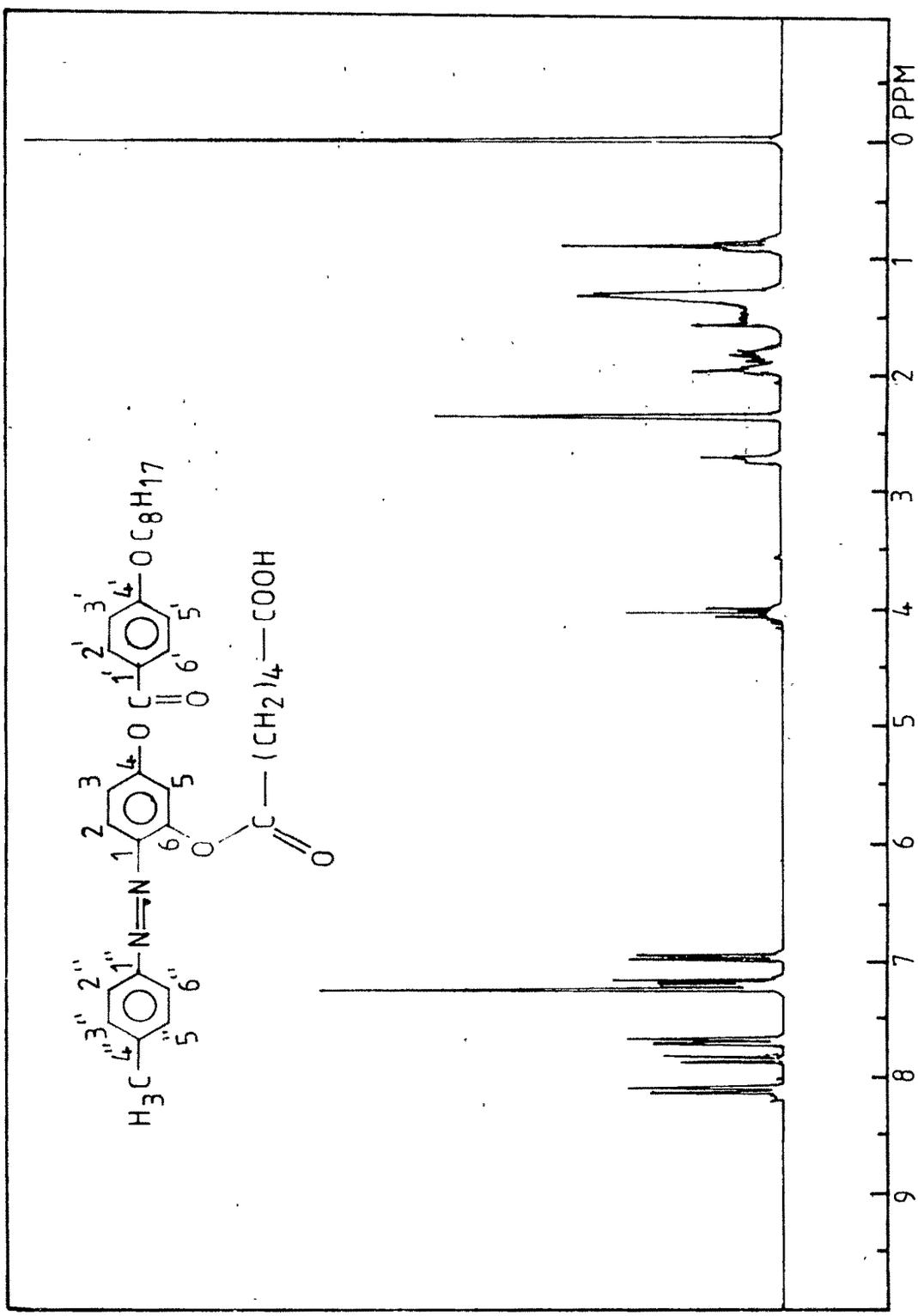


Fig.42 NMR SPECTRA

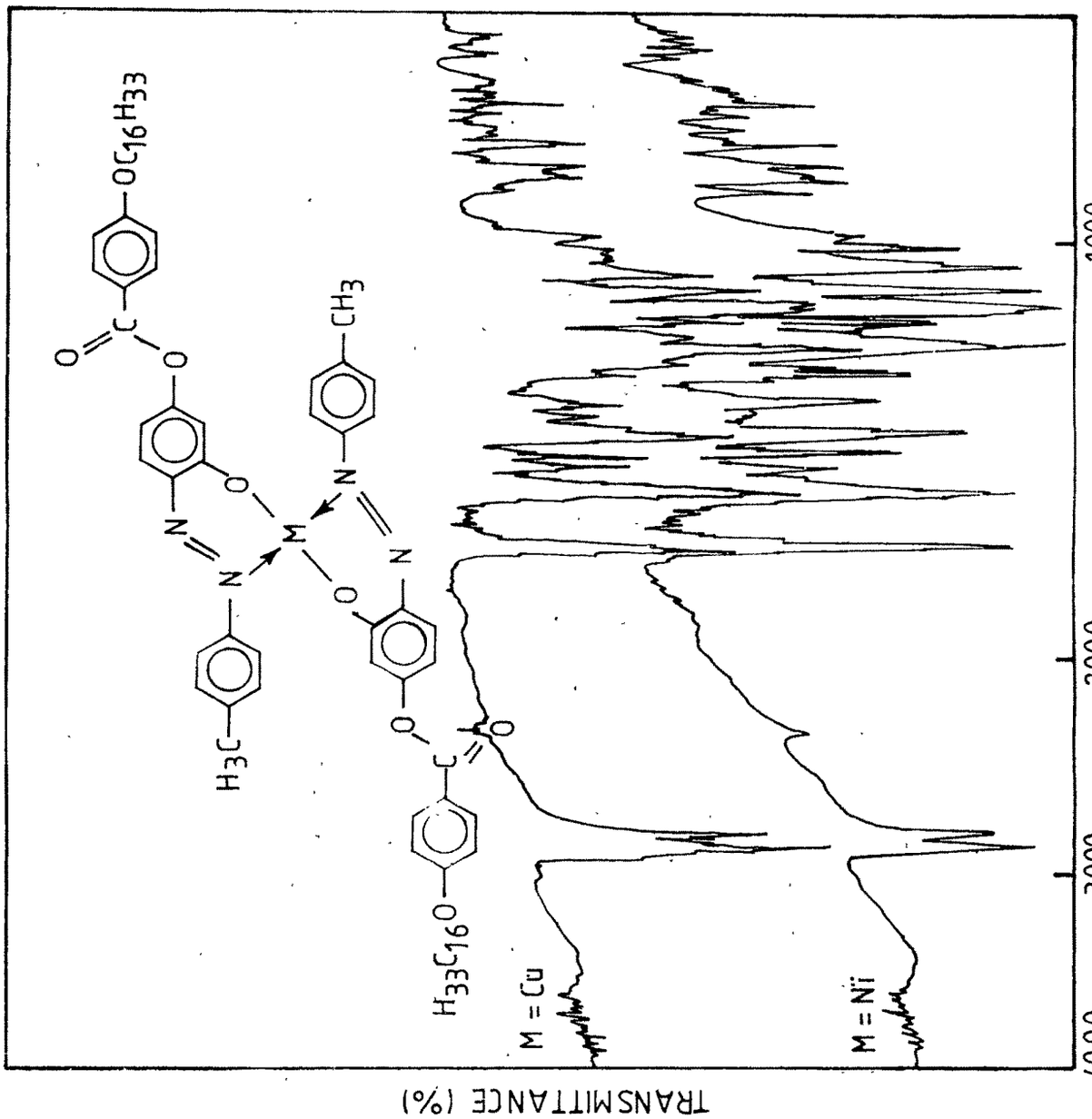
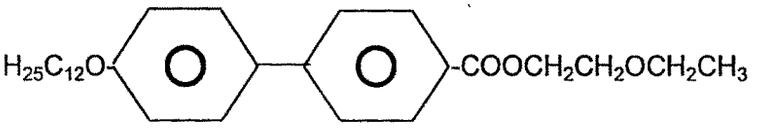

TRANSMITTANCE (%)
WAVENUMBER CM⁻¹
4000
3000
2000
1000
M = Cu
M = Ni
OC16H33
CH3
H3C
H33C16O
M
N
O
C

Fig. 43

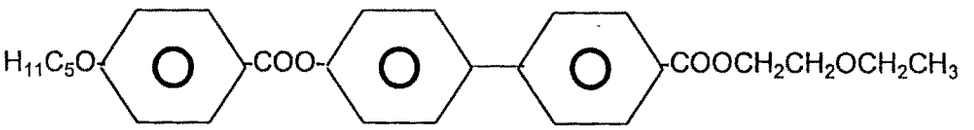
5.0 SYNTHESIS OF DIFFERENT COMPOUNDS FOR COMPARISON WITH DIFFERENT HOMOLOGOUS SERIES.

The following compounds were synthesized and characterised as per the process described previously.



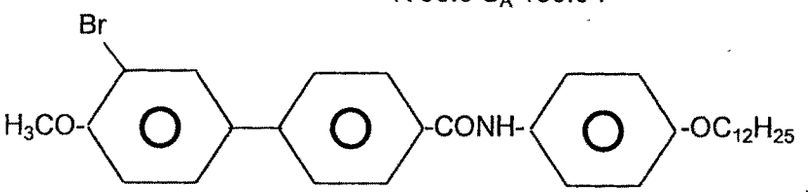
P_1

K 60.0 S_A 73.0 I



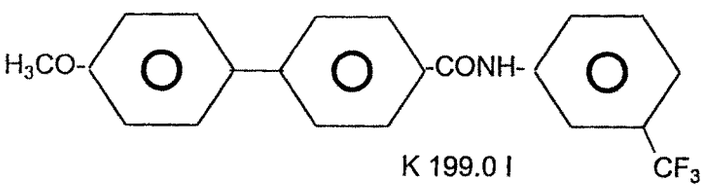
P_2

K 90.0 S_A 166.0 I



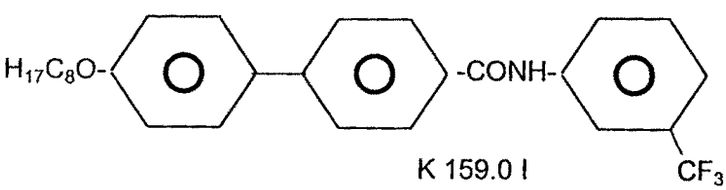
P_3

K 188.0 S_A 218.0 I



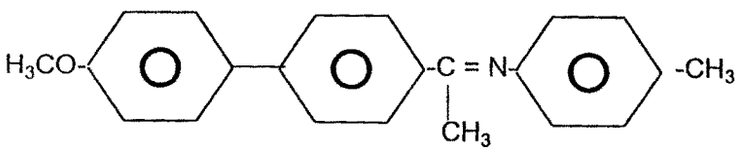
P_4

K 199.0 I



P_5

K 159.0 I



P_6

K 239.0 I

Table - 33a

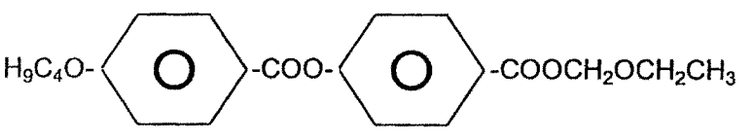
Code No.		Required			Found	
	C	H	N	C	H	N
P_1	76.65	9.25	---	76.20	8.83	---
P_2	73.10	3.72	---	72.69	6.58	---
P_3	67.84	7.07	2.47	67.82	6.83	2.78
P_4	67.38	4.31	3.77	67.42	4.37	3.48
P_5	71.64	6.40	2.98	71.38	6.44	2.79
P_6	83.81	6.67	4.40	83.78	6.43	4.62

6.0 MIXED MESOMORPHISM :

Three binary systems comprising of following members were studied

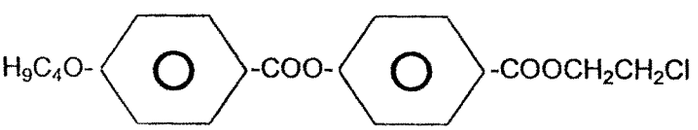
System : A

Component : a



K 76.0 I

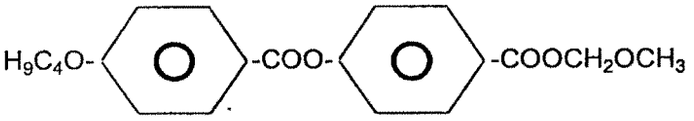
Component : b



K 75.0 I

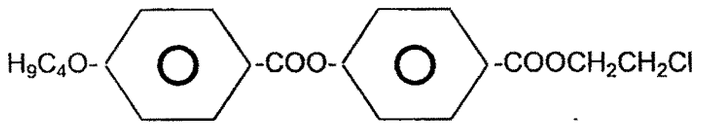
System : B

Component : a



K 75.0 I

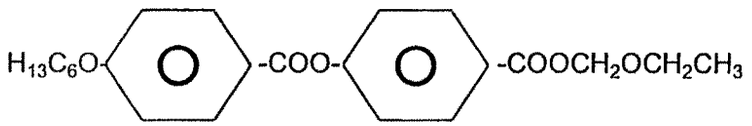
Component : b



K 75.0 I

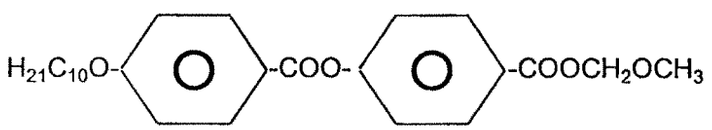
System : C

Component : a



K 43.0 S_A 54.0 I

Component : b

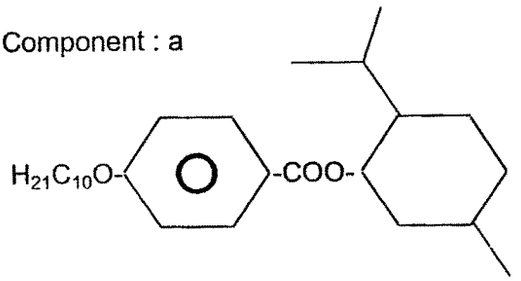


K 40.0 S_A 73.0 I

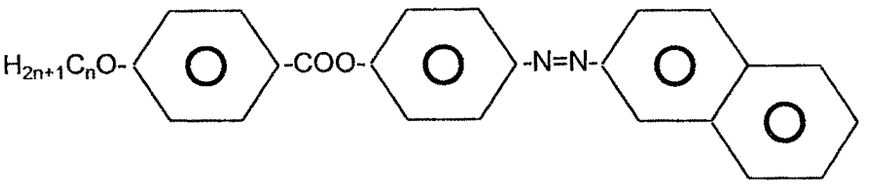
6.1 Doping of a chiral component.

1. System : D-F

Component : a



Component : b



n=10 - System D

n=14 - System E

n=16 - System F

6.2 Preparation of binary mixtures :

The two substances in known proportions were carefully and accurately weighed in a small fusion tube (2" X 1/4") so that the total weight of the mixture was 0.1 gm (exactly weighed). The tube with its contents was then heated in a paraffin bath so as to melt the contents at the possible lowest temperature, when the mixture melted, it was throughly stirred by means of a glass rod to ensure complete mixing of the components. The homogeneous liquid was then quickly cooled by quenching the tube in an icebath. The solid mixture was then removed from the tube and was converted to fine powder by intimately grinding it in an agate mortar. Various mixtures of different proportions were prepared in this way, and their various transition temperatures were studied.

7.0 DETERMINATION OF TRANSITION TEMPERATURES :

The transition temperatures were determined by using a polarzing microscope "Leitz Laborlux 12POL Microscope" provided with a heating stage.

Slides were prepared by two different methods (a). In the first method, the substance is taken on a slide and heated to a little more than mesomorphic temperature at that stage cover slip is placed over it and then it is cooled off (b). In second method, the substance is taken on a slide and cover slip is placed over it and then compound is heated.

The microscope was standardized by taking melting points and / or transition temperatures of very pure but known substances like benzoic acid, succinic acid, p-azoxyanisole, vanillin, p-anisal-p-phentidine, p-azoxyphenetole.

To determine the various transitions a glass slide carrying a thin section of the material with cover slip on it was observed under the microscope. The slide was inserted into the specimen chamber of heating stage and the temperature was raised fast (5 ^{o}C / min) to find approximate transition temperatures. The measurements were then repeated and near the transition to be observed the rate of heating was regulated to about 1 ^{o}C / min. The changing textures over the temperature ranges are carefully observed and recorded as the appearance of focal-conic, plane, homeotropic and threaded structures of smectic and nematic phases emerge under polarised light. All observations were repeated several times, in case of any doubt, the compounds were purified again and then were subjected to the study under microscope afresh.

8.0 DIFFERENTIAL SCANNING CALORIMETRY :

Thermal analysis plays an important role in the characterisation of mesomorphic substances and in the elucidation of structure property effects. Calorimetry is a valuable help to detect polymorphism and can yield some clues to phase transitions. A knowledge of both the temperature and heat of transition is necessary if the principles of physical analysis are to be applied to mesophase forming systems. From this information the transition enthalpy and entropy may be calculated which acts as a key for evaluating the type and degree of order present in systems involving phase changes.

This technique maintained the sample and reference materials isothermal to each other by proper application of electrical energy, as they were heated or cooled at a linear rate The curve obtained is a recording of heat flow dH/dt, in m. cal/sec. as a function of temperature. In the true thermodynamic sense, endotherm curve peak is indicated by a peak in the upward direction (increase in enthalpy) while in exotherm peak is recorded in the opposite direction. In all appearances, the DSC curve looks very similar to that of a DTA curve except for the ordinate axis units. As in DTA the area enclosed by the DSC curve peak is directly proportional to enthalpy change.

Area = k. Δ Hm except that k is independent of temperature.

In the present work, nine members of series 4-methyl-2'-hydroxy 4'(4"-n-alkoxybenzoyloxy) azobenzenes (Table 37) and other mesogens (Table 38) from different homologous series were screened by DSC using Mettler TA 4000 system. All the members were showing endothermic peaks for solid-mesomorphic and mesomorphic-isotropic transitions. The enthalpy and entropy data are given in table. 37, 38.

9.0 FLUORESCENT SPECTRA

Fluorescence is light that is emitted from a molecule after the molecule has absorbed light of a different (and shorter) wavelength. One characteristic feature of fluorescent relation is that the fluorescence stops whenever the irradiating light is removed. Though anthracence is colourless but pure sample of it when viewed in ultra violet light gives off blue visible light which is called fluorescence.

Aromatic hydrocarbons such as benzene, naphthalene, anthracene and fluorene are called luminophores and are considered as basic fluorescing substances. The groups that enhance this fluorescence, or that shift it to the visible region for example -CH=CH-, CO-, -CH=CH-COO-, p-phenylene, -CH=CH=COOH, -CN are called fluorogens. Auxoflores include $-NH_2$ and -OH groups which enhance fluorescence.

n-Dodecyl derivative of series - III was studied for its fluorescent properties. The excitation and emission spectra were recorded for the compound by Schimadzu Rf 540 spectrophotoflurometer at room temperature. The excitation spectra are the record of luminescence intensity at fixed emission as a function of the excitation wavelength. The fluorescence emission spectra in which the excitation wavelength is kept constant and the corresponding wavelength distribution of the emitted radiation is measured.

Fluorescent spectra of n-dodecyl derivative of series - III is represented in Fig. 13.

10.0 FERROELECTRIC MEASUREMENTS :

Both electro optic and dielectric measurements of 4-methyl-2'-4-bis (4"-n-alkoxybenzoyloxy) azobenzene when doped with 10% be weight of chiral dopant (1R,2S,5R) - (-) - menthyl 4-n-dodecyloxy benzoate were carried out by Dr. Raina and his group at Patiala.

The measurements were carried out in a 7.5 μ m thick sample sandwiched between two conducting Indium tin oxide coated glass substrates (LUCKID, U.K.). The substrates have been pre-treated with the polyimide coating. The cells were filled by capillary action at the isotropic phase of the liquid crystal. The sample was then cooled into the liquid crystal phase @ 0.1 °/min. in a LINKAM TP90 and THS600 temperature programmer cum hot stage. The thermal polarising microscopy of the sample was observed using GETNER polarising microscope.

Polarisation measurements

Sawyer-Tower circuit was used to find out that whether the material shows Hysteresis loop i.e. spontaneous polarisation. It was found that at 20 °C, 22 °C, 26°C, and 45 °C, the sample shows elliptical loop which suggests the absence of spontaneous polarisation.

Dielectric measurements

In order to verify the electro-optic results they did dielectric measurements using Impendance Analyser HP4192A in the frequency range 10 Hz to 10 Mhz at zero bias The cell was calibrated using air and benzene as standard references.

Fig. 44 (I) Plot of dielectric constant (real ε' and complex ε") Vs. frequency at a temperature of 26 °C.

From Fig. 44 (I), they observed that the relaxation frequency of the molecules is ~300kHz i.e. molecules relax at a very high frequency. While the relaxation fequency of ferroelectric liquid crystals at a temperature less than Tc* lies in the Hz region.

Fig. 44 (II), Plot of ε" Vs. Temperature, at various frequencies (0.1kHz, 0.5kHz, ---)

Dr. Raina's group observed that with the increase of temperature, ε' remains constant while in the case of FLCs ε' should fall exponentially with the rise of temperature and after Tc*, the value of ε' should remain constant, which again contradicts their results This shows the existence of non-ferroelectric phase.

Fig. 44 (III), Plot of ε" Vs. ε" at 26 °C (Cole-Cole Plot)

The results show that the molecules have got single relaxation time with a relaxation frequency of ~300 kHz.

Fig. 44 (IV), Plot of ε" Vs. ε' at 30 °C (Cole-Cole Plot)

Which again shows that the molecules have got single relaxation time.

Conclusions : Thus from here the conclusion is drawn that the molecules do not show ferroelectricity at any temperature.

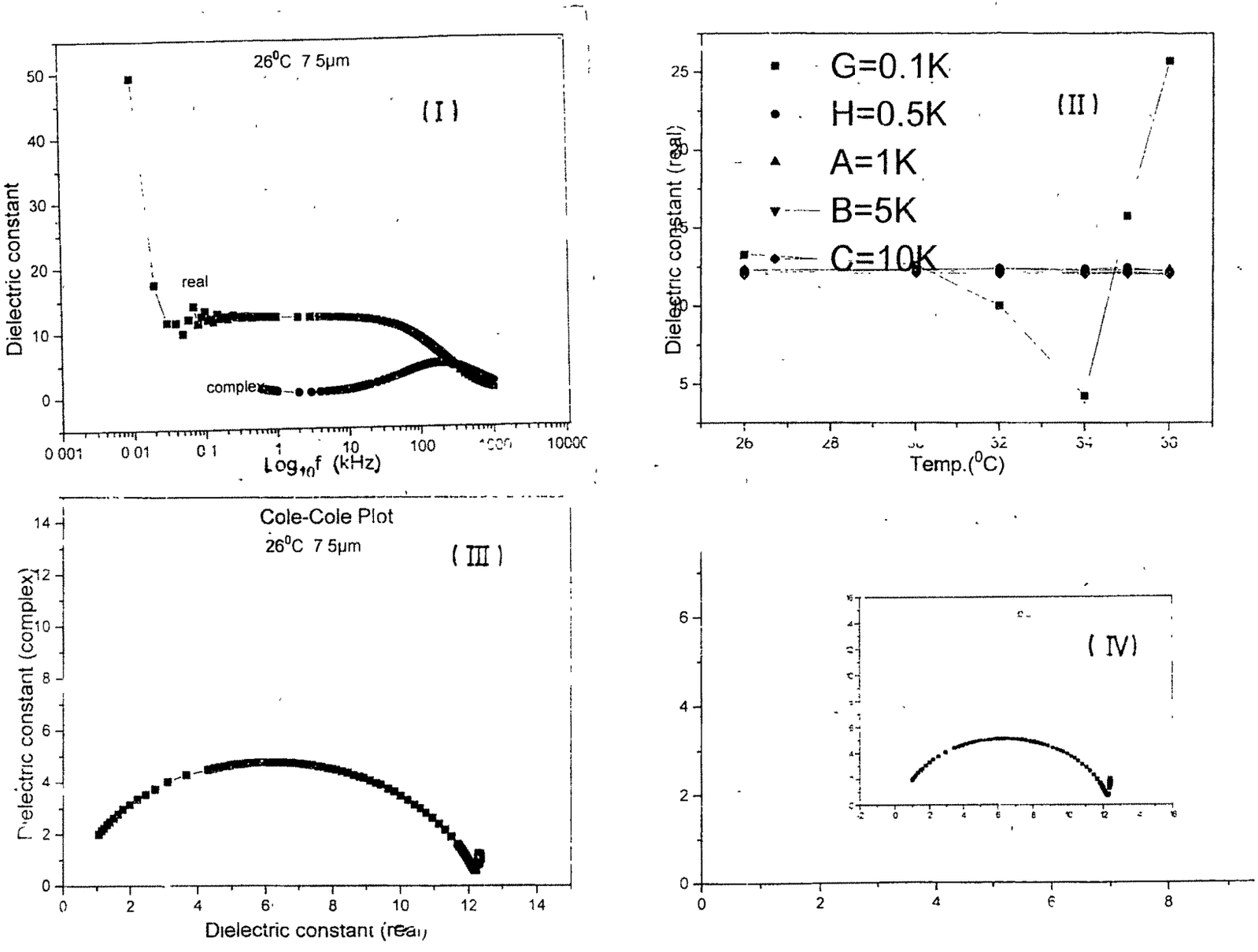

26°C 7.5μm
(I)
Dielectric constant
real
complex
Log10f (kHz)
G=0.1K
H=0.5K
A=1K
B=5K
C=10K
(II)
Dielectric constant (real)
Temp.(°C)
Cole-Cole Plot
26°C 7.5μm
(III)
Dielectric constant (complex)
Dielectric constant (real)
(IV)

Fig. 44.