EXPERIMENTAL

EXPERIMENTAL

1. Preparation of Compounds

1.1 Biphenyl Derivatives

1.1.1 n-Alkyl Halides :

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

1.1.2 Preparation of 4-(4"-n-Alkoxy benzoyloxy)-4'-nitrobiphenyls: series - I

1.1.2 a 4-n-Alkoxy Benzoic Acids :

Commercially available 4-methoxy benzoic acid (anisic acid B.D.H.) was used. Number of other methods (240,297) are known for alkylation of p-hydroxy benzoic acid. However, in the present study, the method developed by Dave and Vora (298) was followed.

p-Hydroxybenzoic acid (0.1 mole), appropriate halide (0.12 mole) and potassium hydroxide (0.25 mole) were dissolved in 100 ml ethanol and refluxed for 7 to 8 hours. Ten percent aqueous potassium hydroxide solution (25 ml) was added and reflux was continued for two hours, to hydrolyze 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. (240).

1.1.2 b 4-n-Alkoxybenzoyl Chlorides (298) :

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.

1.1.2.c 4-Hydroxy-4'-Nitrobiphenyl (299,300) :

4-Hydroxy-4'-nitrobiphenyl was synthesized by the process reported in the literature. It was synthesized by four step method.

(i) Preparation of Benzoyl Chloride :

Benzoyl chloride was prepared by the method described above.

(ii) Benzoyloxy Biphenyl :

4-Hydroxy biphenyl (0.1 mole) was dissolved in 50 ml of dry pyridine and was added slowly, with stirring, to cold benzoyl chloride (0.1 mole) contained in a round bottom flask. The mixture was heated on a water bath for thirty minutes and was allowed to cool up to room temperature. It was acidified with cold 1:1 hydrochloric acid and precipitates obtained were filtered and washed with water and dried. The ester was crystallized from ethanol. Melting point 150 °C. (Reported 149 - 150°C.)(299,300).

(iii) 4-Benzoyloxy-4'-Nitrobiphenyl :

4-Benzoyloxy biphenyl (0.145 mole) was taken in round bottom flask, 310 ml of glacial acetic acid was added in the flask and it was heated up to 80 - 90°C. 100 ml Fuming nitric acid was added slowly in such a way that the temperature remained between 80 - 90°C. After complete addition, the reaction mixture was cooled to room temperature. The solid separated was filtered and washed with water and methanol. The product was crystallized from glacial acetic acid. Melting point is in good accordance with the literature (299,300).

(iv) Hydrolysis of 4-Benzoyloxy-4'-Nitrobiphenyl :

4-Benzoyloxy-4'-nitrobiphenyl (0.18 mole) was taken in round bottom flask, 300 ml of ethanol was added to it and it was heated to reflux. An aqueous solution of potassium hydroxide (40 gms of KOH in 100 ml water) was then added dropwise at reflux. After complete addition, the mixture was further refluxed for 30 minutes and cooled over night. Next day, blue crystals of potassium salt were filtered, washed with tetrahydrofuran until wash was colourless. Pure 4-hydroxy-4'-nitrobiphenyl was obtained by dissolving the salt in minimum amount of boiling water and adding 1:1 hydrochloric acid until acidic pH was obtained. The yellow solid was filtered, washed with water, dried and crystallized from ethanol. Melting point 203°C. (Reported 203 - 204°C.)(299,300).

1.1.2 d Preparation of Biphenyl Esters

4-(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyls :

Series : I

4-(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyls were synthesized by condensing appropriate 4-n-alkoxy benzoyl chloride with 4-hydroxy-4'-nitrobiphenyl.

4-Hydroxy-4'-nitrobiphenyl (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxy benzoyl 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 recrystallized several times from acetic acid until constant transition temperatures were obtained. The transition temperatures, elemental analysis and IR spectral data are recorded in tables 3, 4 and 5, respectively.

1.1.3 Preparation of optically active 4-(4"-β-methyl butoxy benzoyloxy)-4'-nitrobiphenyl.

Optically active mesogen analogous to butoxy derivative of series-I was synthesized.

1.1.3.1 Preparation of S(+) 2-methyl butyl bromide :

50 gms of hydrobromic acid (48%) was taken in a round bottom flask. 15 gms (8.2 ml) of concentrated sulphuric acid was added in portions with constant

shaking, 17.6 gms (22.0 ml) of S(-)-2-methyl-1-butanol was added followed by the addition of 12.0 gms (6.5 ml) of conc. H_2SO_4 (98%) in portions with shaking. The whole mass was refluxed gently on wire gauze for 2-3 hours. Optically active bromide separated above the acids. The reaction mass was cooled up to room temperature. Bromide layer was separated and washed with water, hydrochloric acid, water, 5 percent sodium bicarbonate solution and water. Bromide was dried over anhydrous calcium chloride and distilled. B.P. 120°C. Reported 121°C (301).

1.1.3.2 Preparation of 4(β-methyl butoxy) benzoic acid and 4(β-methyl butoxy) benzoyl chloride.

S(+)-4(β-methyl butoxy)benzoic acid and its acid chloride were synthesized by the procedure described in section 1.1.2 a & b respectively. Melting point of S(+)-4(β-methyl butoxy) benzoic acid 120°C.

1.1.3.3 Preparation of 4-hydroxy-4'-nitrobiphenyl.

4-Hydroxy-4'-nitrobiphenyl was prepared by the method described in section 1.1.2.c.

1.1.3.4 Preparation of optically active 4-(4"-β-methyl butoxy benzoyloxy)-4'-nitrobiphenyl

4-Hydroxy-4'-nitrobiphenyl (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly to cold 4(β-methyl butoxy) benzoyl chloride (0.01 mole). The mixture was refluxed on water bath for an hour and was allowed to stand over night. It was acidified with 1:1 cold hydrochloric acid. Precipitates obtained were filtered and washed with cold dilute sodium hydroxide solution followed by water. Final product was recrystallized several times from glacial acetic acid till constant transition temperatures were obtained.

Elemental Analysis :

	C%	H%	N%
Required	71.11	5.68	3.45
Found	71.24	5.68	2.92

IR spectral vibrations (stretching and bending)(cm^{-1}):

2950-2850, 1725, 1600, 1510-1520, 1350, 1280, 1210, 1170, 1070, 850. (Fig. 23.); $K \xrightarrow{167^\circ C} S_A \xrightarrow{205^\circ C} S_{mx} \xrightarrow{215^\circ C} \overset{*}{N} \xrightarrow{225^\circ C} Iso$

1.1.4 Preparation of 4-(n-Alkanoyloxy)-4'-nitrobiphenyl : Series - II

1.1.4.1 n-Alkanoyl Chlorides :

n-Alkanoyl chlorides were prepared by the method described in section 1.1.2.b.

1.1.4.2 Preparation of 4-hydroxy-4'-nitrobiphenyl

4-Hydroxy 4'-nitrobiphenyl was synthesized by the method described in section 1.1.2.c.

1.1.4.3 Preparation of Esters :

4-(n-Alkanoyloxy)-4'-nitrobiphenyl :

4-(n-Alkanoyloxy)-4'-nitrobiphenyls were synthesized by condensing appropriate n-alkanoyl chloride with 4-hydroxy-4'-nitrobiphenyl.

Respective alkanoyl chloride (0.01 mole) was dissolved in dry benzene (10 ml) in a 100 ml round bottom flask. 4-Hydroxy-4'-nitrobiphenyl (0.01 mole) was dissolved in 10 ml dry pyridine and was slowly added with stirring to cold solution of 4-n-alkanoyl chloride in benzene. The mixture was stirred for two hours at 50-60 °C and was allowed to stand over night. It was then acidified with 1:1 cold hydrochloric acid. Benzene was evaporated and the reaction product was extracted from aqueous phase with ether. Ether layer was washed with water, dilute potassium hydroxide solution and with water. Ether extract was dried and then evaporated. Solid obtained was further purified by crystallization from ethanol.

The transition temperatures, elemental analysis and IR spectral data are given in table 6, 7 and 8, respectively.

1.1.5 Preparation of 4-n-Alkoxy-4'-nitrobiphenyls Series - III

Gray (302, 303) has synthesized a few homologues.

1.1.5.1 Potassium salt of 4-hydroxy-4'-nitrobiphenyl.

Potassium salt of 4-hydroxy-4'-nitrobiphenyl was synthesized as described in section 1.1.2.c.

1.1.5.2 4-n-Alkoxy-4'-nitrobiphenyls:

The common alkylation methods (240,304) failed in alkylation of 4-hydroxy-4'-nitrobiphenyl. A modified method described here was used for alkylation.

The potassium salt of 4-hydroxy-4'-nitrobiphenyl (0.01 mole) was dissolved in 50 ml of dry

DMF. To this solution (0.12 mole) alkyl halide was added. The whole mass was then refluxed for three to four hours on sandbath. The mixture was cooled upto room temperature then poured into cold water. It was then extracted with solvent ether. Ether layer was washed with water, dilute potassium hydroxide solution and water. Ether extract was dried over anhydrous calcium chloride and finally ether was evaporated. Solid obtained was further purified by recrystallization from alcohol several times till constant transition temperatures were obtained.

Transition temperatures, elemental analysis and IR spectral data are given in tables 9. 10 and 11 respectively.

1.1.6 Preparation of diesters of trans -1,4-cyclohexane dicarboxylic acid and terephthalic acid with 4-hydroxy-4'-nitrobiphenyl.

Diacid chlorides of both the compounds were prepared by the same method as described in section 1.1.2.b.

(i) Di-(4-Nitrobiphenyl) trans 1-4-cyclohexane dicarboxylate (MT_3)

(ii) Di-(4-Nitrobiphenyl) terephthalate (MT_4)

Diesters were synthesized by condensing appropriate diacid chloride with 4-hydroxy-4'-nitrobiphenyl.

The diacid chloride (0.01 mole) was dissolved in about 5 ml of dry pyridine. The solution of 4-hydroxy-4'-nitrobiphenyl (0.02 mole) in 10 ml of dry pyridine was added slowly to cold solution of diacid chloride. The mixture was heated on waterbath for about 1.5 hours and was allowed to stand over night. It was acidified with cold 1:1 hydrochloric acid. Precipitates were filtered and washed with water, dilute sodium hydroxide solution and water. The resulting diesters were recrystallized several times from DMF until constant transition temperatures were obtained.

Elemental Analysis

	Calculated			Found		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
MT_3	67.80	4.59	4.95	67.76	4.98	5.09
MT_4	68.57	3.57	5.00	69.01	3.96	4.61

IR spectral data (Bending and Stretching vibrations) (cm^{-1})

MT_3 1730, 1710, 1600, 1510, 1470, 1280, 1210, 1160, 1070, 880, 850, 760. (Fig: 47.b)

MT_4 1730, 1600, 1520, 1485. 1350, 1250-80, 1200, 1115, 1090, 1000, 850, 800, 750, 700. (Fig: 47.b)

Transition Temperatures

MT_3 K $\xrightarrow{307\,^{\circ}C}$ N $\xrightarrow{>360\,^{\circ}C}$ Iso. (d)

MT_4 K $\xrightarrow{315\,^{\circ}C}$ N $\xrightarrow{>360\,^{\circ}C}$ Iso. (d)

(d) decomposition.

2.0 Cholesteryl Derivatives :

2.1. Cholesteryl Derivatives with Rigid and Flexible spacers :

2.1.1 Dicholesteryl Carbonates : Series IV

Cholesteryl chloroformate (0.02 mole, recrystallized three times from dry acetone) and 50 ml dry benzene were taken in a 200 ml round bottom quickfit flask. The contents were rapidly mixed with oxyglycols, glycols, dihydroxy aromatic compounds or amino phenols (0.01 mole). 4 ml of anhydrous pyridine and 40 ml of dry benzene was added to the reaction mixture. The reaction mixture was stirred for 2-3 hours at about 38-40°C. The mixture was then filtered to separate the precipitates of pyridine hydrochloride and other insoluble materials. The filtrate was concentrated under vacuum to remove excess of benzene, then methanol was added to the solution and the precipitates obtained were filtered and dried. The precipitates were crystallized from chloroform-acetone mixture till constant transition temperatures were obtained. The transition temperatures, elemental analysis and IR spectral data are given in tables 12.b, 13 and 14, respectively.

2.1.2 Dicholesteryl Carbamates : Series V

Dicholesteryl Carbamates were synthesized by condensing different diamines (0.01 mole) with cholesteryl chloroformate (0.02 mole) as described above.All the compounds were recrystallized from chloroform-acetone mixture till constant transition temperatures were obtained.

The transition temperatures, elemental

analysis, IR spectral data are given in table 15, 16 and 17 respectively.

2.1.3 Cholesteryl 4-n-alkoxy phenyl carbamates: Series VI

2.1.3.a Synthesis of Alkoxy Anilines :

4-n-Alkoxy anilines can be synthesized by different routes (304,306). In the present study the following route was followed as it gives over all better yields of 4-n-alkoxy anilines (306).

(i) Synthesis of 4-n-alkoxy acetanilides :

Paracetamol (0.1 mole) anhydrous potassium carbonates (0.15 mole) and alkyl bromides (0.15 mole) and dry acetone (60 ml) were taken in round bottom flask. The reaction mixture was refluxed on waterbath for 8 to 10 hours. The whole mass was then added to water and extracted with ether. The ether was evaporated and the residual solids, 4-n-alkoxy acetanilides were directly used for hydrolysis.

(ii) Hydrolysis of 4-n-alkoxy acetanilides to 4-n-alkoxy anilines :

A mixture of 4-n-alkoxy acetanilide (0.146 mole) water (70 ml) and concentrated hydrochloric acid (45 ml) were stirred for 10-12 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 extract was dried and concentrated at reduced pressure to give an oil which was purified by distillation.

The higher members separated as solid and were filtered directly, without ether extraction. Melting points and boiling points agree well with the reported values (304,306).

2.1.3.b Cholesteryl 4-n-alkoxy phenyl carbamates :

Cholesteryl 4-n-alkoxy phenyl carbamates were synthesized by condensing appropriate 4-n-alkoxy aniline (0.01 mole) with cholesteryl chloroformate (0.01 mole) as described in section 2.1.1. All the compounds were recrystallized from chloroform-absolute alcohol mixture till constant transition temperatures were obtained.

Transition temperatures, elemental analysis and IR spectral data are recorded in table 18,19 and 20, respectively.

2.2.1 Preparation of model compounds with N, N'-hexane-α,ω-diylbis (trimellitimide) and p-cresol (model compound no.1), 4-hydroxy-4'-ethoxy azobenzene (model compound no. 2)

2.2.1.a. Preparation of N,N'-hexane-α,ω-diylbis (trimellitimides)(307)

An α, ω diamino hexane (0.1 mole) was dissolved in 100 ml DMF (dry), 0.25 mole of trimellitic anhydried was added and the resulting solution was refluxed for 2 hours under stirring. Acetic anhydride (0.5 mole) was then added and the reaction mixture was refluxed for two more hours. It was then cooled to room temperature and poured in to 1 litre of ice cold water. Precipitated diacid was isolated by filtration. The product was recrystallized from DMF-water. Melting point is in good accordance with the literature (307).

2.2.1.b Preparation of 4-hydroxy-4'-ethoxy azobenzene ;

4-hydroxy-4'-ethoxy azobenzene was synthesized by using conventional method of diazotization and coupling (308).

4-Ethoxy aniline (0.1 mole) was dissolved in 1:1 hydrochloric acid (100 ml) and solution was cooled to 0 °C. This was diazotized by adding saturated sodium nitrite solution (0.1 mole) with constant stirring, maintaining faint possitive 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 4-ethoxy benzene diazonium chloride was coupled with phenol (0.1 mole) in alkaline 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 recrystallized from aqueous ethanol till constant melting point was obtained.M.P 120 °C, (reported 121°C) (309).

2.2.2 Preparation of model compounds M-1 and M-2 :

Model compounds M-1 and M-2 were prepared by condensing diacid chloride of N,N'-hexane α,ω -diylbis (trimellitimide) with p-cresol and 4-hydroxy 4'-ethoxy azobenzene, respectively.

2.2.2.a. Preparation of diacid chloride of N-,N'-Heaxane α,ω-diylbis (trimellitimide).

The diacid chloride of above mentioned compound was synthesized by the method described in the section 1.1.2.b.

2.2.2.b. Preparation of esters (Model compounds M-1 and M-2)

p-Cresol (0.02 mole) was dissolved in dry pyridine (10 ml) and was slowly added to cold diacid chloride solution of N,N' hexane-α,ω -diylbis (trimellitimide)(0.01 mole). The reaction mixture was heated on water bath for about an hour and was allowed to stand over night. It was acidified with cold 1:1 hydrochloric acid. Precipitates obtained were filtered and washed with water, sodium bicarbonate solution and water. Using the similar procedure model compound M-2 was prepared using 4-hydroxy-4'-ethoxy azobenzene. Both the model compounds were crystallised from appropriate solvents.

Elemental Analysis

	Calculated (%)			Found (%)		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
M_1	70.82	4.97	4.35	71.13	4.34	4.46
M_2	68.42	4.82	9.21	68.00	4.36	8.92

IR spectral Data (Bending & Stretching vibrations) Cm^{-1}.

M_1 : 2800, 1770, 1730, 1710, 1600, 1500, 1390, 1280, 1250, 1190, 1160, 1095, 1050, 870, 800, 720.

M_2 : 2800, 1780, 1750, 1720, 1600, 1490, 1410, 1290, 1250, 1150, 1080, 1050, 840, 720. (Fig:41.b.)

Transition Temperatures

M_1 K $\xrightarrow{237^\circ C}$ Iso.

M_2 K $\xrightarrow{240^\circ C}$ N $\xrightarrow{320^\circ C}$ Iso (d)

(d) - decomposition.

2.3.1 Dicholesteryl imide esters of N,N'-alkane α,ω-diyl bis (trimellitimides): Series VII:

Dicholesteryl imide esters of N,N'-alkane,α - ω diyl bis (trimellitimides) were synthesized by condensing appropriate quantity of diacid chloride of N,N' alkane α,ω-diyl bis (trimellitimide) with cholesterol.

2.3.1.a Synthesis of N,N' alkane α,ω -diyl bis (trimellitimides)

N,N' Alkane α,ω -diyl bis (trimellitimides) were synthesized by the method described earlier in section 2.2.1.a by using different diamino alkanes. Melting points are in good accordance with the literature (307) table 21.a.

2.3.1.b Diacid chlorides of N,N'alkane α,ω - diyl bis (trimellitimides) :

Diacid chlorides of above compounds were synthesized by the method described in section 1.1.2.b.

2.3.1.c Dicholesteryl imide esters :

The esterification was carried out by condensing appropriate diacid chloride with cholesterol following the procedure of Dave and Vora (310).

0.02 Mole of cholesterol and 0.01 mole of corresponding diacid chloride were taken in round bottom flask. To this, 20 ml N,N'dimethylaniline was added as solvent and reaction mixture was heated for two hours on an oil-bath between 120°C - 145°C. The whole mass was allowed to cool then poured in ice-cold water. The blue mass was filtered off and washed with acetone. The dicholesteryl imide esters were recrystallized from chloroform-acetone mixture till constant transition temperatures were obtained.

Transition temperatures, elemental analysis and IR spectral data are recorded in tables 21.b, 22 and 23, respectively.

2.4.1 Cholesteryl esters with phthalimide moiety.

Two model compounds (Fig.13K ,L) were synthesized with cholesterol and phathalimide moiety.

2.4.1.a Preparation of phathalimide derivatives :

N-substituted phthalimides were synthesized by the method described in section 2.2.1.a.

N-phthaloyl glycine (P.G.) M.P. 194 °C (Reported 192°C) (311)

N-phthaloyl-4-amino benzoic acid (PAB) M.P. >300 °C.

Elemental Analysis

	C(%)	H(%)	N(%)
Required	67.42	3.37	5.2
Found	67.84	3.62	5.04

2.4.1.b Preparation of acid chlorides of PG and PAB

Acid chlorides were prepared as described in the section 1.1.2.b by heating PG and PAB with excess of thionyl chloride.

2.4.1.c. Preparation of cholesteryl esters with mono imide linkages.

Equimolar proportion (0.01 mole) of cholesterol and appropriate acid chloride of PG and PAB were taken in round bottom flask. Freshly distilled N,N'-dimethyl aniline (20 ml) was added as solvent. The whole mass was heated in an oil-bath upto 120°C for two hours. After heating, the whole mass was added to ice cold water. The blue solid was filtered and washed with dilute alcohol or with acetone to remove N,N'-dimethyl aniline, washings gave white mass which was recrystallized from alcohol or chloroform-acetone mixture.

MT_1 Cholesteryl ester of N-phthaloyl glycine [Cholesteryl-2-amino (N-phthaloyl) acetate].

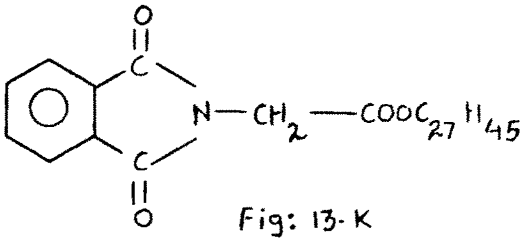


Fig: 13-K

MT_2 Cholesteryl ester of N-phthaloyl-4-amino benzoic acid [Cholesteryl 4-amino (N'-phthaloyl) benzoate]

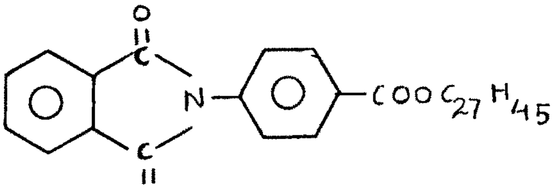


Fig: 13-L

Elemental Analysis

	Calculated (%)			Found(%)		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
MT_1	77.48	8.90	2.44	77.03	8.84	2.86
MT_2	79.37	8.35	2.20	78.98	8.81	2.04

IR spectral data (Bending & stretching vibrations) cm^{-1}

MT_1 2850, 1750, 1720, 1420, 1395, 1215, 1120, 960, 720. (Fig:47.a)

MT_2 2900, 2800, 1790, 1720, 1600, 1515, 1470, 1395, 1275, 1120, 880, 710. (Fig:47.a)

Transition Temperatures :

MT_1

$$\begin{tikzcd} K \arrow[rr, "166^\circ C"] & & Iso \arrow[dl, "91^\circ C"] \\ & S \arrow[ul, "87^\circ C"] & \end{tikzcd}$$

MT_2 $K \xrightarrow{210^\circ C} Ch \xrightarrow{322^\circ C} Iso\ (d)$

d - decomposition.

3.0 Optically Active Ester Amides (Chiral compounds).

3.1.1 Optically active S(+)-4(4'-β-methyl butoxy benzoyloxy)-4"-n-Alkoxy benzoyloxy benzanilides Series : VIII:

S(+)-2-methyl butyl bromide, 4(β-methyl butoxy) benzoic acid and 4(-β-methyl butoxy) benzoyl chloride were synthesized by methods described in section 1.1.3.1, 1.1.2.a and 1.1.2.b respectively.

3.1.2 Preparation of S(+)-4(β-methyl butoxy)-4'-hydroxy benzanilide.

p-Amino phenol (0.01 mole) was taken in dry pyridine (10 ml) and was added to cold S(+)-4(β-methyl butoxy) benzoyl chloride (0.01 mole). The whole mass was heated for an hour on a water bath and allowed to stand over night. It was acidified with cold 1:1 hydrochloric acid and the precipitates were filtered and washed with water. The resultant amido compound was crystallized from alcohol. M.P. 187°C.

Elemental Analysis

	C(%)	H(%)	N(%)
Required	72.24	7.02	4.68
Found	72.08	6.62	4.23

IR spectral data (Bending & stretching vibrations) Cm^{-1} 3350, 2950, 1730, 1650, 1600, 1510, 1410, 1260, 1190, 1160, 1070, 840, 760. Fig: 45-a

3.1.3.a. Preparation of 4-n-alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides.

4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the methods described in sections 1.1.2.a and 1.1.2.b, respectively.

3.1.3.b. Preparation of S(+) 4-(4'-β-methyl butoxy benzoyloxy)-4"-n-alkoxy benzoyloxy benzanilides.

Series : VIII:

S(+) 4-(β-methyl butoxy)-4'-hydroxy benzanilides (0.01 mole) was dissolved in dry pyridine (10 ml.) and was added slowly with stirring to cold 4-n-alkoxy benzoyl chloride (0.01 mole). The mixture was heated on water-bath with stirring for an hour and was allowed to stand over night. It was acidified with cold 1:1

hydrochloric acid, the precipitates were filtered, washed with water, dilute sodium hydroxide solution and water. The solid ester amides were recrystallized from acetic acid till constant transition temperatures were obtained. The transition temperatures, elemental analysis and IR spectral data are recorded in tables 24, 25 and 26, respectively.

4.0 Synthesis of New Mesogens with Typical structural units.

4.1 Synthesis of 4-Ethoxy-4'-carboxy-propoxy azobenzene. (MT_5)

4.1.1 Synthesis of potassium salt of 4-hydroxy-4'-ethoxy azobenzene :

4-Hydroxy -4'-ethoxy azobenzene was synthesized by the method described in section 2.2.1.b. Five gms of 4-hydroxy-4'-ethoxy azobenzene was treated with 10 ml. alcoholic potassium hydroxide solution. After that alcohol was evaporated and resulting solid was used as potassium salt of 4-hydroxy-4'-ethoxy azobenzene.

4.1.2 Synthesis of MT_5

Five gms. of potassium salt of 4-hydroxy-4'-ethoxy azobenzene and 7 ml of γ-butyrolactone were taken in a round bottom flask and heated in an oil-bath upto 160 C°(till whole mass solidified). Resulting solid was washed with alcohol, benzene and then was acidified with 1:1 HCl and washed with water. Solid was filtered and was recrystallized from benzene.

4.2. Synthesis of S(+) Ethyl 4(4'-β-methyl butoxy benzoyloxy) benzylidene-4"amino benzoate (MT_6)

4.2.1.a Synthesis of S(+) 4-β-methyl butoxy benzoic acid and its acid chloride.

S(+)4(β-methyl butoxy) benzoic acid and its acid chloride were synthesized by the methods described in section 1.1.3.1 and 1.1.3.2.

4.2.1.b Synthesis of S(+) 4(4'-β-methyl butoxy benzoyloxy)-benzaldehyde:

Above compound was synthesized by condensing S(+) 4-β-methyl butoxy benzoyl chloride with 4-hydroxy benzaldehyde.

4-Hydroxy benzaldehyde (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with stirring to cold acid chloride. The mixture was heated on water-bath for an hour and was allowed to stand over night. It was acidified with cold 1:1 hydrochloric acid. The precipitates were washed with water, cold dilute sodium hydroxide solution followed by water. Aldehyde was crystallized from alcohol.

4.2.2 Synthesis of Schiff base.

The equimolar quantities of S(+) 4(4'-β-methyl butoxy benzoyloxy) benzaldehyde (0.01 mole) and ethyl 4-amino benzoate (0.01 mole) were condensed by refluxing them in ethanol (25 ml) for two hours. The Schiff base was crystallized from ethanol.

Elemental Analysis

	Calculated			Found		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
MT_5	65.85	6.09	8.54	66.21	5.69	8.24
MT_6	73.20	6.32	3.05	73.54	6.12	2.84

Transition Temperatures

MT_5

$$\begin{tikzcd}
K \arrow[rr, "186^\circ C"] & & Iso \arrow[dl, "185^\circ c"] \\
& N \arrow[ul, "184^\circ c"] &
\end{tikzcd}$$

MT_6

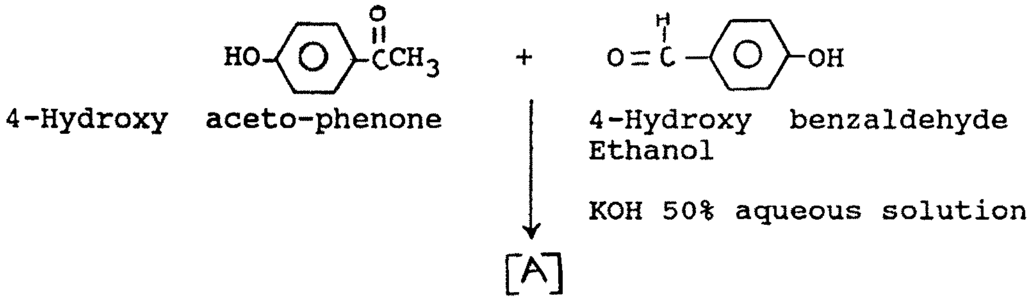
$$\begin{tikzcd}
K \arrow[rr, "147^\circ C"] & & S(A) \arrow[r, shift left, "170^\circ c"] \arrow[dl, "129^\circ c"] & \overset{*}{N} \arrow[l, shift left] \arrow[r, shift left, "206^\circ C"] & Iso \arrow[l, shift left] \\
& SC^{*} \arrow[ul, "127^\circ c"] & & &
\end{tikzcd}$$

5. Synthesis of fluorescent thermotropic polymers having chalcone repeating units in the main chain.

5.1.1 Synthesis of 4,4'-dihydroxy chalcone

Simplest method for the synthesis of chalcone involves Claisen-Schmidt reaction (312). This is the reaction of aceto-phenone with benzaldehyde in the presence of aqueous alkali, resulting in the formation of α, β unsaturated ketone (312).

4,4'-dihydroxy chalcone (4,4'-dihydroxy benzylidene acetophenone) was synthesized according to the hot condensation process described by Geissman and Clinton (313).

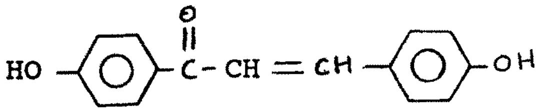


4-Hydroxy aceto-phenone

4-Hydroxy benzaldehyde
Ethanol

KOH 50% aqueous solution

[A]



[A] 4,4'-dihydroxy chalcone.

13.6 gms (0.1 mole) 4-hydroxy acetophenone and 13.2 gms (0.1 mole) 4-hydroxy benzaldehyde were dissolved in minimum amount of ethanol. 55 ml of 50% potassium hydroxide solution was added to the above solution. The flask was heated at 50 °C for twenty hours. The solution was acidified by cold 6N hydrochloric acid. Yellow crystalline solid separated, which was filtered and washed with water. It was recrystallized from aqueous ethanol. m.p. 204°C (Reported 204 °C) (313).

5.1.2 Synthesis of α,ω bis (4-carboxy phenoxy)-Oligo ethers

5.1.2.a Synthesis of dichlorides from dietheylene glycol, triethylene glycol and tetraethylene glycol (314,315).

Triethylamine (11 ml) was added in diethylene glycol (20 ml) which was taken in 200 ml round bottom flask. 40 ml. of thionyl chloride was added slowly with stirring during 3 to 4 hours. A white solid separated which partially dissolves as the reaction proceeds. The reaction mixture was refluxed for 40 minutes and was allowed to cool. Finally, it was poured into ice-cold water and extracted with chloroform. Chloroform layer was washed with water several times and dried over anhydrous calcium chloride. Chloroform was finally evaporated and resulting liquid obtained was dichloride.

Same way dichlorides from triethylene glycol and tetraethylene glycol were prepared. They were then further purified by distillation under reduced pressure.

5.1.2 b Synthesis of α,ω bis (4-carboxy phenoxy)-
oligo ethers.

Three diacids (DA- 1 to 3) were synthesized by the same method reported in the literature for synthesis of 1,2-Bis(4'-carboxyphenoxy)ethane. (316,317).

27.6 gms of p-hydroxy benzoic acid (0.2 mole) was dissolved in 100 ml 22.4% potassium hydroxide solution (0.4 mole) and 30 ml of alcohol in round bottom flask. 20.68 gms of appropriate dichloride (0.11 mole) was added to the flask and the whole mass was refluxed for 8-10 hours. Reaction mixture was then allowed to cool, then acidified with cold 1:1 hydrochloric acid. Solid mass obtained was filtered and washed with water and dilute alcohol. Diacids obtained were recrystallized several times from appropriate solvent till constant melting points were obtained.

Elemental Analysis

		C(%)	H(%)
DA I	Required	62.43	5.20
	Found	62.00	5.40
DA II	Required	61.54	5.64
	Found	61.05	5.74
DA III	Required	60.83	5.99
	Found	60.35	6.01

Melting points :

DA I 320 - 322 °C

DA II 228°C

DA III 177°C

IR spectra is given in figure : 50.a

5.1.2.c Synthesis of diacid chloride of diacids DA I-III.

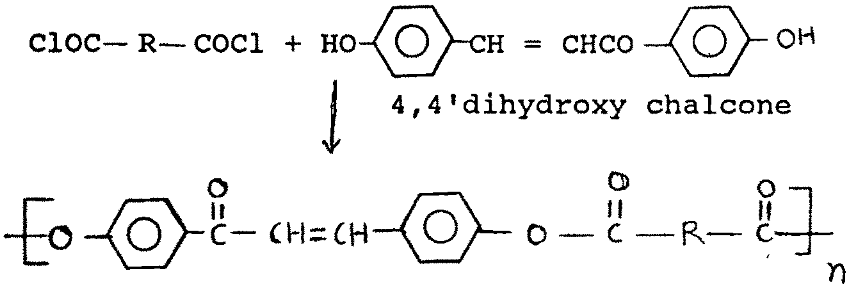
Respective diacid (0.005 mole) and excess of thionyl chloride in round bottom flask were taken and heated on a water-bath till the evolution of hydrochloric acid gas ceased. A few drops of pyridine was used as a catalyst. Excess of thionyl chloride was distilled off under reduced pressure. The diacid chloride was used in the reaction without further purification.

5.1.2.d Polycondensation of different diacidchlorides with 4,4'-dihydroxy chalcone.

Polycondensation was carried out to synthesize polyesters with 4,4'-dihydroxy chalcone repeating unit by solution polycondensation reaction using pyridine as a solvent.

(i) $$\text{HOOC—R—COOH} \xrightarrow[\text{Pyridine (Catalyst)}]{\text{SOCl}_2} \underset{\text{Diacid chloride}}{\text{ClOC—R—COCl}}$$

(ii)



The appropriate diacid chloride (0.005 mole) was dissolved in 10 ml dry pyridine and cooled to (5 - 10°C) in an ice-bath. The solution of 4,4'-dihydroxy chalcone (0.005 mole) in 5 ml dry pyridine was added to the acid chloride with constant stirring. The reaction mixture was guarded against moisture absorption. The temperature of mixture was allowed to rise to room temperature (28 - 30°C) and stirred for two more hours. It was finally poured in to ice-hydrochloric acid mixture and solid separated was filtered washed with water followed by alcohol to remove unreacted monomers. All the three polymers were purified by solvent non-solvent method. DMF was used as solvent and alcohol was used as non-solvent.

Elemental Analysis

		C(%)	H(%)
P_1	Required	72.00	4.73
	Found	68.41	4.93
P_2	Required	70.71	5.05
	Found	66.74	5.17
P_3	Required	69.59	5.33
	Found	68.43	5.34

Transition Temperatures:

Polymer	Transition Temperatures °C	
	Nematic	Isotroptic
P_1	162.0	201.0
P_2	77.0	139.0
P_3	—	76.0*

*Gives intense birefringence upto 106 °C, solidifies as glass.

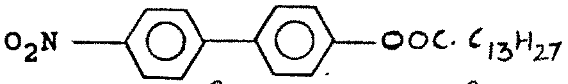
IR spectral data is recorded in table 27. Solubility behavior was also studied which is represented in table 28.

6.0 Mixed Mesomorphism :

Three binary systems comprised of following members were studied.

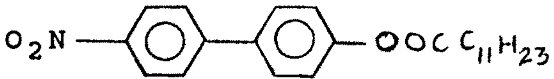
System : A

Component : a



$$K \xrightarrow{64.7\,^{\circ}C} S_A \xrightarrow{78.6\,^{\circ}C} Iso.$$

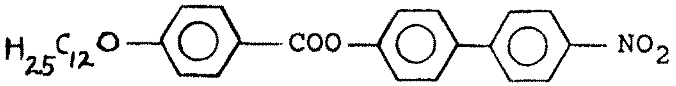
Component : b



$$K \xrightarrow{58.8\,^{\circ}C} S_A \xrightarrow{71.1\,^{\circ}C} Iso$$

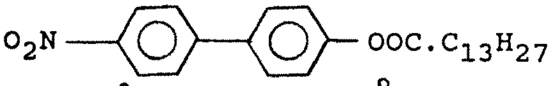
System - B

Component : a



$$K \xrightarrow{93\,^{\circ}C} S_A \xrightarrow{229\,^{\circ}C} Iso.$$

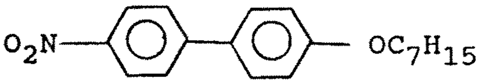
Component : b



$$K \xrightarrow{64.7\,^{\circ}C} S_A \xrightarrow{78.6\,^{\circ}C} Iso.$$

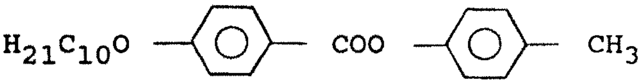
System - C

Component : a



$$\begin{tikzcd}
K \arrow[rr, "37.0\,^{\circ}C"] & & N \arrow[r, "40.0\,^{\circ}C"] \arrow[dl, "32.4\,^{\circ}C"] & Iso. \\
& S_m \arrow[ul] & &
\end{tikzcd}$$

Component : b (318)



$$\begin{tikzcd}
K \arrow[rr, "56.0^{\circ}C"] & & N \arrow[r, "60.5\,^{\circ}C"] \arrow[dl, "51.0\,^{\circ}C"] & \text{Iso.} \\
& S_m \arrow[ul] & &
\end{tikzcd}$$

Preparation of 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 content 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 by the microscopic method described below.

7.0 Determination of Transition Temperatures :

The transition temperatures were determined by using a polarizing microscope "Leitz Loborlux 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 made to cool 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, vaniline, p-anisal-p-phenetidine, 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 in to the specimen chamber of heating stage and the temperature was raised fast (5 °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°C per 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 a fresh. Compounds in which decomposition was observed, fresh slide was prepared each time for recording the correct transition temperatures.

8. Differential Scanning Calorimetry

The term "differential scanning calorimetry" has become a source of confusion in thermal analysis in the past several years. This confusion is understandable because at the present time there are two entirely different types of instruments which use the same name. These two instruments are different in designs of which one is actually a differential thermal analysis apparatus. The instruments are (a) differential scanning calorimeters which are heat flow recording instruments $(dg/dt)\Delta T=0$ (Perkin-Elmer, Deltatherm and others). (b) Differential scanning calorimeters which are differential temperature recording or DTA instruments $(\Delta T \neq 0)$ (Dupont, Stone, Fisher, Linses and others).

The term differential scanning calorimetry (DSC) was first used by Weston et al., (319) to describe the instrument technique developed by the Perkin-Elmer corporation. 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 mcal/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 an 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.

$$\text{Area} = K \cdot \Delta H_m$$

except that K is independent of temperature.

In the present work, calorimetric study was carried out for number of series on Mettler TA 4000 system to study the thermodynamic aspects of mesophases.

The data for enthalpy and entropy changes at different transitions are recorded in tables 29-34.

9. Viscometric study

Many methods for measurement of viscosity are reported (320,321) but those which make use of the capillary are well suited for our purpose. It is a unique property that dilute polymer solution has much higher viscosity than that of pure solvent.This is because, the presence of the dissolved macromolecules in the solution increases the energy dissipation in the laminiar flow over that for the pure solvent flow by the polymer segments. This large difference in viscosity and various functions derived there from are usually measured to produce information about the nature of micro structure of the polymer under study. It will be proper to define viscosity functions which are being estimated for this purpose.

The ratio of the viscosity of a dilute polymer solution (η) to that of a pure solvent (ηo) of equal density and of equal hydrokinetic pressure is approximately equal to the polymer solvent efflux-time ratio in the capillary viscometer. The latter ratio is designated as the relative viscosity (η_{rel}) or as the viscosity ratio (322).

$$\eta_{rel} = \frac{\eta}{\eta_0}$$

Because $[\eta_{rel}]$ approaches 1 and not zero as the solution becomes more dilute, the relative viscosity obviously does not denote the polymer's ability to increase the viscosity of the dispersion medium. To compensate for this discrepancy, the relative viscosity is diminished by 1; a new term results that is designated as the specific viscosity $[\eta_{sp}]$.

The specific viscosity relationship may be expressed by the equivalent form :

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

where η is the viscosity of the solution and η_0 that of the solvent.

The specific viscosity is not yet the intensive function derived because it increases with concentration. When the specific viscosity is divided by the concentration, expressed in a new quantity known as the reduced viscosity $[\eta_{red}]$, increment per unit solute concentration at given concentration or the viscosity number is obtained.

$$\eta_{red} = \eta_{sp}/C$$

where C is concentration, g/dl.

Viscosity may also be expressed by logarithmic relation (323), termed either the inherent viscosity $[\eta_{inh}]$ or the logarithmic viscosity number and is defined as

$$\eta_{inh} = \ln \eta_{rel}/C$$

where C is concentration in g/dl.

Ususally the reduced and inherent viscosities have different values for a given concentration, the latter being lower. Neither of this term is independent of concentration but they are usually linear functions of concentration in dilute solutions which can be extrapolated to a common intercept as the concentration approaches zero (324). The common limiting value of either of these functions in infinitely dilute solution is called the intrinsic viscosity $[\eta]$, the limiting viscosity number.

$$[\eta] = \left[\frac{\eta_{sp}}{C}\right]_{C \to 0}$$

The intrinsic viscosity is the intensive property which permits the determination of molecular weight and the solution dimension of macromolecules.

The linear relationship between the reduced viscosity and the concentration is expressed by the Huggin's equation (325). It is employed to estimate intrinsic viscosity.

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C$$

In the relation K' is Huggin's constant and is obtained by plotting η_{sp}/C versus C. The intercept and k' is calculated from the value of the slope which is equal to $k'[\eta]$.

Similarly Kraemer (323) relationship

$$\frac{\ln \eta_{rel}}{c} = [\eta] - k''[\eta]^2 c$$

can be applied to the experimental data and (η) can be determined from the plot of

$$\frac{\ln \eta_{rel}}{c} \text{ vs } c$$

The methods known as one point methods are also used to calculate intrinsic viscosity $[\eta]$ which avoids entirely the use of some constants such as K' and K". These one point methods have certain inbuilt limitations. They assume the linear behaviour between C and η_{sp}/C and/or $\ln \eta_{rel}$. Other modifications are also used which involve the constants. In the present study our main interest was the comparison of the viscosity data with the similar polymeric systems, hence, the following equation was used which is recommended for the one point method (326).

$$\eta = \frac{3 \ln \eta_{rel} + \eta_{sp}}{4c}$$

where C is concentration in g/dl.

9.1 Experimental

Mesogenic polymers were characterized by measuring their viscosity. Standardized suspended type Ubbelhode viscometer was used for the measurement of viscosity of the polymer samples in suitable solvents. The viscometer was washed with chromic acid, rinsed several times with distilled water and finally with acetone and dried.

Solvents used for preparing the polymer

solutions were purified by distillation before use.

Solvents were filtered through G-3 sintered glass funnel. The solvent was carefully introduced in the clean and dry viscometer held vertically in the thermostate and allowed to stand for ten minutes to attain the constant temperature. The average flow time was measured by taking the three independent readings.

The required amount of well powdered and dried polymer was dissolved in suitable solvent. The clear solution was filtered through G-3 sintered glass funnel. The solution thus prepared was carefully introduced in a viscometer held vertically in thermostate. It was allowed to attain the thermostate temperature. The flow time was measured atleast three times and the average flow time was noted. From the mean efflux time different viscosities were calculated and are summarized in table 35 a and 35 b.

10.0 IR Spectral study

IR spectral study is highly useful in the characterization of organic materials. Mesogenic materials were screened by using Nujol/KBr pellets in the range of infra-red frequency. IR spectra are given in fig. 17-a,c, 23, 28.a,b, 32, 36, 41.a,b, 45.a,b, 47.a,b, 50.a,b.

11.0 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 enhances this fluorescence, or that shift it to the visible region for examples - CH=CH-, CO-, -CH = CH-$\underset{\underset{O}{\|}}{C}$O-, p-phenylene, -CH=CH-COOH-,-CN are called fluorogens . Auxoflores include $-NH_2$ and -OH groups which enhance fluorescence.

Three polymers containing chalcone groups were studied for their fluorescent properties. The excitation and emission spectra were recorded for the compounds in solution,[solutions were prepared in N-methyl-2-pyrrolidone] by Schimadzu Rf 540 spectrophotofluorometer 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 polymers are represented in fig. 52.

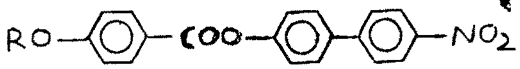
12.0 NMR spectra

NMR spectra of representative member of series

I-V and VII using $CdCl_3$ solvent for characterization of synthesized compounds were taken, NMR are given in fig.18.a, b, c, 29,33,41 c

Table : 3

4(4"-n-Alkoxy benzoyloxy)-4'-nitrobiphenyl



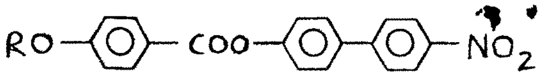
Transition Temperatures °C

Sr. No.	R n-alkyl group	Transition Temperatures °C Smectic A	Nematic	Isotropic
1.	Methyl	-	184	285
2.	Ethyl	-	166	284
3.	Propyl	-	150	266
4.	Butyl	(119)*	153	255
5.	Pentyl	128	170	244
6.	Hexyl	105	206	239
7.	Heptyl	103	220	234
8.	Octyl	101	229	233
9.	Decyl	93	-	231
10.	Dodecyl	93	-	229
11.	Tetradecyl	95	-	224
12.	Hexadecyl	98	-	220
13.	Octadecyl	101	-	215

( )* monotropic value.

Table : 4

4(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyl

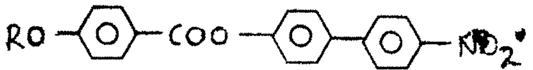


Elemental Analysis.

Sr. No.	R n-alkyl Group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1.	Methyl	68.77	4.30	4.01	68.39	4.68	3.67
2.	Ethyl	69.42	4.68	3.86	69.03	5.11	3.47
3.	Propyl	70.03	5.04	3.71	69.63	5.23	3.44
4.	Butyl	70.59	5.37	3.58	70.16	5.55	3.55
5.	Pentyl	71.11	5.68	3.46	70.70	5.78	3.07
6.	Hexyl	71.60	5.97	3.34	71.20	6.35	3.02
7.	Heptyl	72.06	6.24	3.23	71.65	6.63	3.44
8.	Octyl	72.48	6.49	3.13	72.06	6.66	3.26
9.	Decyl	73.26	6.95	2.95	72.81	7.30	2.82
10.	Dodecyl	73.96	7.35	2.78	73.84	7.64	3.18
11.	Tetradecyl	74.58	7.72	2.64	74.11	8.09	2.69
12.	Hexadecyl	75.13	8.05	2.50	74.69	8.30	2.43
13.	Octadecyl	75.64	8.35	2.38	75.51	8.58	2.45

Table : 5

4(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyl



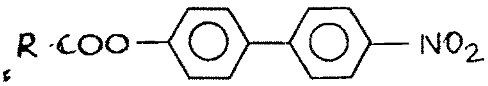
IR Spectra

Bending and Stretching Vibrations (cm^{-1})

R = Ethyl	R = n-Heptyl	R = n-Octadecyl
1730	2800	2800
1600	1730	1730
1515	1600	1600
1340	1510	1515
1260	1350	1350
1210	1255	1255
1165	1210	1210
1070	1165	1165
850	1070	1070
750	1005	1005
-	850	860
-	755	750

Table : 6

4-(n-Alkanoyloxy)-4'-nitrobiphenyl



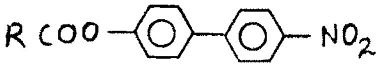
Transition Temperatures °C

Sr. No	R n-alkyl group	Transition Temperatures °C		
		Smectic	Nematic	Isotropic
1.	Hexyl	-	-	64.1
2.	Heptyl	-	(46.4)*	52.9
3.	Octyl	-	(52.7)	55.1
4.	Nonyl	(57.8)	(59.4)	63.2
5.	Undecyl	58.8	-	71.1
6.	Tridecyl	64.7	-	78.6
7.	Pentadecyl	73.5	-	81.9

( )* monotropic value.

Table : 7

4(n-Alkanoyloxy)4'-nitrobiphenyl

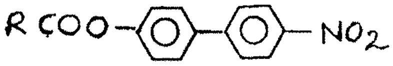


Elemental Analysis.

Sr. No.	R n-alkyl group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1.	Hexyl	69.72	6.42	4.28	70.12	6.70	4.09
2.	Heptyl	70.38	6.74	4.12	70.18	6.95	3.64
3.	Octyl	70.98	7.04	3.94	71.24	6.62	3.53
4.	Nonyl	71.54	7.32	3.79	71.18	7.22	3.74
5.	Undecyl	72.54	7.81	3.53	72.98	7.96	3.70
6.	Tridecyl	73.41	8.24	3.29	73.04	7.94	3.58
7.	Pentadecyl	74.17	8.61	3.09	73.79	8.23	3.17

Table : 8

4(n-alkanoyloxy)-4'-nitrobiphenyl



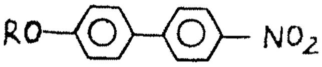
IR spectra

Bending and stretching Vibrations (cm^{-1})

R = n-Hexyl	R = n-Nonyl	R = n-Pentadecyl
2800	2800	2800
1740	1760	1760
1600	1600	1600
1520	1520	1520
1490	1490	1490
1345	1340	1350
1170	1140	1140
840	835	845
760	760	-

Table : 9

4-n-Alkoxy-4'-nitrobiphenyl



Transition Temperatures °C

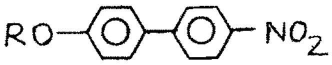
Sr. No.	R n-alkyl group	Transition Temperatures °C Smectic	Nematic	Isotropic
1.	Butyl	-	-	77.8
2.	+ Pentyl	-	-	57.8
3.	+ Hexyl	-	-	69.9
4.	+ Heptyl	(32.4)*	37.0	40.0
5.	+ Octyl	50.0	-	63.4
6.	Decyl	(69.5)	-	74.3
7.	Dodecyl	67.6	-	71.0
8.	Tetradecyl	(74.4)	-	75.8
9.	Hexadecyl	(79.8)	-	82.8
10.	Octadecyl	-	-	86.4

( )* Monotropic value.

\+ Reported by Gray (302,303)

Table : 10

4-n-Alkoxy-4'-nitrobiphenyl

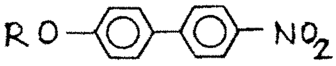


Elemental Analysis.

Sr. No.	R n-alkyl group	Calculated (%) C	H	N	Found (%) C	H	N
1.	Butyl	70.85	6.27	5.16	71.23	6.46	4.97
2.	Decyl	74.36	8.17	3.99	74.01	8.60	3.87
3.	Dodecyl	75.19	8.62	3.65	74.80	8.64	4.04
4.	Tetradecyl	75.91	9.00	3.41	76.33	9.41	3.83
5.	Hexadecyl	76.54	9.34	3.19	76.88	9.38	3.58
6.	Octadecyl	77.09	9.64	2.99	77.43	9.69	3.46

Table : 11

4-n-Alkoxy-4'-nitrobiphenyl

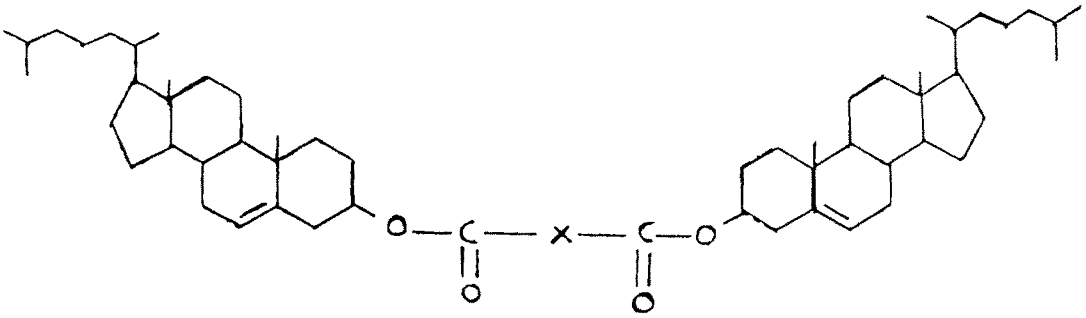


IR Spectra

Bending and stretching Vibrations (cm^{-1}).

R = n-Butyl	R = n-Decyl	R = n-Dodecyl
1600	2900	2800
1520	1600	1600
1350	1510	1515
1260	1330	1345
1205	1250	1255
1115	1180	1180
1050	1100	1100
1010	1030	1030
840	830	830
760	755	760

TABLE :- 12·a



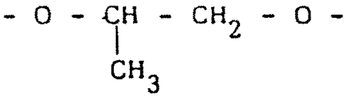
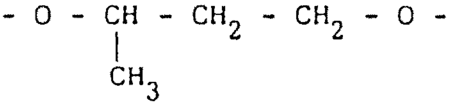
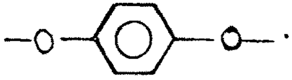
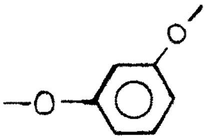
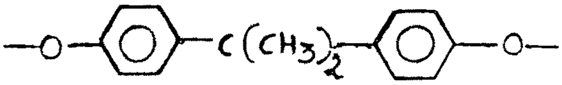
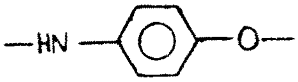
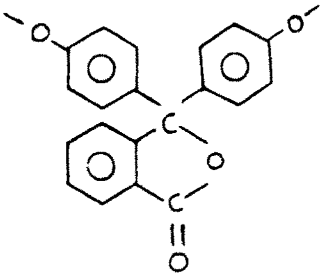
X	Code No.
$-(CH_2CH_2O)_2-O-$	CC - 1
$-O-(CH_2CH_2O)_2-CH_2CH_2-O-$	CC - 2
$-O-(CH_2CH_2O)_3-CH_2CH_2-O-$	CC - 3
$-O-CH_2-CH_2-O-$	CC - 4
 $-O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-O-$	CC - 5
$-O-CH_2-CH_2-CH_2-CH_2-O-$	CC - 6
 $-O-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-O-$	CC - 7
	CC - 8
	CC - 9
	CC - 10
	CC - 11
	CC - 12
$-O-(CH_2-CH_2-O)_n-$	CC - 13

Table : 12.b

Dicholesteryl Carbonate with Rigid and Flexible spacers.

$H_{45}C_{27}OOCO-X-OCOOC_{27}H_{45}$

Transition Temperatures. °C

Sr. No.	Code No.	Transition Temperatures °C			
		$K_1 - K_2$	Smectic	Cholesteric	Isotropic
1.	CC-1	-	-	(126)*	160
2.	CC-2	-	-	172	252
3.	CC-3	-	(90)	(111)	122
4.	CC-4	126	-	177	178
5.	CC-5	-	-	160	188
6.	CC-6	-	-	180	254
7.	CC-7	-	-	166	204
8.	CC-8	174	-	222	264(d)
9.	CC-9	-	-	-	230
10.	CC-10	-	-	166	197
11.	CC-11	-	-	169	262(d)
12.	CC-12	-	-	-	235
13.	CC-13	-	(+)	-	106

( )* Monotropic value.

(d) Decomposition

(+) From room temperature.

Table : 13

Dicholesteryl Carbonates with Rigid and Flexible Spacers.

$H_{45}C_{27}OOCO-X-OCOOC_{27}H_{45}$

Elemental Analysis

Sr. No.	Code No.	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1.	CC-1	77.42	10.54	-	77.31	10.67	-
2.	CC-2	76.39	10.47	-	76.01	10.03	-
3.	CC-3	75.44	10.41	-	75.21	10.89	-
4.	CC-4	78.55	10.61	-	78.00	10.21	
5.	CC-5	78.66	10.66	-	78.38	11.04	-
6.	CC-6	78.77	10.72	-	78.36	11.09	-
7.	CC-7	78.77	10.72	-	78.32	11.01	-
8.	CC-8	79.66	10.06	-	79.18	10.50	-
9.	CC-9	79.66	10.06		79.91	10.49	-
10.	CC-10	80.99	9.83	-	80.83	10.33	-
11.	CC-11	79.74	10.18	1.5	80.12	10.55	1.06
12.	CC-12	79.86	8.93	-	79.44	9.28	-
13.	CC-13	73.51	7.95	-	69.20	8.37	-

Table : 14

Dicholesteryl Carbonates with Rigid and Flexible Spacers.

$H_{45}C_{27}OOCO-X-OCOOC_{27}H_{45}$

IR Spectral Data

Bending and Stretching Vibrations (cm^{-1})

CC-1	CC-5	CC-10	CC - 12
2950	2900	2900	2900
1745	1740	1755	1770
1480	1465	1505	1505
1370-80	1370-80	1465	1465
1270	1250-80	1370-80	1370-80
1145	990	1250-60	1250
1005	775	1010	840
800		940	750-60
		830	
		780	

Table : 15

Dicholesteryl Carbamates with Rigid and Flexible Spacers.

$H_{45}C_{27}OOCHN-R-NHCOOC_{27}H_{45}$

Transition Temperatures °C

Sr. No.	R	Transiton Temperatures °C		
		Smectic	Cholesteric	I sotropic
1.	$-(CH_2)_2-$	(215)*	-	233
2.	$-(CH_2)_3-$	195	-	210
3.	$-(CH_2)_4-$	161	-	209
4.	$-(CH_2)_5-$	151	-	199
5.	$-(CH_2)_6-$	169	-	198
6.	$-(CH_2)_8-$	(134)	152	177
7.		-	271	284

( )* Monotropic values

Table : 16

Dicholesteryl Carbamates with Rigid and Flexible Spacers.

$H_{45}C_{27}OOCHN-R-NHCOOC_{27}H_{45}$

Elemental Analysis

Sr. No.	R	Calculated (%) C	H	N	Found (%) C	H	N
1.	$-(CH_2)_2-$	78.33	10.86	3.17	77.91	10.63	3.56
2.	$-(CH_2)_3-$	78.84	10.91	3.12	78.52	10.73	3.63
3.	$-(CH_2)_4-$	78.95	10.96	3.07	78.51	11.01	3.59
4.	$-(CH_2)_5-$	79.05	11.02	3.02	78.61	10.93	3.41
5.	$-(CH_2)_6-$	79.15	11.06	2.98	78.86	11.37	3.4
6.	$-(CH_2)_8-$	79.34	11.16	2.89	79.78	11.53	2.73
7.		79.83	10.30	3.00	79.62	10.53	3.19

Table : 17

Dicholesteryl Carbamates with Rigid and Flexible Spacers

$H_{45}C_{27}OOCHN-R-NHCOOC_{27}H_{45}$

IR spectra

Bending and stretching Vibrations (cm^{-1})

R = $-(CH_2)_4-$	R = $-(CH_2)_6-$	R= $-C_6H_4-$
3340	3350	3450
2915	2925	2950
1650	1700	1710
1480	1530	1545
1420	1470	1410
1200	1255	1310
1090	1140	1200
990	1010	1060
750	780	840

Table : 18

Cholesteryl 4-n-alkoxy phenyl carbamates

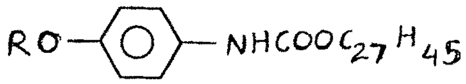
Transition Temperatures °C.

Sr. No.	R n-alkyl group	Transition Temperatures °C		
		Smectic	Cholesteric	Isotropic
1.	Methyl	(98)*	139	189
2.	Ethyl	-	144	180
3.	Propyl	(149)	150	171
4.	Butyl	170	172	174
5.	Pentyl	157	-	174
6.	Hexyl	133	-	177
7.	Heptyl	130	-	173
8.	Octyl	124	-	173
9.	Decyl	118	-	171
10.	Dodecyl	115	-	169
11.	Tetradecyl	122	-	165
12.	Hexadecyl	114	-	165
13.	Octadecyl	111	-	156

( )* Monotropic values.

Table : 19

Cholesteryl 4-n – alkoxy phenyl carbamates



Elemental Analysis

Sr. No.	R n-alkyl group	Calculated (%) C	H	N	Found (%) C	H	N
1.	Methyl	78.56	9.91	2.62	78.29	9.99	3.02
2.	Ethyl	78.69	10.02	2.55	78.47	10.12	3.14
3.	Propyl	78.86	10.12	2.49	78.47	10.03	2.83
4.	Butyl	79.03	10.23	2.43	78.61	9.78	2.31
5.	Pentyl	79.19	10.32	2.37	79.34	10.58	2.71
6.	Hexyl	79.34	10.41	2.31	78.93	10.50	2.75
7.	Heptyl	79.48	10.56	2.26	79.11	10.41	2.73
8.	Octyl	79.62	10.58	2.21	79.18	10.58	2.60
9.	Decyl	79.88	10.74	2.12	79.41	10.30	2.47
10.	Dodecyl	80.12	10.88	2.03	79.66	10.70	2.41
11.	Tetradecyl	80.33	11.02	1.95	80.28	11.08	2.17
12.	Hexadecyl	80.54	11.14	1.88	80.08	10.75	1.73
13.	Octadecyl	80.72	11.25	1.81	80.81	11.30	2.25

Table : 20

Cholesteryl 4-n-alkoxy phenyl carbamates

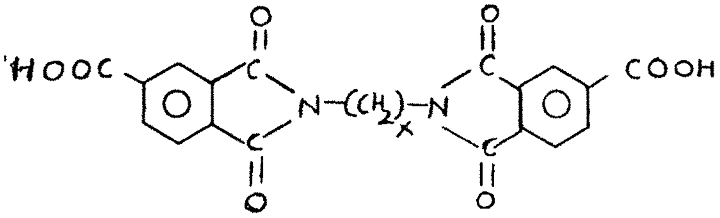
IR spectral Data

Bending and stretching Vibrations (cm^{-1})

R = ~~n-~~Methyl	R = n-Dodecyl	R = n-Octadecyl
3450	3495	3400
2950	2940	2950
1735	1680	1710
1520	1480	1530
1210	1160	1220
1050	1005	1050
825	-	830

Table : 21.a

N-N'Alkane-∝,ω -Diylbis (Trimellitimides)

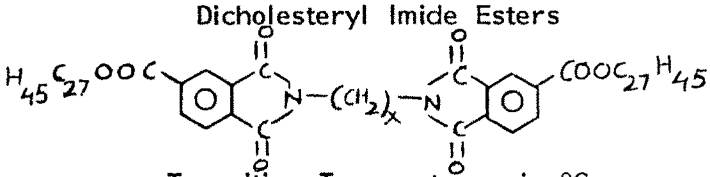


Melting points °C

Sr. No.	x No. of CH_2 units	Melting points °C
1	2	> 310
2	3	> 310
3	4	343 - 345
4	5	244 - 248
5	6	321 - 322
6	8	242 - 243

Table : 21.b

Dicholesteryl Imide Esters



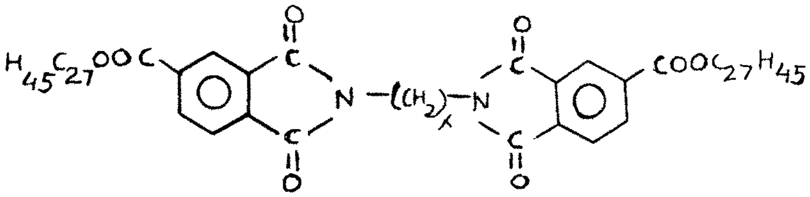
Transition Temperatures in °C

Sr. No.	x No. of CH_2 units	Transition Temperatures °C Cholesteric	Isotropic
1.	2	-	294 (d)
2.	3	221	247 (d)
3.	4	256	277 (d)
4.	5	221	259 (d)
5.	6	224	264 (d)
6.	8	215	262 (d)

d - Decomposition

Table : 22

Dicholesteryl Imide Esters.

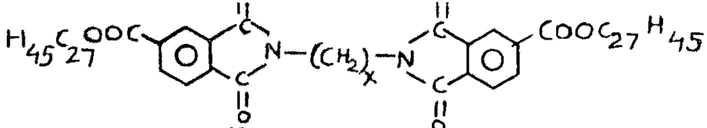


Elemental Analysis

Sr. No.	x No. of CH_2Units	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1.	2	77.62	8.74	2.45	77.34	8.52	2.62
2.	3	77.72	8.80	2.42	77.37	9.17	2.28
3.	4	77.75	8.87	2.39	77.32	8.82	2.78
4.	5	77.91	8.94	2.36	78.32	9.06	2.63
5.	6	78.00	9.00	2.33	78.41	9.31	2.34
6.	8	78.17	9.12	2.28	78.60	9.52	2.03

Table : 23

Dicholesteryl Imide Esters



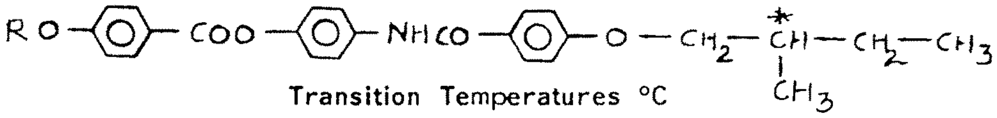
IR spectral Data

Bending and stretching Vibrations (cm^{-1})

x = 5	x = 8
2850	2850
1780	1780
1720	1730
1400	1400
1370	1380
1290	1245
1255	1185
1190	1090
1095	735
730	

Table : 24

S(+)4(4'-β-Methyl butoxy benzoyloxy)-4"-n-alkoxy benzoyloxy benzanilides.



Transition Temperatures °C

Sr. No.	R n-alkyl group	Transition Temperatures °C Smectic-B	Smectic-C	Smectic-A	Cholesteric	Isotropic
1	Propyl	-	-	-	**	194**
2	Butyl	-	-	-	(202)*	206
3	Pentyl	-	-	-	196	204
4	Hexyl	-	-	-	189	200
5	Heptyl	-	-	-	185	200
6	Octyl	-	-	-	183	197
7	Decyl	-	-	-	190	196
8	Dodecyl	183	-	(186)	187	190
9.	Tetradecyl	-	167	170	-	188
1(	Hexadecyl	-	171	176	-	186 (d)
1	Octadecyl	-	174	182	-	186

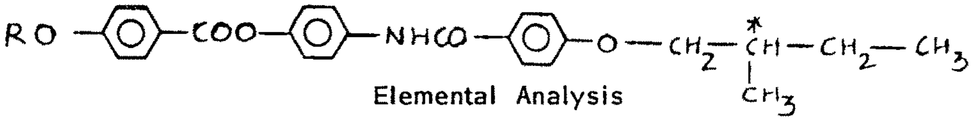
( )* Monotropic values.

(d) Decomposition

** : Monotropic Ch phase is seen in thin section of slide.

Table : 25

S(+)4(4'-B-Methylbutoxy benzoyloxy)-4"-n-alkoxy benzoyloxy benzanilide

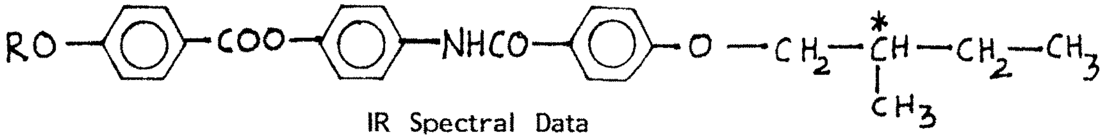


Elemental Analysis

Sr. No.	R n-alkyl group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1.	Propyl	72.88	6.72	3.04	72.46	6.31	3.18
2.	Butyl	73.26	6.95	2.95	72.86	6.82	3.34
3.	Pentyl	73.62	7.16	2.86	73.31	6.78	2.86
4.	Hexyl	73.96	7.36	2.78	73.58	7.04	3.12
5.	Heptyl	74.27	7.54	2.71	74.66	7.56	2.34
6.	Octyl	74.58	7.72	2.64	74.13	7.32	2.64
7.	Decyl	75.13	8.05	2.50	74.73	8.16	2.87
8.	Dodecyl	75.64	8.35	2.38	75.20	8.14	2.51
9.	Tetradecyl	76.09	8.62	2.28	75.69	8.31	2.12
10.	Hexadecyl	76.52	8.86	2.18	76.16	8.44	2.09
11.	Octadecyl	76.90	9.04	2.08	76.53	9.41	2.35

Table : 26

S(+)4(4'-β-Methyl butoxy benzoyloxy)-4"-n-alkoxybenzoyloxy benzanilides.



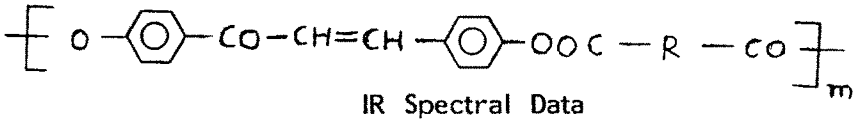
IR Spectral Data

Bending and stretching Vibrations (cm^{-1})

R = Hexyl	R = Dodecyl	R = Hexadecyl
3375	3400	3400
2950	2940	2925
1730	1730	1725
1650	1660	1650
1600	1610	1600
1515	1520	1515
1260	1265	1260
1200	1205	1200
1165	1180	1175
1075	1080	1080
840	850	850
760	765	760

Table : 27

Polymers



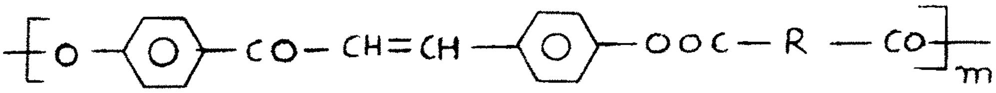
IR Spectral Data

Bending and Stretching Vibrations (cm^{-1})

P_1	P_2
3430	3400
1680-90	1730
1615	1600
1565	1510
1450	1420
1210	1260
1160	1210
1110	1160
1000-1020	1050
705	755

Table : 28

Solubility Behaviour of Polymers



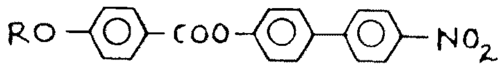
Solvents	P_1	P_2	P_3
Ethyl acetate	(-)	(-)	(-)
Benzene	(-)	(-)	(-)
Xylene	(-)	(-)	(-)
THF	(-)	(-)	(-)
DMF	(+)	(+)	(+)
DMSO	(-)	(-)	(+)
N-Methyl 2-Pyrrolidone	(+)	(+)	(+)

Soluble : (+)

Insoluble : (-)

Table : 29

4(4"-n-Alkoxy benzoyloxy) 4'-n-nitrobiphenyl



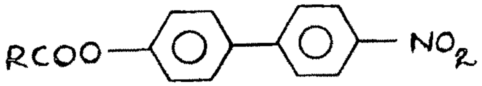
Calorimetric Data

Sr. No.	R n-alkyl group	Transition state	Weight in Mg.	Heating rate °C/min.	Peak Temp. °C (microscopic reading)	H J/g	S J//g.k.	Total S J/g.k.
1.	Methyl	K-N	2.9	10	184.4 (184)	149.09	0.326	
		N-Iso	-	-	278.9 (285)	7.30	0.013	0.339
2.	Ethyl	K-N	3.1	10	163.0 (166)	113.62	0.261	
		N-Iso			272.5 (284)	10.83	0.019	0.280
3.	Propyl	K_1-K_2	6.9	10	91.8	4.10	0.011	
		K_2-N			147.6 (150)	98.10	0.233	0.238
		N-Iso			259.1 (266)	2.37	0.005	
4.	Butyl	K-N	7.6	10	153.5 (153)	103.24	0.242	0.248
		N-Iso			247.7 (255)	3.26	0.006	
		Iso-N			243.3 (254)	3.68	0.007	
		N-S	-		117.6 (117)	6.43	0.016	
		S-K			104.0 (107)	20.90	0.056	
5.	Pentyl	K-S	13.5	20	129.8 (128)	95.58	0.237	
		S-N			168.3 (170)	0.22	0.0005	0.242
		N-Iso			241.1 (244)	1.84	0.004	

Sr. No.	R n-alkyl group	Transition state	Weight in Mg.	Heating rate °C/min.	Peak Temp. °C (microscopic reading)	H J/g	S J/g.k.	Total S J/g.k.
6.	Hexyl	K-S	8.6	10	117.9 (105)	80.01	0.205	0.211
		S-N			202.4 (206)	0.50	0.001	
		N-Iso			234.7 (239)	2.62	0.005	
7.	Heptyl	K-S	7.1	10	109.6 (103)	109.60	0.286	0.295
		S-N			218.4 (226)	2.58	0.005	
		N-Iso			231.7 (234)	1.83	0.004	
8.	Octyl	K_1-K_2	6.8	10	100.0 (97)	-	-	0.235
		K_2-S			104.6 (101)	86.43	0.229	
		S-N			227.4 (229)	1.93	0.004	
		N-Iso			235.2 (233)	1.11	0.002	
9.	Decyl	K_1-K_2	5.0	10	90.0 (91)	-	--	0.152
		K_2-S			93.0 (93)	47.78	0.131	
		S-Iso			229.5 (231)	10.39	0.021	
10.	Dodecyl	K_1-K_2	3.6	10	91.0 (91)	-	-	0.279
		K_2-S			94.3 (93)	94.06	0.256	
		S-Iso			226.0 (229)	11.56	0.023	
11.	Tetradecyl	K-S .	5.5	10	96.6 (95)	97.54	0.264	0.288
		S-Iso.			220.9 (224)	11.93	0.024	
12.	Hexadecyl	K-S	3.7	10	99.8 (98)	107.71	0.289	0.315
		S-Iso			217.6 (220)	12.81	0.026	
13.	Octadecyl	K-S	4.0	10	101.7 (101)	141.27	0.377	0.407
		S-Iso			213.2 (210)	14.58	0.030	

Table : 30

4(n-Alkanoyloxy)4'-Nitrobiphenyl

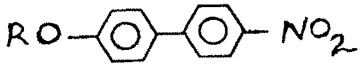


Calorimetric Data

Sr. No.	R n-alkyl group	Transition state	Weight in Mg.	Heating rate °C/min.	Peak Temp.°C (microscopic reading)	H J/g	S J/g.k.
1.	Heptyl	K-Iso.	3.5	2	52.2 (52.9)	73.15	0.225
		Iso-N	-	-	44.9 (46.4)	0.76	0.002
2.	Octyl	K-Iso	3.5	5	54.5 (55.1)	96.16	0.294
		Iso-N	-	-	48.7 (52.7)	0.50	0.002
3.	Nonyl	K-Iso.	4.3	5	62.5 (63.2)	84.51	0.252
		Iso-N	-	-	57.8 (59.4)	1.02	0.003
		N-S	-	-	55.6 (57.8)	0.48	0.001
4.	Undecyl	K-S	2.7	2	58.0 (58.8)	89.35	0.269
		Sm-Iso	-	-	71.0 (71.1)	6.90	0.020
5.	Tridecyl	K-S	3.6	10	67.4 (64.7)	120.15	0.371
		S-Iso	-	-	77.9 (78.6)	10.20	0.029
6.	Pentadecyl	K-Sm	3.0	10	74.4 (73.5)	102.81	0.296
		S-Iso	-	-	84.2 (81.9)	10.76	0.030

Table : 31

4-n-Alkoxy-4'-nitrobiphenyl



Calorimetric Data

Sr. No.	R n-alkyl group	Transition state.	Weight in Mg.	Heating Rate °C/Min	Peak Temp.°C (Miscroscopic reading)	H J/g.	S J/g.k.
1.	Octyl	K-S	5.5	2	50.0 (50.3)	66.82	0.207
		S-Iso.	-	-	56.1 (63.4)	1.98	0.006
2.	Decyl	K-Iso.	2.8	5	70.9 (74.3)	120.86	0.351
		Iso-S	-	-	65.6 (69.5)	6.85	0.020
3.	Dodecyl	K-S	2.4	2	67.4 (67.0)	98.73	0.290
		S-Iso.	-	-	70.4 (71.0)	6.38	0.019
4.	Tetradecyl	K-Iso.	2.1	5	74.1 (75.8)	112.64	0.324
		Iso-S	-	-	73.0 (74.4)	7.63	0.022
5.	Hexadecyl	K-Iso	2.3	5	78.8 (82.8)	132.87	0.377
		Iso-S	-	-	76.7 (79.8)	10.67	0.031

TABLE - 32

Dicholesteryl Carbonate with Rigid and Flexible Spacers

$H_{45}\,C_{27}\,OOCO - X - OCOO - C_{27}\,H_{45}$

Code No.	Transition State	Transition Tempature^{0}C (Microscopic reading)	Δ H J/G	Δ S J/G.K.
CC-1	K_1-K_2	145	-	-
	K_2-I	162(160)	-	-
	I-Ch	122.7(126)	3.227	0.008
CC-2	K -Ch	179.7(172.0)	41.781	0.092
	Ch-Iso	263.2(252.0)	0.918	0.002
CC-3	K-Iso	121(122)	52.575	0.133
	Iso-Ch	100.9(111)	1.117	0.003
	Ch-Sm	(90)	-	-
CC-4	K_1-K_2	103.7	0.451	0.001
	K_2-K_3	122.2(126)	22.841	0.058
	K_3-Iso	169 6(178)	40.096	0:09
	Iso-Ch	160.7(177)	1.449	0.003
CC-5	K-Ch	148.5(160)	30.103	0.0714
	Ch-Iso	190.5(188)	0.532	0.001
CC-6	K-Ch	181.4(180)	67.399	0.149
	Ch-Iso	252.4(254)	2.317	0.004
CC-7	K-Ch	170.7(166)	44.239	0.099
	Ch-Iso	— (204)	-	-
CC-8	K_1-K_2	163.3(174)	15.828	0.036
	K_2-Ch	236.1(222)	23.083	0.045
	Ch-Iso	266.8(264)	3.847	0.007
CC-10	K-Ch	165.9(166)	Total ΔH	—
	Ch-Iso	189.4(197)	30.775	—
CC-11	K-Ch	165.7(169)	23.66	0.054
	Ch-Iso	263.1(262)	02.609	0 005

TABLE - 33

Cholesteryl 4-n-Alkoxy Phenyl Carbamates

$RO-C_6H_4\ NHCOO\ C_{27}\ H_{45}$

Sr. No.	R n-alkyl	Weight mg	Transition state	Heating rate °C/min	Peak Temp °C (Microscopic reading)	ΔH J/g	ΔS J/g°K	Total ΔS J/g°k
1.	Methyl	16.2	K - Ch	15	140.9(139)	56.765	0.137	
			Ch - Iso		189.6(189)	2.023	0.004	0.141
2.	Ethyl	13.3	K - Ch	10	139.7(144)	39.764	0.096	
			Ch - Iso		183.4(180)	1.209	0.002	0.096
3.	Propyl	18.7	K1 - K2	15	106.9(120)	8.891	0.023	
			K2 - Ch		152.6(150)	39.690	0.093	
			Ch - Iso		176.6(171)	0.736	0.002	0.118
			Iso - Ch		166.8(168)	1.470	0.003	
			Ch - Sm		138.8(149)	0.909	0.002	
4.	Butyl	15.7	● K - Iso	10	173.6(174)	68.433	0.153	0.153
			- Iso - Ch		168.4( )	0.812	0.002	
			Ch - S		158.2( )	3.0550	0.007	
			S - K		116( )	34 407	0.088	
5.	Pentyl	17.9	K - S	15	159 (157)	46.967	0.108	
			S - Iso		172.7(174)	5.807	0.013	0.121
6.	Hexyl	18.0	K1 - K2	10	123(122)	–	–	
			K2 - S		134.9(133)	77.059	0.189	
			S - Iso		176(177)	25 89	0.057	0.246
7.	Heptyl	18.0	K1 - K2	10	105.3(101)	33.792	0.089	
			K2 - S		126.8(130)	10.403	0.026	
			S - Iso		165.4(173)	7.959	0.018	0.133
8.	Octyl	14.7	K1 - K2	15	109.3(107)	14.025	0.036	
			K2 - S		125.1(124)	19.172	0.048	
			S - Iso		173.5(173)	10.377	0.023	0.023
9	Decyl	14.7	K - S	15	119.0(118).	56.640	0.144	
			S - Iso		170.7(171)	12.505	0.028	0.172

10	Dodecyl	18.1	K1 - K2	15	94.9( )	1.859	0.005	
			K2 - S		117.1(115)	42.812	0.109	
			S - Iso		168.5(169)	11 437	0.026	0.14
11	Tetradecyl	12.4	K - S	15	123.8(122)	53.274	0.134	
			S - Iso		163.1(165)	11.233	0.026	0.16
12	Hexadecyl	13.6	K - S	15	116.4(114)	43.322	0.111	
			S - Iso		158.5(165)	6 7221	0 016	0.127
13	Octadecyl	15.8	K1 - K2	15	102.6(103)	9.438	0.025	
			K2 - S		112.9(112)	29.600	0.077	
			S - Iso		153.8(156)	10 724	0.025	0.127

● Enantiotropic Ch & Sm phases were not detected by DSC

TABLE - 34

S(+)-4-(4′-β-Methyl butoxy benzoyloxy)-4″-n-Alkoxy benzoyloxy benzanilides

Calorimetric Data

Sr. No.	R n-alkyl	Weight mg	Heating °C/min	Transition state	Peak Temp°C (Microscopic reading)	ΔH J/g	ΔS J/g.k
1.	Butyl	10	10	K-I	204.2(206)	75.251	0 157
				I-Ch	197.1(202)	1.454	0.003
				Ch-K	190.4(194)	53.968	0.116
2.	Pentyl	13	5	K-I	197.7(204)	69.476	0.147
				I-Ch	198.4(202)	2.026	0.004
				Ch-K	187.3(186)	54.851	0.119
3.	Hexyl	13	5	K-I	190 6(200)	121.94	0.263
				I-Ch	184 2(197)	3.261	0.007
				Ch-K	177.1(183)	77.660	0.173
4.	Octyl	10	5	K-Ch	186.7(183)	50.630	0.11
				Ch-I	195.4(197)	2.054	0.004
5.	Decyl	12	5	K_1-K_2	164.1(163)	4.916	0.012
				K_2-Ch	190.0(190)	50.08	0.108
				Ch-I	196.8(196)	3.422	0.007
6.	Dodecyl	12	10	K-I	186.1(190)	77.155	0.168
				I-Ch	185.3(189)	1 078	0.002
				Ch-K	181.8	70.971	0.156
7.	Hexadecyl	13	8	K-I	171.4	41.549	0.093
				I-K	166.1	36 226	0.088

Table : 35 a.

Viscosity Data of Polymers

Solvent : DMF for P_1, N-methyl 2-Pyrrolidene for P_2 and P_3.

Temperature : 26°C

Concentration : 0.5 %

Viscosity	P_1	P_2	P_3
ηrelative	1.084	1.0814	1.066
ηspecific	0.084	0.0813	0.066
ηreduced	0.168	0.163	0.132
ηinherent	0.161	0.156	0.128
ηintrinsic	0.162	0.158	0.129

Table : 35 b

Viscosity Data of Polymers.

Solvents : DMF for P_1, N-Methyl 2-Pyrrolidone for P_3.

Temperature 26 °C

Polymer	Concentration %	η_{rel}	$\eta_{sp.}$	$\eta_{intrinsic}$ (dl/gm) One Pt. method	$\eta_{intrinsic}$ (dl/gm) Graphical
P_1	1.00	1.185	0.185	0.173	
	0.75	1.133	0.133	0.169	0.16
	0.50	1.084	0.084	0.162	
	0.25	1.038	0.038	0.149	
P_3	1.00	1.147	0.147	0.139	
	0.75	1.104	0.104	0.134	0.125
	0.50	1.066	0.066	0.129	
	0.25	1.032	0.032	0.126	