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Synthesis and characterization of homologous series with chiral (*S*)-1-methylpropyl terminal substituent

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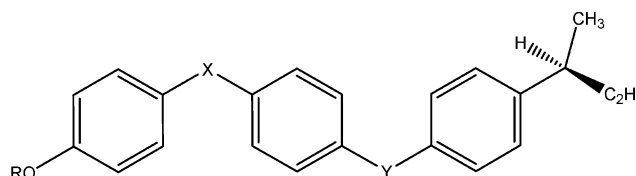
Homologous series of liquid crystalline azoesters and azomethine esters consisting of a (*S*)-1-methylpropyl group attached in one of the terminal positions have been synthesized and thermally characterized. All twenty-four derivatives from both series, namely, the 4-(4-*n*-alkoxybenzoyloxy)-4'-1-(*S*)-methylpropylazobenzenes and 4-(4-*n*-alkoxybenzoyloxy)benzylidene-4'-1-(*S*)-methylpropylanilines exhibit mesomorphism. The lower members of the homologous series show a chiral nematic phase while the higher members show smectic C*, smectic A as well as chiral nematic mesophases. The homologues have been characterized using IR, NMR and UV-Visible, spectroscopies, X-ray diffraction and DSC. Their mesomorphic properties are compared with those of structurally related homologous series.

1. Introduction

Azo dye liquid crystals have attracted much attention for potential use in optical storage applications because of their easy availability, reasonable photo-fatigue resistance and the marked transformation of their molecular shape upon *E* to *Z* photoisomerization [1–7]. Azo dyes have a reasonable dichroic ratio for reflective liquid crystal devices which are of considerable interest owing to their remarkably lower power consumption [8]. Three-layered G–H (guest–host) systems with subtractive colour mixing of yellow, magenta and cyan are expected to be used in developing full colour reflective displays [9, 10]. Also, the chiral smectic C phase of liquid crystals possessing ferroelectric or anti-ferroelectric characteristics have a permanent polarization without the presence of an external electric field and can improve the response time of liquid crystalline modulators [11]. Therefore, chiral azo dye liquid crystals are the focus of much research, given those highly desirable properties.

Earlier we have reported a number of non-chiral homologous series which have been found to exhibit mesomorphism which has been attributed to their molecular geometry and molecular forces arising therefrom [12, 13]; however, a great deal of interest has grown in recent years in ferroelectric liquid crystals in terms of both fundamental and applied research [14, 15]. Therefore, in the present study we have synthesized

two homologous series, with a terminal chiral *sec*.butyl group and azo/azomethine groups as one of the central linkages for series I/II. Their mesomorphic properties are studied in order to obtain a better understanding of the relationship between molecular structure and the appearance of the SmC* phase. The general molecular structure of the series is:



Series I: X = –COO–, Y = –N=N–; series II: X = –COO–, Y = –CN=N–.

2. Experimental

2.1. Materials

4-(*S*)-1-Methylpropylaniline, 4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, *n*-alkyl bromides and all other chemicals were obtained from Fluka, BDH, Merck or Aldrich, and used as received.

2.2. Characterization

The microanalysis of the homologues was carried out using a Perkin-Elmer 240C Elemental Analyser. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer, ¹H NMR spectra on a Bruker 300 spectrophotometer. The textures of the liquid crystalline

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phases and transition temperatures were studied using a Leitz Laborlux 12 POL polarizing microscope provided with a Kofler heating stage. The thermal properties of the homologues were investigated by differential scanning calorimetry (DSC Mettler TA-4000 system).

2.3. Synthesis of series I: 4-(4-*n*-alkoxybenzoyloxy)-phenylazo-4'-1-(*S*)-methylpropylbenzenes (Figure 1)

2.3.1. 4-Hydroxyphenylazo-4'-1-(*S*)-methylpropylbenzene

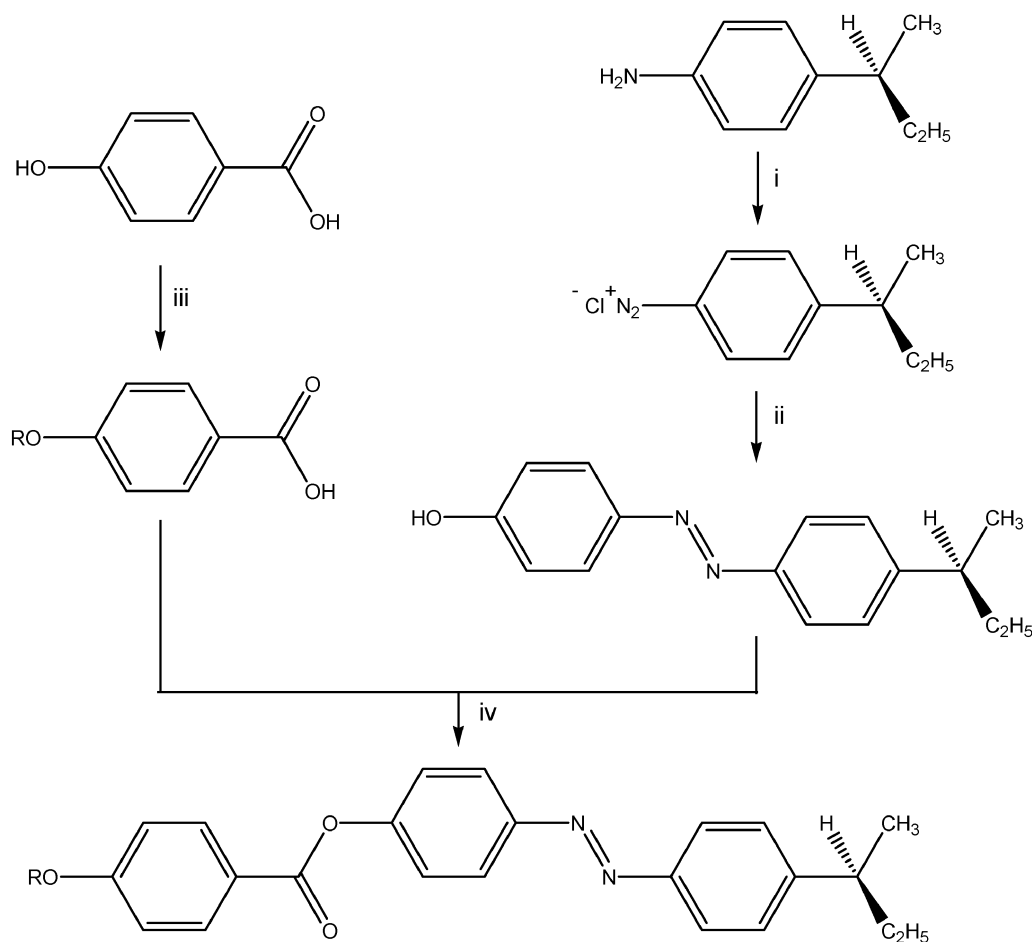
The dye was prepared by a known procedure in two steps [16].

2.3.2. 4-*n*-Alkoxybenzoic acids. These were synthesized by the method of Dave *et al.* [17].

2.3.3. 4-(4-*n*-Alkoxybenzoyloxy)phenylazo-4'-1-(*S*)-methylpropylbenzenes.

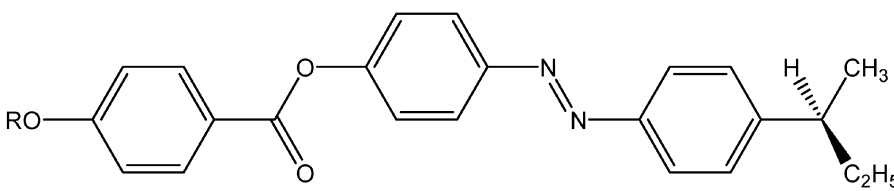
N,N' -Dicyclohexylcarbodiimide (DCC, 1.58 mmol) was dissolved in a solution

of 4-hydroxyphenylazo-4'-1-(*S*)-methylpropylbenzene (1.44 mmol), 4-*n*-alkoxybenzoic acid (1.44 mmol) and 4-(dimethylamino)pyridine (DMAP, 0.14 mmol) in 20 ml dry dichloromethane (DCM, 20 ml) and the solution stirred at room temperature for 12 h under a condenser fitted with a silica gel guard tube. The precipitated material was filtered and the filtrate concentrated. The residue was washed successively with water, saturated aqueous NaHCO_3 and 5 % aqueous NaOH to remove any unreacted acid and phenol. The precipitate was again washed with water and the final product recrystallized from ethanol until constant transition temperatures were obtained; these are recorded in table 1. The elemental analysis of all the compounds were found to be satisfactory and are recorded in table 2 FTIR (KBr cm^{-1}): 3041($\gamma\text{C-H}$, aromatic), 2945($\gamma\text{C-H}$, asym. $-\text{CH}_3$), 2922($\gamma\text{C-H}$, symm. $-\text{CH}_3$), 2869, 2851($\gamma\text{C-H}$, methylene), 1731($\gamma\text{C=O}$, ester), 1607, 1510, 1465($\gamma\text{C=C}$, aromatic),

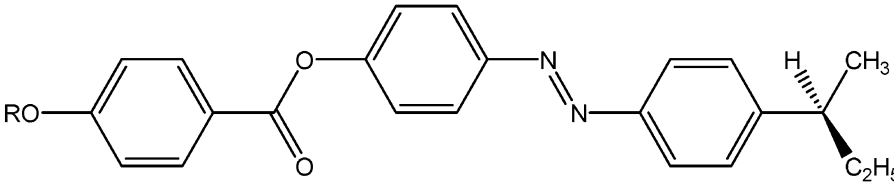


Where $R = \text{C}_n\text{H}_{2n+1}$ $n = 1$ to 8, 10, 12, 14 and 16

Figure 1. Synthetic route for series I compounds. (i) NaNO_2 , HCl, $0-5^\circ\text{C}$ (ii) aq. NaOH, Phenol $0-10^\circ\text{C}$, HCl (iii) *n*-Alkyl bromide, KOH, Alcohol (iv) DCC, DMAP, CH_2Cl_2 (DCM).

Table 1. Transition temperatures of 4-(4-*n*-alkoxybenzoyloxy)phenylazo-4'-1-(*S*)-methylpropylbenzenes (series I).


<i>R</i> = <i>n</i> -alkyl group	Transition temperatures/°C						I		
	Cr	SmC*	SmA	N*	I				
Methyl	•	117	—	—	—	•	175	•	
Ethyl	•	120	—	—	—	•	188	•	
Propyl	•	119	—	—	—	•	168	•	
Butyl	•	114	—	—	—	•	172	•	
Pentyl	•	98	—	—	—	•	158	•	
Hexyl	•	88	—	—	—	•	155	•	
Heptyl	•	73	—	—	—	•	152	•	
Octyl	•	65	—	—	—	•	151	•	
Decyl	•	68	•	75	•	82	•	143	•
Dodecyl	•	75	•	94	•	110	•	142	•
Tetradecyl	•	67	•	99	•	115	•	139	•
Hexadecyl	•	63	•	100	•	116	•	127	•

Table 2. Elemental analysis for 4-(4-*n*-alkoxybenzoyloxy)phenylazo-4'-1-(*S*)-methylpropylbenzenes (series I).


<i>R</i> = <i>n</i> -alkyl group	Calculated/%			Found/%		
	C	H	N	C	H	N
Methyl	74.22	6.18	7.22	74.20	6.15	7.25
Ethyl	74.62	6.46	6.96	74.61	6.45	6.98
Propyl	75.00	6.73	6.73	74.96	6.72	6.74
Butyl	75.34	6.97	6.51	75.31	6.95	6.52
Pentyl	75.67	7.20	6.30	75.65	7.19	6.32
Hexyl	75.98	7.42	6.11	75.98	7.41	6.12
Heptyl	76.27	7.62	5.93	76.25	7.60	5.95
Octyl	76.54	7.82	5.76	76.51	7.81	5.78
Decyl	77.04	8.17	5.44	77.03	8.15	5.45
Dodecyl	77.44	8.48	5.16	77.44	8.45	5.17
Tetradecyl	77.89	8.77	4.91	77.85	8.74	4.93
Hexadecyl	78.26	9.03	4.68	78.22	9.01	4.50

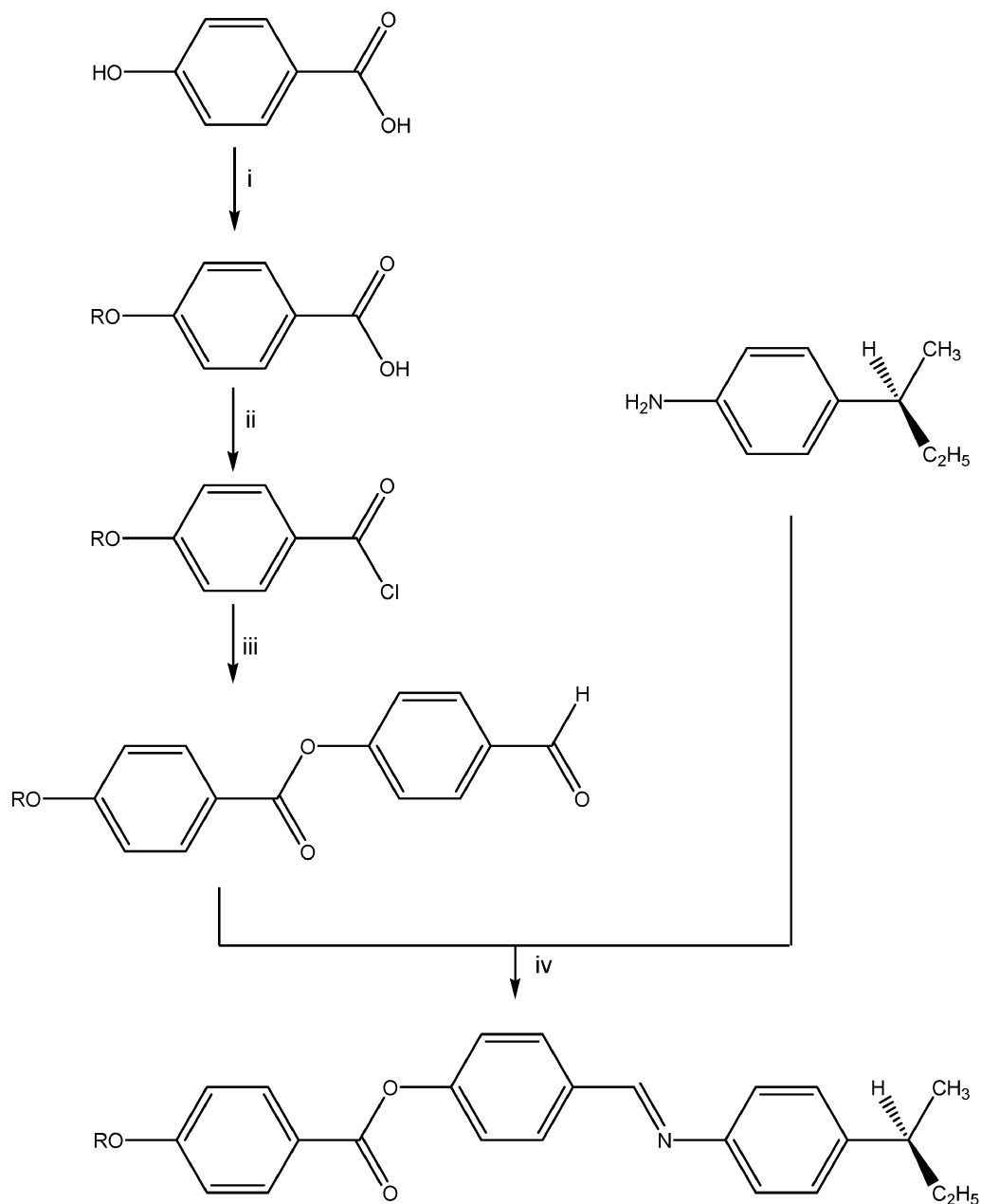
1421(γ N=N), 1265(γ C-O-C, asymm.), 1065(γ C-O-C, symm). H NMR (CDCl₃, 300 MHz, δ ppm, standard TMS): *Decyl* 0.8(t, 3H, -CH₃), 0.9(t, 3H, -CH₃), 1.25(d, 3H, -CH(CH₃)-CH₂-), 1.3-1.6(m, 14H, alkyl

chain), 1.7(quintet, 2H, -CH₂-CH₂-O-), 1.8(m, 2H, -CH-CH₂-CH₃), 2.7(m, 1H, -CH-CH₂-CH₃), 4.1(t, 2H, -CH₂-CH₂-O-), 7.0(d, 2H, H⁶), 7.35(2 × d, 4H, H⁴, H⁵), 7.8(d, 2H, H²), 7.95(d, 2H, H¹), 8.15(d, 2H, H³);

Dodecyl 0.85(t, 3H, $-\text{CH}_3$), 0.9(t, 3H, $-\text{CH}_3$), 1.3(d, 3H, $-\text{CH}(\text{CH}_3)-\text{CH}_2-$), 1.35–1.6(m, 18H, alkyl chain), 1.65(quintet, 2H, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.8(m, 2H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 2.7(m, 1H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 4.0(t, 2H, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 7.0(d, 2H, H^6), 7.35(2 × d, 4H, H^4, H^5), 7.85(d, 2H, H^2), 7.95(d, 2H, H^1), 8.15(d, 2H, H^3).

2.4. Synthesis of series II: 4-(4-*n*-alkoxybenzoyloxy)-benzylidene-4'-1-(*s*)-methylpropylanilines (Figure 2)

2.4.1. 4-*n*-Alkoxybenzoic acids; 4-*n*-alkoxybenzoyl-chlorides. These were synthesized by the method of Dave *et al.* [17].



Where $\text{R} = \text{C}_n\text{H}_{2n+1}$ $n = 1$ to 8, 10, 12, 14 and 16

Figure 2. Synthetic route for series II compounds. (i) *n*-Alkyl bromide, Alcohol, KOH (ii) SOCl_2 (iii) dry Pyridine, 4-Hydroxy benzoic acid, HCl (iv) Ethanol, glacial Acetic acid.

2.4.2. 4-(4-*n*-Alkoxybenzoyloxy)benzaldehydes. These were synthesized by the reported method [18].

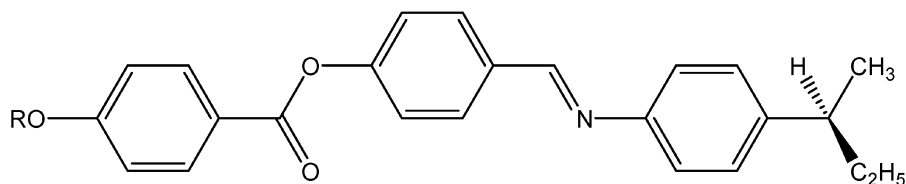
2.4.3. 4-(4-*n*-Alkoxybenzoyloxy)benzylidene-4'-1-(s)-methylpropylanilines. These were synthesized by taking equimolar quantities of appropriate 4-(4-*n*-alkoxybenzoyloxy)benzaldehydes and 4-1-(S)-methylpropylaniline in the minimum quantity of ethanol with a few drops of glacial acetic acid and refluxing the mixture for a period of 4 to 6 h. The products were filtered, dried and recrystallized from ethanol until constant transition temperatures were obtained; these are recorded in table 3. The elemental analysis of all the compounds were found to be satisfactory and are recorded in table 4. FTIR (Nujol, KBr pellets cm^{-1}): 3053($\gamma\text{C-H}$, aromatic), 2954($\gamma\text{C-H}$, asym. $-\text{CH}_3$), 2920($\gamma\text{C-H}$, symm. $-\text{CH}_3$), 2871, 2850($\gamma\text{C-H}$, methylene), 1731($\gamma\text{C=O}$, ester), 1608, 1512, 1471($\gamma\text{C=C}$, aromatic), 1421($\gamma\text{N=N}$), 1267($\gamma\text{C-O-C}$, asymm.), 1069($\gamma\text{C-O-C}$, symm). H NMR (CDCl_3 , 200 MHz, δ ppm, standard TMS): *Propyl* 0.85(t, 3H, $-\text{CH}_3$), 1.1(t, 3H, $-\text{CH}_3$), 1.25(d, 3H, $-\text{CH}(\text{CH}_3)-\text{CH}_2-$), 1.6(quintet, 2H, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.85(m, 2H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 2.65(m, 1H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 4.0(t, 2H, $-\text{CH}_2-\text{CH}_2-\text{O}-$), 7.0(d, ^2H , H^6), 7.25(d, 2H, H^5), 7.35(d, 2H, H^2), 7.4(d, 2H, H^4), 8.00(d, 2H, H^1), 8.15(d, 2H, H^3), 8.5(s, 1H, $-\text{CH}=\text{N}-$).

3. Results and discussion

All twelve homologues of series I (with azo as one of the central linkages), from methyl to hexadecyl are liquid crystalline in nature (table 1). The homologues with short *n*-alkyl chains ($n=1$ to 8 exhibit the chiral nematic (cholesteric) phase; however, higher derivatives from $n=10$ to 16, show in addition the ferroelectric smectic C^* phase along with the smectic A phase. The dependence of transition temperatures on the number of carbon atoms in the *n*-alkyl chain is shown in figure 3. The N^*-I transition temperatures decrease on two curves giving an alternation as the parity of the chain is varied but which merge at the C_6 derivative. The SmC^*-SmA and $\text{SmA}-\text{N}^*$ transition curves increase as the series is ascended. The $\text{Cr}-\text{M}$ transition temperatures rise initially from the C_1 to C_2 members and then fall up to the C_8 homologue; they then rise again upto the C_{12} homologue and fall till the last C_{16} homologue. The mesophase range of the chiral smectic phase increases at the expense of the chiral N^* phase. The SmC^* phase shows a broken focal-conic texture whereas the chiral nematic phase shows a plane texture; the SmA phase shows a focal-conic fan-shaped texture. The series shows mesophase ranges between 49 and 86°C .

All twelve homologues of series II (with azomethine as one of the central linkages) are liquid crystalline in

Table 3. Transition temperatures of 4-(4-*n*-alkoxybenzoyloxy)benzylidene-4'-1-(S)-methylpropylanilines (series II).

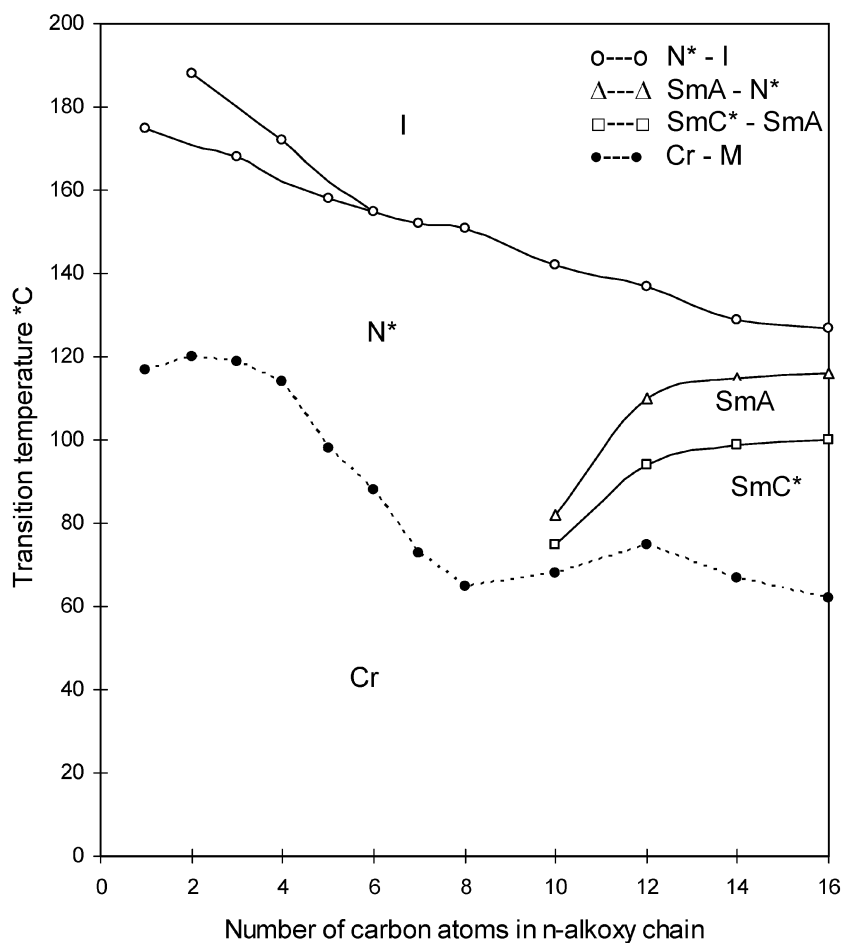


<i>R</i> = <i>n</i> -alkyl group	Transition temperatures/ $^\circ\text{C}$							
	Cr		SmC^*		SmA	N^*	I	
Methyl	•	104	—	—	—	•	181	•
Ethyl	•	111	—	—	—	•	187	•
Propyl	•	128	—	—	—	•	173	•
Butyl	•	114	—	—	—	•	173	•
Pentyl	•	(95) ^a	—	—	•	107	164	•
Hexyl	•	99	—	—	•	106	163	•
Heptyl	•	93.5	—	—	•	112	158	•
Octyl	•	64	•	85	•	120	154	•
Decyl	•	62	•	90	•	127	150	•
Dodecyl	•	59	•	95	•	136	145	•
Tetradecyl	•	69	•	100	•	137	140	•
Hexadecyl	•	54	•	105	—	—	133	•

^aValue in parenthesis indicates monotropic transition.

Table 4. Elemental analysis for 4-(4-*n*-alkoxybenzoyloxy)benzylidene-4'-1-(*S*)-methylpropylanilines (series II).

<i>n</i> -alkyl group	Calculated/%			Found/%			
	C	H	N	C	H	N	N
Methyl	77.51	6.45	3.61	77.50	6.44	3.63	
Ethyl	77.80	6.73	3.49	77.78	6.72	3.50	
Propyl	78.07	6.98	3.37	78.04	6.95	3.39	
Butyl	78.32	7.22	3.26	78.28	7.19	3.28	
Pentyl	78.55	7.44	3.16	78.55	7.41	3.18	
Hexyl	78.77	7.65	3.06	78.75	7.64	3.08	
Heptyl	78.98	7.85	2.97	78.96	7.82	2.98	
Octyl	79.17	8.04	2.88	79.15	8.03	2.90	
Decyl	79.53	8.38	2.72	79.51	8.36	2.75	
Dodecyl	79.85	8.68	2.58	79.84	8.66	2.59	
Tetradecyl	80.14	8.96	2.46	80.13	8.95	2.48	
Hexadecyl	80.40	9.21	2.34	80.39	9.20	2.35	

Figure 3. Transition temperatures versus the number of carbon atoms in the *n*-alkoxy chain for 4-(4-*n*-alkoxybenzoyloxy)-phenylazo-4'-1-(*S*)-methylpropylbenzenes (series I).

nature (table 3); the chiral nematic phase is exhibited from the methyl homologue and remains up to the tetradecyl homologue. The smectic A phase commences from the C₅ homologue as a monotropic phase, which becomes enantiotropic in the hexyl homologue; however in the C₈ to C₁₆ members, an additional smectic C* phase is observed. The chiral nematic phase is not seen in the hexadecyl homologue, which exhibits only SmC* and SmA phases. The dependence of the transition temperatures on the number of carbon atoms in the *n*-alkyl chain is shown in figure 4. The N*-I transition temperatures fall on distinct curves giving on alternation as the parity of the chain is varied; the curves merge at the C₇ member. The SmA-N* transition curve shows a rising tendency as the series is ascended; similarly the SmC*-SmA transition curve also shows a rising tendency from the C₈ to C₁₆ homologue. The series exhibits mesophase ranges between 45 and 90°C. The textures of the SmC*, SmA and N* phase are similar to those seen for series I.

The enthalpy changes associated with the phase transitions for some of the members of each of series were measured using differential scanning calorimetry (DSC); the data are listed in table 5, and figure 5 shows the DSC traces. The DSC curves confirm the transition temperatures measured using polarizing microscopy.

The photochemical properties of some of the homologues of series I were evaluated in chloroform solution; they show an absorption maximum at about 360 nm (figure 6) and weak shoulders at about 440 nm which are related to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, of the azobenzene *trans*-configuration. The C₁₂ homologue of series I exhibits a *trans-cis* photoreactive process with successive decrease in the absorbance maximum at 360 nm and increase in the maximum at 440 nm on irradiation with 360 nm light; the photochemical process is shown in figure 6. In the early stage of the irradiation (0.5 min) the absorbance at 360 nm decreased steadily, indicating simple *trans-cis* isomerization. However, with further irradiation

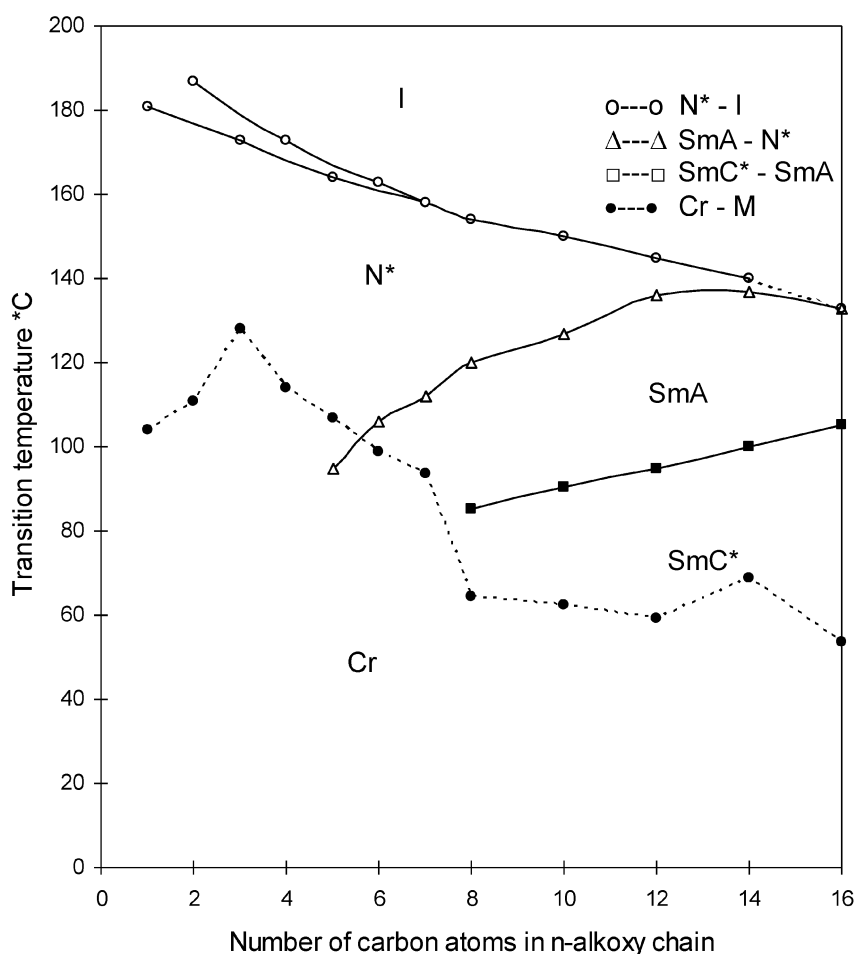


Figure 4. Transition temperatures versus the number of carbon atoms in the *n*-alkoxy chain for 4-(4-*n*-alkoxybenzoyloxy)-benzylidene-4'-1-(*S*)-methylpropylanilines (series II).

Table 5. DSC data for selected homologues of series I and II compounds.

Series	Homologues of the series	Heating rate/ $^{\circ}\text{C min}^{-1}$	Transition temperature/ $^{\circ}\text{C}$		$\Delta H/\text{J g}^{-1}$	$\Delta S/\text{J g}^{-1} \text{K}^{-1}$
I	7	10	Cr-N*	73.30	38.20	0.11
			N*-I	152.00	1.90	0.0044
I	10	10	Cr-SmC*	67.70	70.30	0.206
			SmC*-SmA	74.50	2.80	0.0081
			SmA-N*	81.80	—	
			N*-I	142.00	1.70	0.0041
I	16	10	Cr-SmC*	62.70	61.00	0.181
			SmC*-SmA	100.00	2.30	0.0061
			SmA-N*	116.00	—	
			N*-I	126.90	1.60	0.004
II	7	10	Cr-SmC*	93.5	46.60	0.1271
			SmC*-N*	113.00	2.60	0.0067
			N*-I	159.00	1.80	0.0042
II	8	10	Cr-SmC*	64.00	70.36	0.208
			SmC*-SmA	85.40	0.80	0.0022
			SmA-N*	122.00	1.20	0.0030
			N*-I	154.00	1.60	0.0037
II	10	10	Cr-SmC*	62.60	44.30	0.132
			SmC*-SmA	90.40	—	
			SmA-N*	127.00	—	
			N*-I	150.60	1.80	0.0042
II	14	10	Cr-SmC*	69.00	83.10	0.2429
			SmC*-SmA	100.00	1.70	0.0045
			SmA-N*	137.20	0.80	0.0019
			N*-I	139.90	2.00	0.0048
II	16	10	Cr-SmC*	53.80	38.20	0.1168
			SmC*-SmA	105.40	1.50	0.0039
			SmA-I	132.40	1.90	0.0046

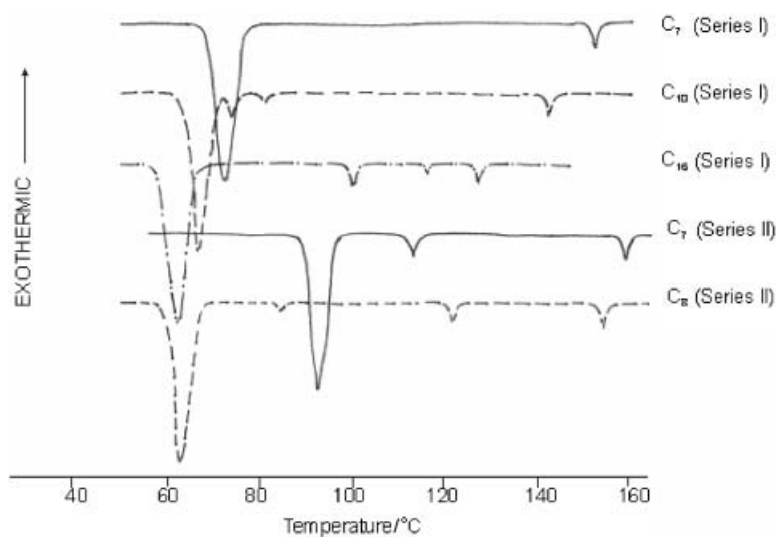


Figure 5. DSC thermograms of mesogens of series I and series II.

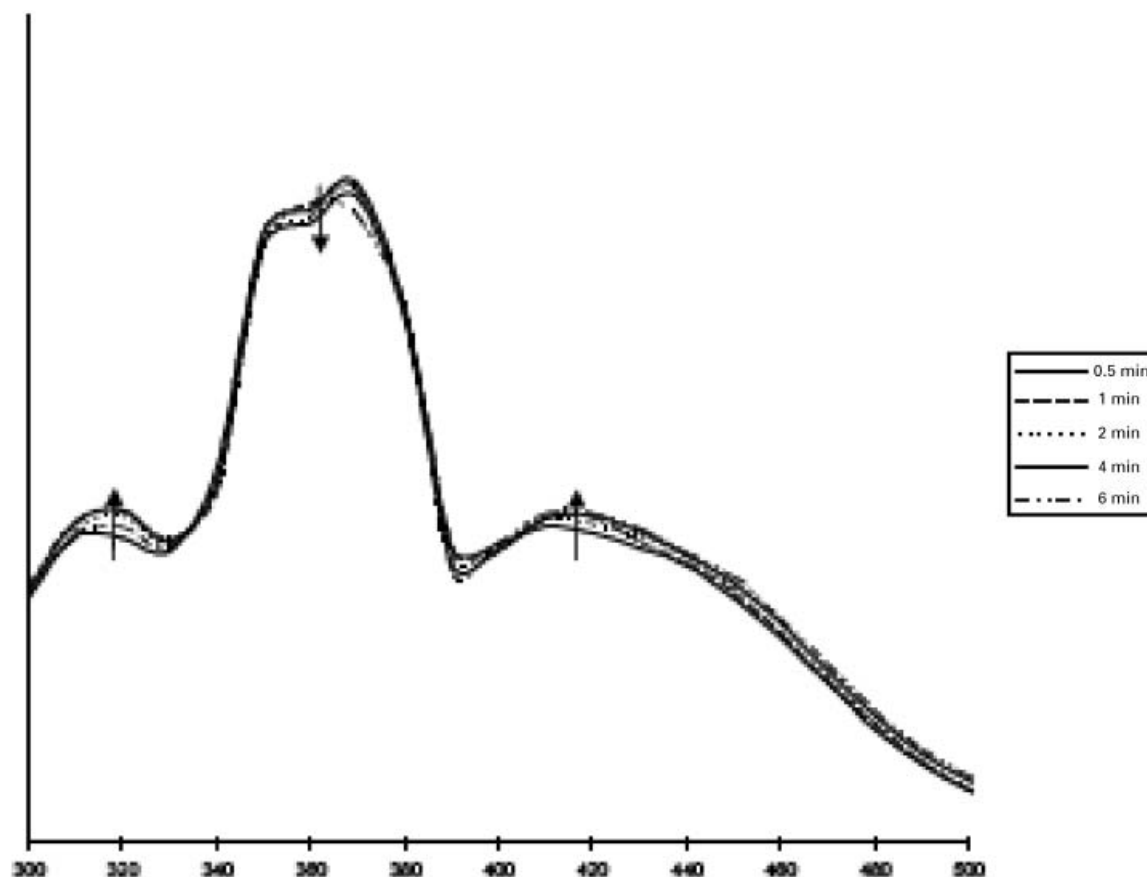


Figure 6. UV-visible spectra of the C_{12} homologue of series I.

(0.5–2 min), the absorbance increased smoothly, and the spectra became much broader. These processes may be related to the reorganization of the azobenzene chromophores during the *trans-cis*-isomerisation due to insufficient free volume caused by the strong H-aggregation and perpendicular alignment of the chromophores.

The N^* , SmA and SmC^* phases of the compounds were also confirmed by X-ray diffraction. For example, figure 7 presents the temperature-dependent X-ray diffractograms obtained from a powder sample of compound C_{12} (series I) at 85 and 100°C. A weak, broad reflection in the wide angle (associated with lateral packing) and a sharp reflection at low angle (associated with smectic layers) are seen clearly. Curve (a) presents a diffuse reflection at about 5.3 Å, which corresponds to the lateral spacing of two mesogenic groups. A sharp first order reflection at 33.64 Å and second order reflection at 17.51 Å are seen, which correspond to the smectic layers. The optical texture of compound C_{12} (series I) reveals a simple fan-shaped texture in this temperature range. Both results are consistent with a smectic A phase. When the temperature was decreased from 95 to 90°C, the layer spacing of

the first order reflection decreased from 33.64 to 32.92 Å, see curve (b). On further cooling from 90 to 85°C, the layer spacing of the first order reflection continued to decrease from 32.92 to 32.42 Å, see curve (c). This presents strong evidence for the formation of the tilted chiral smectic phase. These results are also in agreement with the optical microscopic observation which reveals a broken fan texture. The data obtained indicate that in the SmC^* phase the layer thickness decreases gradually as the temperature decreases.

The mesophase ranges of the two series under study are compared with structurally similar series. Table 6 shows the average mesophase range for the homologous series selected for comparative study. The molecular geometry of the series under comparison (figure 8) shows that all the series are structurally similar, consisting of three aromatic cores, ester and azo or azomethine central linkages, and *n*-alkoxy as one of the terminal groups. Molecules of series I, A and B differ only in one of their terminal moieties; series I has the *sec*-butyl group, series A has the *n*-butyl group and series B has the *iso*-propyl group. Similarly, series II and C differ only in one of their terminal groups; series II

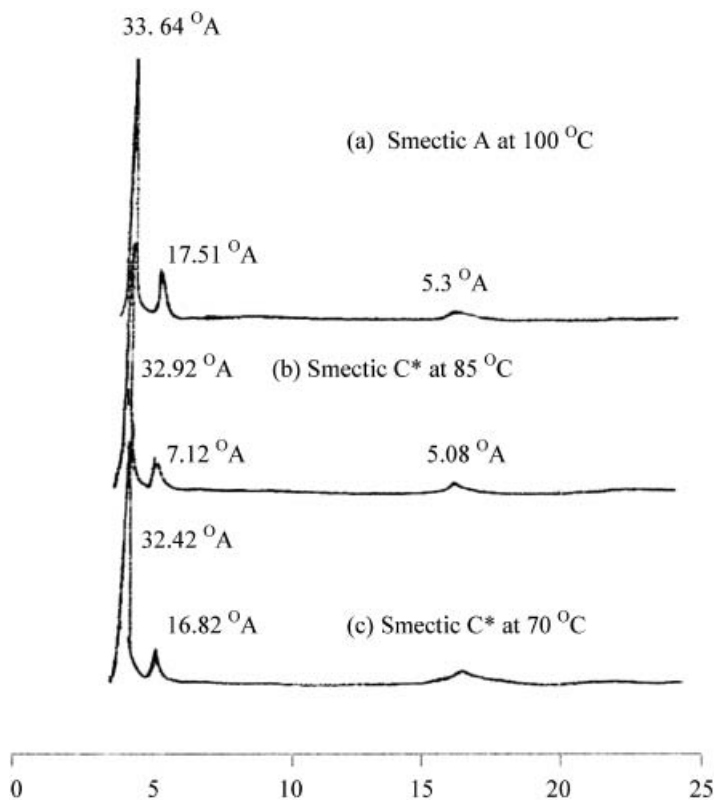


Figure 7. Temperature-dependent WAXD diagrams for compound C_{12} of series I at (a) 100°C , (b) 85°C , (c) 70°C .

has the *sec*-butyl group and series C has the *iso*-propyl group.

When comparing series B, I and A an increase in the nematic and smectic mesophase range is observed with increasing number of methylene units in the terminal group. Branching in the terminal group causes disruption in the molecular packing, which reduces the transition temperature and melting point as well as the mesophase range compared with the unbranched analogues. Therefore, series A has high nematic mesophase ranges than the branched series I and B. However, as predicted by Coates [22], branching introduces the tilted smectic phase into the series. We also observe similar behaviour in series I and II, which exhibit the tilted SmC^* phase.

The molecules of series I and II resemble each other in all aspects, except in one of their central linkages; series II has an azomethine central linkage, whereas series I has azo central linkage. The nematic phase range of series I is greater than that of series II, whereas the smectic mesophase range of series II is greater than that of series I. It is also seen that the onset of smectic phase behaviour in series II is earlier at the C_5 member, while it is at the C_{10} homologue in I. The azomethine linkage of series II is less coplanar than the azo linkage of series I, which enhances lateral attractions resulting in a larger smectic mesophase range and earlier onset of the smectic phase.

Comparing series II and C, it is observed that the nematic mesophase range of C is greater than that of II,

Table 6. Average mesophase range ($^{\circ}\text{C}$).

Series	Nematic	Smectic	Commencement of smectic phase
I	61.2 (C_1 – C_{12})	33.5 (C_{10} – C_{16})	C_{10}
II	48.28 (C_1 – C_{14})	69.32 (C_8 – C_{16})	C_5
A	127.9 (C_1 – C_9)	—	—
B	46.5 (C_1 – C_{12})	32.33 (C_{12} – C_{16})	C_8
C	51.8 (C_1 – C_{12})	40.2 (C_8 – C_{16})	C_7

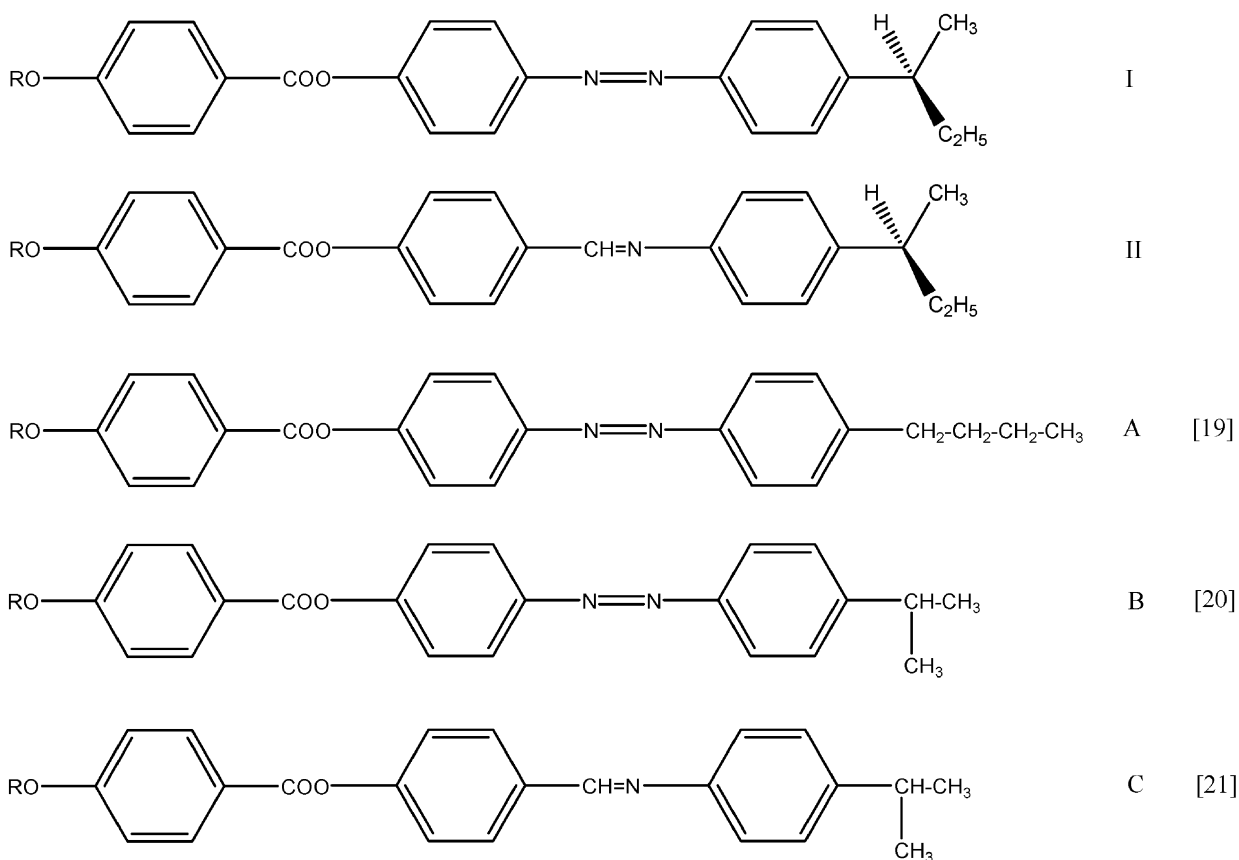


Figure 8. Molecular structures of molecules in series I, II, A, B & C.

whereas the smectic mesophase range of II is greater than that of C; this may be due to additional methylene units in the terminal group in series II, which gives rise to weaker end-on attractions but higher lateral attractions than those of series C. For the same reason the onset of the smectic phase behaviour is at the C_5 derivative in series II, whereas in series C, it is at a later stage at the C_7 derivative.

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