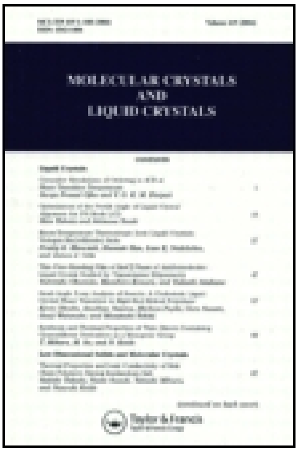

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Synthesis of Liquid Crystals with Lateral Methyl Group and Study of Their Mesomorphic Properties

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Synthesis of Liquid Crystals with Lateral Methyl Group and Study of Their Mesomorphic Properties

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Two new homologous series consisting of central azo and ester linkage and methyl groups at the central as well as terminal benzene rings are synthesized and their mesomorphic properties are studied. Between these two series; Series I has lateral methyl group on terminal benzene ring where as series II has lateral methyl groups at central as well as terminal benzene cores. All the homologues of series I and II are mesogenic in nature; series I exhibits nematic phase from C1 to C14 members whereas C16 member shows smectic C mesophase alongwith nematic mesophase on the other hand all the members of series II are nematogenic in nature. The nematic phase of the series I and II shows marble/schlieren texture and the smectic phase shows schlieren texture of smectic C variety. The mesomorphic properties of both the series are compared with each other and also with other structurally related series to evaluate the effect of lateral methyl group at central as well as terminal benzene core on mesomorphism.

Keywords Azo-ester mesogen; homologous series; lateral methyl group; mesomorphism; nematic; smectic C

Introduction

Mesomorphic behavior of mesogens depends on the molecular structures of molecules and molecular forces arising, therefore, a slight change in the molecular geometry brings about considerable change in its mesomorphic properties [1–15]. Lateral substitution makes molecules broad and plays an effective role in mesogenic properties of a mesogenic compound. Literature survey indicates that the study of lateral substitution at central and terminal benzene ring is rare however [3,6,12–15]. Recently our group has reported the effect of lateral substitution on mesogenic properties of Fluoro aniline derivatives [14]. Keeping this in view, we have synthesized two new homologous series consisting of azo and ester central linkages and lateral methyl groups at central as well as terminal benzene core in order to study the effect of lateral methyl group on mesomorphism.

Experimental

4-Hydroxy benzoic acid, the appropriate n-alkyl halides, 2,4-dimethylaniline, phenol, and 2-methyl phenol were used as received. Solvents were dried and distilled prior to use.

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Microanalyses of some of the representative compounds were performed on a Perkin Elmer Series II 2400-CHN analyzer; infrared (IR) spectra were recorded on a Shimadzu IR-408, and nuclear magnetic resonance (NMR) spectra were measured on a Varian mercury-300 spectrometer. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL optical polarizing microscope provided with a Kofler heating stage. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-60.

1. 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the reported method [16].
2. 4-Hydroxyphenylazo-2′,4′-dimethylbenzene, 3-methyl-4-hydroxyphenylazo-2′, and 4′-dimethylbenzene were prepared by a known method [17].
3. The series I, namely 4-(4′-n-alkoxybenzoyloxy)-phenylazo-2″, 4″-dimethyl benzenes; and series II viz. 4-(4′-n-alkoxybenzoyloxy)-3-methylphenylazo-2″, 4″-dimethylbenzenes were synthesized by adding drop wise a cold solution of 4-hydroxy phenylazo-2″, 4″-dimethylbenzene (for series I); and 3-methyl-4 hydroxyphenylazo-2″, 4″-dimethylbenzene (for series II), in dry pyridine to a cold solution of 4-n-alkoxy benzoyl chlorides. The mixture was allowed to stand overnight at room temperature. It was acidified with 1:1 cold HCl and the separated solid was filtered and column chromatographed on silica gel (60–120 mesh) with 1% ethyl acetate – petroleum ether (60–80°C) (1:99) mixture as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallized repeatedly from ethyl acetate – petroleum ether until constant transition temperatures were obtained. These are recorded in Tables 1 and 2 respectively for series I and II. The elemental analyses of C8 member (series I) and C6 member (Series II) were found to be satisfactory (Table 3). The synthetic route of the series is shown in Scheme 1.

FTIR (Nujol, KBr pellets, cm^{-1}) were recorded on a Shimadzu IR-408.

Table 1. Transition temperature (°C) of Series I. Series I: 4-(4′-n-alkyloxybenzoyloxy)-phenylazo-2″, 4″-dimethylbenzenes

	Transition temperature (°C)		
R = n-Alkyl group	Smectic C	Nematic	Isotropic
Methyl	–	136	234
Ethyl	–	127	214
Propyl	–	125	202
Butyl	–	111	167
Pentyl	–	91	161
Hexyl	–	92	143
Heptyl	–	94	144
Octyl	–	80	164
Decyl	–	93	152
Dodecyl	–	73	128
Tetradecyl	–	55	83
Hexadecyl	54	62	75

Table 2. Transition temperature (°C) of Series II. Series II: 4-(4′-n-alkyloxybenzoyloxy) 3-methylphenyl azo-2″, 4″- dimethylbenzenes

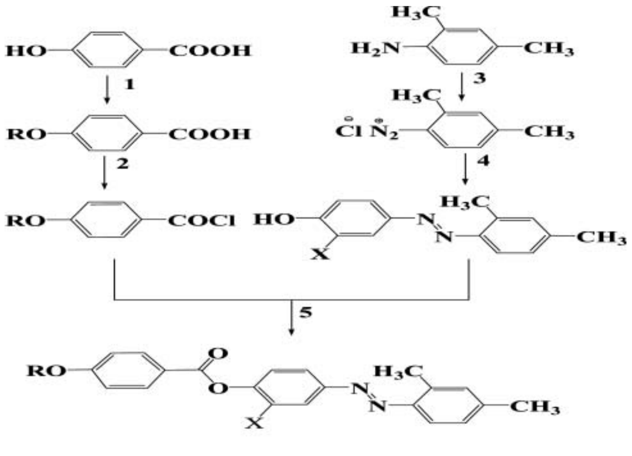
	Transition temperature (°C)		
R = n-Alkyl group	Smectic C	Nematic	Isotropic
Methyl	–	135	162
Ethyl	–	115	188
Propyl	–	92	138
Butyl	–	90	155
Pentyl	–	93	134
Hexyl	–	95	145
Heptyl	–	78	94
Octyl	–	56	93
Decyl	–	44	84
Dodecyl	–	45	68
Tetradecyl	–	52	70
Hexadecyl	–	55	76

Series I: 4-(4′-n-octyloxybenzoyloxy)-phenylazo-2″, 4″-dimethylbenzene.

2925–2858 (C—H St, Alkyl CH_3, SP^3 hybridization), 1734 (—C=O— St. of ester), 1606 (—N=N— St.), 1517–1479 (—C=C— St. of Aromatic ring), 1469 (—C—H bending of —CH_2—), 1262 (Aromatic ether St.), 1075(—C—O— St. of ester), 878 (strong —C—H— bending for 1:2:4 tri substituted benzene ring), 759 (weak —C—H— bending for —$(CH_2)_7$—) cm^{-1}.

Series II: - 4-(4′-n-hexyloxybenzoyloxy) 3-methylphenyl azo-2″, 4″- dimethylbenzene.

2954–2857 (C—H St, Alkyl CH_3, SP^3 hybridization), 1734 (—C=O— St. of ester), 1601 (—N=N— St.), 1577–1503 (—C=C— St. of Aromatic ring), 1477 (—C—H bending



Note: X = --H (for Series I), –CH_3 (for Series II)
R = C_nH_{2n+1}, where n = 1 to 8, 10, 12, 14, 16
(1) Alcohol, KOH, n-RBr, (2) $SOCl_2$, (3) HCl, $NaNO_2$, H_2O/0--5°C, (4) phenol or 2-methyl phenol, aq.NaOH, at 0--10°C, pH 8--12, and (5) Dry Pyridine, 1:1 cold HCl

Scheme 1. Synthetic route for Series I and II.

Table 3. Elemental analysis

		Theoretical			Practical		
Series	Homologue	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
I	C8	75.92	7.40	6.10	75.51	7.67	6.27
II	C6	75.66	7.25	6.30	75.40	7.75	6.35

of —CH_2—), 1247 (Aromatic ether St.), 1061(—C—O— St. of ester), 893 (strong —C—H— bending for 1:2:4 tri substituted benzene ring), 725 (weak —C—H— bending for —$(CH_2)_5$—) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm, standard TMS) were recorded on Varian mercury 300 ($CDCl_3$, 300 MHz, δ ppm, standard TMS).

Series I: 4-(4′-n-octyloxybenzoyloxy)-phenylazo-2″, 4″-dimethylbenzene.

δ = 0.89 (t, 3H, —CH_3), 1.29–1.82 (m, 14H, 7(—CH_2—)), 1.85 (Qunt, 2H, —$COCH_2$), 2.38 (s, 3H, Ar—CH_3), 2.69 (s, 3H, Ar—CH_3), 4.04 (t, 3H, —OCH_2), 6.95–8.15 (m, 11H, Ar—H).

Series II: 4-(4′-n-hexyloxybenzoyloxy) 3-methylphenyl azo-2″, 4″-dimethylbenzene.

δ = 0.90 (t, 3H, aliphatic —CH_3), 1.35–1.82 (m, 14H, 5(-CH_2-)), 1.85 (Qunt, 2H, —$COCH_2$), 2.32 (s, 3H, Ar—CH_3), 2.37 (s, 3H, Ar—CH_3) 2.68 (s, 3H, Ar—CH_3), 4.04 (t, 3H, —OCH_2), 6.95–8.15 (m, 11H, Ar—H).

Results and Discussion

In the present investigation, twelve homologues from each of the two series; viz. 4-(4′-n-alkyloxybenzoyloxy)-phenylazo-2″, 4″-dimethylbenzenes (series I); 4-(4′-n-alkyloxybenzoyloxy) 3-methylphenyl azo-2″, 4″-dimethylbenzenes (series II), were synthesized and their mesomorphic properties were studied.

All the twelve homologues of series I are mesogens (Table 1); the nematic phase commences from the very first derivative and remains upto the tetradecyl derivative, whereas the smectic C phase is observed only in the hexadecyl derivative. Figure 1 shows the plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that Cr—M transitions show overall falling tendency from the methyl to octyl derivative and then a slight rising tendency at the 10th homologue and then the curve shows falling tendency upto hexadecyl derivative. The N—I curve shows overall falling tendency with a jump at the C8 derivative as the series is ascended. The nematic phase of the series shows marble/schlieren texture whereas the smectic phase shows schlieren texture of the smectic C variety.

All the twelve homologues of series II are mesogens (Table 2); the nematic phase commences from the very first derivative and remains upto the last hexadecyl derivative. Smectic phase is absent in the entire series; thus, all homologues are nematogens. Figure 2, shows plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that the N—I curve shows an odd–even effect in the initial members upto C6 derivative, then the N—I curve shows falling tendency from C7 to C12 member with slight rise at C10 homologue; from C12 upto C16 homologue the N—I curve shows slight rising tendency as the series is ascended. The Cr—M transitions show initially falling tendency upto C3 derivative and then rising tendency upto C6 derivative, then the Cr—M curve shows

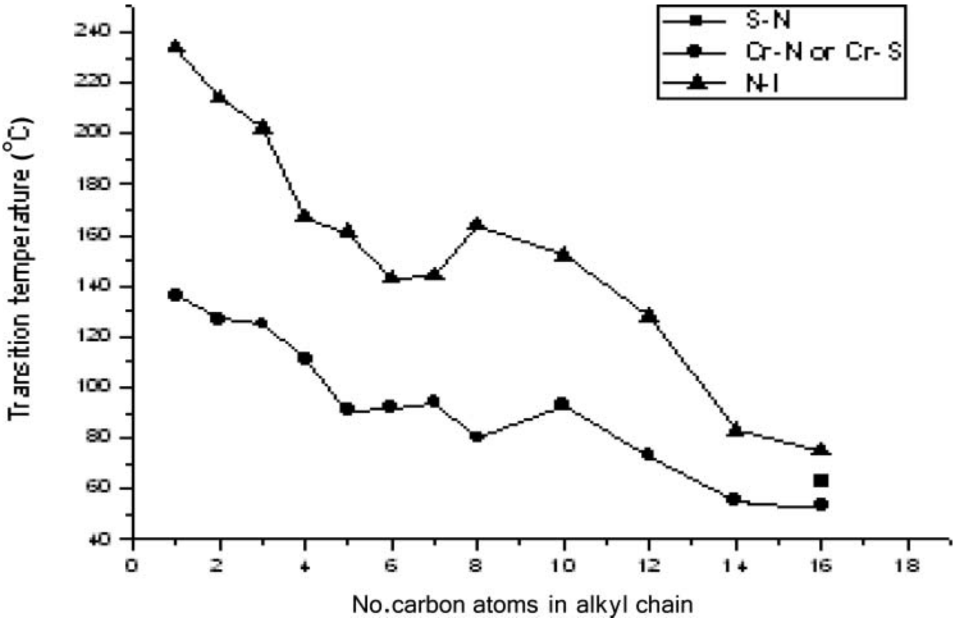


Figure 1. Series I: 4-(4′-n-alkyloxybenzoyloxy)-phenylazo-2″, 4″-dimethylbenzenes.

overall falling tendency with slight increase from C12 to C16 derivative. The nematic phase of the series shows the same Marble/Schlieren texture as that of the series I.

Figure 3 shows polarizing optical microscopic images of Marble and Schlieren texture of nematic phase of compound C8 of series I and C6 of series II respectively.

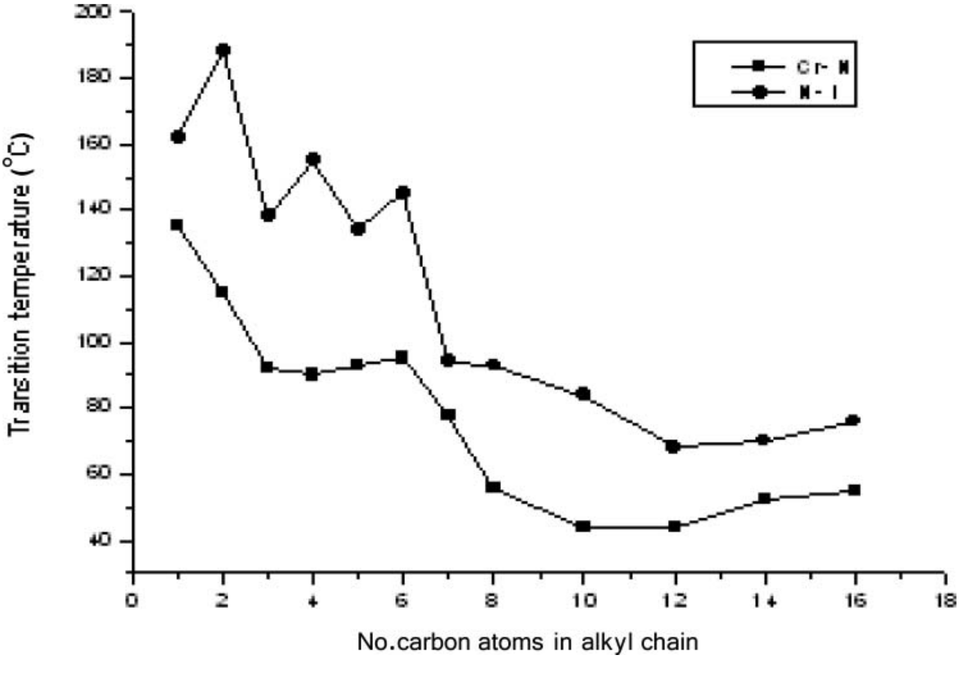
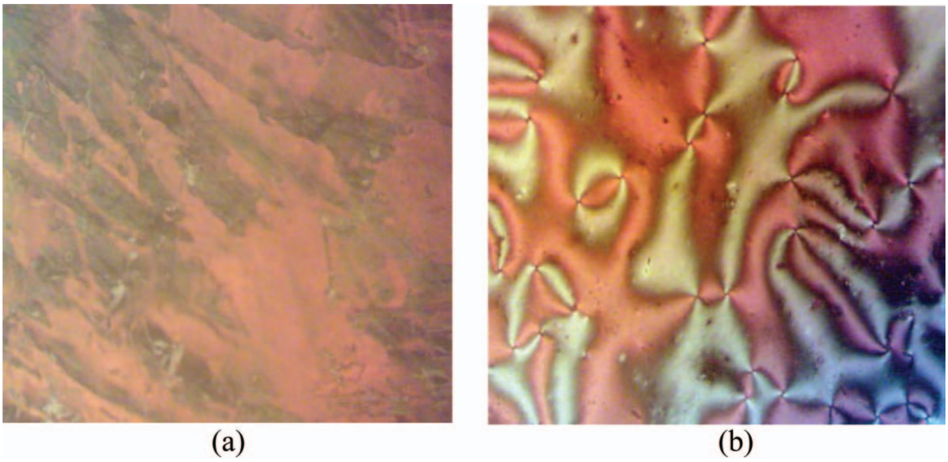


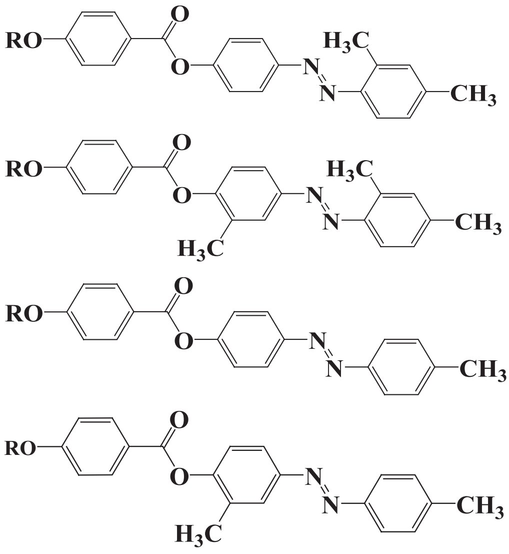
Figure 2. Series II: 4-(4′-n-alkyloxybenzoyloxy)-3-methylphenylazo-2″, 4″-dimethylbenzenes.



(a) (b)

Figure 3. Textures of mesophase observed under polarizing optical microscope. (a) Marble texture of nematic phase of compound C8 Series I at 114°C on cooling. (b) Schlieren texture of the nematic phase of Compound C6 Series II at 121°C on cooling.

Series I and II are compared with each other and structurally related homologous series [8,15]. Figure 4 shows molecular structures of the series in comparison and Table 4 shows Thermal stabilities of smectic and nematic mesophase of these series under comparison. Series II is purely nematogenic as it does not exhibit smectic mesophase till C16 derivative studied, whereas series I shows smectic C mesophase in the C16 homologue alongwith nematic phase; this can be due to introduction of one more lateral methyl group in the central benzene ring in series II. Both series I and II have lower N—I thermal stability than series A; this can be due to the introduction of lateral methyl group in the aromatic core



…………… (I)

…………. (II)

………….. (A) [8]

…………. (B) [15]

Figure 4. Molecular structures of the series in comparison.

Table 4. Average thermal stabilities (°C)

Series	Smectic-isotropic (°C) or smectic–nematic (°C)	Nematic-isotropic (°C)	Commencement of smectic mesophase
1	62 (C_{16})	155.6 (C_1–C_{16})	C_{16}
2	–	117.2 (C_1–C_{16})	–
A	106.5 (C_{10}–C_{16})	242 (C_1–C_8)	C_{10}
B	–	147.5 (C_8 and C_{16})	–

of series I and II, which forces apart the long molecular axes of the molecules, thereby lowering the N—I stability [2]. The introduction of the lateral methyl group in series I as well as in series II changes the molecular conformation and broadens the molecules, which decreases, the transition temperatures and thermal stabilities of smectic and nematic mesophase [2,14,15]. This factor is a direct result of an increase in the thickness of the molecule [18]. The increased dissymmetry resulting from the lateral methyl group leads to less effective molecular packing in the crystal lattice, and therefore, lowers the crystal to mesophase transition temperature as shown in Tables 1 and 2 [15]. Thus, the effect of substitution, which leads to an increase in molecular breadth, is that the long narrow molecules will be forced further apart so reducing the strength of the intermolecular lateral attractions. Both smectic and nematic mesophases depend to a greater or lesser extent on these cohesive forces to maintain the parallel orientation of the molecules. Therefore, substitution leading to an increase in molecular breadth will decrease the smectic and nematic thermal stabilities, which is actually found in the present series I and II [2].

When the two homologues of series B Viz. C8 and C16 are compared with C8 and C16 homologues of series II, it is found that the N—I stability of C8 and C16 homologues of series B is higher than those of series II; it seems that the introduction of lateral methyl group in the central benzene ring in series II has much pronounced effect in the reduction of transition temperature, N—I thermal stability and thereby mesophase range [2]. The N—I thermal stability of series II is lower than that of series I which can be due to increase in breadth of the molecule of series II due to introduction of one more methyl group in the central benzene ring [2]. These results are in agreement with our previous results of the substitution of lateral methyl group in central benzene core [14]. The commencement

Table 5. DSC analysis

Series	Member	Heating rate (°C/min)	Transition temperature (°C)	H = J/g	S = J/g.K
I	Octyl	10	Cr–M 79.50	77.42	0.2195
			N–I 164.29	2.72	0.0062
I	Hexadecyl	10	Cr–M 52.74	1.00	0.0031
			S–N 60.38	17.88	0.0536
			N–I 74.54	0.37	0.0011
II	Hexyl	10	Cr–M 93.10	107.55	0.2936
			N–I 139.02	2.70	0.0065

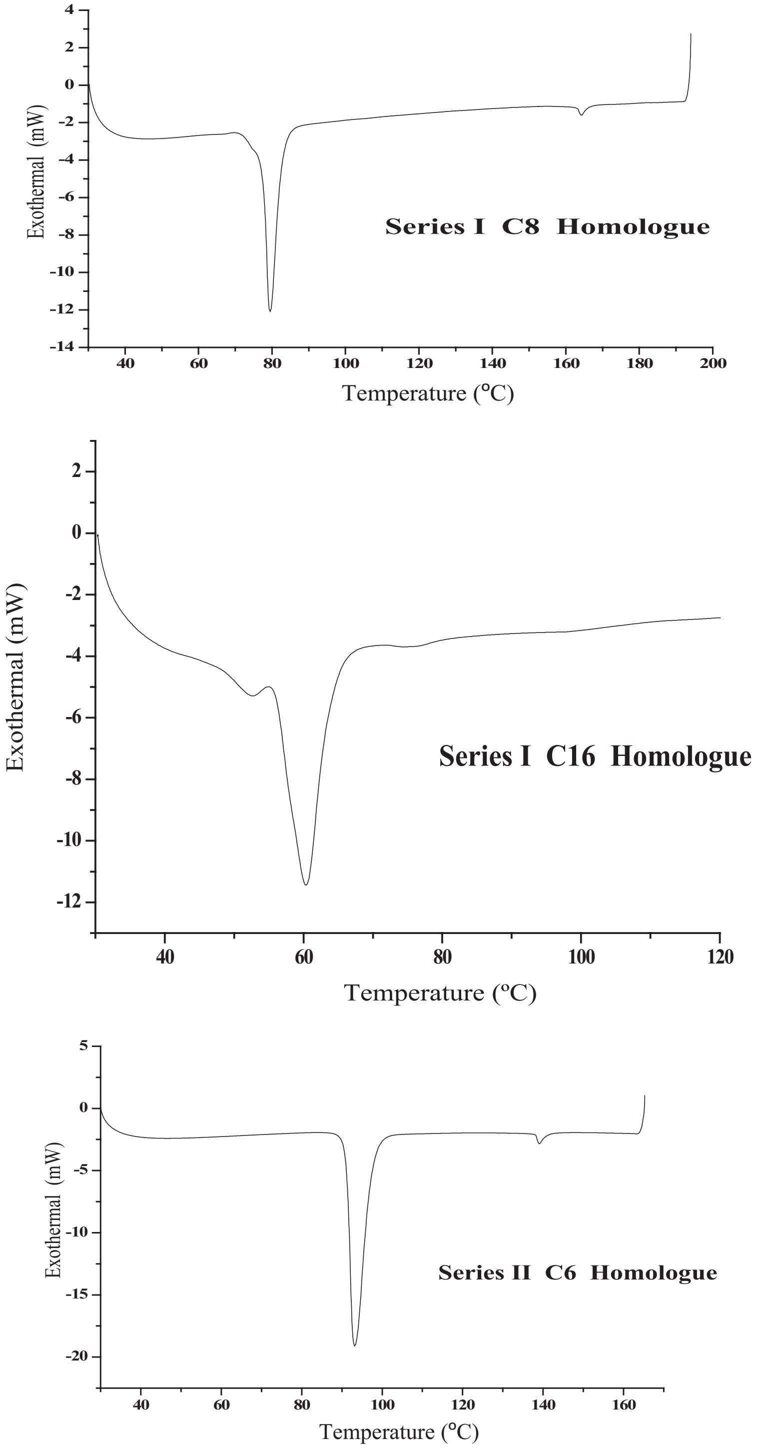


Figure 5. DSC curves.

of smectic mesophase in series I is at a later C16 homologue as compared to laterally unsubstituted series A where it is at an early C10 homologue.

Two homologues from series I (C8, C16) and one homologue from series II (C6) were analyzed by DSC; their data are given in Table 5 whereas Figure 5 shows DSC curves of these homologues.

Conclusion

The introduction of methyl group in lateral position at terminal and central benzene core decreases thermal stabilities of smectic and nematic mesophases. The commencement of smectic mesophase is delayed with introduction of lateral methyl group in terminal benzene ring in series I whereas with introduction of one more lateral methyl group in central benzene core, the smectic phase is altogether eliminated.

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