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Synthesis and study of 4-(4′-*n*-alkoxybenzoyloxybenzoyl)-4′′-*n*-butoxyanilides

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Thirteen compounds with ester and amide linkages were synthesized and their mesogenic properties evaluated. Methyl to *n*-propyl derivatives exhibit nematic phases, *n*-butyl to *n*-decyl derivatives exhibit smectic and nematic mesophases, whereas *n*-dodecyl to *n*-octadecyl derivatives exhibit only smectic phases. All the smectic homologues exhibit smectic C phases. Middle members of the homologous series exhibit polymorphism of smectic mesophase. A plot of transition temperatures versus number of carbon atoms in the alkoxy chain reveals an odd–even effect for nematic–isotropic transition temperatures. Nematic–isotropic and smectic–cholesteric thermal stabilities of the prepared compounds (series I) are higher compared to those of previously reported compounds, series A, B and C. The results indicate that a simple reversal of a central linkage has a dramatic effect on the appearance of smectic mesophase in a homologous series. The structures of the synthesized compounds were characterized using elemental analysis, thin-layer chromatography and spectral data.

1. Introduction

The mesomorphic behaviour of an organic compound is basically dependent on its molecular architecture in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties.

A number of mesogenic homologous series have been reported that have –COO–, –CH=N–, –N=N–, –CH=CH–, –CH=CHCOO–, –C=C–, –C≡C–, etc, groups as their central linkages. Many mesogenic homologous series contain two central linkages, both of which may either be ester [1–3] or azomethine groups [4, 5] or one of which may be ester and the other azomethine [6, 7]. In the literature there are few reports of mesogenic compounds having amide linkages. However, to the best of our knowledge, the first homologous series containing a (–NHCO–) amide group as one of the central linkages was reported by Vora and Gupta [8]. Soon after that Kalyvas and McIntyre [9] and Patel [10] reported a symmetrical homologous series having ester and amide central linkages. In addition, Brown [11] also mentioned that compounds with –CONH– linkages may exhibit mesomorphism.

More recently, many researchers have synthesized mesogenic polyester-amides and model compounds having amide and ester linkages [12–16]. These studies indicated that 'amide' linkages, although raising the melting point, are also smectogenic, enhance mesogenic character and impart stability to the compounds. It has been observed by Griffin *et al.* [17] and others [9, 18] that reversal of the central linkage results in some remarkable differences in liquid crystalline properties. In consequence, synthesis of a homologous series having reversal of amide linkage would enable comparison with other similar homologous series. Moreover, it was suspected that reversal of the amide linkage may induce a smectic C phase. With this in view, the homologous series (series I) shown in figure 1 was synthesized and their mesogenic properties studied.

2. Experimental

2.1. *Instrumentation*

Microanalysis of the synthesized compounds was carried out using a Coleman carbon–hydrogen analyser. IR spectra and FTIR spectra were recorded on a Perkin-Elmer spectrophotometer and NICOLET Impact-400 FTIR, respectively. NMR spectra were recorded on a Hitachi NMR R-1200 instrument. Liquid crystalline properties were investigated using Leitz-Labourlux 12 Pol (Germany) polarizing optical microscope provided with a Kofler heating stage. ESI-MS were recorded on a LC-MS Shimadzu-2010 instrument.

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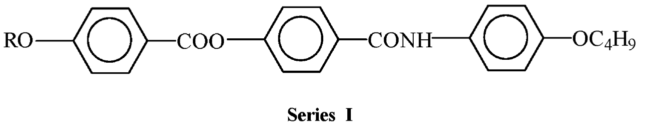


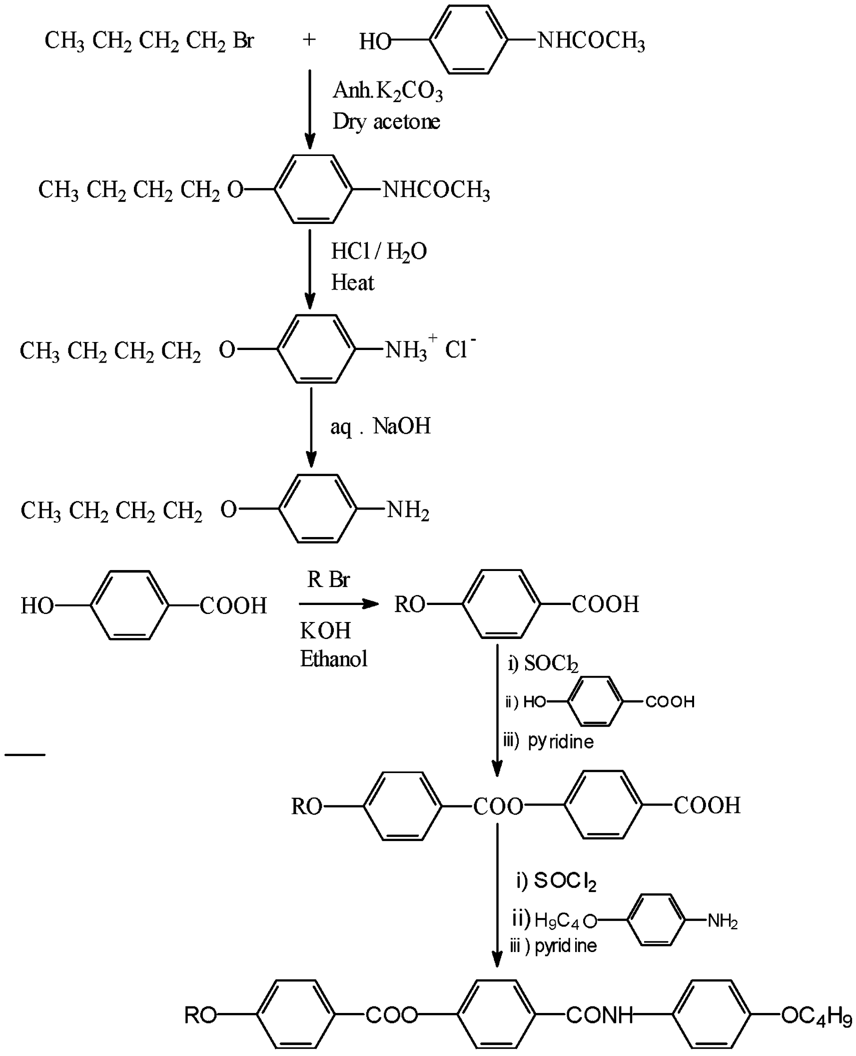
$R = n\text{-}C_mH_{2m+1}$, m = 1–8, 10, 12, 14, 16, 18

Figure 1. Structure of the series I compounds.

2.2. *Synthesis and characterization*

The route adopted for the synthesis of the mesogens is shown in scheme 1. 4-*n*-Alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chlorides were synthesized by the modified method of Dave and Vora [19]. 4-*n*-Alkoxybenzoyloxybenzoic acids and their chlorides were synthesized by methods described in the literature [20–22]. 4-*n*-Butoxy aniline was synthesized by the method reported in the literature [23, 24].

2.2.1. 4-(4′-n-alkoxybenzoyloxybenzoyl)-4′′-*n*-butoxyanilides (I). The respective 4-*n*- alkoxybenzoyloxybenzoyl chloride (0.01 mol) was dissolved in 5 ml of dry pyridine. A solution of 4-*n*-butoxyaniline (0.01 mol) in 10 ml of dry pyridine was added slowly to a cold solution of the above acid chloride. The mixture was heated on a water-bath for about half an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid. Precipitates were filtered and washed with water followed with diluted sodium hydroxide solution and water. The resulting ester–amide compounds were recrystallized several times from DMF until constant transition temperatures were obtained (table 1). The yield of purified ester–amide compounds varied between 65% and 70%. The elemental analysis of all the compounds gave satisfactory results (table 2).



Scheme 1. Synthetic route to series I compounds.

Table 1. Phase transition temperatures of series I compounds.

Compound	R = C_nH_{2n+1}	Transition temperatures /°C
1	CH_3	Cr 207.0 N 254.0 I
2	C_2H_5	Cr 242.0 N 287.0(d) I
3	C_3H_7	Cr 210.0 N 275.0 I
4	C_4H_9	Cr 172.0 SmC 193.0 N 293.0(d) I
5	C_5H_{11}	Cr 202.0 SmC 226.2 N 282.0(d) I
6	C_6H_{13}	Cr 174.0 SmC 230.0 N 296.0(d) I
7	C_7H_{15}	Cr 203.0 SmC 234.0 SmA 259.0 N 284.0(d) I
8	C_8H_{17}	Cr 179.0 SmC 227.0 SmA 247.0 N 264.0 I
9	$C_{10}H_{21}$	Cr 171.0 SmC 218.0 SmA 233.5 N 261.0 I
10	$C_{12}H_{25}$	Cr 174.2 SmC 239.0 I
11	$C_{14}H_{29}$	Cr 159.0 SmC 231.0 I
12	$C_{16}H_{33}$	Cr 148.0 SmC 224.0 I
13	$C_{18}H_{37}$	Cr 138.0 SmC 217.0 I

Cr = crystal, SmC = smectic C, SmA = smectic A, N = nematic, I = isotropic, d = decomposition.

Table 2. Elemental analysis of series I compounds.

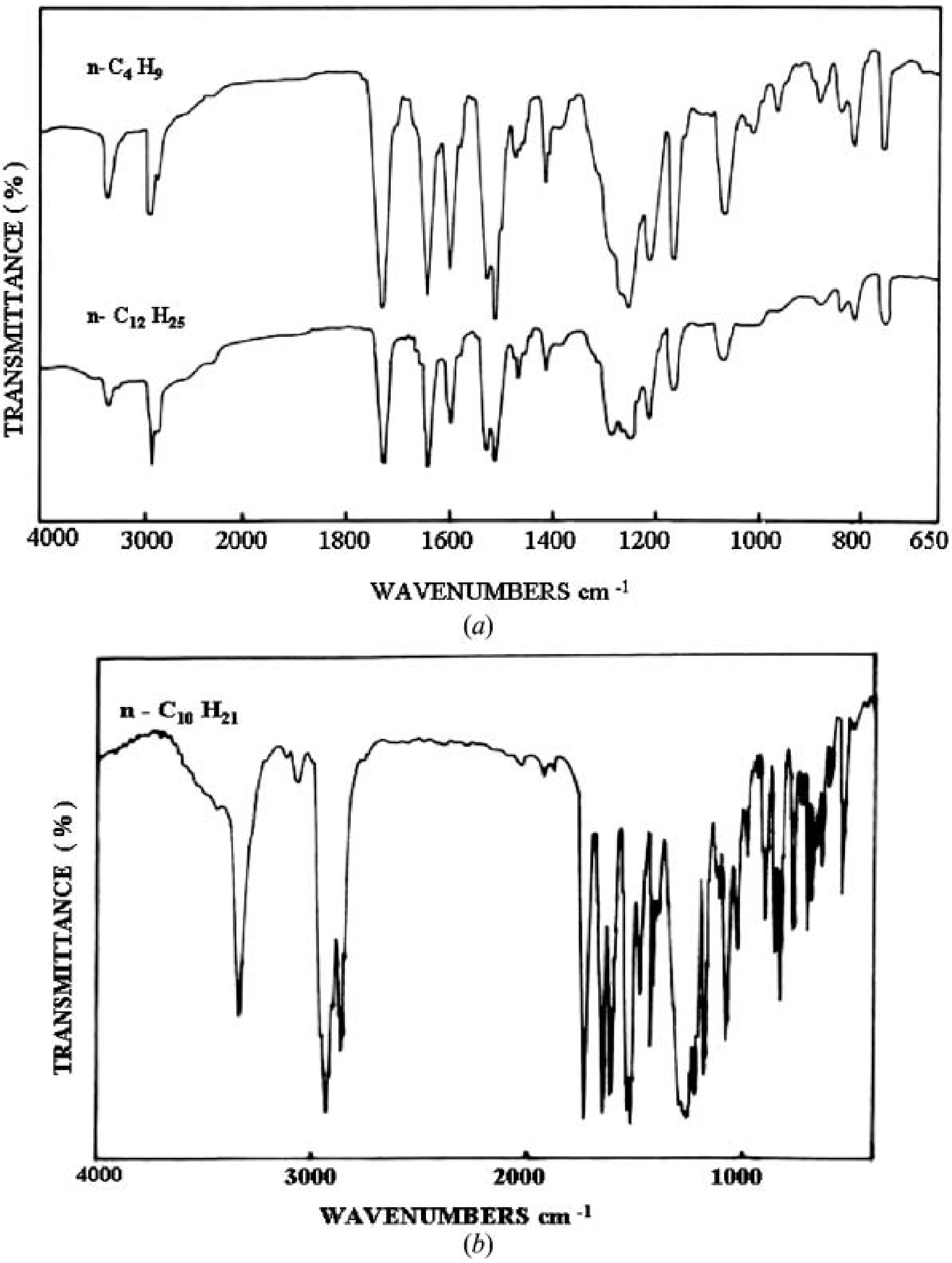
		% Found (% Calculated)		
Compound	R=C_nH_{2n+1}	C	H	N
1	CH_3	71.63 (71.60)	5.87 (5.97)	3.43 (3.34)
2	C_2H_5	72.12 (72.06)	6.24 (6.24)	3.15 (3.23)
3	C_3H_7	72.37 (72.48)	6.44 (6.49)	3.13 (3.13)
4	C_4H_9	71.35 (72.88)	6.42 (6.73)	3.14 (3.04)
5	C_5H_{11}	72.86 (73.26)	6.85 (6.95)	2.78 (2.95)
6	C_6H_{13}	73.51 (73.62)	7.35 (7.16)	2.83 (2.86)
7	C_7H_{15}	74.12 (73.96)	7.47 (7.36)	2.65 (2.78)
8	C_8H_{17}	74.26 (74.28)	7.49 (7.54)	2.73 (2.71)
9	$C_{10}H_{21}$	74.67 (74.86)	7.93 (7.89)	2.46 (2.57)
10	$C_{12}H_{25}$	75.63 (75.39)	8.16 (8.20)	2.20 (2.44)
11	$C_{14}H_{29}$	75.79 ((75.88)	8.53 (8.49)	2.24 (2.33)
12	$C_{16}H_{33}$	76.25 (76.31)	8.85 (8.74)	2.13 (2.23)
13	$C_{18}H_{37}$	76.59 (76.71)	8.93 (8.98)	2.20 (2.13)

2.2.2. Spectral analysis of 4-(4′-*n*-alkoxybenzoyloxybenzoyl)-4′′-*n*–butoxyanilides. The IR (KBr) spectrum of the *n*-butoxy derivative is shown in figure 2a: –NH stretching of secondary amide, 3350 cm^{-1}; –NH bending vibrations, 1640 cm^{-1}; stretching vibration of C=O of amide, 1610 cm^{-1}; C–H bending of alkene (–CH_2 –),1510 cm^{-1}; C–H bending of aromatic ring, 750 cm^{-1}; carbonyl stretching of aromatic ring of ester, 1730 cm^{-1}; C–H stretching and bending vibrations of –CH_3, 2900 cm^{-1} and 1410 cm^{-1}; C–H of aromatic ring, 1600 cm^{-1} and 1200 cm^{-1}.

IR (KBr) spectrum of the *n*-dodecyloxy derivative (figure 2a): –NH stretching of secondary amide, 3350 cm^{-1}; –NH bending vibrations, 1640 cm^{-1}; stretching vibration of C=O of amide, 1600 cm^{-1}; C–H bending of alkene (–CH_2 –), 1510 cm^{-1}; C–H bending of aromatic ring, 755 cm^{-1}; carbonyl stretching of aromatic ring of ester, 1730 cm^{-1}; C–H stretching and bending vibrations of –CH_3, 2900 cm^{-1} and 1410 cm^{-1}; C–H of aromatic ring, 1600 cm^{-1} and 1210 cm^{-1}.

FTIR (KBr) spectrum of *n*-decyloxy derivative (figure 2b): –NH stretching of secondary amide, 3331 cm^{-1}; –NH bending vibrations, 1645 cm^{-1}; stretching vibration of C=O of amide, 1605 cm^{-1}; C–H bending of alkene (–CH_2–), 1517 cm^{-1}; C–H bending of aromatic ring, 760 cm^{-1}; carbonyl stretching aromatic ring of ester, 1731 cm^{-1}; C–H stretching and bending vibrations of –CH_3, 2931 cm^{-1} and 1414 cm^{-1}; C–H of aromatic ring, 1605 cm^{-1} and 1212 cm^{-1}.

For the n-dodecyloxy derivative, ^{1}H NMR (90 MHz, $CDCl_3$) (see figure 3): δ 0.9–1.7 (m, 30 H of two alkyl chains at C-4′ and C-4′′), 4.25 (t, 4H of two methylene groups in the alkoxy chain at C-4′ and C-4′′), 7.11 (d, 4H at C-3′, C-5′, C-3′′ and C-5′′), 7.45 (d , 4H at C-3, C-5 and C-2′′, C-6′′), 8.05 (d, 4H at C-2 and C-6), 8.25 (d, 4H at C-2′ and C-6′), 9.1 (S, 1H of –CONH–).



(*a*)

(*b*)

Figure 2. (a) Representative IR spectra of 4-(4′-*n*-alkoxybenzoyloxybenzoyl)-4′′-*n*-butoxyanilides for R = *n*-C_4H_9 and *n*-$C_{12}H_{25}$. (b) Representative FTIR spectrum of 4-(4′-*n*-decyloxybenzoyloxybenzoyl)-4′′-*n*-butoxyanilide.

ESI-MS: *n*-pentyloxy derivative, [$M^+ + Na^+$, relative intensity (%)] 310(7), 338.5(100), 360.3(78), 376.1(9), 391.3(9), 347.2(10), 476.7(7), 498.3(8); *n*-decyloxy derivative, [$M^+ + Na^+$, relative intensity(%)] 245.4(7), 310.4(8), 338.4(100), 360.3(60), 415.2(12), 437.5(10), 568(7).

3. Results and discussion

Vora and co-workers [25, 26] and Gupta [27] have studied a number of mesogenic series with ester and amide central linkages and also a mesogenic series having two amide linkages. The observations of Vora *et al.* made it clear that, compared to an ester and azomethine linkage, an amide central linkage enhances smectic and nematic phases and the enhancement is more in the case of smectic mesophases.

For the synthesis of series I, the intermediates 4-*n*-alkoxybenzoic acids and 4-*n*-alkoxybenzoyloxybenzoic acids were synthesized, both of which are mesogenic in nature. As shown in table 1, the lower derivatives (C_1 to

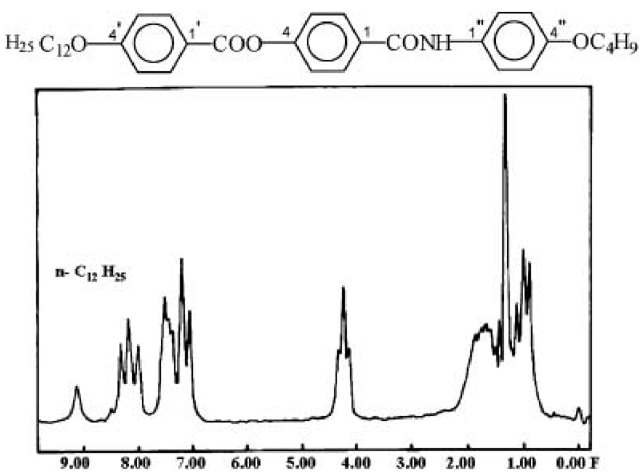


Figure 3. ^{1}H NMR spectrum of 4-(4′-*n*-dodecyloxybenzoyloxybenzoyl)-4′′-*n*-butoxyanilide.

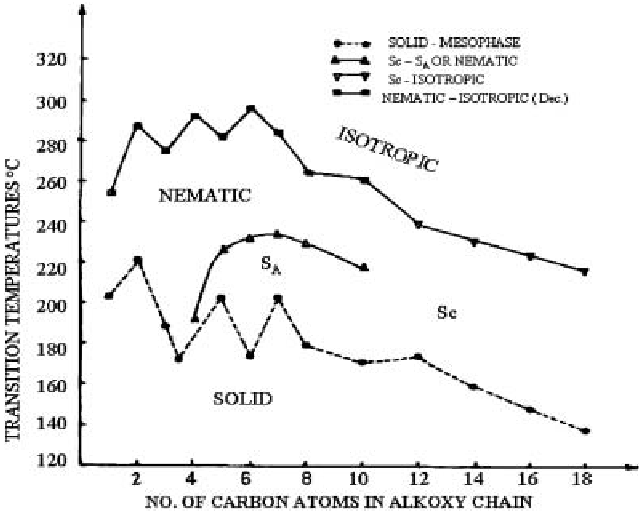


Figure 4. Transition temperatures versus number of carbon atoms in alkoxy chain of series I compounds.

C_3) of series I were found to exhibit only nematic phases, the middle derivatives (C_4 to C_{10}) exhibit smectic and nematic mesophases and higher derivatives (C_{12} to C_{18}) exhibit only a smectic C (SmC) phase. All of the smectic homologues exhibit SmC phases.

A plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits an odd–even effect for nematic–isotropic transition temperatures (figure 4). The odd–even effect in molecules forming liquid crystals has been explained by Gray [28, 29].

The average thermal stabilities of different mesogenic homologous series are compared and recorded in table 3. The average thermal stabilities of 4-(4′-*n*-alkoxybenzoyloxybenzoyl)-4′′-n-butoxyanilided (series I) are compared with those of the 4-(4′-*n*-alkoxybenzoyloxy)-4′′-*n*-butoxybenzanilides (series A) [30], 1,4-bis(4′-*n*-alkoxybenzoyloxy)- aminophenols (series B) [10] and 4-(4′-*n*-alkoxybenzoyloxy)-4′′-*n*-heptyloxybenzanilides (series C) [8].

Reference to the geometry of series I and series A, B and C (figure 5) indicates that one of the central linkage amide (–CONH–) is reversed in all three series A, B and C as (–NH-CO–) in the molecules.

In the present series the nitrogen of amide linkage is attached to terminal phenyl ring and can take part in group resonating structures along with terminal *n*-butoxy group with contributes to polarizability of the molecules of series I. In the case of series A, B and C, the nitrogen of amide linkage is attached to a central phenyl group, which is attached to another phenyl ring via an ester linkage. This would cause difference in the polarizability of molecules of series I, A, B and C. Molecules of series I and A differ only by reversal of amide linkage. Molecules of series B and C differ from the molecules of series I at one end of the molecules only. At one end molecules of series B and C have alkoxy group and *n*-heptyloxy group.

Reference to table 3 indicates that nematic/isotropic and smectic/nematic or isotropic thermal stabilities of series I compounds are higher than those of series A, B and C. The difference between series I and A is only of reversal of amide linkage; the thermal stabilities of series I are higher than those of series A as explained earlier. Series B and C have other factors playing at one end due to difference in the end group as well as reverse amide linkage. The net result of different forces lead to lower thermal stabilities for the smectic and nematic phases in series B and C compared to those of series I.

An interesting aspect of the present series is that it exhibits polymorphism of smectic phases. Ten members

Table 3. Average thermal stabilities (°C) of series I, A, B and C compounds.

	(I)	(A)	(B)	(C)
Transition	R′ = C_4H_9	R′ = C_4H_9	R = R′	R′ = C_7H_{15}
Nematic to isotropic (C_1 to C_{10})	279.38	256.75	250.94	231.81
Smectic to nematic/isotropic (C_4 to C_{18})	237.64	-	203.43	211.71
Commencement of smectic mesophase	C_4	-	C_6	C_2

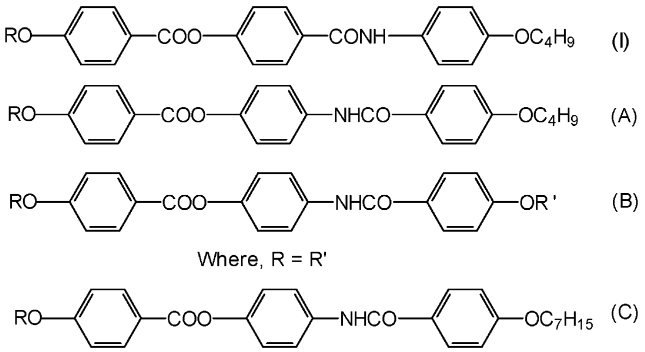


Figure 5. Comparative geometry of series I, A, B and C compounds.

of series I exhibit SmC phases and three members exhibit smectic A (SmA) phases.

In the present series, SmA (focal conic texture) and SmC (broken fan shaped texture) phases are inferred from textures observed under a polarizing microscope (figures 6–7) .

4. Conclusion

A new mesogenic homologous series with reversal of amide central linkage has been synthesized. *n*-Butyl to *n*-decyl derivatives exhibit smectic and nematic mesophases. *n*-Dodecyl to *n*-octadecyl derivatives exhibit only SmC phases. All the smectic homologues exhibit SmC phases. Middle members exhibit polymorphism of smectic mesophases. A plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits an odd–even effect for the nematic–isotropic transition temperatures. Nematic to isotropic and smectic to nematic or isotropic thermal stabilities of series I are higher than those of series A, B and C. In the present series, SmA (focal conic texture) and SmC (broken fan shaped texture) phases are inferred from textures observed under a polarizing optical microscope.

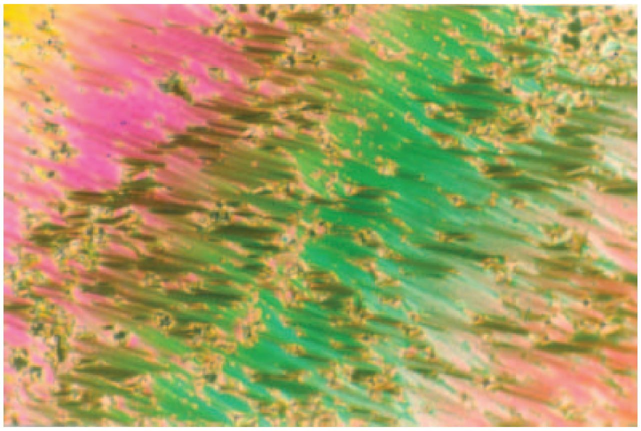


Figure 6. Polarized optical microphotograph of smectic A (focal conic texture) liquid crystalline phase of 4-(4′-*n*-decyloxybenzoyloxybenzoyl)-4″-*n*-butoxyanilide on cooling at 224°C.

Figure 7. Polarized optical microphotograph of smectic C (broken fan shaped texture) liquid crystalline phase of 4-(4′-*n*-octyloxybenzoyloxybenzoyl)-4″-*n*-butoxyanilide on heating at 196°C.

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