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Preliminary communication

Azomesogens containing an ethoxyethyl terminal chain: synthesis and characterization†

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Two homologous mesogenic series, the ethoxyethyl 4-(4′-*n*-alkoxyphenylazo)benzoates (I) and the ethoxyethyl [4-(4′-*n*-alkoxybenzoyloxy)phenylazo]-4″-benzoates (II), both containing a terminal ethoxyethyl chain, have been synthesized. In series I, all nine members synthesized exhibit only an enantiotropic smectic A mesophase. In series II, all 12 homologues exhibit an enantiotropic nematic mesophase; a smectic A phase appears in the *n*-butyloxy derivative as a enantiotropic phase and persists through to the *n*-hexadecyloxy member. The mesomorphic properties of both series are compared with each other and also with the properties of other structurally related series to evaluate the effects of the ethoxyethyl chain on mesomorphism.

1. Introduction

Terminal groups present in a molecule have their own importance because of their polarity. It has been found that terminally substituted compounds exhibit more stable mesophases than do unsubstituted mesogenic compounds. Any terminal group which increases the molecular polarizability, without significantly increasing the molecular breadth, increases the thermal stability of the resulting mesophase.

A number of homologous series of mesogenic esters with normal [1–3] and branched [4–8] terminal alkyl chains have been reported previously. However our literature survey indicated that, compared with mesogenic esters with normal and achiral branched terminal alkyl chains, liquid crystalline esters having chains containing differing kinds of atoms are very rare. To distinguish these from branched alkyl groups, we will refer to them as broken terminal alkyl chains. Weygand *et al.* [9] have studied the alkyl chain CH_3OCH_2O–, which combines two ether functions as a terminal substituent. Rather few compounds have been examined, but the data shows that mesomorphic properties disappear entirely or the compounds have lower nematic thermal stabilities than the analogous compounds containing the $CH_3CH_2CH_2O$– group.

More recently, liquid crystalline dimers comprising cholesteryl esterimide groups linked via oligo(ethylene oxide) chains, as well as homologous mesogenic series of cholesteryl esterimides with oxyethylene and methylene tails, have appeared in the literature [10, 11]. Chiang *et al.* [12, 13] studied the effects of ethoxyethoxyethoxy (EO) and butoxyethoxyethoxy (BO) chains on mesomorphism. They observed that the BO-containing liquid crystals have greater SmC* phase stability than the corresponding EO-containing materials. We have reported [14] methoxyethyl and ethoxyethyl esters of 4-(4-*n*-alkoxybenzoyloxy)benzoic acids as well as methoxyethyl *trans*-4-(4′-*n*-alkoxybenzoyloxy)-α-methyl cinnamates. All three homologous mesogenic series exhibited smectic A mesophases at ambient temperatures. We have also reported [15] the binary mixtures of such compounds which show room temperature smectogenic properties and over a wide range of temperatures. Recently we reported [16] a homologous series containing an ethoxyethyl chain and based on three phenyl rings and ester and azomethine central linkages, which exhibited nematic and/or smectic mesophases. We have observed therefore that a broken terminal alkyl chain adversely affects the mesophase thermal stability, but does not eliminate mesomorphism.

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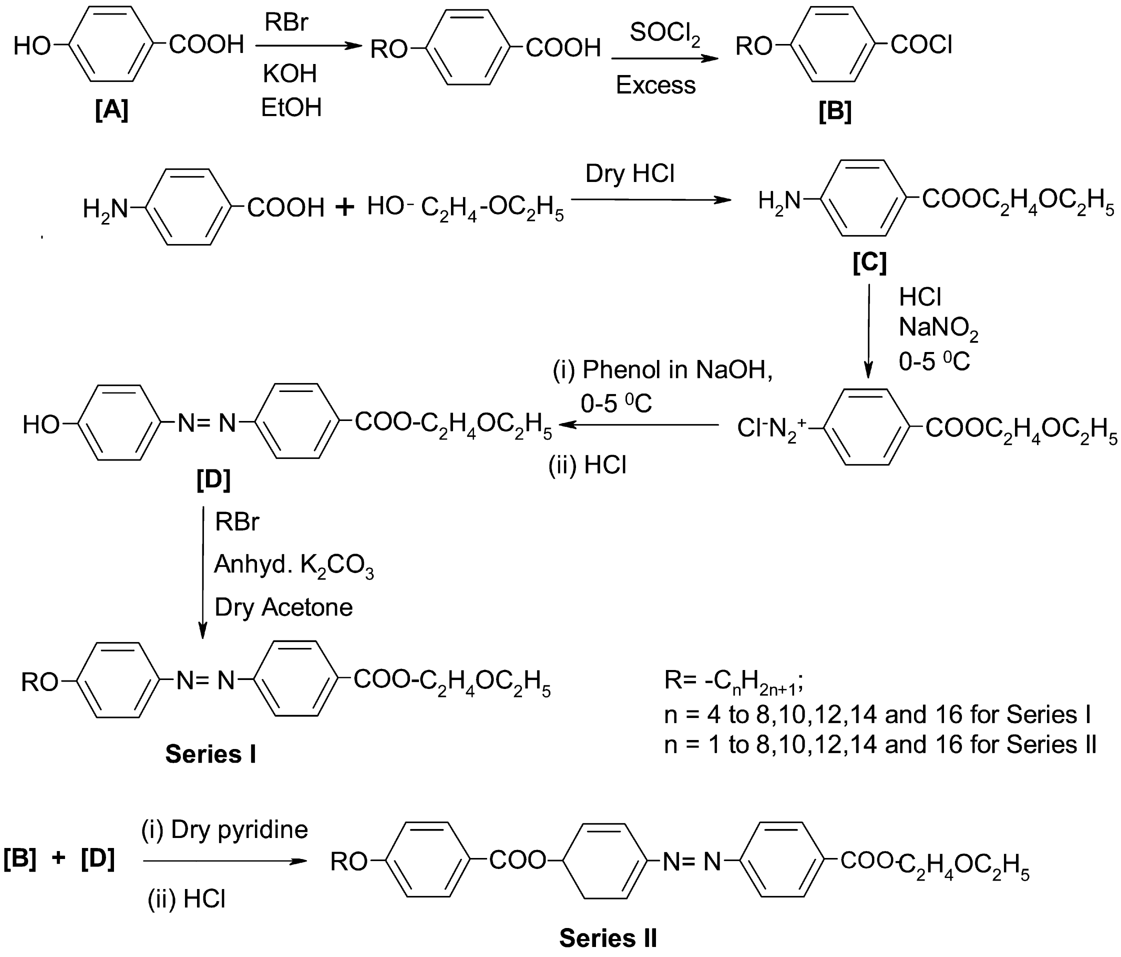
2. Experimental

4-Hydroxybenzoic acid, the appropriate *n*-alkyl halides, 4-aminobenzoic acid, ethoxyethanol, phenol and anhydrous K_2CO_3 were used as received. Solvents were dried and distilled before use. Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyser, and the values obtained are in close agreement with those calculated. IR spectra were determined for KBr pellets, using a Shimadzu IR-408 spectrophotometer. ^1H NMR spectra were obtained with a Perkin-Elmer R-32 spectrometer using tetramethylsilane (TMS) as internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference; $CDCl_3$ was used as solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope equipped with a heating stage. The enthalpies of transitions, reported as $J\,g^{-1}$, were measured on a Mettler TA-4000 system, at a scanning rate of $5°C\,min^{-1}$. The calorimeter was calibrated using pure indium as standard.

The synthetic route to compounds of series I and II is illustrated in the scheme. 4-*n*-Alkoxybenzoic acids [**A**] and 4-*n*-alkoxybenzoyl chlorides [**B**] were synthesized by the modified method of Dave and Vora [17]. Ethoxyethyl-4-aminobenzoate [**C**] was synthesized by the esterification of 4-aminobenzoic acid with 2-ethoxyethanol as described earlier [16]. The ester was crystallized several times from carbon tetrachloride until a constant melting point was obtained. The melting point of the product is 82°C (reported [16] 82°C). Ethoxyethyl 4-(4′-*n*-hydroxyphenylazo)benzoate [**D**] was synthesized by coupling the diazonium salt of ethoxyethyl 4-aminobenzoate with phenol [18]. The crude dye was crystallized repeatedly from aqueous ethanol until a constant melting point of 142°C was obtained.

Elemental analysis: found C 64.68, H 5.66, N 9.15; $C_{17}H_{18}N_2O_4$ requires C 64.97, H 5.73, and N 8.92%. The IR spectrum of the compound showed a broad peak associated with intermolecular hydrogen-bonded phenolic –OH between 3600 and $3200\,cm^{-1}$. The



Scheme 1. Synthetic route to series I and II compounds.

–COO– stretching vibrations were seen at 1700 cm^{-1}. Other signals observed were at 1600, 1500, 1470, 1375, 1260, 1140, 1040, 820 cm^{-1}.

2.1. *Synthesis of series I compounds*

Ethoxyethyl 4-(4′-*n*-hydroxyphenylazo)benzoate (0.1 mol), the appropriate *n*-alkyl halide (0.15 mol) and anhydrous K_2CO_3 (0.15 mol) were added to dry acetone (60 ml). The mixture was heated under reflux using a water bath for 8 h; the whole mass was then added to water. The solid was separated, dried and triturated by stirring for 30 min with 10% aqueous sodium hydroxide solution and washed with water. The insoluble product was thus separated from the reactants. Finally the products were crystallized from ethanol until constant transition temperatures were obtained. The elemental analyses of all compounds of series I were found to be satisfactory, and are listed in table 1.

IR (*n*-octyloxy derivative): 2920, 1725 (–COO–), 1605 (–N–N–), 1500, 1465, 1380, 1265, 1140, 1020, 840 cm^{-1}. ^1H NMR (*n*-octyloxy derivative, 300 MHz): δ 0.90 (t, 3H, $-CH_3$ at C-4′), 1.25–1.50 (m, 10H, 5 X $-CH_2-$), 1.70–1.90 (m, 5H, Ph–O–C–CH_2– and –O–C–CH_3), 3.45–3.65 (quart., 2H, –OCH_2– at C-1), 3.80 (t, 2H, $PhOCH_2$–), 4.05 (t, 2H, –COO–C–CH_2–), 4.50 (t, 2H, –$COOCH_2$–), 7.00 (d, $J=9$ Hz, 2H, ArH at C-3′ and C-5′), 7.85–7.95 (m, 4H, ArH at C-2′, C-6′, C-3 and C-5), 8.20 (d, $J=9$ Hz, 2H, ArH at C-2 and C-6).

2.2. *Synthesis of series II compounds*

Ethoxyethyl 4-(4′-*n*-hydroxyphenylazo)benzoate (0.02 mol) was dissolved in dry pyridine (5 ml) and a cold solution of a 4-*n*-alkoxybenzoyl chloride (0.02 mol) in dry pyridine (5 ml) was added slowly with constant stirring with ice bath cooling. The mixture was allowed to stand overnight at room temperature, and was then acidified with cold 1:1 aqueous hydrochloric acid. The solid was separated, dried and triturated by stirring for 30 min with 10% aqueous sodium hydroxide solution and washed with water. The insoluble product was thus separated from the reactants. Finally all the products were crystallized from acetic acid until constant transition temperatures were obtained. The elemental analyses of all compounds of series II were found to be satisfactory and are listed in table 1.

IR (*n*-butyloxy derivative): 2920, 1720 (–COO–), 1640 (–N–N–), 1600, 1500, 1405, 1300, 1265, 1060, 840 cm^{-1}. ^1H NMR (*n*-butyloxy derivative, 60 MHz): δ 0.90–2.00 (m, 10H, $-(CH_2)_2-CH_3$ and –O–C–CH_3), 3.40–3.85 (m, 4H, $PhOCH_2$– and –OCH_2– at C-1″), 4.05 (t, 2H, –COO–C–CH_2–), 4.50 (t, 2H, –COO–CH_2–), 7.00 (d, $J=9$ Hz, 2H, ArH at C-3′ and C-5′), 7.35 (d,

Table 1. Elemental analysis for series I and II compounds.

	$R=-C_nH_{2n+1}$ n	Molecular formula	% Required(found) C	H	N
Series I					
	4	$C_{21}H_{26}N_2O_4$	68.11(68.26)	7.03(7.24)	7.57(7.47)
	5	$C_{22}H_{28}N_2O_4$	68.75(68.89)	7.29(7.47)	7.29(7.33)
	6	$C_{23}H_{30}N_2O_4$	69.35(69.48)	7.54(7.65)	7.04(7.14)
	7	$C_{24}H_{32}N_2O_4$	69.90(69.84)	7.77(7.96)	6.80(6.88)
	8	$C_{25}H_{34}N_2O_4$	70.42(70.77)	7.98(7.86)	6.57(6.35)
	10	$C_{27}H_{38}N_2O_4$	71.37(71.42)	8.37(8.64)	6.17(6.50)
	12	$C_{29}H_{42}N_2O_4$	72.20(72.24)	8.71(8.43)	5.81(5.92)
	14	$C_{31}H_{46}N_2O_4$	72.94(73.21)	9.02(9.24)	5.49(5.64)
	16	$C_{33}H_{50}N_2O_4$	73.61(73.56)	9.29(9.34)	5.20(5.27)
Series II					
	1	$C_{25}H_{24}N_2O_6$	66.96(67.18)	5.36(5.47)	6.25(6.51)
	2	$C_{26}H_{26}N_2O_6$	67.53(67.25)	5.63(5.26)	6.06(5.84)
	3	$C_{27}H_{28}N_2O_6$	68.07(68.19)	5.88(6.04)	5.88(5.80)
	4	$C_{28}H_{30}N_2O_6$	68.57(68.62)	6.12(6.23)	5.71(5.74)
	5	$C_{29}H_{32}N_2O_6$	69.05(68.89)	6.35(5.98)	5.56(5.52)
	6	$C_{30}H_{34}N_2O_6$	69.50(69.22)	6.56(6.55)	5.41(5.61)
	7	$C_{31}H_{36}N_2O_6$	69.92(70.06)	6.77(6.54)	5.26(5.45)
	8	$C_{32}H_{38}N_2O_6$	70.33(70.24)	6.96(7.05)	5.13(5.29)
	10	$C_{34}H_{42}N_2O_6$	71.08(70.90)	7.32(7.56)	4.88(4.67)
	12	$C_{36}H_{46}N_2O_6$	71.76(71.64)	7.64(7.81)	4.65(4.92)
	14	$C_{38}H_{50}N_2O_6$	72.38(72.78)	7.94(8.21)	4.44(4.22)
	16	$C_{40}H_{54}N_2O_6$	72.95(72.82)	8.21(8.30)	4.26(4.13)

$J=9$ Hz, 2H, ArH at C-3 and C-5), 7.85–8.25 (m, 8H, ArH at C-2, C-6, C-3″, C-5″, C-2′, C-6′, C-2″ and C-6″).

3. Results and discussion

As a preliminary investigation, the mesophases exhibited by series I and II were examined using a polarizing optical microscope. Thin films of the samples were obtained by sandwiching them between a glass slide and a cover slip. All the compounds of series I and II show mesomorphism. On cooling the isotropic liquid in an untreated slide, focal-conic textures characteristic of the smectic A phase were-observed for compounds of series I. In series II compounds, on cooling the isotropic liquid small droplets appeared which coalesced to give classical schlieren (threaded) textures characteristic of the nematic phase. On further cooling, the higher members ($n \geq 4$) showed focal-conic textures characteristic of the smectic A mesophase. The associated enthalpies of transition of two derivatives of each of series I and II were measured by differential scanning calorimetry. Data are recorded in table 2. Enthalpy changes of the various transitions agree well with the existing related literature value [19].

Series I: ethoxyethyl 4-(4′-n-alkoxyphenylazo)benzoates. Nine compounds of series were synthesized and their mesogenic properties evaluated. All the compounds exhibit an enantiotropic smectic A mesophase; transition temperatures are recorded in table 3. The plot of transition temperature against the number of carbon atoms in the alkoxy chain (figure 1) shows a steady fall in the smectic–isotropic transition temperature with increasing chain length.

Series II: ethoxyethyl [4-(4′-n-alkoxybenzoyloxy) phenylazo]-4″-benzoates. All 12 members synthesized exhibit an enantiotropic nematic mesophase. A smectic A mesophase appears in the *n*-butyloxy derivative as an enantiotropic phase and remains in the series up to the *n*-hexadecyloxy derivative; transition temperatures are recorded in table 3. The entire homologous series II exhibits mesomorphism. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (figure 2) shows a smooth decrease in the

3

Table 2. DSC data for series I and II compounds.

Series	*n*	Transition	Peak temperature°C	ΔH/J g^{-1}	ΔS/J g^{-1} K^{-1}
I	8	Cr–Sm A	59.1	33.82	0.1018
		Sm A–I	77.7	1.53	0.0044
	14	Cr–Sm A	64.7	24.76	0.0733
		Sm A–I	77.7	1.26	0.0036
II	12	Cr–Sm A	95.4	62.7^a	0.1702
		Sm A–N	176.0	0.71	0.0016
		N–I	—	^{b}	—
	16	Cr–Sm A	74.0	26.3	0.0758
		Sm A–N	141.2	0.91	0.0022
		N–I	158.5	1.34	0.0031

[a] Total enthalpy including any other Cr–Cr transition.
[b] The enthalpy could not be measured.

Table 3. Transition temperatures(°C) of the series I and II compounds.

n	Cr		Sm A		N		I
Series I							
4	●	78.0	●	89.0	—	—	●
5	●	75.0	●	88.0	—	—	●
6	●	79.0	●	86.0	—	—	●
7	●	66.1	●	83.5	—	—	●
8	●	61.4	●	82.0	—	—	●
10	●	76.2	●	79.8	—	—	●
12	●	72.0	●	78.6	—	—	●
14	●	62.0	●	78.0	—	—	●
16	●	67.1	●	77.6	—	—	●
Series II							
1	●	152.0	—	—	●	244.0	●
2	●	143.0	—	—	●	238.0	●
3	●	132.0	—	—	●	227.0	●
4	●	103.0	●	152.0	●	219.5	●
5	●	85.5	●	173.0	●	213.0	●
6	●	87.0	●	176.0	●	211.0	●
7	●	94.0	●	174.0	●	209.0	●
8	●	93.5	●	172.0	●	205.5	●
10	●	90.0	●	170.0	●	198.0	●
12	●	95.5	●	169.0	●	192.0	●
14	●	95.0	●	167.0	●	187.0	●
16	●	87.0	●	158.5	●	182.5	●

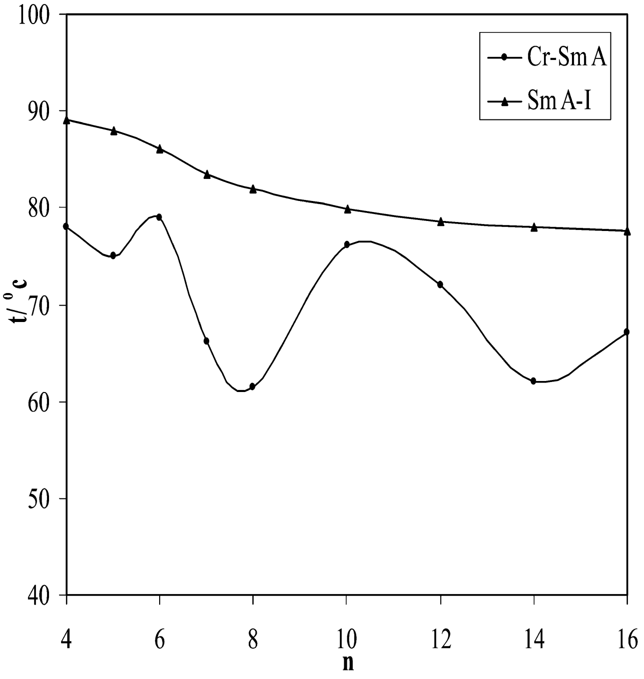


Figure 1. The phase behaviour of series I compounds.

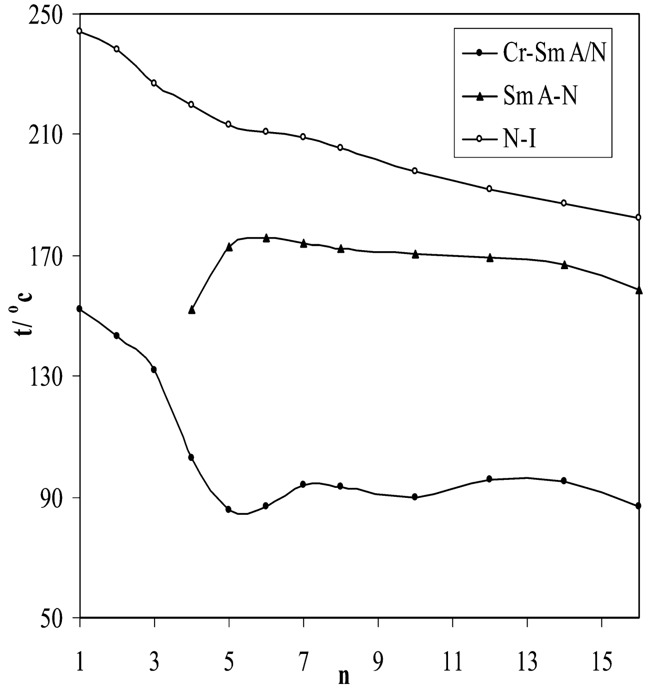


Figure 2. The phase behaviour of series II compounds.

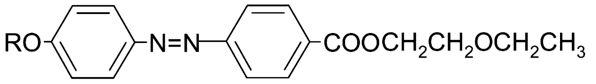
nematic–isotropic transition temperature with increasing chain length. In series II smectic mesophase appears earlier and exhibits a steep increase in the smectic–nematic transition temperature, before eventually decreasing on increasing the terminal chain length.

Table 4 summarizes the average mesophase range, average thermal stabilities and molecular structures of series I and II and the structurally related series A [14], B [20] and C [16] reported in the literature. Series II exhibits smectic and/or nematic mesophases whereas series I exhibits only a smectic mesophase. Also the comparison of n-decyl to *n*-hexadecyl ethers in series I and II shows that the average relative mesophase range and thermal stabilities of the smectic phase in series II are greater by 65.1 and 87.6°C, respectively, compared with series I. The mesogenic cores of series II are longer than those of series I because of the third aromatic ring and a central ester linkage. Gray [21] has explained that an increase in the length of a molecule, as a result of its enhanced anisotropy of polarizability, increases the intermolecular cohesive forces which are responsible for induction of the nematic phase, so also explaining the higher average smectic thermal stabilities of series II.

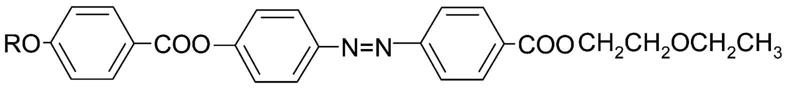
The smectic thermal stabilities of series I are higher than those of the structurally related series A. Gray [21] also noted that a compound which requires more thermal energy to disorganize the molecular arrangement of the smectic phase has a greater smectic thermal stability. As can be seen in table 4, more thermal energy has to be supplied to disorganize the molecular

Table 4. The average mesophase length (°C) average thermal stabilities (°C) and molecular structure of series I, II, A, B and C compounds.

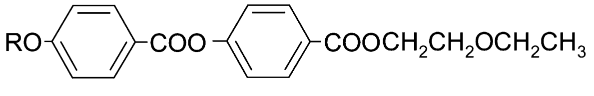
	Mesophase length		Thermal stabilities		
Series	N(C_1–C_6)	Sm(C_{10}–C_{16})	N(C_1–C_6)	Sm(C_{10}–C_{16})	Commencement of Sm phase
I	—	9.17	—	78.48	C_4
II	70.75	74.25	225.4	166.1	C_4
A	—	11.50	—	70.75	C_5
B	—	12.00	—	92.50	C_4
C	27.00	60.00	198.8	151.6	C_2



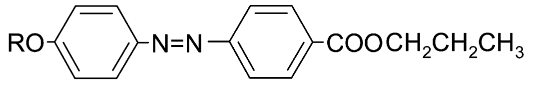
Series I



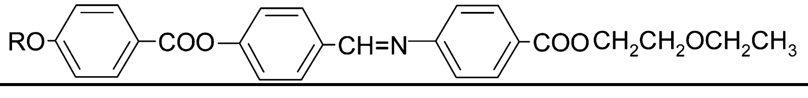
Series II



Series A



Series B



Series C

arrangement of the smectic phase of compounds of series I, as indicated by the fact that the average Sm–I transition temperatures are higher by 7.7°C than for compounds of series A. The slightly higher smectic thermal stabilities of series I may probably be due to the presence of the central –N–N– linkage which is more coplanar than the central –COO– linkage and allows the molecules to pack more efficiently, and hence that the smectic thermal stabilities of series I are a little higher than for series A. The average smectic mesophase temperature range of series I is lower than for series A. The thermal stability of a mesophase is a more important factor in relating mesomorphic behaviour to chemical constitution, since the temperature range of a mesophase is determined partly by the unpredictable nature of the crystal–mesophase transition temperature.

Reference to table 4 indicates that the average width and thermal stability of the smectic mesophase of series I are reduced by 2.8 and 14.0°C, respectively, compared with series B. The molecules of series I and B differ only at one terminus, the $-OC_2H_5$ terminal group of series I being replaced by $-CH_3$. Similar results from Wegand *et al.* [9] and this laboratory [14, 16] were noted in § 1.

Reference to table 4 also indicates that the average smectic and nematic mesophase temperature range, as well as the thermal stabilities of series II, are higher than for series C. The series differ only in the central linkage. In series II there is an azo central linkage whereas in series C there is an azomethine central linkage. As an azo central linkage is more coplanar than an azomethine central linkage, the explanation given previously would probably hold also in the comparison of these two series. However data for a wider range of similar series would help in further understanding such trends.

4. Conclusion

In this article we have presented the synthesis and characterization of two new mesogenic homologous series of azobenzene derivatives containing a terminal ethoxyethyl chain. Series I is purely smectogenic as it is a short two-phenyl ring system, whereas series II exhibits nematic as well as smectic A phase due to the presence of an additional phenyl ring along with an ester linkage. Although the broken alkyl chain is believed to be deleterious to mesomorphic behaviour, compounds containing such chains can exhibit mesomorphic properties with good thermal stabilities if properly designed.

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