

Azomesogens with methoxyethyl tail: Synthesis and characterization

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MS received 9 March 2004; revised 11 January 2005

Abstract. Two new mesogenic homologous series are synthesized from methoxyethyl 4-(4'-hydroxyphenylazo) benzoate. In series I the phenolic –OH group is alkylated, whereas in series II it is esterified with 4-*n*-alkoxybenzoyl group. In series I, all the nine members synthesized exhibit only enantiotropic smectic A mesophase. In series II, all the twelve homologues exhibit enantiotropic nematic mesophase. Smectic A mesophase appears from the *n*-decyloxy derivative as a enantiotropic phase and persists till the last *n*-hexadecyloxy member. The mesomorphic properties of both the series are compared with each other and also with the properties of other structurally related series to evaluate the effect of the methoxyethyl tail on mesomorphism.

Keywords. Azomesogens; methoxyethyl tail; smectic A; nematic.

1. Introduction

Terminal substituents play a significant role in promoting liquid crystalline properties in a mesogen. The terminal substituents generally consist of either a homologue alkoxy or alkyl group or a compact unit such as nitro, cyano, halogen etc.^{1,2} A number of mesogenic homologous series of achiral esters with branched alkyl tail are also reported in the literature.^{3,4} However, a literature survey indicates that liquid crystalline esters with tails comprising different kinds of atoms are very rare. To distinguish these tail groups from branched alkyl groups, we will refer to them as broken alkyl terminal groups or chains. Weygand *et al*⁵ have reported few compounds with alkyl chain combining two ether functions as a terminal substituent e.g. CH₃OCH₂O–. They observed that the mesomorphic property disappears entirely or they have lower nematic thermal stabilities than the analogous compounds containing the group CH₃CH₂CH₂O–.

Later on Chiang *et al*⁶ studied effect of ethoxyethoxy and butoxyethoxyethoxy tails on mesomorphism. Earlier, we have reported⁷ three mesogenic homologous series of esters having methoxyethyl and ethoxyethyl tails. All the three mesogenic homologous series exhibited smectic A mesophase at ambient temperatures. We have also reported⁸ binary sys-

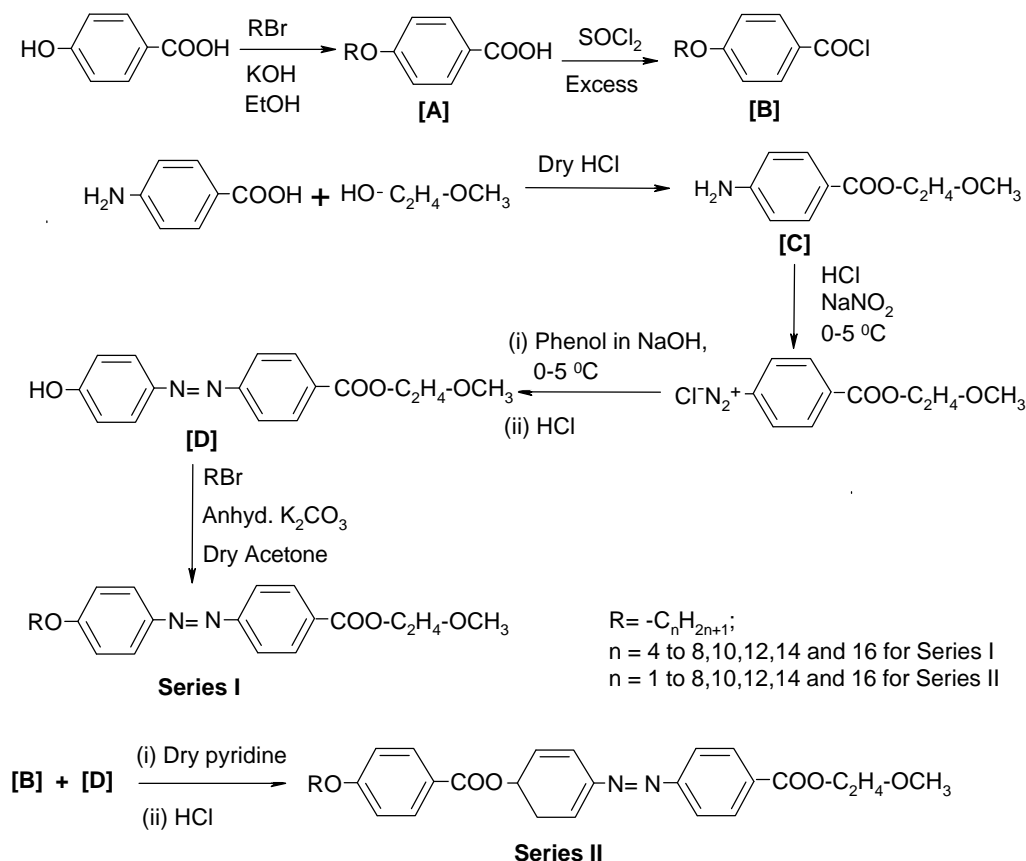
tems of such compounds with room temperature smectogenic properties and over a wide range of temperatures. Recently, we reported⁹ studies on the extensive mesogenic homologous series of Schiff's base esters having ethoxyethyl tails, which exhibited nematic and/or smectic mesophases with good thermal stabilities. We have therefore observed that such a broken alkyl chain at the terminus of a molecule adversely affects the mesophase thermal stability, but does not eliminate mesomorphism. In order to study further the effect of broken alkyl terminal chains on mesomorphism, two homologous series of azomesogens having methoxyethyl tails have been synthesized.

2. Experimental

2.1 Characterization

Microanalyses of the compounds were carried out on a Coleman carbon–hydrogen analyzer and the values obtained are in close agreement with those calculated. IR spectra were determined as KBr pellets, using a Shimadzu IR-408 spectrophotometer. ¹H NMR spectra were obtained with a Perkin–Elmer R-32 spectrometer using tetramethylsilane (TMS) as the internal reference standard. The chemical shifts are quoted as *d* (parts per million) downfield from the reference. CDCl₃ was used as a solvent for all

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Scheme 1. Synthetic route to series I and II.

the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage. The enthalpies of transitions reported as joules per gram, were determined from thermograms obtained on a Mettler TA-4000 system, adopting a scanning rate of 5°C/min. The calorimeter was calibrated using pure indium as standard.

2.2 Synthesis

4-Hydroxybenzoic acid, the appropriate *n*-alkyl bromides (BDH), 4-amino benzoic acid, 2-methoxyethanol, phenol, anhydrous K₂CO₃ and thionyl chloride (Sisco Chem.) were used as received. All the solvents were dried and distilled prior to use.

Compounds of the new series I and II were prepared following the pathway shown in scheme 1.

2.2a 4-*n*-Alkoxybenzoic acids (A) and 4-*n*-alkoxybenzoyl chlorides (B): These compounds were synthesized by a modified method.¹⁰

2.2b Methoxyethyl-4-aminobenzoate (C): This was synthesized by the esterification of 4-aminobenzoic acid with 2-methoxyethanol as described earlier.⁹

2.2c Methoxyethyl 4-(4-hydroxyphenylazo) benzoate (D): The compound D was synthesized by using the diazotization of methoxyethyl 4-aminobenzoate and coupling it with phenol.¹¹ The crude dye was crystallized repeatedly from aqueous ethanol till a constant melting point was obtained. m.p.: 212°C. Elemental analysis: found C 63.58, H 5.96, N 9.27%, C₁₆H₁₈N₂O₄ requires C 63.86, H 5.79, and N 9.14%. The IR spectrum of the compound showed a broad peak of intermolecular hydrogen-bonded phenolic -OH between 3500 and 3200 cm⁻¹. The -COO- stretching vibrations were seen at 1690 cm⁻¹. Other signals observed were at 1600, 1500, 1475, 1380, 1240, 1140, 840 cm⁻¹.

2.2d General procedure for synthesis of series I compounds: Compound D (0.1 mol), the appropri-

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

Compound	R = $-\text{C}_n\text{H}_{2n+1}$ $n =$	Formula	% Required (% found)		
			C	H	N
<i>Series I</i>					
1	4	$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$	67.41(67.23)	6.74(6.84)	7.86(7.47)
2	5	$\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4$	68.11(6.48)	7.03(7.43)	7.57(7.69)
3	6	$\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4$	68.75(68.90)	7.29(7.61)	7.29(6.93)
4	7	$\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_4$	69.35(69.48)	7.54(7.52)	7.04(7.41)
5	8	$\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_4$	69.90(69.74)	7.77(7.53)	6.80(6.74)
6	10	$\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}_4$	70.91(71.20)	8.18(8.46)	6.36(6.18)
7	12	$\text{C}_{28}\text{H}_{40}\text{N}_2\text{O}_4$	71.79(71.62)	8.55(8.54)	5.98(5.81)
8	14	$\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}_4$	72.58(72.42)	8.87(8.69)	5.65(5.48)
9	16	$\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_4$	73.28(72.38)	9.16(9.38)	5.34(5.65)
<i>Series II</i>					
1	1	$\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_6$	66.36(66.48)	5.07(5.17)	6.45(6.82)
2	2	$\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_6$	66.96(67.16)	5.36(5.31)	6.25(6.55)
3	3	$\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_6$	67.53(67.12)	5.63(5.71)	6.06(6.27)
4	4	$\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_6$	68.07(68.35)	5.88(5.91)	5.88(5.72)
5	5	$\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_6$	68.57(68.46)	6.12(6.48)	5.71(5.92)
6	6	$\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_6$	69.05(68.76)	6.35(6.83)	5.55(5.64)
7	7	$\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_6$	69.50(69.84)	6.56(6.87)	5.41(5.08)
8	8	$\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_6$	69.92(70.04)	6.77(6.48)	5.26(5.37)
9	10	$\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_6$	70.71(70.58)	7.14(7.02)	5.60(5.79)
10	12	$\text{C}_{35}\text{H}_{44}\text{N}_2\text{O}_6$	71.43(71.88)	7.48(7.52)	4.76(4.41)
11	14	$\text{C}_{37}\text{H}_{48}\text{N}_2\text{O}_6$	72.08(72.17)	7.79(8.03)	4.54(4.32)
12	16	$\text{C}_{39}\text{H}_{52}\text{N}_2\text{O}_6$	72.67(72.77)	8.67(8.70)	4.35(4.13)

ate *n*-alkyl bromide (0.15 mol) and anhydrous K_2CO_3 (0.15 mol) were added to dry acetone (60 ml). The mixture was refluxed on a water bath for eight hours. The whole mass was then added to the 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, all the products were crystallized from ethanol till constant transition temperatures were obtained. Results of elemental analysis of all the compounds of series I were found to be satisfactory, and are listed in table 1. IR and ^1H NMR spectral data of *n*-decyloxy derivative are given below.

IR spectrum (ν_{max} , cm^{-1}): 2920, 1720 ($-\text{COO}-$), 1605 ($-\text{N}=\text{N}-$), 1500, 1465, 1400, 1255, 1140, 1020, 845 cm^{-1} .

^1H NMR (200 MHz): **d** 0.90 (*t*, 3H, $-\text{C}-\text{CH}_3$), 1.20–1.50 (*m*, 16H, $8 \times -\text{CH}_2-$), 1.70–1.90 (*m*, 2H, $\text{PhO}-\text{C}-\text{CH}_2-$), 3.45 (*s*, 3H, $-\text{OCH}_3$), 3.75 (*t*, 2H, $\text{PhO}-\text{CH}_2-$), 4.05 (*t*, 2H, $-\text{COO}-\text{C}-\text{CH}_2-$), 4.50 (*t*, 2H, $-\text{COOCH}_2-$), 7.00 (*d*, $J = 9$ Hz, 2H, ArH at C-3' and C-6'), 7.80–7.95 (*m*, 4H, ArH at C-2', C-6', C3 and C-5), 8.20 (*d*, $J = 9$ Hz, 2H, ArH at C-2 and C-6).

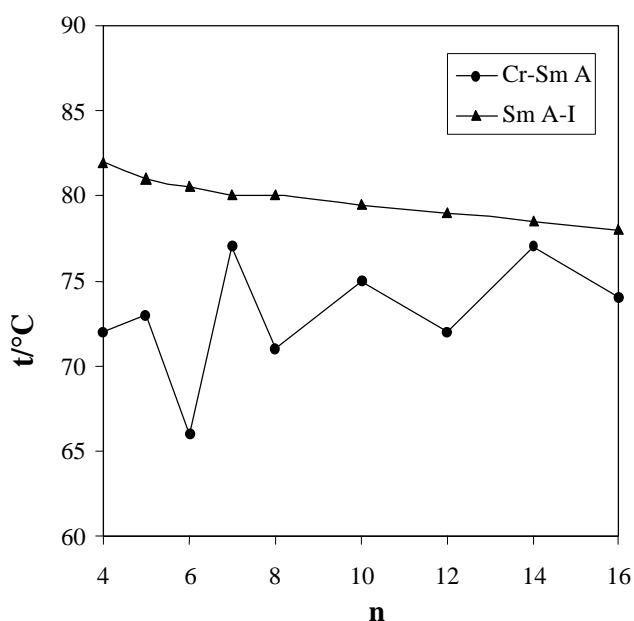
2.2e General procedure for synthesis of series II compounds: Compound D (0.02 mol) was dissolved in dry pyridine (5 ml) and a cold solution of 4-*n*-alkoxy benzoyl chloride (0.02 mol) in dry pyridine (5 ml) was added slowly to it in an ice bath with constant stirring. The mixture was allowed to stand overnight at room temperature. It was 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 then washed with water. The insoluble product was thus separated from the reactants. Finally all the products were crystallized from acetic acid till constant transition temperatures were obtained. Elemental analyses of all compounds of series II were satisfactory and are listed in table 1. IR and ^1H NMR spectral data of *n*-tetradecyloxy derivative are given below.

IR spectrum (ν_{max} , cm^{-1}): 2920, 1725 ($-\text{COO}-$), 1608 ($-\text{N}=\text{N}-$), 1510, 1415, 1265, 1172, 1080, 848.

^1H NMR (200 MHz): **d** 0.90 (*t*, 3H, $-\text{C}-\text{CH}_3$), 1.30–1.65 (*m*, 22H, $11 \times -\text{CH}_2-$), 1.80–1.90 (*m*, 2H, $\text{PhO}-\text{C}-\text{CH}_2-$), 3.45 (*s*, 3H, $-\text{OCH}_3$), 3.78 (*t*, 2H, PhOCH_2-), 4.05 (*t*, 2H, $-\text{COO}-\text{C}-\text{CH}_2-$), 4.55 (*t*,

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

Series	R = $-C_nH_{2n+1}$ $n =$	Transition	Peak temperature (°C)	ΔH (Jg ⁻¹)	ΔS (Jg ⁻¹ K ⁻¹)
I	6	Cr-Sm A	66.7	21.64	0.0637
		Sm A-I	79.3	1.38	0.0039
	10	Cr-Sm A	75.4	19.26	0.0553
		Sm A-I	80.1	2.17	0.0062
II	10	Cr-Sm A	103.2	24.35	0.0647
		Sm A-N	164.1	0.08	0.0002
		N-I	229.7	1.26	0.0025
	14	Cr-Sm A	82.9	32.41	0.0911
		Sm A-N	156.3	1.07	0.0025
		N-I	219.7	0.09	0.0002

**Figure 1.** Phase behaviour of series I.

2H, $-\text{COOCH}_2-$), 7.00 (*d*, $J = 9$ Hz, 2H, ArH at C-3' and C-5'), 7.40 (*d*, $J = 9$ Hz, 2H, ArH at C3 and C-5), 7.95–8.05 (*m*, 4H, ArH at C-2, C-6, C-3'' and C-5''), 8.05–8.25 (*m*, 4H, ArH at C-2', C-6', C-2'' and C-6'').

3. Results and discussion

As preliminary investigation, the mesophases exhibited by compounds of series I and II were examined by using an optical polarizing 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 on an ordinary slide, focal-conic textures characteristic of the smectic A

phase are observed for compounds of series I. In series II compounds, on cooling the isotropic liquid small droplets appear, which coalesce to classical schlieren (threaded) textures characteristic of the nematic phase. On further cooling, higher members ($n = 10$) show focal-conic texture characteristic of the smectic A mesophase.

Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results; therefore we may draw conclusions concerning the nature of the phases which occur during the transitions. In the present study, enthalpies of two derivatives of each series I and II were measured by differential scanning calorimetry. Data are recorded in table 2. Enthalpy values of the various transitions agree well with the existing related literature values¹² which fact has helped in further confirmation of the mesophase type.

3.1 Series I: Methoxyethyl-4-(4*n*-alkoxyphenylazo) benzoates

Nine compounds have been synthesized and their mesogenic properties are evaluated. All the compounds synthesized exhibit enantiotropic smectic A mesophase. The transition temperatures are recorded in table 3.

Plots of transition temperatures against the number of carbon atoms in the alkoxy chain (figure 1) show steady fall in smectic-isotropic transitions.

3.2 Series II: Methoxyethyl [4-(4*n*-alkoxybenzoyloxy) phenylazo]-4²-benzoates

All the twelve members synthesized exhibit enantiotropic nematic mesophase. Smectic A mesophase

appears from the *n*-butyloxy derivative as an enantiotropic phase and remains up to the *n*-hexadecyloxy derivative. The transition temperatures are recorded in table 4.

The entire homologous series II exhibit mesomorphism. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (figure 2) shows a smooth falling tendency for nematic–isotropic transition temperatures throughout the series. Series II also exhibit falling tendency of smectic–nematic transition temperatures for higher homologues. Table 5 summarizes the average mesophase range and average thermal stabilities as well as molecular structure of the present series I and II and the structurally related series A,^{7a} B¹³ and C^{7b} reported in the literature. Table 4 shows that series I exhibits only the smectic mesophase, whereas series

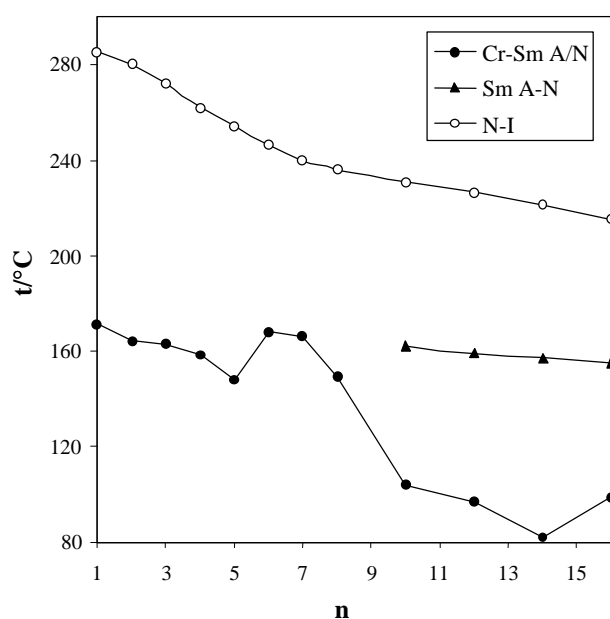


Figure 2. Phase behaviour of series II.

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

Compound	n =	Cr	Sm A	I
1	4	• 72.0	• 82.0	•
2	5	• 73.0	• 81.0	•
3	6	• 66.0	• 80.5	•
4	7	• 77.0	• 80.0	•
5	8	• 71.0	• 80.0	•
6	10	• 75.0	• 79.5	•
7	12	• 72.0	• 79.0	•
8	14	• 77.0	• 78.5	•
9	16	• 74.0	• 78.0	•

II exhibits smectic and/or nematic mesophases. Also the comparison of *n*-decyl to *n*-hexadecyl ethers in series I and II shows that the average relative mesophase length and thermal stabilities of the smectic phase in the series II are greater by 60.75°C and 79.50°C respectively compared to series I. The reference to molecular structure indicates that the molecules of series II are longer than the molecules of series I because of the third aromatic ring and a central ester linkage. Gray¹⁴ has explained that increase in the length of the molecules, as a result of its polarisability, increases the intermolecular cohesive forces which would be responsible for induction of nematic mesophase as well as the wider mesophase length and the higher average smectic thermal stabilities of series II molecules.

The smectic thermal stabilities of series I are higher as compared with those of the structurally related series A. Gray¹⁴ also defined that a compound which requires more thermal energy to disorganize the molecular arrangement of the smectic phase has greater smectic thermal stability. It can be seen from table 4 that more thermal energy has to be supplied to disorganize the molecular arrangement of the smectic phase of compounds of series I, as can be evidenced by the fact that the average Sm-I transition temperatures are higher by 8.00°C than those of compounds of series A. The slightly higher smectic thermal stabilities of series I may probably due to the presence of the –N=N– central linkage which is more coplanar than the –COO– central linkage and allows packing of the molecules such that the smectic thermal stabilities of series I become higher than those of series A. The average smectic mesophase length of series I molecules are lower than those of 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 may be determined partly by the unpredictable nature of the crystal-mesophase temperature.

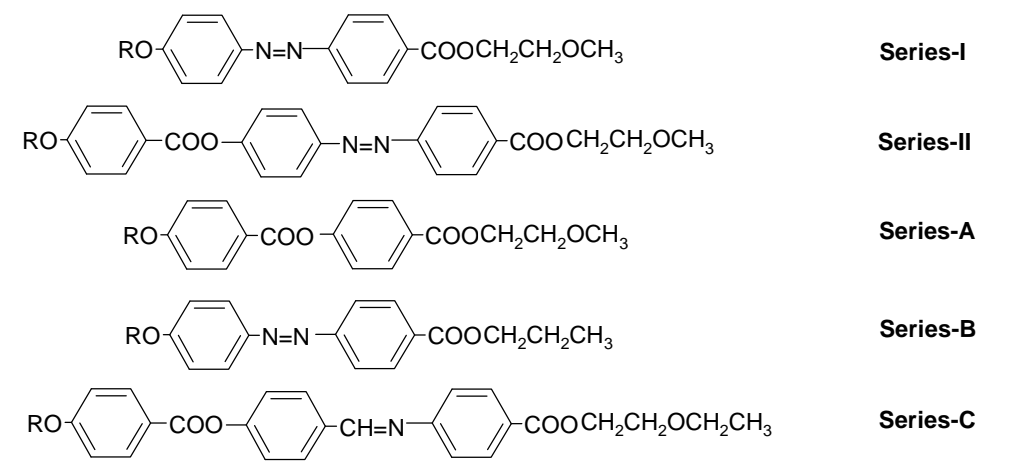
Reference to table 5 indicates that the average width and thermal stabilities of the smectic mesophase of series I are lowered by 7.50°C and 13.75°C respectively, compared to series B. The molecules of series I and series B differ only at one terminus. The –OCH₃ terminal group of series I is replaced by –CH₃ in series B. Weygand *et al*⁵ have studied an alkyl chain combining two ether functions, e.g. CH₃OCH₂O–. Relatively few compounds have been examined, but the data show that the mesomorphic

Table 4. Transition temperatures (°C) of the series II.

Compound	$n =$	Cr		Sm A		N		I
10	1	•	171	–	–	•	285	•
11	2	•	164	–	–	•	280	•
12	3	•	163	–	–	•	272	•
13	4	•	158	•	–	•	262	•
14	5	•	148	•	–	•	254	•
15	6	•	168	•	–	•	246	•
16	7	•	166	•	–	•	240	•
17	8	•	149	•	–	•	236	•
18	10	•	104	•	162	•	231	•
19	12	•	97	•	159	•	226	•
20	14	•	82	•	157	•	221	•
21	16	•	99	•	155	•	215	•

Table 5. The average mesophase length, average thermal stabilities and molecular structure of series I, II, A, B and C.

Series	Mesophase length		Thermal stabilities		Commencement of Sm phase
	N(C ₁ -C ₆)	Sm(C ₁₀ -C ₁₆)	N(C ₁ -C ₆)	Sm(C ₁₀ -C ₁₆)	
I	–	4.25	–	78.75	C ₄
II	87.83	65.00	267.83	158.25	C ₁₀
A	–	21.00	–	70.75	C ₅
B	–	12.00	–	92.50	C ₄
C	27.00	60.00	198.8	151.6	C ₂



property disappears entirely or they have lower nematic thermal stabilities than the analogous compounds containing the CH₃CH₂CH₂O– terminal substituent. Earlier, we⁷ have also observed that the broken alkyl chain at the terminus adversely affects mesophase thermal stabilities. In the present investigations also we have made the same observations.

Reference to table 5 also indicates that the average smectic and nematic mesophase length as well as thermal stabilities of present series II are higher than

for series C. Both the series differ by the central linkage and the terminal chain. In series II there is an azo central linkage and methoxyethyl tail, whereas in series C there is an azomethine central linkage and ethoxyethyl tail. As an azo central linkage is more coplanar than an azomethine central linkage, probably the explanation given in the forgoing discussion would hold well in the comparison of these two series. Moreover, earlier also we^{7a} have observed that ethoxyethyl mesophase thermal stabilities affects

more adversely as compared to the methoxyethyl tail. However, data for more such series would help in understanding these trends.

4. Conclusions

In this article we have presented the synthesis and characterization of two new mesogenic homologous series of azobenzene derivatives containing ethoxyethyl tails, as azobenzene derivatives are more stable compared to Schiff base derivatives. Series I is purely smectogenic as it is a short two-phenyl rings system, whereas series II exhibit nematic as well as smectic A mesophases due to the presence of an additional phenyl ring along with an ester linkage. Though the broken alkyl tail is believed to be deterrent to mesomorphic behaviour, the compounds exhibit mesomorphic properties with good thermal stabilities if properly designed.

Acknowledgements

The authors thank Prof S M Joshi, and Dr N D Jadav for encouragement.

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