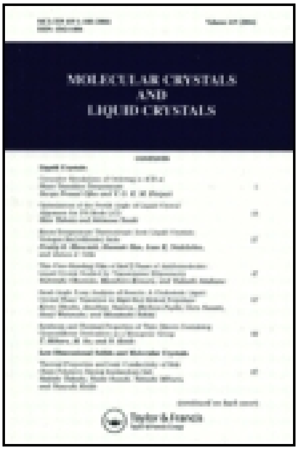

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Mesogenic Schiff's Base Esters with a Methoxyethyl Tail

A. K. Prajapati [a] & N. L. Bonde [a]

[a] Applied Chemistry Department, Faculty of Technology and Engineering, Kalabhavan M. S. University of Baroda, Vadodara, India

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Mesogenic Schiff's Base Esters with a Methoxyethyl Tail

A. K. Prajapati
N. L. Bonde
Applied Chemistry Department, Faculty of Technology and Engineering,
Kalabhavan M. S. University of Baroda, Vadodara, India

Two new mesogenic homologous series, each consisting of a methoxyethyl tail and a Schiff's base central linkage, have been synthesized by condensing 2-methoxyethyl 4-aminobenzoate with different 4-n-alkoxybenzaldehydes or 4-n-alkoxybenzoyloxybenzaldehydes to give series I and series II, respectively, and their mesomorphic behavior was studied. In series I, 2-methoxy ethyl 4-(4′-n-alkoxybenzylidine)aminobenzoates, the n-butoxy derivative is nonmesogenic whereas higher homologues exhibit the SmA mesophase. In series II, 2-methoxyethyl 4″-[4-(4′-n-alkoxybenzoyloxy)benzylidene]aminobenzoates, all the twelve compounds synthesized exhibit mesomorphism. Methoxy to n-octyloxy derivatives exhibit an enantiotropic nematic mesophase. The smectic A mesophase commences from n-propoxy derivative and persists up to the last homologue synthesized. 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.

Keywords: liquid crystals; methoxyethyl tail; Schiff's base esters

1. INTRODUCTION

Liquid-crystalline properties are highly sensitive to the molecular shape, lateral substituent, terminal substituent, hydrogen bonding, bridging group, breadth-to-length ratio etc.; all these effects are very well studied and reported in the literature [1–3].

The influence of the terminal substituent has a particular importance. Early reviews suggest that molecules of mesogenic compounds should contain moderately dipolar terminal groups. It has also been found that terminally substituted compounds exhibit higher

Address correspondence to A. K. Prajapati, Applied Chemistry Department, Faculty of Technology and Engineering, Kalabhavan M. S. University of Baroda, P.B. No. 50, Vadodara 390 001, India. E-mail: akprajapati@yahoo.co.uk

mesophase stability than unsubstituted compounds. It is also very well known that the terminal substituent increases the overall polarizability of the molecule without increasing its breadth and hence it has the higher mesophase stability. Generally in a liquid-crystalline compound, the end groups are compact units like –CN, $-NO_2$, or flexible chains such as *n*-alkyl or *n*-alkoxy [4–8]. There have been few research papers indicating a branch chain at the terminal position [9–11]. Booth *et al.* have described the synthesis and characterization of three achiral-branched alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)-3-fluorobenzoates that show SmC_{alt} and overlying SmA phases [12].

There are also very few examples that have a broken alkoxy terminal chain. Weygand *et al.* [13] have reported mesogenic properties of an alkyl chain combining two ether functions as a terminal substituent. Chiang *et al.* [14,15] studied the effect of ethoxyethoxyethoxy and butoxyethoxyethoxy tails on mesomorphism. They reported that the latter unit has greater Smetic C (SmC^*) thermal stability than the former unit. Earlier we have reported methoxyethyl and ethoxyethyl esters of 4(4′-*n*-alkoxybenzoloxy)benzoic acids [16] as well as methoxyethyl trans-4(4′-*n*-alkoxybenzoyloxy)-α-methylcinnamates [17]. All the three mesogenic homologous series exhibited the smectic A mesophase at ambient temperatures. To study the effect of an azo central linkage on thermal stability, we have reported mesogenic homologous series of azomesogens with an ethoxyethyl [18] and a methoxtethyl tail [19]. We [20] have also synthesized a mesogenic homologous series of Schiff's base esters containing an ethoxyethyl tail and evaluated the effect of a Schiff's base linkage and an ethoxyethyl tail on mesomorphism. From all these studies we have observed that such terminal chains adversely affect the mesophase thermal stability but do not eliminate mesomorphism. In continuation of our work on a substituted ethyl tail, we have synthesized two new mesogenic homologous series with a methoxyethyl tail and evaluated the effect of a methoxyethyl tail and a Schiff's base linkage on mesomorphism.

2. EXPERIMENTAL

2.1. Materials

4-Hydroxybenzoic acid, 4-hydroxybenzaldehyde, 4-aminobenzoic acid, 1-bromoalkanes, potassium hydroxide, potassium carbonate, thionyl chloride, and 2-methoxyethanol were used as received. Solvents were dried and distilled prior to use.

2.2. Characterization

Microanalyses of the compounds were performed on a Perkin Elmer Series 2400 elemental analyzer. IR spectra were determined using KBr pellets, using a Shimandzu IR-408 specrophotometer. ^{1}H NMR spectra were obtained with a Bruker Dpx 200 spectrometer, using tetramethylsilane (TMS) as an internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference. $CDCl_3$ was used as a solvent. The liquid-crystalline properties of the compounds were investigated on a Leitz Laborlux 12 POL microscope equipped with a heating stage. The enthalpies of transitions reported as J/g were determined from thermograms obtained on a Universal V3.0G TA instrument adopting a rate of 5°C/min. The calorimeter was calibrated using pure indium as the standard.

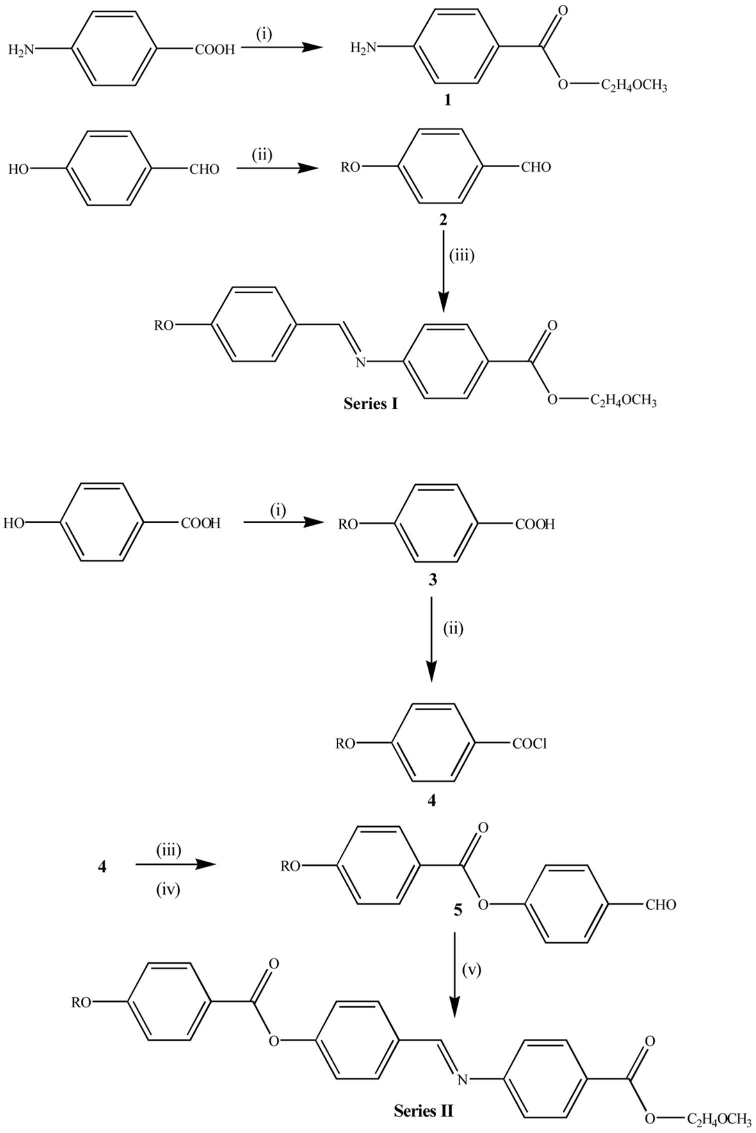
2.3. Synthesis

The synthetic routes of both series are illustrated in Scheme 1.

2-Methoxyethyl 4-aminobenzoate **(1)** was synthesized by the esterification of 4-aminobenzoic acids with 2-methoxyethanol [21]. The ester was crystallized repeatedly until a constant melting point was obtained, resulting in a white solid product. Mp: 58°C; yield: 67%. Elemental analysis: found C 61.74, H 6.82, N 7.05; $C_{10}H_{13}NO_3$ requires C 61.53, H 6.67, N 7.17%. The Fourier transform infrared (FTIR) spectrum of the compound showed two bands for N—H stretching vibrations of a free amino group at 3453 and 3360 cm^{-1}. The ester (–COO–) stretching vibrations were seen at 1686 cm^{-1}. The other signals observed were at 1634 (N—H bending vibration), 1607, 1520, 1445, 1310, 1275, 1310, 1105, 840 cm^{-1}.

4-*n*-Alkoxybenzaldehydes **(2)** were prepared by the method of Gray and Jones [22].

2-Methoxyethyl 4-(4′-*n*-alkoxybenzylidine)aminobenzoates (Series I) was prepared as follows: nine Schiff's bases of series XI were synthesized by condensing equimolar quantities of 2-methoxyethyl 4-aminobenzoate **(1)** and the appropriate 4-*n*-alkoxybenzaldehyde **(2)** in boiling ethanol. All the Schiff's bases were crystallized from methanol until constant transition temperatures were obtained. Yield: 83–91%. The elemental analysis of all the compounds were found to be satisfactory, and all are listed in Table 1. IR and ^{1}H NMR spectral data of *n*-dodecyloxy and *n*-tetradecyloxy derivatives as representative members are given below.



SCHEME 1 (a) (i) Dry HCL, $CH_3OC_2H_4OH$, reflux; (ii) R Br, K_2CO_3, acetone, reflux; (iii) EtOH, **1**, AcOH (cat.), reflux; Series I: $R = -C_nH_{2n+1}$, n = 4–8, 10, 12, 14, and 16; (b) (i) RBr, KOH, EtOH; (ii) $SOCl_2$ (excess); (iii) 4-hydroxy benzaldehyde, pyridine; (iv) cold aqueous 1:1 HCl; (v) EtOH, **1**, AcOH (cat.), reflux; Series II: $R = -C_nH_{2n+1}$, n = 1–8, 10, 12, 14, and 16.

TABLE 1 Elemental Analysis for Series I and II Compounds

Compound no.	$R = C_nH_{2n+1}$ n	Molecular formula	% Required (found)		
			C	H	N
Series I					
1	4	$C_{21}H_{25}NO_4$	74.34(74.61)	7.37(7.69)	4.13(3.77)
2	5	$C_{22}H_{27}NO_4$	74.79(74.92)	7.65(7.50)	3.97(3.54)
3	6	$C_{23}H_{29}NO_4$	75.20(74.82)	7.9(7.53)	3.81(3.62)
4	7	$C_{24}H_{31}NO_4$	75.59(75.83)	8.14(8.32)	3.67(3.83)
5	8	$C_{25}H_{33}NO_4$	75.95(75.61)	8.35(8.61)	3.54(3.54)
6	10	$C_{27}H_{37}NO_4$	76.6(76.87)	8.75(8.98)	3.31(3.04)
7	12	$C_{29}H_{41}NO_4$	77.16(77.61)	9.09(8.84)	3.1(3.29)
8	14	$C_{31}H_{45}NO_4$	77.66(77.53)	9.39(9.16)	2.92(3.18)
9	16	$C_{33}H_{49}NO_4$	78.11(77.69)	9.66(9.73)	2.76(2.43)
Series II					
10	1	$C_{25}H_{23}NO_6$	69.28(69.59)	5.31(5.62)	3.23(3.46)
11	2	$C_{26}H_{25}NO_6$	69.8(69.54)	5.59(5.30)	3.13(2.84)
12	3	$C_{27}H_{27}NO_6$	70.28(70.49)	5.86(5.42)	3.04(2.93)
13	4	$C_{28}H_{29}NO_6$	70.73(70.81)	6.11(5.92)	2.95(3.29)
14	5	$C_{29}H_{31}NO_6$	71.17(70.98)	6.34(6.65)	2.86(2.54)
15	6	$C_{30}H_{33}NO_6$	71.57(71.36)	6.56(6.61)	2.78(2.97)
16	7	$C_{31}H_{35}NO_6$	71.95(72.37)	6.78(6.99)	2.71(2.94)
17	8	$C_{32}H_{37}NO_6$	72.32(72.04)	6.97(7.02)	2.64(2.17)
18	10	$C_{34}H_{41}NO_6$	72.99(72.81)	7.33(6.91)	2.5(2.84)
19	12	$C_{36}H_{45}NO_6$	73.59(73.21)	7.67(7.38)	2.39(2.03)
20	14	$C_{38}H_{49}NO_6$	74.15(74.53)	7.97(7.81)	2.28(2.61)
21	16	$C_{40}H_{53}NO_6$	74.65(74.79)	8.24(8.51)	2.14(1.80)

2-Methoxyethyl 4-(4′-n-dodecyloxybenzylidine)-aminobenzoate

IR spectrum (KBr) ν_{max}/cm^{-1}: 2921 ($\nu_{C-H,}$ aliphatic), 2847, 1702(–COO–), 1594(–CH=N–), 1511, 1416, 1168, 1099, 839.

^{1}H NMR spectrum ($CDCl_3$, 200 MHz): δ 8.35 (s, 1H, –CH=N–), 8.08 (d, $J = 8.7$ Hz, 2H, ArH at C-2 and C-6), 7.84 (d, $J = 8.4$ Hz, 2H, ArH at C-2′ and C-6′), 7.19 (d, $J = 8.7$ Hz, 2H, ArH at C-3 and C-5), 6.98 (d, $J = 9$ Hz, 2H, ArH at C-3′ and C-5′), 4.48 (t, $J = 4.4$ Hz, 2H, $-COOCH_2C-$), 4.03 (t, $J = 4.4$ Hz, 2H, $Ar-O-CH_2-$), 3.74 (t, $J = 5.1$ Hz, 2H, $-COOCCH_2-$), 3.44 (s, 3H, $-O-CH_3$), 1.82 (m, 2H, $ArOCCH_2-$), 1.27–1.58 (m, 18H, 9x$-CH_2-$), 0.88 (t, $J = 6$ Hz, 3H, $-CH_3$).

2-Methoxyethyl 4-(4′-n-tetradecyloxybenzylidine)-aminobenzoate

IR spectrum (KBr) ν_{max}/cm^{-1}: 2918 ($\nu_{C-H,}$ aliphatic), 2850, 1718 (–COO–), 1593 (–CH=N–), 1512, 1419, 1168, 1109, 841.

^{1}H NMR spectrum ($CDCl_3$, 200 MHz): **δ** 8.35 (s, 1H, −CH=N−), 8.08 (d, $J = 8.7$ Hz, 2H, ArH at C-2 and C-6), 7.84 (d, $J = 8.0$ Hz, 2H, ArH at C-2′ and C-6′), 7.19 (d, $J = 8.7$ Hz, 2H, ArH at C-3 and C-5), 6.98 (d, $J = 9$ Hz, 2H, ArH at C-3′ and C-5′), 4.48 (t, $J = 4.6$ Hz, 2H, $-COOCH_2C-$), 4.03 (t, $J = 6.4$ Hz, 2H, $Ar-O-CH_2$), 3.74 (t, $J = 5.1$ Hz, 2H, $-COOCCH_2-$), 3.44 (s, 3H, $-O-CH_3$), 1.82 (m, 2H, $ArOCCH_2-$), 1.27–1.58 (m, 22H, 11x$-CH_2-$), 0.88 (t, $J = 6$ Hz, 3H, $-CH_3$).

4-*n*-Alkoxybenzoic acid **(3)** and 4-*n*-alkoxybenzoyl chloride **(4)** were synthesized by the method of Dave and Vora [23].

4-*n*-Alkoxybenzoylxoy-4′-benzaldehydes **(5)** were synthesized by the method of Dave and Kurian [24].

2-Methoxyethyl 4″-[4-(4′-*n*-alkoxybenzoyloxy)benzylidene]aminobenzoates (Series II) were synthesized as follows:

The corresponding 4-*n*-alkoxybenzoylxoy-4′-benzaldehyde (0.01 mol) **(5)** was dissolved in dry ethanol and was added dropwise to the round-bottom flask containing 2-methoxyethyl 4-aminobenzoate (0.01 mol) **(1)**, which was previously dissolved in dry ethanol. The resulting reaction mixture was refluxed for 2 h. The crude product was repeatedly crystallized from dry ethanol to give a white solid compound. The elemental analysis of all the compounds were found to be satisfactory and are recorded in Table 1. IR and ^{1}H NMR spectral data of *n*-tetradecyloxy derivative as a representative member are given below.

2-Methoxyethyl 4″-[4-(4′-n-tetradecyloxybenzoyloxy)-benzylidene]aminobenzoate

IR spectrum (KBr) ν_{max}/cm^{-1}: 2919 ($\nu_{C-H,}$ aliphatic), 2851, 1711 (−COO−), 1599 (−CH=N−), 1513, 1414, 1171, 1116, 844.

^{1}H NMR spectrum ($CDCl_3$, 400 MHz): **δ** 8.44 (s, 1H, −CH=N−), 8.1 (m, 4H, ArH at C-2′, C-6′, C-2″ and C-6″), 7.96 (d, $J = 8.7$ Hz, 2H, ArH at C-2 and C-6), 7.36 (d, $J = 8.6$ Hz, 2H, ArH at C-3″ and C-5″), 7.26 (d, $J = 9$ Hz, 2H, ArH at C-3 and C-5), 7.0 (d, $J = 9$ Hz, 2H, ArH at C-3′ and C-5′), 4.5 (t, $J = 4.7$ Hz, 2H, $-COOCH_2-$), 4.02 (t, $J = 6.4$ Hz, 2H, $ArOCH_2-$), 3.75 (t, $J = 5.0$ Hz, 2H, $-COOCCH_2-$), 3.4 (s, 3H, $-OCH_3$), 1.82 (m, 2H, $Ar-O-C-CH_2-$), 1.26 (m, 22H, 11x$-CH_2-$), 0.9 (t, 3H, $-CH_3$).

3. RESULTS AND DISCUSSION

3.1. Optical Microscopic Studies

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.

Series I

First member synthesized ($n = 4$) of the series I is nonmesogenic. On cooling from the isotropic liquid in an ordinary slide, n-pentyloxy to n-hexadecyloxy derivatives of the series I show the focal conic texture characteristic of SmA phase.

Series II

On cooling from the isotropic liquid, the methoxy to n-octyloxy derivatives of series II show the threaded/marble texture characteristic of nematic mesophase, which on further cooling ($n \geq 3$), transforms into the focal conic texture of a SmA mesophase. On cooling from the isotropic liquid, the n-decyloxy to n-hexadecyloxy derivatives show focal conic textures of the SmA mesophase.

3.2. DSC Studies

As representative cases, the associated enthalpies of transition of the n-dodecyloxy derivative of series I as well as the n-decyloxy and the n-tetradecyloxy derivatives of series II were measured by differential scanning calorimetry (DSC). Data are recorded in Table 2. Enthalpy changes of the various transitions agree well with the existing related literature value [25].

3.3. The Phase Behavior

Series I: 2-Methoxyethyl 4-(4′-n-alkoxybenzylidine)-aminobenzoates

Nine compounds were synthesized, and their mesogenic properties were evaluated. The n-butoxy derivative is nonmesogenic, but the n-pentyloxy derivative exhibits a monotropic SmA phase, whereas for n-hexyloxy, all the members exhibit an enantiotropic SmA mesophase. The transition temperatures are recorded in Table 3. A plot of transition temperatures against the number of carbon atoms in the alkoxy chain is shown in Fig. 1. The SmA–I curve rises steeply at first, which reaches to maxima for the n-heptyloxy derivative before falling progressively.

Series II: 2-Methoxyethyl 4″-[4-(4′-n-alkoxybenzoyloxy)-benzylidene]aminobenzoates

All the twelve compounds synthesized exhibit mesomorphism. The methoxy to n-octyloxy derivatives exhibit an enantiotropic nematic mesophase. The SmA mesophase commences from the n-propyloxy

TABLE 2 Transition Temperatures (°C) of the Series I and II Compounds

Compound no.	R = $-C_nH_{2n+1}$ n	Cr		SmA		N		I
Series I								
1	4	●	71	—	—	—	—	●
2	5	●	(61)*	●	—	—	75	●
3	6	●	63	●	—	—	77	●
4	7	●	59	●	—	—	83	●
5	8	●	57	●	—	—	81	●
6	10	●	42	●	—	—	77	●
7	12	●	58	●	—	—	68	●
8	14	●	61	●	—	—	67	●
9	16	●	60	●	—	—	66	●
Series II								
10	1	●	161	—	—	●	219	●
11	2	●	158	—	—	●	217	●
12	3	●	136	●	156	●	215	●
13	4	●	134	●	154	●	211	●
14	5	●	135	●	148	●	207	●
15	6	●	127	●	146	●	202	●
16	7	●	120	●	145	●	197	●
17	8	●	117	●	148	●	192	●
18	10	●	115	●	—	—	174	●
19	12	●	114	●	—	—	163	●
20	14	●	117	●	—	—	158	●
21	16	●	101	●	—	—	146	●

Notes. ( )*, monotropic value; Cr, crystalline solid; Sm A, Smectic A phase; Sm C, Smectic C phase; N, Nematic phase; I, isotropic liquid phase; ●, phase exists; and —, phase does not exist.

derivative and persists up to the final homologue synthesized. The transition temperatures are recorded in Table 3. A plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Fig. 2) shows smooth falling tendencies for the N-I and the SmA–I

TABLE 3 DSC Data for Series I and II

Series	Compound no.	Transition	Peak temp. (°C)	ΔH (J/g)	ΔS(J/gK)
I	7	Cr-Sm A	57.00	41.30	0.2464
		Sm A-I	67.50	2.06	0.0311
II	18	Cr-Sm A	115.56	18.65	0.0480
		Sm A-I	174.07	2.19	0.0050
	20	Cr-Sm A	118.18	17.80	0.0460
		Sm A-I	156.83	3.96	0.0120

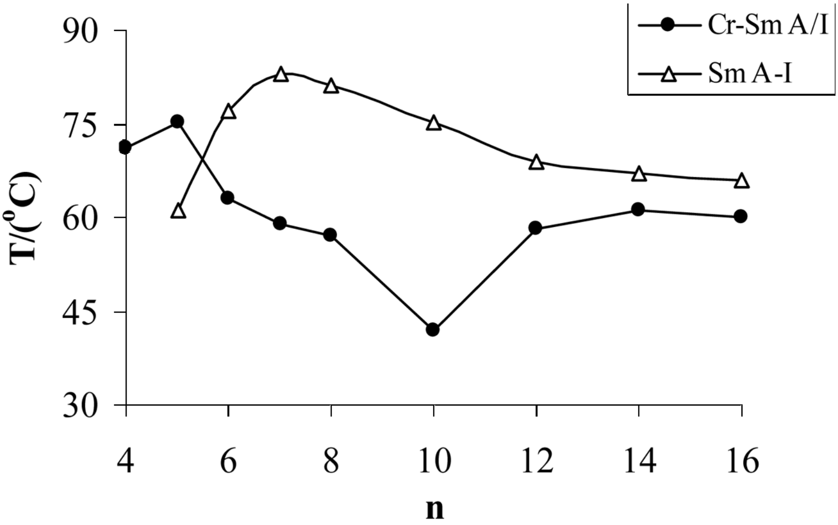


FIGURE 1 Phase behavior of series I.

transition temperatures with increasing chain length. The SmA–N transition temperatures a show smooth falling and then a rising tendency for the *n*-octyloxy homologue of the series.

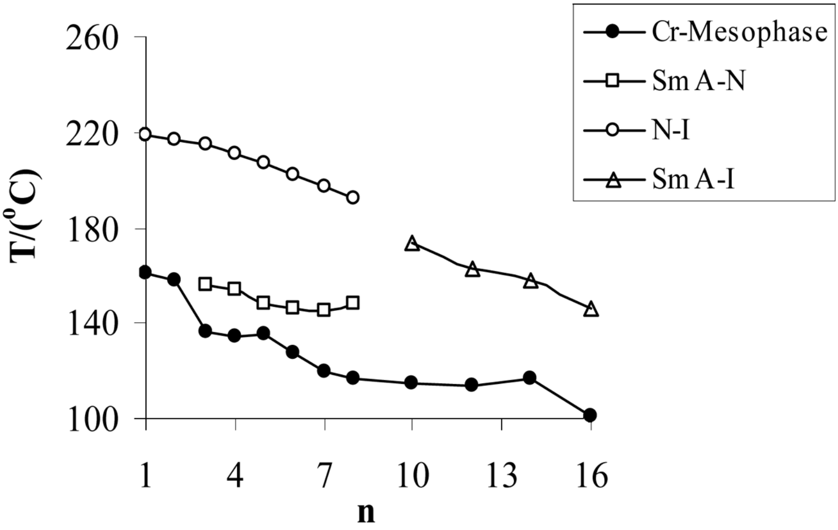


FIGURE 2 Phase behavior of series II.

3.4. Mesogenic Properties and Molecular Constitution

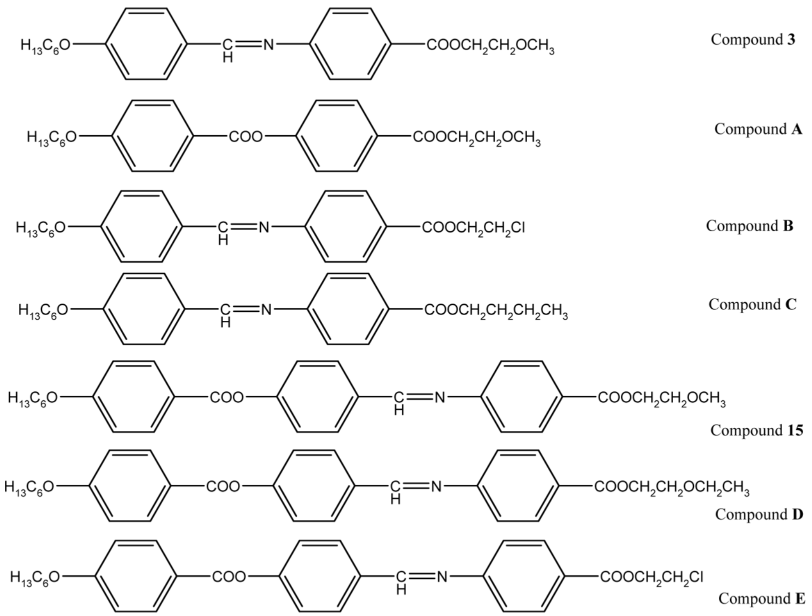
It is well known that thermotropic liquid crystals are highly sensitive to the molecular constitution. It is of prime importance from the chemist's point of view to find the effect of alteration in molecular core to the mesogenic properties of the compound. As mentioned previously, the thermal stability and mesophase length as a measure of mesomorphism can be correlated with the molecular constitution of the compounds.

Table 4 and Scheme 2 summarize the mesophase range (width of mesophase), thermal stability, and molecular structures of the *n*-hexyloxy derivative of present series I and II (compounds **3** and **15**) and structurally related compounds **A** [16], **B** [26], **C** [27], **D** [20], and **E** [26]. Table 4 indicates that compound **3** exhibits an enantiotropic SmA mesophase, whereas compound **15** exhibits on enantiotropic SmA phase as well as the enantiotropic nematic mesophase. The smectic mesophase range and smectic phase thermal stability of compound **15** is greater by 9°C and 73°C than those of compound **3**. Reference to the molecular structure of both the compounds indicates that compound **15** differs from compound **3** in the number of benzene rings and central linkages. Compound **15** is longer than that of compound **3** because of the additional phenyl ring and ester central linkage. Gray [28] has explained that the increase in the length of the molecule, as a result of its polarizability, increases the intermolecular cohesive forces that would be responsible for the induction of the nematic mesophase and the higher smectic phase thermal stabilities of compound **15** than of compound **3**.

The smectic mesophase range and smectic mesophase thermal stability of compound **3** is higher by 6°C and 34°C than those of

TABLE 4 Comparison of Mesophase Length (°C), Thermal Stabilities (°C), and Molecular Structure of Compounds **3**, **16**, **A**, **B**, **C**, **D**, and **E**

Compound no.	Mesophase length		Thermal stabilities		Commencement of Smectic phase
	Sm	N	Sm	N	
3	14	—	77	—	5
A	8	—	43	—	5
B	23	—	88	—	5
C	16.5	—	84.5	—	2
15	23	52	150	202	3
D	78	6.5	183.5	190	2
E	21	61	190	251	3



SCHEME 2

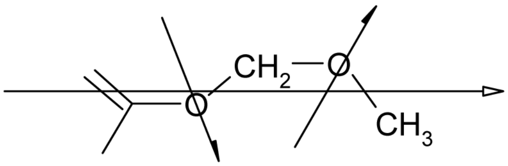
compound **A** (Table 4); both the compounds differ only at the central linkage. Compound **3** has an azomethine (–CH=N–) central linkage, whereas compound **A** has an ester (–COO–) central linkage. The azomethine central linkage is more coplanar and provides such packing to the molecules that the smectic phase thermal stability increases. It is also known that the liquid-crystalline properties are enhanced most when all the rings are conjugated; *i.e.*, the liquid crystal transition temperatures are highest when the entire system is linked through central linking groups involving multiple bonds (*e.g.*, −CH=N− or −CH=CH–). But the central ester linkage does not link the system through a multiple bond, and hence the mesogenic thermal stability of a system connected via a azomethine linkage is higher.

Reference to Table 4 indicates that the smectic mesophase range and smectic mesophase thermal stability of compound **3** is lower by 9°C and 11°C respectively than those of compound **B**. The molecular structural difference between compound **3** and **B** lies in the terminal position. The ester tail is changed from a methoxy group for compound **3** to a chloro group for compound **B**. The more polar chloro group enhances the polarizability of the molecule of compound **B** and hence the mesophase thermal stability. This is also reflected in the comparison of compounds **15** and **E** where the smectic mesophase thermal stability of compound **15** is lower by 40°C and the nematic mesophase range as well as nematic mesophase thermal stabilities are lower by 9°C and 49°C, respectively, than those of compound **E**.

From Table 4 we can see that the smectic mesophase range and smectic mesophase thermal stability of compound **3** is lower by 2.5°C and 7.5°C respectively than those of compound **C**. Both the compounds differ at one terminus only. The ester tail is methoxyethyl for compound **3**, whereas it is an n-butyl chain for compound **C**. Weygand *et al.* [13] have reported mesogenic properties of an alkyl chain combining two ether functions as a terminal substituent, *e.g.*, CH_3OCH_2O-. Few compounds have been examined, but the data show that the mesomorphic property disappears entirely or has lower nematic thermal stabilities than the analogous compounds containing the group $CH_3CH_2CH_2O-$. Attempts have been made to explain this effect in terms of differences in the linear nature of the two groups (one compound contains one and the other contains two oxygen atoms), but it is quite likely that the reason lies in some interaction between the two ether dipoles. For example, the effective dipole moment of the group CH_3OCH_2O- may be a weaker resultant dipole along the axis of the chain (Scheme 3).

Probably because of the same reason, the smectic mesophase range and smectic mesophase thermal stability of compound **3** is lower, as it contains a broken alkyl chain (methoxyethyl chain) at the terminus, than for compound **C**, which has an n-butyl tail. Previously, we [16–20] have also observed that a broken alkyl chain at the terminus adversely affects the smectic thermal stability.

Table 4 shows that the nematic mesophase length of compound **15** is lower by 45.5°C, whereas the nematic thermal stability is higher by 12°C, than those of compound **D**. Table 4 also shows that the smectic mesophase length and smectic mesophase thermal stability of compound **15** is lower by 55°C and 23.5°C than those of compound **D**. Reference to the molecular structure of both these compounds, indicates that both the compounds differ only at one terminal chain. In compound **D** one more methylene unit is present at the terminal



SCHEME 3 Partial dipole cancellation in the group $-OCH_2OCH_3$.

broken alkyl ester chain. The addition of the methylene group decreases the strength of the terminal intermolecular cohesions. However, the addition of a methylene group does increase the polarizability of the molecule of compound **D**. Such increase in the molecular polarizability tends to increase the smectic mesophase thermal stability of compound **D** more than compound **15**. We would also expect the lateral intermolecular attractions to increase as the chain length grows, thus compound **15** has a higher nematic thermal stability than compound **D**, whereas addition of one methylene group adversely affects the smectic mesophase thermal stability, which agrees well with our earlier work [16,17].

4. CONCLUSION

In this article we have presented the synthesis and characterization of two new mesogenic homologous series of Schiff's base esters containing methoxyethyl tails. Series I is purely smectogenic as it is a short two-phenyl-ring system, whereas the compounds of series II exhibit the nematic phase as well as the smectic A phase with good mesophase range and higher thermal stabilities due to the presence of an additional phenyl ring along with an ester linkage. The study indicates that though the broken alkyl tail is believed to be detrimental to mesomorphic behavior, the compounds exhibit mesomorphic properties with good thermal stabilities if properly designed.

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REFERENCES

[1] Vill, V. (1996). *Liq. Cryst. 2.0 Database: Liquid Crystalline Compounds for Personal Computers*, Fijitsu Kyushu System FQA Ltd.: Fukuoka.

[2] Demus, D. & Zascjke, H. (1984). *Flussige Kristalle in Tabellen II*, VEB Deutscher Verlag fur Grundstoffindustroc: Leipzing.

[3] Kelkar, H. (1980). In: *Handbook of Liquid Crystals*, Kelkar, H. & Hatz, R. (Eds.), Verlag Chemie Gmbh: Weinheim.

[4] Gray, G. W. & Harrison, K. J. (1971). *Mol. Cryst. Liq. Cryst.*, *13*, 37; *Smp. Faraday Soc.*, *5*, 54.

[5] Collings, P. J. & Hird, M. (1997). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis: New York, 61–63.

[6] Shah, N. H., Vora, R. A., & Jadav, N. D. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 291.

[7] Chudgar, N. K., Rathnam, S., Shah, A. N., & Sharma, H. C. (1994). *Mol. Mat.*, *4*, 283.

[8] Agrawal, Y. K. & Rajput, S. J. (1990, 1997). *J. Indian Chem. Soc.*, *67*, 369; *74*, 689.

[9] Gray, G. W. & Kelly, S. M. (1984). *Mol. Cryst. Liq. Cryst.*, *104*, 335.

[10] Matsunaga, Y. & Miyajima, N. (1984). *Bull. Chem. Soc. Jpn.*, *57*, 1413.

[11] Vora, R. A., Prajapati, A. K., & Kevat, J. B. (2000). *Mol. Cryst. Liq. Cryst.*, *357*, 229.

[12] Booth, C. J., Dunmer, D. A., Goodby, J. W., Haley, J., & Toyne, K. J. (1996). *Liq. Cryst. 20*, 387.

[13] Weygand, C., Gabler, R., & Bircon, N. (1941). *J. Prakt. Chem.*, *158*, 266.

[14] Chiang, Y. H., Ames, A. E., Gaudiana, R. A., & Adams, T. G. (1991). *Mol. Cryst. Liq. Cryst.*, *208*, 85.

[15] Chiang, Y. H., Ames, A. E., & Nieman, A. (1998). *Mol. Cryst. Liq. Cryst.*, *312*, 95.

[16] Vora, R. A. & Prajapati, A. K. (1994). *J. Mys. Univ. Secn. B*, *33A*, 61.

[17] Vora, R. A. & Prajapati, A. K. (2001). *Proc. Indian Acad. Sci. (Chem. Sci.)*, *113*(2), 95.

[18] Prajapati, A. K. & Pandya, H. M. (2004). *Liq. Cryst.*, *31*, 889.

[19] Prajapati, A. K. & Pandya, H. M. (2005). *J. Chem. Sci.*, *117*(3), 255.

[20] Prajapati, A. K., Sharma, H. C., & Chudgar, N. K. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 813.

[21] Vogel, A. I. (1989). In: *A Text Book of Practical Organic Chemistry*, 5th ed., E.L.B.S. and Longman Group Ltd.: UK, 897.

[22] Gray, G. W. & Jones, B. (1954). *J. Chem. Soc.*, 1467.

[23] Dave, J. S. & Vora, R. A. (1970). In: *Liquid Crystals and Ordered Fluids*, Johnson, J. F. & Porter, R. S. (Eds.), Plenum Press: New York, 477.

[24] Dave, J. S. & Kurian, G. (1975). *J. Phys.*, *C1*, 403.

[25] Marzotko, D. & Demus, D. (1975). *Pramana Suppl.*, *1*, 189.

[26] Prajapati, A. K., Bonde, N. L., & Patel, H. N. (2005). *Phase Transitions*, *78*(6), 507.

[27] Fishel, D. L. & Patel, P. R. (1972). *Mol. Cryst. Liq. Cryst.*, *17*, 139.

[28] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London, 208, 212, 213, 219, 221, 224.