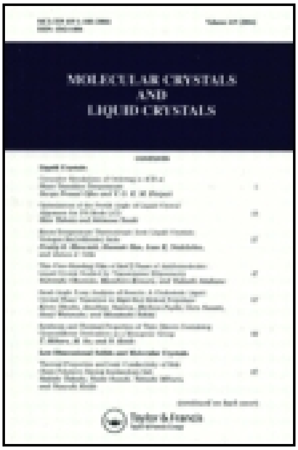

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Mesomorphic Behaviour of Schiff Base Esters-I: (a) p(p′-n-Alkoxybenzoyloxy)benzylidene-p″ -anisidines (b)p(p′ -n-Alkoxybenzoyloxy)benzylidene-p″ -toluidines

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Mesomorphic Behaviour of Schiff Base Esters—I:

(a) *p*(*p*′-*n*-Alkoxybenzoyloxy)benzylidene-*p*″-anisidines
(b) *p*(*p*′-*n*-Alkoxybenzoyloxy)benzylidene-*p*″-toluidines†

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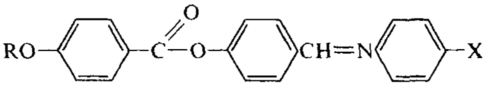
Two homologous series of liquid crystalline Schiff base esters of the following structural formula are synthesized by condensing *p*(*p*′-*n*-alkoxybenzoyloxy)benzaldehydes with *p*-anisidine and *p*-toluidine.



I $X = OCH_3$ $R = C_1—C_{18}$
II $X = CH_3$ $R = C_1—C_{18}$

All the members of the two series exhibit mesomorphism with good phase length and thermal stability. In both series I and II, all the members show enantiotropic nematic properties up to the longest chain length studied. Smectic mesophase begins in series I with the dodecyl derivative as a monotropic phase, becomes enantiotropic with the tetradecyl homolog and continues to be enantiotropic through the octadecyl derivative. However, in series II, the smectic phase begins with the much shorter heptyl derivative as a monotropic phase, becomes enantiotropic with an alkyl group longer than the nonyl chain and continues to be enantiotropic through the octadecyl derivative.

In both the series, the plots of the transition temperatures against the number of carbon atoms in the alkoxy chain behave in the normal manner and exhibit the usual odd–even effect for nematic–isotropic transition temperatures. The smectic–nematic transition temperatures lie on a rising curve which does not merge with the falling nematic–isotropic transition curve.

The thermal properties of both the series are compared with those of the other related series. The influence of the terminal MeO and Me groups on mesomorphism is discussed.

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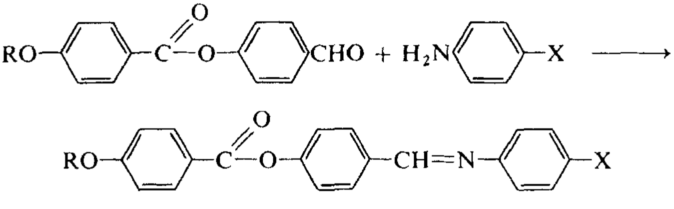
† Presented at the VI International Liquid Crystal Conference, Kent, Ohio, USA, 1976.

INTRODUCTION

Mesomorphic homologous series of varying molecular structure are known. Most of these are Schiff bases, acids and esters. A few mesomorphic homologous series comprising both an ester linkage and an azomethine group in the same molecule have been studied. Dave and Patel[1] and Fishel and Patel[2] studied homologous series of Schiff base aliphatic esters. These esters are purely smectogenic in nature. Gray and Harrison[3] studied different *p*-substituted benzylideneaminocinnamates of alkyl and aryl esters. These exhibit smectic and nematic mesophases. The esters containing asymmetric carbon atom in the alkyl chain exhibit cholesteric mesophases. We in our earlier studies reported the mesomorphic behaviour of a homologous series of *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates of cholesterol[4] wherein the higher members exhibit smectic and cholesteric mesophases. Here we present the mesomorphic behaviour of two homologous series of Schiff base esters which exhibit both smectic and nematic mesophases.

RESULTS AND DISCUSSION

These two homologous series consisting of fourteen Schiff base esters each, were prepared by the following synthetic route:



I X = OCH$_3$ R = C$_1$—C$_{18}$
II X = CH$_3$ R = C$_1$—C$_{18}$

The melting points and transition temperatures of these series are compiled in Tables I and II.

All the members of the two series exhibit mesomorphism with good phase length and thermal stability. In both series I and II, all the derivatives exhibit enantiotropic nematic properties. In series I the smectic mesophase begins with the dodecyl derivative as a monotropic phase, becomes enantiotropic with the tetradecyl homolog and continues to be enantiotropic through the octadecyl derivative, the last homolog studied. In series II, however, the smectic phase begins with the much shorter heptyl derivative as a monotropic smectic phase, becomes enantiotropic with an alkyl group longer than

TABLE I

$p(p'$-n-Alkoxybenzoyloxy)benzylidene-p''-anisidines
$RO\cdot C_6H_4\cdot CO_2\cdot C_6H_4\cdot CH{=}N\cdot C_6H_4\cdot OCH_3$

Alkyl group (R)	Transition temperatures in °C		
	Smectic	Nematic	Isotropic
Methyl	—	153.5	305.0
Ethyl	—	133.0	301.5
Propyl	—	125.0	280.0
Butyl	—	118.5	277.0
Pentyl	—	121.0	259.0
Hexyl	—	101.0	257.0
Heptyl	—	102.0	242.0
Octyl	—	102.5	240.5
Nonyl	—	103.0	230.0
Decyl	—	112.0	225.5
Dodecyl	(100.5)	116.0	210.5
Tetradecyl	115.0	118.0	202.0
Hexadecyl	116.0	130.0	194.0
Octadecyl	105.0	145.0	188.0

Value in parenthesis indicates monotropy.

TABLE II

$p(p'$-n-Alkoxybenzoyloxy)benzylidene-p''-toluidines
$RO\cdot C_6H_4\cdot CO_2\cdot C_6H_4\cdot CH{=}N\cdot C_6H_4\cdot CH_3$

Alkyl group (R)	Transition temperatures in °C		
	Smectic	Nematic	Isotropic
Methyl	—	129.0	274.5
Ethyl	—	135.0	270.0
Propyl	—	136.0	255.5
Butyl	—	124.0	251.5
Pentyl	—	119.5	235.0
Hexyl	—	119.0	230.0
Heptyl	(75.0)	99.0	220.0
Octyl	(91.5)	110.5	215.5
Nonyl	(108.0)	112.5	208.5
Decyl	106.5	121.5	202.5
Dodecyl	99.5	142.5	193.5
Tetradecyl	95.0	155.0	184.0
Hexadecyl	91.0	160.5	178.0
Octadecyl	88.0	159.0	171.5

Values in parenthesis indicate monotropy.

the nonyl chain and continues to be enantiotropic through the octadecyl derivative, the last homolog studied.

In both the series, the plots of the transition temperatures against the number of carbon atoms in the alkoxy chain exhibit smooth relationship. The nematic–isotropic transition temperatures lie on two falling curves exhibiting the normal odd–even effect, the even members occupying the upper curve as usual. The smectic–nematic curves, in both the series rise smoothly but they do not merge with the descending nematic–isotropic transition curves. However, in series II the smectic–nematic curve rises to a maximum through the C_{14} derivative and then falls off, which is not the case in series I (Figs. 1 and 2).

Table III summarizes the average thermal stabilities and the commencement of the smectic mesophase in homologs

p(*p*′-*n*-alkoxybenzoyloxy)benzylidene-*p*″-anisidines (A)

p(*p*′-*n*-alkoxybenzoyloxy)benzylidene-*p*″-toluidines (B)

and compares these with those of

biphenyl *p*-*n*-alkoxybenzoates[5] (C)

p-*n*-alkoxybenzylideneaminobiphenyls[6] (D)

methyl *p*-*n*-alkoxybenzylidene-*p*′-aminobenzoates[1] (E)

The geometry of these series is shown in Figure 3.

The average nematic thermal stability of series (A) is higher than that of series (B) whereas the average smectic thermal stability of series (A) is lower than that of series (B). The molecular geometry of the two series is similar the only difference being in the terminal substituents; series (A) has a methoxy substituent at one end of the molecule and series (B) has a methyl substituent at the corresponding end of the molecule.

TABLE III

Average thermal stabilities in °C

Series	A	B	C	D	E
Nematic–isotropic (C_1–C_{18})	243.7	220.7	132.3	169.2 (C1–C10)	—
Smectic–isotropic (C_{12}–C_{18})	123.4	154.2	116.6	150.1	114.7
Commencement of smectic phase	C_{12}	C_7	C_9	C_5	C_4

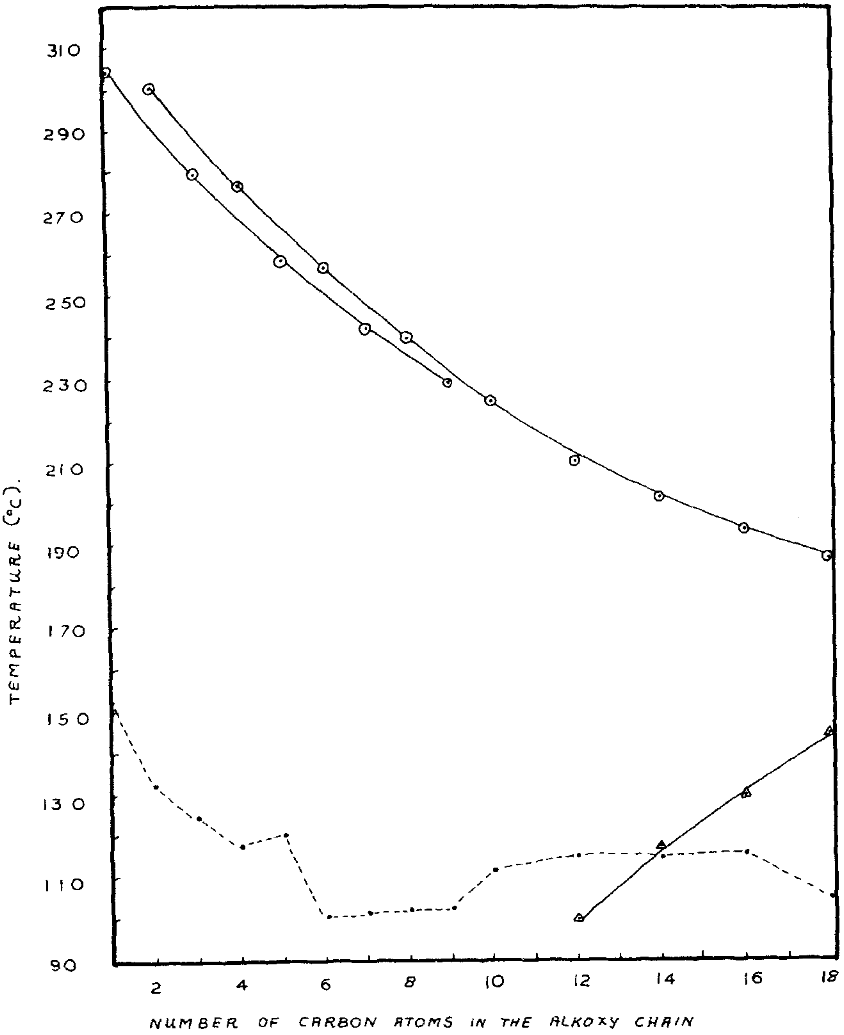


FIGURE 1 *p*(*p*′-*n*-Alkoxybenzoyloxy)benzylidene-*p*″-anisidines.
•----•, solid–mesomorphic; △——△, smectic–nematic; ⊙——⊙, nematic–isotropic.

It has been observed that in a homologous series, whereas a terminal methoxy group enhances the nematic thermal stability, it reduces the smectic thermal stability. The thermal stability orders of terminal substituents for smectic and nematic mesophases in mesomorphic compounds have been deduced by Gray[7] in which MeO > Me for the nematic order and Me > MeO for the smectic order. A similar order for nematic mixed liquid

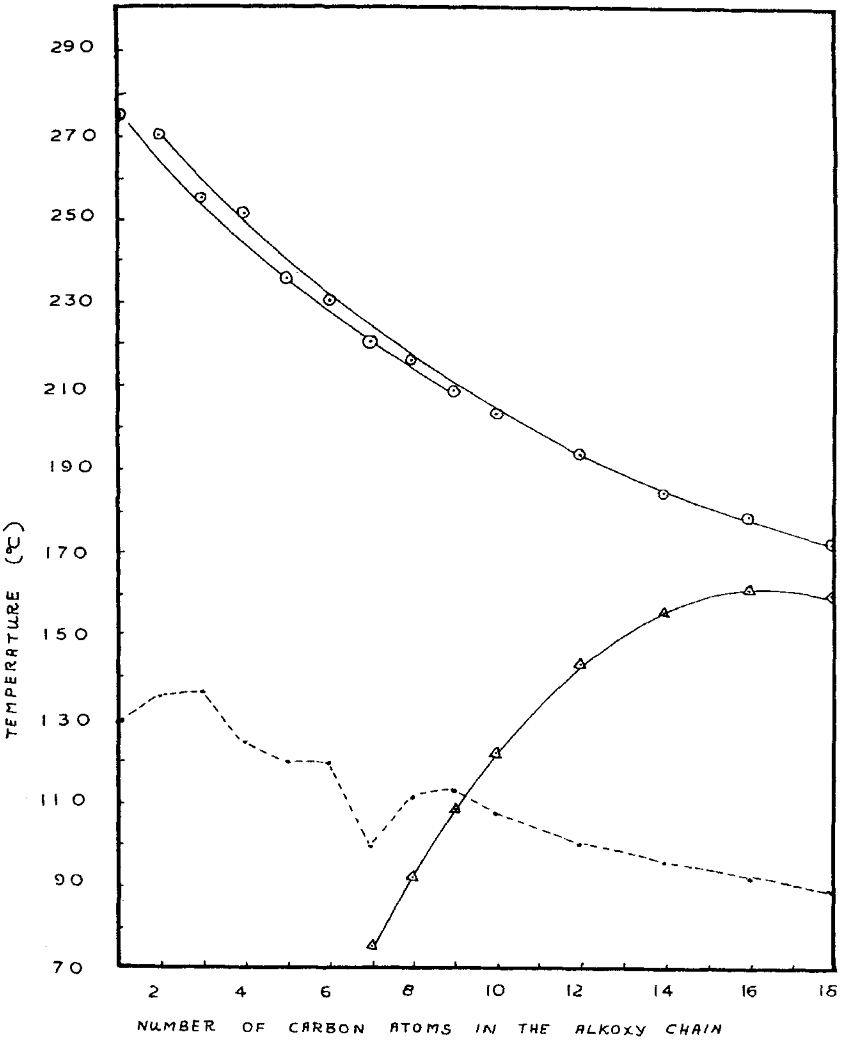


FIGURE 2 $p(p'$-n-Alkoxybenzoyloxy)benzylidene-p''-toluidines.
•----•, solid–mesomorphic; △——△, smectic–nematic; ⊙——⊙, nematic–isotropic.

crystal formation is also obtained by Dave and Dewer[8] in which MeO > Me.

The thermal stabilities of series (A) are higher than those of series (C); the increase in the nematic thermal stability is more than that in the smectic thermal stability. Molecules of series (A) are longer as well as more polarized than those of series (C). Further, compared with series (C), series (A) possesses an azomethine group in its molecules which will make the molecules of

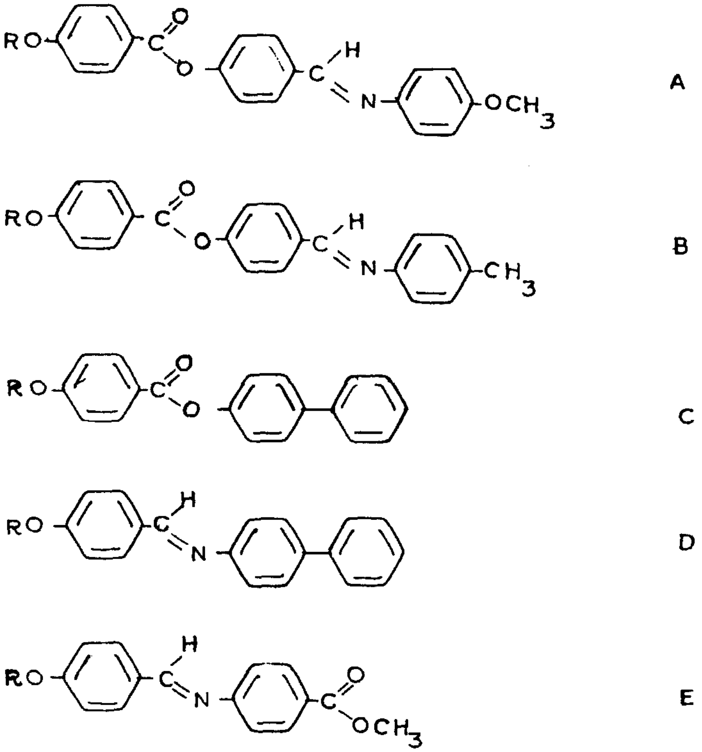


FIGURE 3

series (A) a little less coplanar. The first effect should increase the nematic thermal stability whereas the second effect will affect the smectic thermal stability which is the case.

Similar is the case when series (B) and (C) are compared. Further, the difference in the smectic thermal stabilities of series (B) and (C) is more than the difference in the smectic thermal stabilities of series (A) and (C); this can be attributed to the presence of MeO and Me groups in the two series.

The nematic thermal stability of series (A) is higher than that of series (D) whereas the smectic thermal stability of series (A) is lower than that of series (D). Structurally series (D) is similar to series (C) and therefore, the effect should have been the same but series (D) possesses an azomethine group in its molecules in place of a carboxy group in the molecules of series (C). Therefore, whereas the nematic thermal stability of series (A) which is long and more polarized, is no doubt higher than that of series (D), (of course not to the same extent as compared with that of series (C)), the smectic thermal stability of series (D) containing an azomethine group is not depressed to the same extent as in series (C); thus the smectic thermal stability of series (A) is less than that of series (D).

Same arguments should apply when series (B) and (D) are considered. The nematic and smectic thermal stabilities of series (B) are higher than those of series (D) but not to the same extent as compared with series (C). This can be ascribed to the presence of —COO— and —CH═N— groups in the two series.

Compared with series (E), series (A) and (B) are longer and more polarized. Naturally series (A) and (B) should be thermally more stable with respect to both nematic and smectic mesophases of series (E). But the nematic mesophase is completely absent in series (E). This can be attributed to the strong dipole moment of the carboalkoxy group in series (E), operating at an angle to the long axis of the molecule, thus helping the molecules to adopt a layer lattice.

In series (A) the smectic phase appears at the dodecyl derivative whereas it commences at the heptyl derivative in series (B). This is because the MeO group has an adverse effect on smectic mesophase. Series (C) is shorter and less broad than series (A) and so the smectic phase appears early in series (C) at the nonyl derivative. However, in series (B) the smectic phase appears at the heptyl derivative which is earlier than in series (C). This can be attributed to the presence of the Me group in series (B). In series (D) the smectic phase appears at the pentyl derivative which is earlier than in series (A) and (B). As discussed earlier molecules of series (A) and (B) are less coplanar compared with those of series (D). The commencement of the smectic phase is earliest in series (E), at the butyl derivative. As explained earlier the molecules of series (E) adopt a layer lattice arrangement and naturally the commencement of the smectic mesophase should be early in this series.

EXPERIMENTAL

A Preparation of compounds

(1) *p(p′-n-Alkoxybenzoyloxy)benzeldehydes* These were prepared by reacting different *p-n*-alkoxybenzoyl chlorides and *p*-hydroxybenzaldehyde in presence of pyridine as described elsewhere.[9]

(2) *Schiff bases* Equimolecular amounts of the aldehydes and amines (0.02 mol) were refluxed for 1 hour in ethanol (20 ml) in a round bottom flask. On cooling, the crude Schiff base separated which was collected by filtration. It was recrystallized from ethanol or benzene–ethanol mixture into fine white needles. The melting points and transition temperatures of the

compounds are summarized in Tables I and II. All these compounds gave satisfactory elemental analysis.

B Determination of transition temperatures

These were determined as described elsewhere.[4]

Acknowledgement

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