Unusual Mesogenic Behavior of Laterally Di- and Tri-Substituted Schiff Bases

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Three homologous Schiff base series, with basic skeleton of *N*-[4-(4′-*n*-alkoxybenzoyloxy)-3-methoxybenzylidene]aniline have been synthesized. The position and nature of the substitutent on the aniline moiety have been changed to find out their effects on the mesomorphism. Series I, with a 3-chloro substitutent do not exhibit mesomorphism. Series II, with a 2-methyl substituent in the aniline moiety exhibit monotropic smectic phase from the middle members of the series. However, Series III, having 5-chloro-2-methyl substituents behave like a normal nematogenic series.

It is now well known that the lateral substituents like chloro and methyl reduce the crystal-mesophase and transition temperatures very effectively.[1,2] In our earlier studies[3,4] the effect of lateral methoxyl group on the transition temperatures of mesogenic systems was evaluated. Demus et al.[5—7] have reported compounds with lateral long chain substituents and have established a new molecular concept of liquid crystals. Bapat and Ghatage[8] have synthesized number of laterally substituted mesogenic compounds and used in gas–liquid chromatography. They reported that the laterally substituted liquid crystals have advantages over other liquid crystalline compounds in separation of intricate mixtures of isomeric products. Recently Takenaka[9] have reported ferroelectric liquid crystals with lateral alkoxyl group. Gray et al.[10—12] have reported compounds with lateral chloro and fluoro substituents. Chloro substituted compounds could be useful in two frequency switching devices. With this in view and also to get the ambient liquid crystals it was decided to have one or two more lateral substituents with methoxyl group and to evaluate their effect on mesomorphic systems. The results obtained are quite unusual. Even with the three lateral substituents the crystal–mesophase transition temperatures were not depressed to the extent so as to give ambient mesogens.

Experimental

4-*n*-Alkoxybenzoic acids, their acid chlorides[13] and 4-(4′-*n*-alkoxybenzoyloxy)-3-methoxybenzaldehydes[3] were synthesized by the reported methods. The Schiff bases were synthesized by condensing aldehydes with appropriate anilines in ethanol. The Schiff bases were recrystallized several times from ethanol till constant transition temperatures were obtained. The transition temperatures are given in Table 1.

The elemental analysis were satisfactory.

From the microscopic observations the smectic mesophase exhibited by Series II and III appears like smectic ‘C’ type.

The optical observations were made by using microscope, Leitz Labour Lux 12 POL.

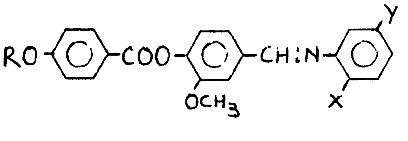

Table 1.

R		Transition temperatures/°C		
		Smectic	Nematic	Isotropic
Series I :	X = H			
	Y = Cl			
	C_5H_{11}	—	—	90.0
	C_8H_{17}	—	—	96.0
	$C_{12}H_{25}$	—	—	60.0
Series II :	X = CH_3			
	Y = H			
	C_7H_{15}	—	—	80.0
	C_8H_{17}	(42.5)[a,b]	—	75.5
	$C_{10}H_{21}$	(45.0)[b]	—	70.0
	$C_{12}H_{25}$	(44.0)[b]	—	82.0
	$C_{14}H_{29}$	(43.0)[b]	—	80.0
	$C_{16}H_{33}$	(42.0)[b]	—	75.0
Series III :	X = CH_3			
	Y = Cl			
	CH_3	—	(116.0)[c,d]	129.0
	C_2H_5	—	(146.0)[d]	147.0
	C_3H_7	—	105.0	126.0
	C_4H_9	—	110.0(118.2)[e]	130.0(139.0)[e]
	C_5H_{11}	—	85.0	119.0
	C_6H_{13}	—	90.0	120.0
	C_7H_{15}	—	82.5	99.0
	C_8H_{17}	—	83.0	104.0
	$C_{10}H_{21}$	(65.0)	88.0(94.8)[e]	101.0(108.0)[e]
	$C_{12}H_{25}$	(81.0)	82.0	93.0
	$C_{14}H_{29}$	(80.0)	(87.0)	91.5
	$C_{16}H_{33}$	(57.0)	—	80.0

a) Values in the parantheses indicate monotropic transition temperature. b) Values obtained on rapid cooling. c) Values in the parathesis indicate monotropic transition temperature. d) Values obtained on rapid cooling. e) DSC Values.

Results and Discussion

Series I: *N*-[4-(4′-*n*-Alkoxybenzoyloxy)-3-methoxybenzylidene]-3-chloroaniline. Pentyloxy, octyloxy, and dodecyloxy derivatives of the series were synthesized by condensing equimolar quantities of 3-chloroaniline with appropriate 4-(4′-*n*-alkoxybenzoyloxy)-3-methoxybenzaldehydes as described in experimental section. All the members are non-mesogenic in nature. This non-mesogenic tendency of the compounds may be attributed to the two lateral groups present, which increases the breadth of the molecules. Vora and Patel[14)] have reported similar compounds without central methoxyl substituent and with chloro group in ortho position (Series A). The series behave like a normal nematogenic series and methoxy to hexadecyloxy derivatives are mesogenic in nature. The Series I with group in meta position increase the breadth of molecule more than in Series A and destroy the mesomorphism. The geometries of the series are given in Fig. 1.

Series II : *N*- [4- (4′- *n*- Alkoxybenzoyloxy)- 3-methoxybenzylidene]-2-methylaniline. The series with a lateral methoxyl group ortho to the ester linkage and a lateral methyl group ortho to azomethine linkage exhibit mesomorphism from octyloxy derivative onwards.

The series exhibit monotropic smectic phase. The monotropic smectic phase is obtained only on quenching. On slow cooling crystallization takes place before the commencement of mesophase. The smectic mesophase is obtained between 40—45°C. The smectic mesophases of homologues are intermiscible and hence of the same type. By contact method and by mixture study smectic phase was identified as smectic C phase.

Vora and Patel[15)] have reported two homologous series without the central methoxyl substituent and trifluoromethyl or methyl group in meta position on the aniline moiety. Series with meta trifluromethyl group (Series B) exhibits smectic phase from hexyloxy derivative, while series with methyl group (Series C) behave like normal nematogenic series.

Series III : *N*- [4- (4′- *n*- Alkoxybenzoyloxy)- 3-methoxybenzylidene]-5-chloro-2-methylanilines. Methoxy to octyloxy derivatives exhibit a nematic phase, decyloxy to tetradecyloxy derivatives are polymesomorphic while hexadecyloxy derivative exhibits only smectic mesophase. The smectic mesophase was observed as a monotropic phase. The methoxy and ethoxy derivatives exhibit nematic mesophase only on quenching. The transition temperatures versus number of carbon atoms in alkoxyl chain exhibit an odd–even effect for nematic-isotropic transitions. The smectic–nematic transitions temperature curve shows a maxima (Fig. 2).

The smectic mesophase of homologues is intermiscible and hence of the same type. To identify the smectic phase, contact method and mixture study with the labelled compounds were carried out. The smectic phase exhibited by the series is of smectic ‘C’ type.

As the Series I is non-mesogenic in nature and Series II shows only monotropic smectic mesophase for middle and higher members, the combination of the two series, i.e. Series III, with three lateral substituents, were least expected to be mesogenic in nature. But contrary to the expectation, the series behave as a normal nematogenic series, but the crystals to mesomorphic or isotropic transition temperatures are not so much depressed. This may be explained by assuming that in the crystal lattice the molecules are packed closely in a manner that the lateral substituents are finding some sort of pockets or gaps so that their breadth increasing effect is not felt to its fullest extent. But of course,

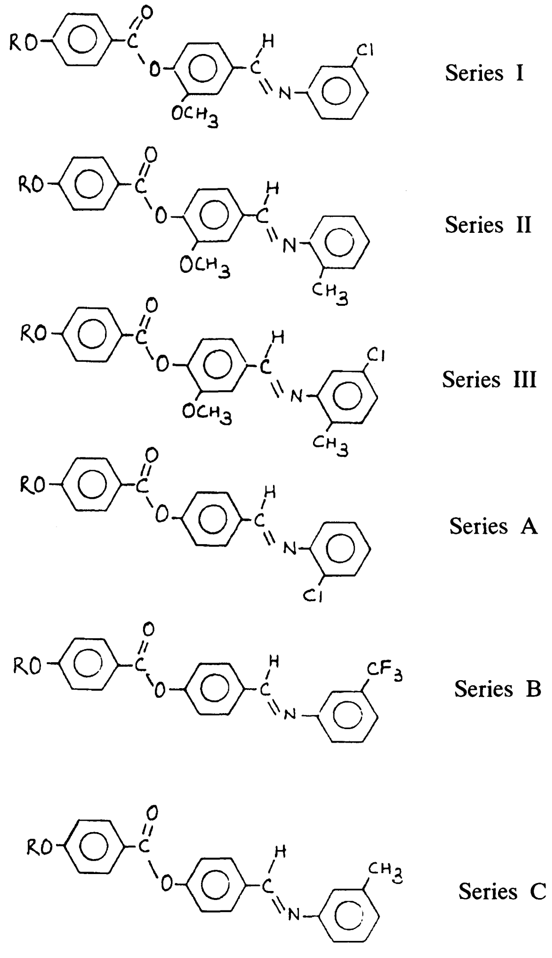

Fig. 1.

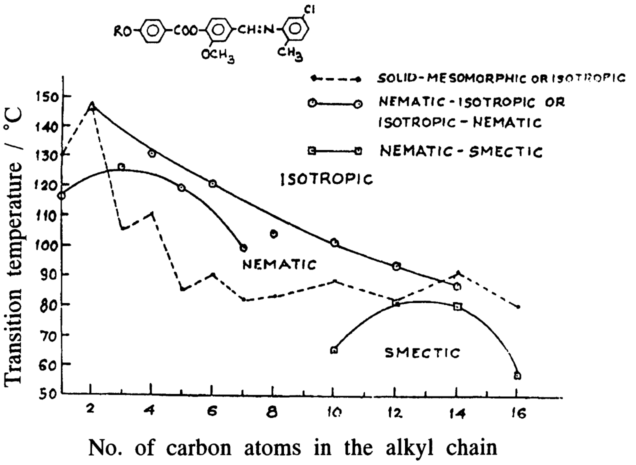

Fig. 2.

only X-ray analysis can throw more light on the crystal structure of the compounds.

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