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Synthesis and Mesomorphic Characterisation of Chiral Homologues

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Chiral liquid crystals have attracted considerable interest as they exhibit a good variety of modulated phases. We have synthesised a homologous series viz., 4-(4¹-n-alkoxy benzoyloxy) benzylidene-4¹¹-1-(s)-methyl propoxy anilines, incorporating a terminal chiral centre, in order to obtain better understanding of the relationship between molecular structure and appearance of SmC* phase in the molecules. It is observed that, in the present series the lower members upto butyl are pure nematogens, while pentyl to hexadecyl derivatives exhibit classical smectic as well as nematic mesophases. An additional smectic C* phase is observed in the middle octyl to dodecyl homologues. The homologues have been characterised by IR, NMR and DSC. Their mesomorphic properties have been compared with structurally related homologous series.

Keywords: Chiral homologues; mesogens; mesomorphism; smectic C; smectic C*; average thermal stabilities

INTRODUCTION

The properties of liquid crystals depend on the structure of liquid crystal molecules. Earlier we have reported number of homologous series with nonchiral centre which have been found to exhibit

mesomorphism and their existence has been attributed to their molecular geometry and molecular forces arising therefrom^{1,2}. However, a great interest has been developed for ferroelectric liquid crystals in both fundamental and applied research because of their application potential in electrooptic devices^{3,4}. Most liquid crystals with chiral mesophases have incorporated a center of chirality.

In the present study we have synthesized a homologous series viz., 4-(4'-n-alkoxybenzoyloxy) benzylidene-4''-1-(s)-methylpropoxy anilines, incorporating a terminal chiral centre, in order to obtain better understanding of the relationship between molecular structure and appearance of SmC* phase in the molecules.

EXPERIMENTAL

The synthetic route for the present homologous series is given in scheme I.

All the chemicals used were of Fluka, B.D.H or Aldrich grade. 4-1-(s) methylpropoxyaniline (A) was synthesized by reported methods from paracetamol^{5, 6}. 4-n-alkoxybenzoic acids, 4-(4'-n-alkoxybenzoyloxy) benzaldehydes were synthesized by reported methods^{7, 8}. 4-(4'-n-alkoxybenzoyloxy) benzylidene -4''-1-(s)-methylpropoxyanilines were synthesized by taking equimolar quantities of appropriate 4-(4'-n-alkoxybenzoyloxy) benzaldehyde and -4-1-(s) methyl propoxyaniline in minimum quantity of ethanol with a few drops of glacial acetic acid and refluxing it for a period of 4 to 6 hours. The products were filtered, dried and recrystallised from ethanol.

All the compounds were analysed by elemental analysis (Table 1) using Coleman USA-CHN analyser and they are in conformity with

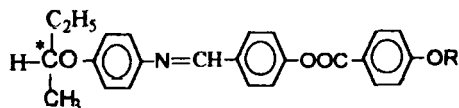
the calculated ones. Transition temperatures and the textures of the mesophases were studied using a Leitz laborlux 12 POL polarising microscope using a Kofler heating stage and few of them have also been studied using a METTLER DSC 20 Differential scanning calorimetry. The analytical data of representative compounds were obtained on a Perkin-Elmer FTIR (FTIR), JEOL FX 200 spectrophotometer (NMR) FTIR: (Nujol, KBr pellets, cm^{-1}) $n\text{-OC}_{10}\text{H}_{21}$: 3413, 2920, 2850, 2869, 1728, 1608, 1508, 1280, 1245, 1207, 1164, 1072, 879, 833.

Proton NMR : (CDCl_3 , 200 MHz, δ , ppm, standard TMS)

$n\text{-OC}_4\text{H}_9$: 1.0 (t, 3H, $-\text{CH}_3$), 1.3 (d, 3H, $-\text{CH}_3$) 1.4-1.9 (m, 6H, 3x- CH_2), 4.05 (t, 2H, $-\text{OCH}_2$), 6.27, 4.25-4.38(m, 1H, $-\text{CH}$ of $^*\text{CH}$) 6.8-8.4 (m, 12H of ArH), 8.5 (s, 1H, $-\text{CH}=\text{N}-$),

RESULTS AND DISCUSSION

In the present study, twelve compounds of the homologous series viz : 4-(4¹-n-alkoxybenzoyloxy)benzylidene-4¹¹-1-(s)-methylpropoxyanilines are synthesised and their mesomorphic properties have been studied. The general molecular structure of the present series is



Where, R is $n\text{-C}_n\text{H}_{2n+1}$; $n = 1-8, 10, 12, 14$ and 16 .

The mesophases were identified according to their textures, which were carried out by optical microscopy classification system reported, by Sackmann and Demus^{9,10} and Gray and Goodby¹¹.

Transition temperatures and mesomorphic properties are summarised in Table 2.

The results show that all the homologues from methoxy to hexadecyloxy are liquid crystalline in nature; compounds with short *n*-alkoxy chain ($n=1$ to $n=4$) exhibit nematic phase. The 5th and 6th derivatives, on cooling exhibit monotropic S_C phase with schleiren texture, which became enantiotropic in the 7th homologue. In the derivatives from $n=8$ to $n=12$, on heating the S_C phase, an additional phase is observed which has been identified as the S_C^* phase based on the lined texture (Fig. 1); and the mesophase range of this S_C^* phase increases with the increase in the methylene units in the *n*-alkoxy chain. However both the S_C^* phase as well as the nematic phase are eliminated in the last two derivatives and the tetradecyloxy and hexadecyloxy homologues exhibit only classical S_C texture.

The observation of textural changes from optical microscopy was confirmed by the DSC for the *n*-octyloxy and *n*-decyloxy compounds. Representative DSC thermograms obtained for compounds are depicted in Fig 2. The pattern showed 4 different peaks corresponding to the peaks of K- S_C , S_C - S_C^* , S_C^* -N and N-I transitions. The enthalpies measured for each phase transition is given.

The magnitude of P_s is a very important property for obtaining a rapid switching speed. The P_s and response times of the decyloxy homologue was taken and it was observed that the saturated value of P_s is 32nC/cm^2 with optimum response times of 67 ms at 126°C . The sample was scanned at 1.0 degree centigrade per minute.

The plot of transition temperatures against the number of carbon atoms in the *n*-alkoxy chain is shown in Fig.3. It is observed that, S-N

transition curve shows a rising tendency as the series is ascended; the N-I transition temperatures fall on two odd even curves, which in turn show an overall falling tendency from methyl to tetradecyl derivatives and both the curves merge at the C₇ derivative. The S_C- S_C* transition curve is almost linear with a maximum mesophase range of 44°C for n=12.

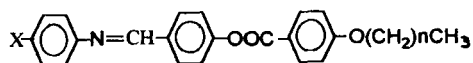
There is a close relationship between mesomorphism and molecular structure of organic compounds. Hence, thermal stability (Table 3) a measure of mesomorphism can be correlated with the molecular constitution of compounds. The present series I can be compared with structurally similar series.

I. 4-(4'-n-alkoxy benzoyloxy) benzylidene-4''-1-(s)- methyl propoxy anilines

A. 4-(4'-n-alkoxy benzoyloxy) benzylidene-4''-n- butyl anilines.¹²

B. 4-(4'-n-alkoxy benzoyloxy) benzylidene-4''-isopropyl anilines.¹³

The general structure of the series in comparison can be given as



SERIES	-X
I	-O*CH(CH ₃)C ₂ H ₅
A	-n-C ₄ H ₉
B	-CH(CH ₃) ₂

TABLE 3 : Average Thermal Stabilities °C

Series	I	A	B
N-I	181.25 (C ₁ -C ₁₆)	222.8 (C ₁ -C ₈)	193.2 (C ₁ -C ₈)
S-N or S-I	120.62 (C ₅ -C ₁₆)	130.2 (C ₆ -C ₁₆)	136.6 (C ₇ -C ₁₆)
Commencement of Smectic Phase	C ₅	C ₆	C ₇

The present series consists of three benzene rings, an ester (COO-) and an azomethine (-CH=N-) linkage and a terminal chiral group -OCH(CH₃)C₂H₅; while the series in comparison differs only at one of the terminal ends. Comparing all the series, series A and B show higher average N-I and S-N thermal stabilities than series I. This can be attributed to the longer n-butyl end group in series A which is more polarisable in nature; while in series B the isopropyl end group does not seem to have fullest breadth increasing effect compared to chiral series I, hence the deterring effect due to branching could be less and mesomorphism could be dominated by polarisability effect of the molecules. However in the present series I the commencement of the smectic phase is earlier at pentyl derivative compared to those at C₆ and C₇ in series A and B respectively, which may be due to the higher lateral attractions caused by the terminal chiral group.

CONCLUSION

The molecular structure plays an important role in the type of mesophase formation and mesophase range. In the present chiral series I, additional SmC* phase appears in the middle members viz, C₈, C₁₀, C₁₂ analogues alongwith Sc phase. The series shows good N-I and S-I thermal stability.

TABLE 1: Elemental Analysis for, p-(p'-n-alkoxy benzoyloxy) benzylidene-p''-1-(s)- methyl propoxy anilines

n-Alkoxy group	% Required			% Found		
	C	H	N	C	H	N
Methoxy	74.44	6.20	3.47	74.41	6.08	3.50
Ethoxy	74.46	6.47	3.35	74.40	6.32	3.39
Propoxy	75.17	6.72	3.25	75.00	6.69	3.27
Butoxy	75.50	6.67	3.14	75.25	6.61	3.20
Pentoxy	75.81	7.18	3.05	75.40	7.05	3.09
Hexyloxy	76.10	7.39	2.96	76.00	7.35	3.01
Heptyloxy	76.38	7.59	2.87	76.20	7.40	2.90
Octyloxy	76.65	7.78	2.74	76.40	7.72	2.85
Decyloxy	77.13	8.13	2.64	77.00	8.10	2.70
Dodecyloxy	77.56	8.44	2.51	77.25	8.32	2.62
Tetradecyloxy	77.95	8.71	2.39	77.60	8.62	2.42
Hexadecyloxy	78.30	8.97	2.28	78.15	8.80	2.32

TABLE 2 : Transition Temperatures for p-(p'-n-alkoxy benzoyloxy) benzylidene-p''-1-(s)- methyl propoxy anilines

n-Alkoxy group	Transition temperatures ⁰ C			
	Smectic C	Smectic C*	Nematic	Isotropic
Methoxy	-	-	100	205
Ethoxy	-	-	85	219
Propoxy	-	-	90	195
Butoxy	-	-	124	202
Pentoxy	(82)	-	104	191
Hexyloxy	(89)	-	100	193
Heptyloxy	100	-	113	188
Octyloxy	81	92.5	116	178
Decyloxy	78	91.0	127	167
Dodecyloxy	66	84.0	128	160
Tetradecyloxy	62	-	-	140
Hexadecyloxy	63	-	-	137

() Values in parentheses show monotropic transitions.

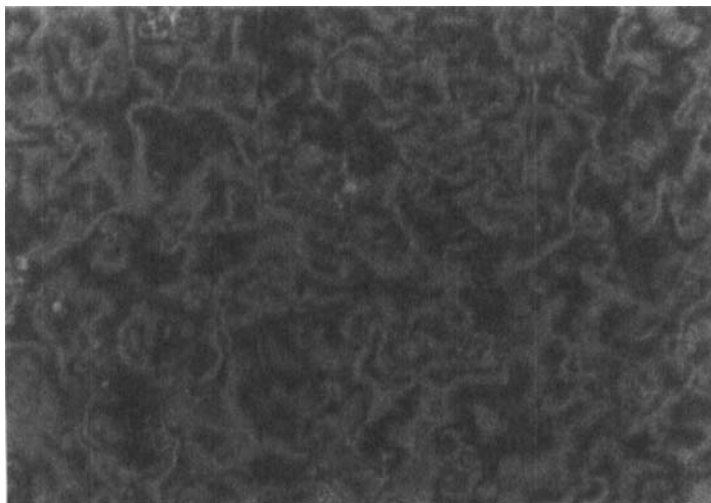
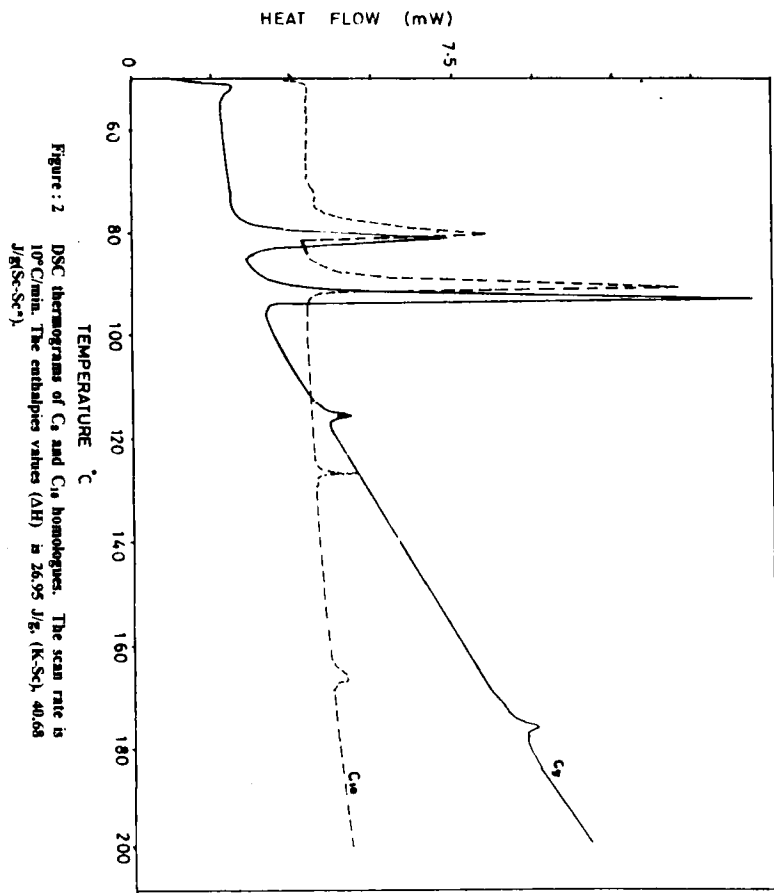


Figure : 1 (a.) Lined texture of Sc* mesophase of decyloxy homologue at 110°, while heating.

See Color Plate XXI at the back of this issue.



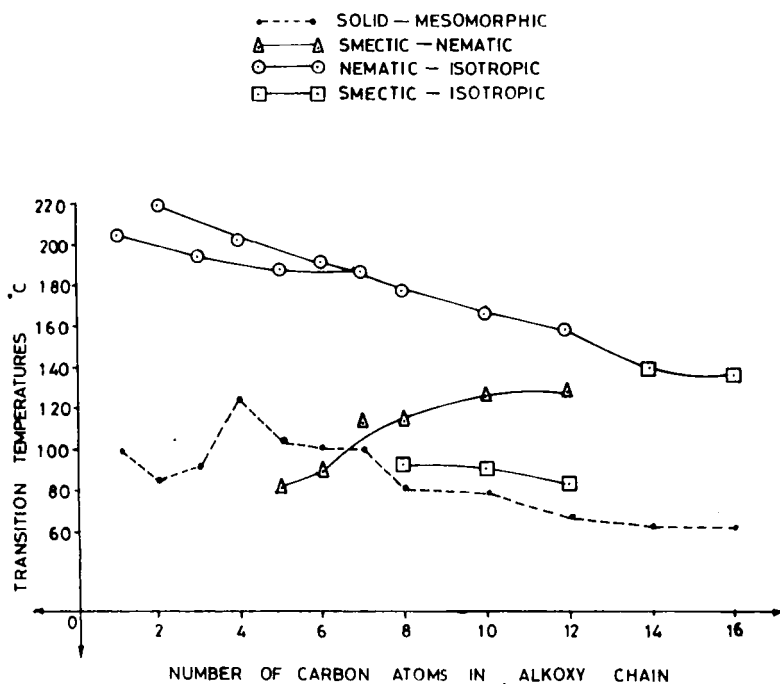
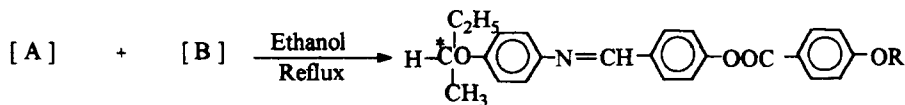
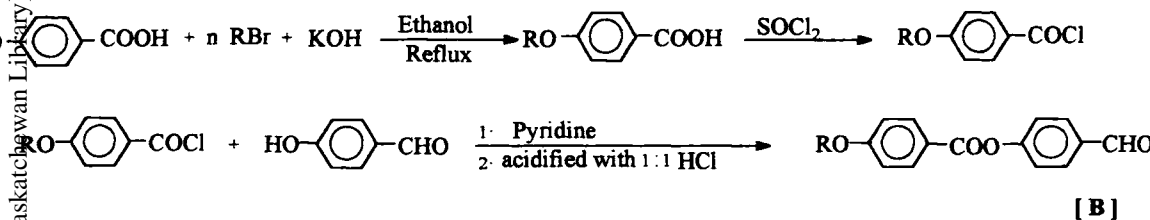
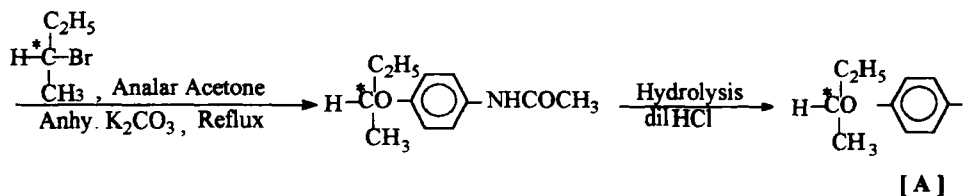


Figure : 3 Transition temperatures °C versus the number of carbon atoms in the n-alkoxy chain for (p-(p'-n-alkoxy benzoyloxy) benzylidene-p''-1-(s)-methyl propoxy anilines.



where $\text{R} = \text{C}_n\text{H}_{2n+1}$; $n = 1-8, 10, 12, 14$ and 16 .

HEME - I : Synthetic route for 4 (4¹-n-alkoxybenzoyloxy)benzylidene-4¹¹-1-(s)-methylpropoxyanilines.

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