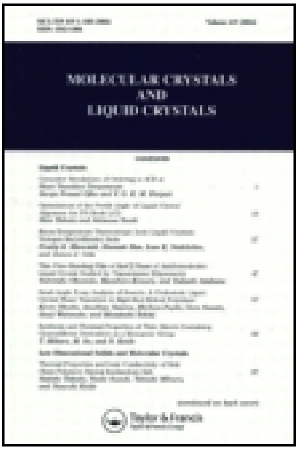

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Effect of Terminal Branching on Mesomorphism

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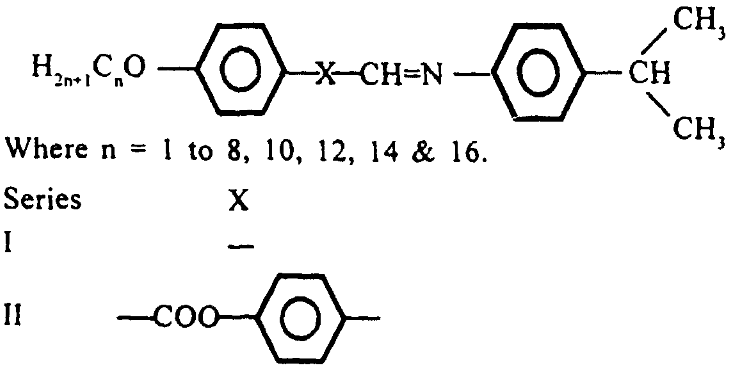
Two new mesogenic homologous series having following general structural formula have been synthesized.

In series-I, n-octyloxy and n-dodecyloxy derivatives exhibit enantiotropic smectic A phase whereas n-decyloxy and n-tetradecyloxy derivatives exhibit monotropic smectic A phase, rest of the members are non-mesogenic. Looking to the terminally branched alkyl group smectogenic tendency of series-I is quite interesting.



In series-II, all the members exhibit enantiotropic nematic phase. The smectic C mesophase commences from the n-heptyloxy derivative and is exhibited alongwith nematic phase till the last n-hexadecyloxy derivative studied. Though branching is known to be less conducive to mesomorphism, it is observed that entire series-II is mesomorphic in nature.

Keywords: Mesogenic p-cumidine derivatives; Effect of terminal branching

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INTRODUCTION

Terminal group present in the molecule have their own importance because of their polarity. It has been found that, terminally substituted compounds exhibit more stable mesophases compared to unsubstituted mesogenic compounds. Generally in a liquid crystalline compounds the end group found, like n-alkyl, n-alkoxy are unbranched or a compact unit like -CN, -NO_2, halogen etc. However a few examples of mesogenic compounds with branched terminal alkyl groups are known[1,2]. According to the systematic studies by Gray and Harrison[3], the branched chain esters have lower liquid crystal stabilities than the unbranched chain esters. When the branching occurs at the first carbon atom of the chain, the effect on liquid crystal thermal stability is the greatest. Movement of branching away from the first carbon atom of the chain towards the end of the chain causes transition temperatures to rise again. Matsunaga et. al.[4,5] also have carried out the systematic studies on the effects of branching of the ester alkyl group on the mesomorphic properties. The replacement of a normal alkyl chain by a branched one can also induce chirality into the system[6].

In order to investigate the effect of terminal branching on mesomorphism, two mesogenic homologous series consisting of a terminal p-cumidine moiety are synthesized and their mesomorphic properties discussed.

EXPERIMENTAL

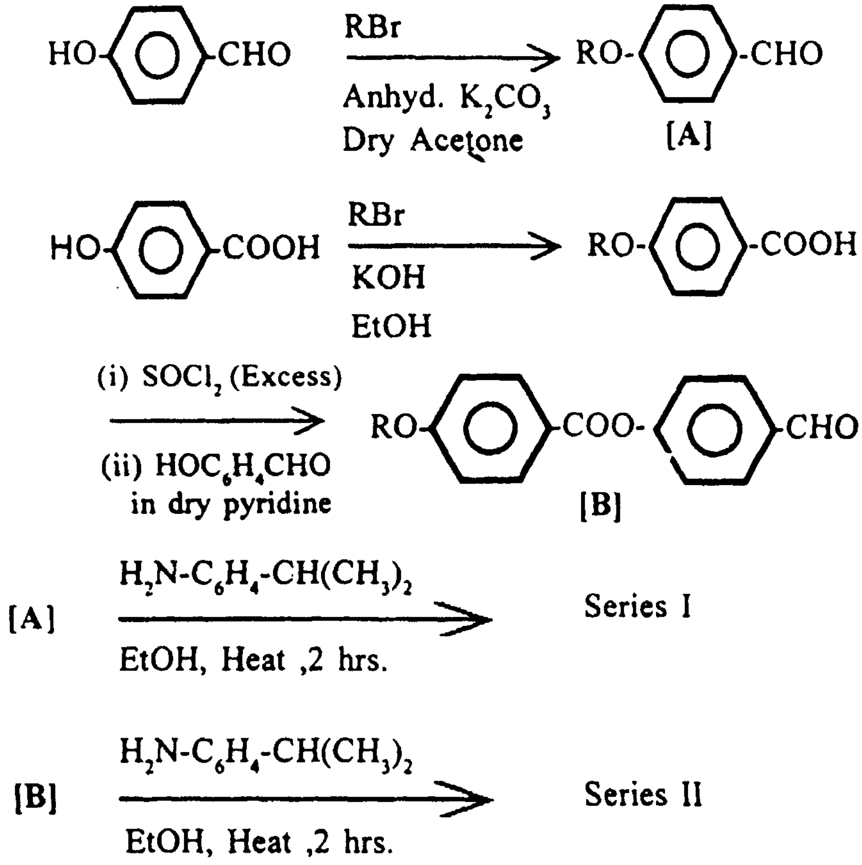
Characterization

Microanalysis of the compounds were performed on a Coleman carbon-hydrogen analyser, and IR spectra were recorded on a Shimadzu IR-408. NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer. Liquid crystalline properties were investigated on a Leitz Labourlux 12 POL microscope provided with a heating stage. DSC were investigated on a Mettler TA-4000 system.

Synthesis

The synthetic route of both the series I & II are illustrated in Scheme 1.

4-n-Alkoxybenzaldehydes were prepared by the method of Gray and Jones[7]. 4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides were synthesized by the modified method of Dave and Vora[8]. 4-n-Alkoxy-benzoyloxy –4′-benzaldehydes were synthesized by the method of Dave and Kurian[9]. The twelve



SCHEME 1 Synthetic route to series I and II

Schiff's bases of series I were synthesized by condensing equimolar quantities of 4-n-alkoxybenzaldehydes and p-cumidine in boiling ethanol. The twelve schiffs bases of series II were prepared by condensing equimolar quantities of 4-n-alkoxybenzoyloxy -4′-benzaldehydes with p-cumidine in boiling ethanol. All the Schiff's bases of series I were crystallized from ethanol and those of series II from n-propanol until constant transition temperatures were obtained. The melting points and transition temperatures are recorded in table I.

The elemental analyses of all the compounds were found to be satisfactory. The elemental data, IR and NMR spectral data for the n-dodecyloxy derivative of series I and n-hexyloxy derivative of series II are given below.

TABLE I Transition temperatures (°C) of the present series I and II

$R=C_nH_{2n+1}$ *n=*	*Transition Temperatures °C*		
Series I	*SmA*	*N*	*I*
1	--	--	71.0
2	--	--	73.0
3	--	--	61.0
4	--	--	66.0
5	--	--	60.0
6	--	--	64.0
7	--	--	58.0
8	56.5	--	59.0
10	(60.0)[a]	--	64.0
12	54.5	--	60.0
14	(64.0)	--	74.0
16	--	--	80.0
Series II	*SmC*	*N*	*I*
1	--	133.0	210.0
2	--	142.0	206.0
3	--	154.0	200.0
4	--	148.0	196.0
5	--	131.0	190.0
6	--	124.0	186.0
7	108.0	118.0	182.0
8	114.0	126.0	176.0
10	110.0	137.0	168.0
12	110.0	145.0	162.0
14	85.0	149.0	157.0
16	82.0	145.0	153.0

a. Values in parantheses indicate monotropy

Elemental data

Series I: Found, C 82.44, H 10.23, N 3.42%. $C_{28}H_{41}NO$ requires C 82.56, H 10.07, N 3.44%.

Series II: Found, C 78.38, H 7.36, N 3.28%. $C_{29}H_{33}NO_3$ requires C 78.56, H 7.45, N 3.16%.

IR (KBr) spectra

Series I: Series I: 2900, 1610 (-CH=N-), 1600, 1470, 1430, 1385 and 1370 (-CH(CH$_3$)$_2$), 1315, 1250, 1150, 830, 760 cm^{-1}.

Series II: 2950, 1725 (-COO-), 1610 (-CH=N-), 1600, 1465, 1430, 1385 and 1365 (-CH (CH$_3$)$_2$), 1310, 1260, 1200, 1070, 885, 765 cm^{-1}.

NMR spectra (solvent CDCl$_3$, standard TMS)

Series I: (60 MHz) δ 0.9 (t, 3H, -CH$_3$), 1.1–1.9 (m, 20H, 10 × -CH$_2$-), 2.4–3.1 (m, 7H, -CH(CH$_3$)$_2$), 3.9 (t, 2H, PhOCH$_2$-), 6.9 (d, J=9Hz, 2H at C-3′ and C-5′), 7.2 (d, J=9Hz, 4H at C-2′, C-6′, C-3 and C-5), 7.8 (d, J=9Hz, 2H at C-2 and C-6), 8.3 (s, 1H, -CH=N-).

Series II: (300 MHz) δ 0.9 (t, 3H, -CH$_3$), 1.2–1.4 (m, 6H, 3 × -CH$_2$-), 1.5–1.9 (qunt., 2H of Ph-O-CH$_2$-CH$_2$), 2.8–3.0 (m, 7H, -CH(CH$_3$)$_2$), 4.05 (t, 2H, PhOCH$_2$-), 6.9 (d, J=9Hz, 2H at C-3′ and C-5′), 7.2 (d, J=9Hz, 2H at C-2′ and C-6′), 7.25 – 7.4 (m, 4H at C-3, C-5, C-3 "and C-5"), 7.95 (d, J=9Hz, 2H at C – 2″ and C 6″), 8.2 (d, J=9Hz, 2H at C-2 and C-6), 8.35 (s, 1H, -CH=N-).

DSC data of n-dodecyloxy derivative of series I and n-heptyloxy and n-dodecyloxy derivatives of series II were determined by adopting a scanning rate of 5°C/ min. (Table II).

TABLE II DSC data of series I and II

Sr. No.	*Series*	*Derivative*	*Transition*	$\Delta H\ J{\cdot}g^{-1}$	$\Delta S\ J{\cdot}g^{-1}\ k^{-1}$
1.	I	n-Dodecyloxy	Cr-SmA	26.87	0.0820
			SmA-I	2.49	0.0075
2.	II	n-Heptyloxy	Cr-SmC	29.75	0.0781
			SmC-N	2 28	0.0058
			N-I	1.42	0.0031
3.	II	n-Dodecyloxy	Cr-SmC	24.27	0.0634
			SmC-N	2.05	0.0049
			N-I	1.23	0.0028

RESULTS AND DISCUSSION

Series I

4-n-Alkoxybenzylidene 4′-isopropylanilines. The n-octyloxy and n-dodecyloxy derivatives exhibit enantiotropic smectic A phase whereas n-decyloxy and n-tetradecyloxy derivatives exhibit monotropic smetic A phase. Rest of the members are non-mesogenic.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figure 1a) exhibits a tendency of rising smectic-isotropic transition in ascending series. Figure 1a also indicates the steep rising tendency of solid – smectic or isotropic transition for n-decyloxy and n-tetradecyloxy derivatives which results in pronounced monotropic smectic nature.

Lower homologues as well as higher homologues of the series I are non-mesogenic. This indicates that isopropyl terminal group disturbs the order when molecules do not have sufficient chain length or very long chain length. Interesting aspects is that even the isopropyl terminal group is present the n-octyloxy to n-tetradecyloxy derivatives exhibit smectic A phase.

Series II

4(4′-n-Alkoxybenzoyloxy) benzylidene 4″-isopropyl anilines. All the members exhibit an enantiotropic nematic phase. The smectic C mesophase commences from the n-heptyloxy homologue and is exhibited along with nematic phase till the last n-hexadecyloxy homologue studied. Though branching is known to be less conducive to mesomorphism, it is observed that the entire series is mesomorphic in nature. This may be attributed to the fact that the series also consists of three aromatic nuclei linked through ester and benzylidene linkages.

The plot of transition temperatures against the number of caron atoms in the alkoxy chain (Figure 1b) shows that the smectic-nematic transition temprature curve rises till the n-tetradecyloxy derivative, which falls slightly in the last derivative. The nematic- isotropic transition temperature shows a smooth falling tendency throughout the series.

Table III summarizes the average thermal stabilities and comparative gemometry of the present series II and the structurally related series A[10] and B[10]. It is known that branching in the alkyl chain adjacent to phenyl ring drastically affects the mesomorphic properties of the system. However it has been pointed out by Gray[11] that if branching does not have maximum breadth increasing effect, then the deterring effect would be less and in some cases polarizibility effect may dominate and there may be enhanced mesomorphic properties. The nematic thermal stabilities of series A are higher than those of series I. Normally a lateral branch, like methyl group will adversely affect the smectic phase and it may be eliminated from the system. It seems that in the present seres II the branched methyl group does not have maximum breadth increasing effect or it finds a pocket in the layer arrangement of smectic phase, whereas its presence on terminus affect the parallel arrangement of molecules required for the nematic

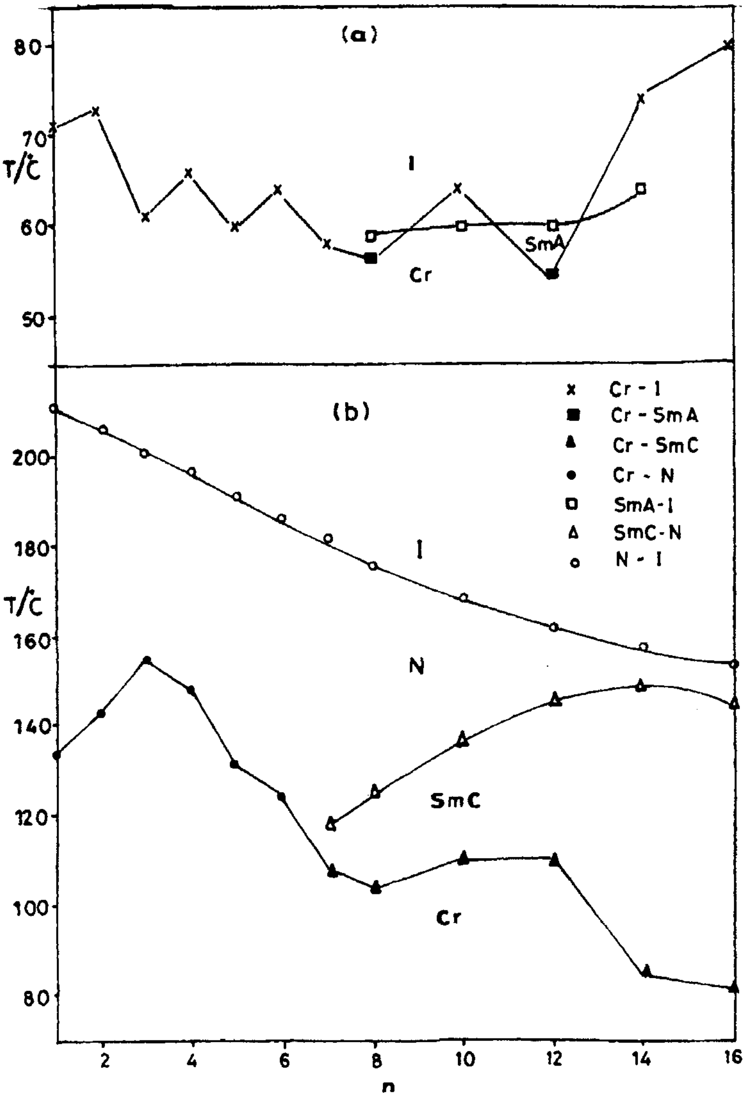
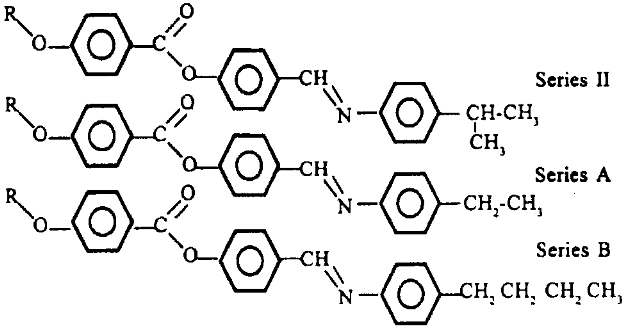


FIGURE 1 The Phase Behaviour for Series I & II

phase. This is reflected in the lower nematic thermal stabilities of series II compared to those of series A. The difference between the smectic thermal stablilties is smaller compared to the nematic thermal stabilities. This show as stated above branched methyl group does not have maximum bradth increasing effect in series II.

TABLE III Average Thermal Stabilities

Series	*II*	*A*	*B*
Smectic-Nematic (C_6-C_{16})	136.6 (C_7-C_{16})	130.3	130.2
Nematic-Isotropic (C_1-C_8)	193.2	232.7	222.8
Commencement of Smectic Phase	C_7	C_6	C_6



Comparative geometry of series II, A and B.

Refrence to table III shows that the defference in the smectic thermal stabilities of series II and B is little whereas nematic thermal stabilities of series B is higher than that of series II. As discussed above, in this case also the difference is in the terminal group at one end only. The explanation given in the forgoing discussion would hold good in the comparison of these two series.

The study indicated that terminal isopropyl group with three phenyl rings having ester and azomethine central linkages exhibit smectic C mesophase along with nematic phase.

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References

[1] W. Kast, *in Landott-Bronstein*, 6th edn., (Springer, Berlin, 1960), Vol. **II**, Part-2a, p. 266.

[2] J.S. Dave, G. Kurian, N.R. Patel and A.P. Prajapati., *Mol. Cryst. Liq. Cryst.*, **112**, 311 (1984).

[3] G.W. Gray and K.J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971); 22, 99 (1971); *Symp. Faraday Soc.*, No. 5, 54 (1971).

[4] Y. Matsunaga and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, **104**, 353 (1984); **16**, 207 (1985); *Bull. Chem. Soc. Jpn.*, **57**, 1413 (1985).

[5] Y. Matsunaga and H. Matsuzaki., *Bull.Chem. Soc. Jpn.*, **62**, 3417 (1989); **63**, 2300 (1990).

[6] G.W. Gray, K.J. Harrison, J.A. Nash and E.P. Raynes, *Electron. Lett.*, **9**, 616 (1973).

[7] G.W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1953).

[8] J.S. Dave and R.A. Vora, *Liquid Crystals and Ordered Fluids*, edited by J.F. Johnson and R.S. Porter (Plenum Press) p. 477 (1970).
[9] J.S. Dave and G. Kurian, *J. Phys.*, **C1**, 403 (1975).
[10] J.S. Dave, G. Kurian and N.R. Patel, *Ind. J. Chem.*, **19A**, 116 (1980).
[11] G.W. Gray, *Molecular Structure and Properties of Liquid Crystals* (Academic Press, London, 1962).