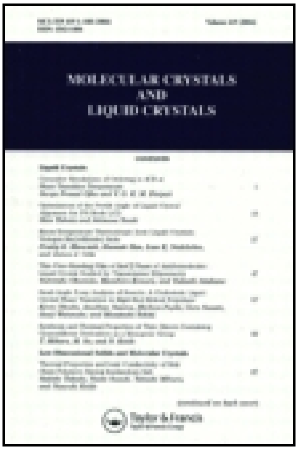

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Liquid Crystals Posessing 1,2,4-Trisubstituted Benzene Derivatives

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Liquid Crystals Posessing 1,2,4-Trisubstituted Benzene Derivatives

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M.S. Univeristy P. B. NO. 51, BARODA – 390 001

The present work deals with synthesis of two homologous series possessing ester and amide linkage and a large lateral aryl substituent. The large lateral group is attached to the main molecule through an amide linkage. Mesogenic amides are rare even when the amide linkage is present in the main molecular framework. However, in the present work the compounds containing amide linkage in lateral moiety also exhibit mesophases of high thermal stability.

INTRODUCTION

Three ring systems incorporating a lateral aryl segment connected to the basic mesogen through a spacer have been reported (1,2,3) to be mesogenic. Connecting a phenyl group with or without a spacer unit to the middle ring of such three ring basic core give compounds with monotropic nematic behaviour only (2-5).

Very few such compounds have been reported to exhibit stable mesophases. One of the factors affecting the stability is presence of spacer. Most of the compounds reported so far have ester linkages connecting the lateral branching to middle aromatic ring. If the ester linkage is replaced by a relatively more rigid amide linkage, there is possibility of obtaining mesophases of good thermal stability. With this in view, the present two homologous series have been synthesized.

EXPERIMENTAL

1. 4-n-alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized as reported in literature (6).
2. 4'-chloro-2-amino-4-hydroxy azobenzene was synthesized as described in the literature (7) using 4-chloroaniline and 3-aminophenol for series 1 and 4'-methoxy-2-amino-4-hydroxy azobenzene was synthesized by using 4-methoxy aniline (p-anisidine) and 3-aminophenol for series 2.
3. 4'-chloro-[2(4''-n-alkoxy benzanilide)-4(4''-n-alkoxy benzoyloxy)] azobenzenes were synthesized by condensing 4'-chloro-2-amino-4-hydroxy azobenzene and appropriate 2 moles of 4-n-alkoxy benzoyl chlorides.
4. 4'-methoxy[2(4''-n-alkoxy benzanilide)-4(4''-n-alkoxy benzoyloxy)] azobenzenes were synthesized by condensing 2 moles of 4-n-alkoxy benzoyl chlorides with 4'-methoxy-2-amino-4-hydroxy azobenzene.

All the compounds synthesized were crystallized several times till constant transition temperatures are obtained. The purity of compounds was checked by TLC.

The compounds were characterized by elemental analysis, IR and NMR spectra.

The compounds were observed under Leitz Laborlux 12 POL polarizing microscope for characterization of mesophases, The smectic mesophase was characterized by miscibility study and DSC.

The transition temperatures for series 1 and 2 are recorded in table 1 and the spectral data are recorded in table 2.

TABLE 1 **Transition temperatures**

R =	Temperatures °C		
n-alkyl group	**Smectic**	**Nematic**	**Isotropic**
Series 1			
Methyl	88.0	----	122.0
Ethyl	80.0	----	130.0
Propyl	72.0	----	128.0
Butyl	99.0	----	133.0
Pentyl	68.0	----	124.0
Hexyl	81.0	----	127.0
Heptyl	78.0	----	121.0
Octyl	70.0	----	118.0
Decyl	72.0	----	110.0
Dodecyl	62.0	----	108.0
Tetradecyl	73.0	----	104.0
Hexadecyl	56.0	----	104.0
Series 2			
Methyl	——	(128.0)*	168.0
Ethyl	——	(140.0)*	178.0
Propyl	——	120.0	149.0
Butyl	(78.0)*	85.0	141.0
Pentyl	75.0	86.0	136.0
Hexyl	79.0	91.0	139.0
Heptyl	76.0	92.0	133.0
Octyl	84.0	99.0	136.0
Decyl	90.0	103.0	130.0
Dodecyl	84.0	105.0	126.0
Tetradecyl	62.0	106.0	119.0
Hexadecyl	50.0	106.0	112.0

* Values in the parentheses indicate monotropy

Table 2 Spectral Data

Homologue	**IR Spectra (cm $^{-1}$)**
Series 1	
n-heptyl	3430, 2920, 2845, 2210, 1733, 1670, 1580, 1510, 1464, 1360, 1320, 1255, 1108, 1040, 982, 846, 752, 680, 633, 585
	NMR Spectra (ppm)
n-heptyl	0.9 δ[6 H, (2 x – C – CH_3), 1.2 – 2.0 δ [20 H, (10 x – CH_2–)], 3.5 – 4 δ[4 H, (2 x Ar – O–CH_2 –)],4.1 δ[1 H, (Ar – NHCO–)],6.8 – 8.5 δ [15 H,Arom.].
	IR Spectra (cm $^{-1}$)
Series 2	
Ethyl	3433, 2926, 2840, 2212, 1736,1669. 1580, 1490, 1462, 1365, 1323, 1251, 1105,1050, 980,848,750,633
	NMR Spectra (ppm)
Ethyl	0.9 δ[6 H, (2 x – C – CH_3)],1.0 – 2.07δ [4 H, (2 x – CH_2–)],3.8δ[3 H, (Ar –O–CH_3)], 4.07 δ[1 H, (Ar – NHCO –)],4.1 – 4.3 δ [4 H,(2xAr–O–CH_2 –)],7.05–8.8 δ[15H, Arom.].

RESULTS AND DISCUSSION

Many mesogens with amide linkage are now known to favour smectogenic tendency (8) when it is present in the main core of a linear molecule. The esteramides synthesized in the present work posess amide linkage in the lateral branching and still exhibit mesophases of good thermal stability and enhanced smectogenic tendency. Series 1 is purely smectic in nature(fig.1). In series 2 both smectic and nematic mesophases are obsrved (fig.2).

Comparison of average thermal stability of series 1 and 2 with series A and B(9) is given in table 3.

Series 1 and 2 have marked higher smectic thermal stabilities and enhanced smectogenic tendency.

Series 1 is purely smectic owing to the presence of chloro group. Methoxy group in series 2 enhances the nematogenic tendency in the series. Series A and B have ester linkages in place of amide lnkage and hence are more nematogenic in nature. Quite a few compounds having structure similar to that of series A & B are known (10) where ester and azo linkages are present. Almost all of these compounds exhibit monotropic nematic phases of low thermal stability. The unexpectedly high mesophase stability of the present two series may be due to the molecular shape and their packing in the anisotropic state. X-ray investigation of similar molecules has helped to understand the packing of such molecules(11).

Five schiff bases with the following structure have been synthesized.

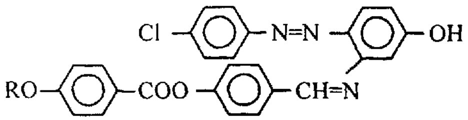


FIGURE 1

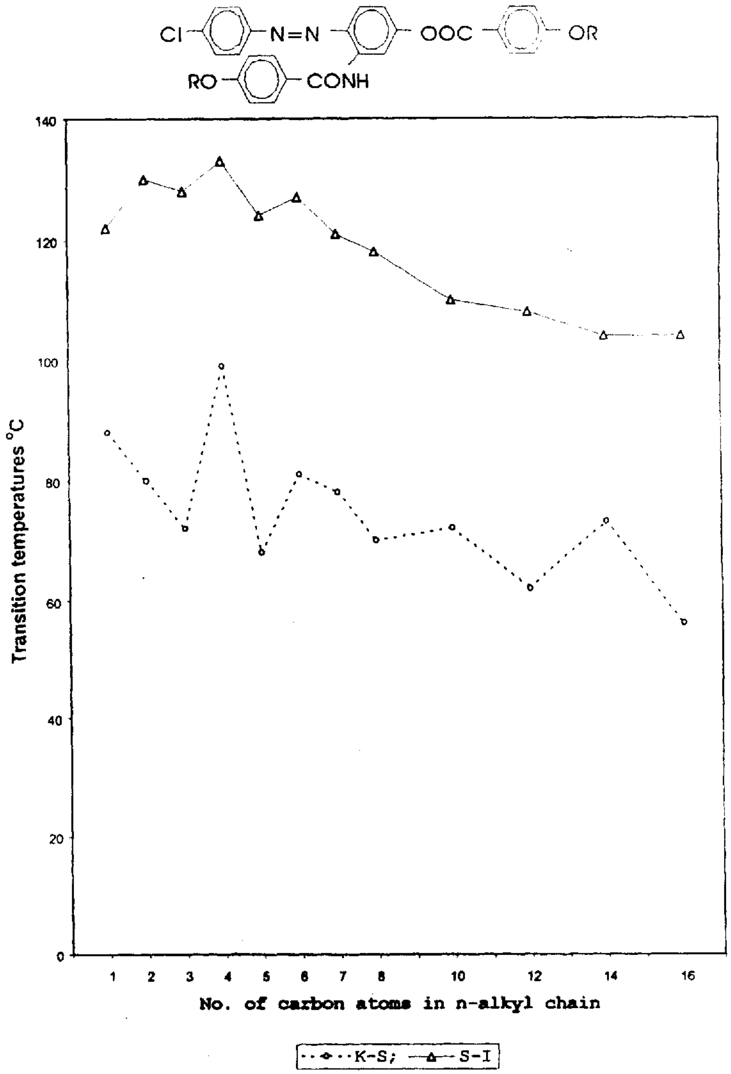

Cl
N=N
OOC
OR
RO
CONH
Transition temperatures °C
0
20
40
60
80
100
120
140
1
2
3
4
5
6
7
8
10
12
14
16
No. of carbon atoms in n-alkyl chain
··◇··K-S; —△—S-I

FIGURE 2

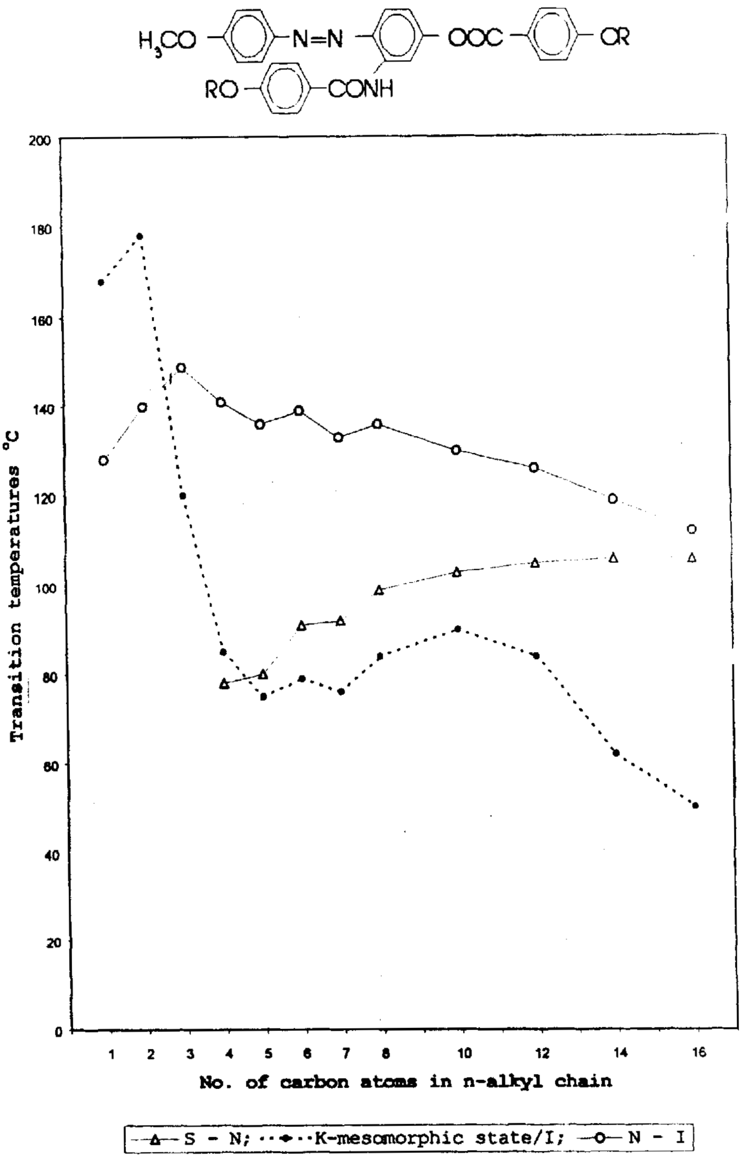

H3CO
N=N
OOC
OR
RO
CONH
Transition temperatures °C
200
180
160
140
120
100
80
60
40
20
0
1
2
3
4
5
6
7
8
10
12
14
16
No. of carbon atoms in n-alkyl chain
S - N;
K-mesomorphic state/I;
N - I

FIGURE 3

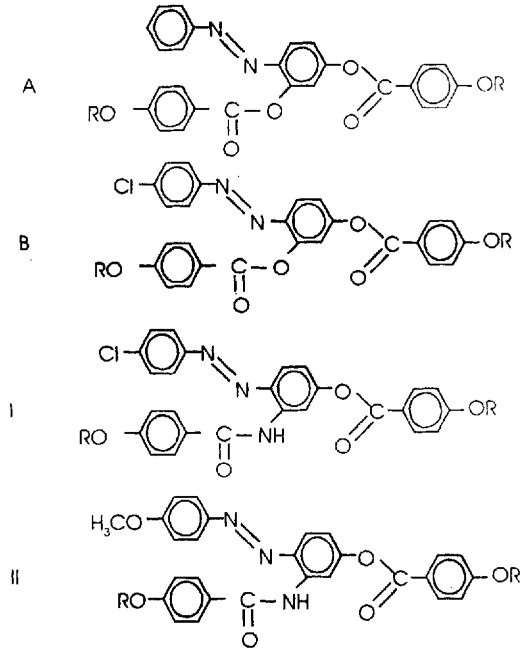
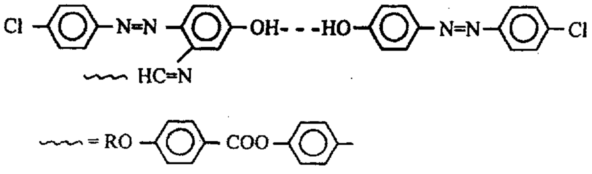


TABLE :3 **Average Thermal Stability °C**

Series	**A**	**B**	**I**	**II**
S-N/I (Homologues)	-	87.25 (C_{10}-C_{16})	119.8 (C_1-C_{16})	95.5 (C_4-C_{16})
N-I (Homologues)	79.62 (C_5-C_{16})	83.5 (C_3-C_{16})	-	138.7 (C_1-C_{16})
Commencement of S Phase	-	C_{10}	C_1	C_4

The transition temperatures are given in table 4a and spectral data are recorded in table 4b.

The schiff bases are thermally very stable. The mesophase range is quite broad. The much higher thermal stability of schiff bases, possessing a long lateral substituent and a terminal phenolic group may be attributed to the intermolecular hydrogen bonding between the molecules. The hydrogen bonding raises the melting point due to the increase in the length of the molecule. The intermolecular hydrogen bonding is confirmed by IR spectroscopy.



Intermolecular hydrogen bonding between molecules of schiff base.

The increased length due to dimer formation responsible for exhibition of mesophases has long been confirmed for alkoxy benzoic acids, but compounds possessing long lateral aryl segments have not been studied much.

ACKNOWLEDGEMENTS

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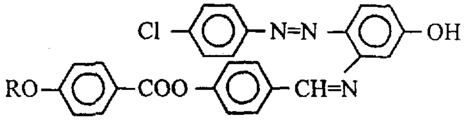

Table 4a **Transition Temperatures**

R =	Temperatures °C		
n-alkyl group	**Smectic**	**Nematic**	**Isotropic**
Hexyl	118.0	130.0	312.0(d)
Octyl	120.0	145.0	305.0
Dodecyl	105.0	289.0	292.0
Tetradecyl	102.0	----	276.0
Hexadecyl	98.0	----	240.0

d=decomposition

Table 4b **Spectral Data**

Homologue	**IR Spectra (cm $^{-1}$)**
n-dodecyl	3433, 2933, 2845, 1728, 1508, 1476, 1421, 1257, 1050, 840, 759
	NMR Spectra (ppm)
n-dodecyl	0.9 δ[3 H, (– C – CH_3), 0.91– 1.84 δ [20 H, (10 x – CH_2–)], 4.3 δ[2H, (Ar –O–CH_2 –)],6.9 – 8.14 δ [15 H,Arom.].

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