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Mesogenic homologous series with a naphthalene moiety

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Interest in the naphthalene unit is increasing considerably. Recently, low and high molecular mass mesogens of naphthalene derivatives exhibiting attractive properties have been reported in the literature. In the present study, three mesogenic homologous series containing a naphthalene moiety have been synthesized. All the homologous series were characterized by elemental analysis and spectroscopic techniques. The behaviour of all three series and their mesophase thermal stabilities are compared with each other and with other structurally related series.

1. Introduction

Dave *et al.* [1, 2], have studied a number of Schiff's base homologous series containing a naphthalene moiety; Wiegand [3] also reported a few Schiff's base compounds containing a naphthalene nucleus. Interest in the naphthalene unit is increasing considerably and recent work on low [4–11] and high [12] molecular mass liquid crystal materials incorporating naphthalene has shown very attractive properties for some of these structures. In the present study three mesogenic homologous series (I, II, III) containing the naphthalene moiety have been synthesized.

Mesomorphic compounds incorporating a phenolic or a primary amino end group are rare [13–16]; Schroeder and Schroeder [17] reported a few such mesogenic compounds. Mesogenic compounds with terminal alcoholic [18] or amino groups [19] are of recent interest. Vora and Gupta [20] for the first time reported two extensive homologous series containing terminal and lateral phenolic groups. The laterally substituted thiol mesogens are yet to be reported. Gray [21] has explained that the rarity of such mesogenic compounds may be due to intermolecular hydrogen bonding and the broadening of the molecules. In order to investigate the influence of the lateral thiol group on mesomorphism we have synthesized a first extensive mesogenic homologous series of Schiff's base esters with a lateral thiol group (series III).

2. Experimental

2.1. *Characterization*

Microanalysis of the compounds was 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 was investigated on a Mettler TA-4000 system.

2.2. *Synthesis*

The synthetic route to series I–III is illustrated in figure 1.

4-*n*-Alkoxybenzaldehydes were prepared by the method of Gray and Jones [22]. 4-*n*-Alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chlorides were synthesized by the modified method of Dave and Vora [23]. 4-*n*-Alkoxybenzoyloxy-4′-benzaldehydes were synthesized by the method of Dave and Kurian [24]. 2-Aminonaphthalene-1-thiol was synthesized by an improved method reported by Valeria *et al.* [25]. The 12 Schiff's bases of series I were synthesized by condensing equimolar quantities of 4-*n*-alkoxybenzaldehydes and 2-aminonaphthalene in boiling ethanol. The 24 Schiff's bases of series II and series III were prepared by condensing equimolar quantities of 4-*n*-alkoxybenzoyloxy-4′-benzaldehydes with 2-aminonaphthalene and 2-aminonaphthalene-1-thiol, respectively in boiling ethanol. All the Schiff's bases of series I were crystallized from ethanol, those of series II and series III from DMF,

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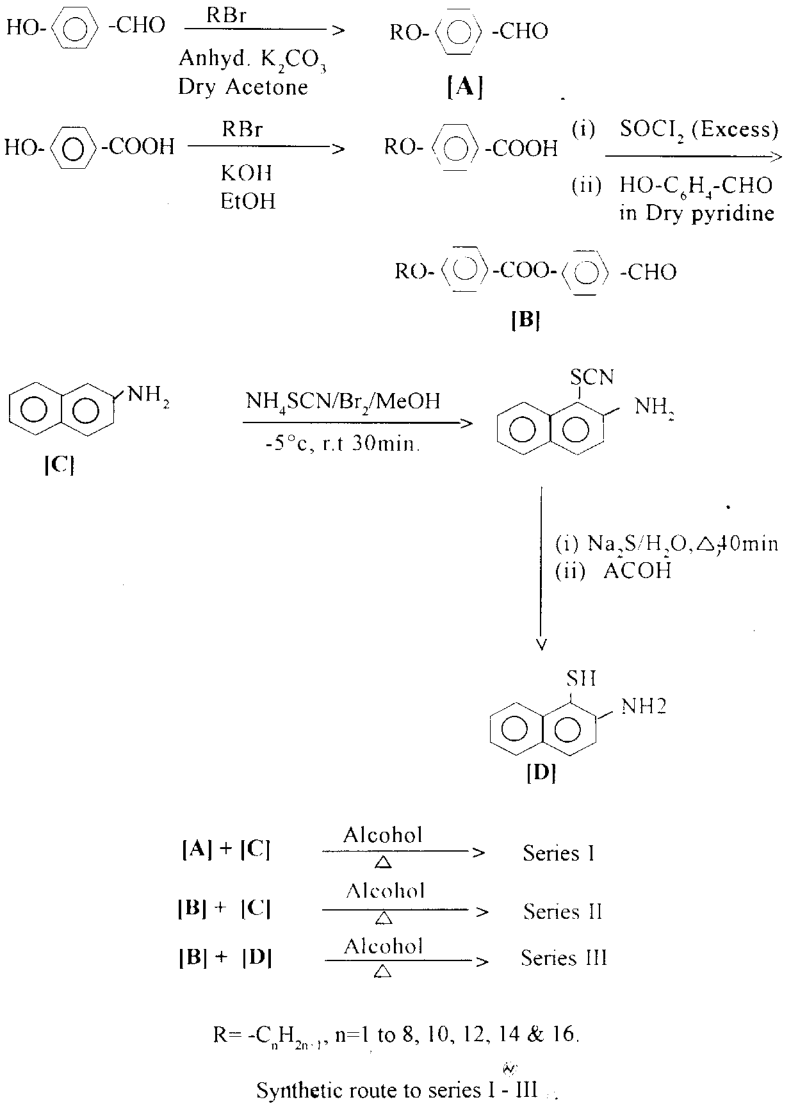


Figure 1. Synthetic route to series I–III.

until constant transition temperatures were obtained. The melting points and transition temperatures are recorded in table 1. The elemental analysis of all the compounds was found to be satisfactory. IR and NMR spectral data are given below.

2.3. *IR (KBr) spectra*

Series I: 2900, 1610 (S, –CH=N–), 1590, 1520, 1475, 1420, 1265, 1180, 850, 760 cm^{-1}.

Series II: 2900, 1730 (S, –COO–), 1605 (S, –CH=N–), 1510, 1470, 1420, 1275, 1205, 1160, 1070, 1010, 840, 755 cm^{-1}.

Series III: 2900, 2345 (W, –SH–), 1730 (S, –COO–), 1610 (S, –CH=N–), 1510, 1470, 1420, 1275, 1205, 1210, 1170, 1075, 1010, 845, 760 cm^{-1}.

2.4. *NMR spectra (solvent $CDCl_3$, standard TMS)*

Series I: (*n*-Dodecyl derivative, 90 MHz) δ 0·90 (t, 3H of terminal methyl group in the alkoxy chain at C-4), 1·0–1·8 (BS, 20H of 10 methylene protons in the alkoxy chain at C-4), 3·95 (t, 2H of $ArOCH_2$ at C-4), 6·8–7·0 (d, $J=9$ Hz 2H at C-3 and C-5), 7·2–7·45 (m, 2H at C-2 and C-6), 7·55–7·8 (m, 7H of naphthalene ring system), 8·35 (s, 1H of –CH=N–).

Series III: (*n*-Dodecyl derivative, 60 MHz) δ 0·90 (t, 3H of terminal methyl group in the alkoxy chain at C-4′), 1·1–1·6 (BS, 20H of 10 methylene protons in the alkoxy chain at C-4′), 3·7–4·2 (m, 3H, 2H of $ArOCH_2$ at C-4 and 1H of –SH– in naphthalene ring),

Table 1. Transition temperatures for series I, II and III compounds.

n	Transition temperatures/°C		
Series I	SmA	N	I
1	—	—	104·0
2	—	—	117·0
3	—	—	122·0
4	—	—	90·0
5	—	—	79·0
6	—	(70·0)[a]	81·0
7	—	(70·0)	88·5
8	—	(76·0)	85·0
10	—	(78·0)	88·0
12	(76·0)	(79·0)	92·0
14	—	—	97·0
16	—	—	100·0
Series II	SmC	N	I
1	—	142·0	270·0
2	—	137·0	267·0
3	—	129·0	254·0
4	—	133·0	249·0
5	—	128·0	239·0
6	—	116·0	235·0
7	(85·0)	120·0	225·0
8	(94·0)	115·0	220·0
10	109·0	141·0	209·0
12	106·0	157·0	198·0
14	101·0	162·0	194·0
16	95·0	155·0	187·0
Series III	SmC	N	I
1	—	188·0	284·0
2	—	187·0	281·0
3	—	191·0	264·0
4	—	184·0	263·0
5	—	170·0	248·0
6	—	163·0	249·0
7	—	150·0	235·0
8	—	145·0	236·0
10	—	136·0	225·0
12	(125·0)	140·0	215·0
14	134·0	143·0	204·0
16	129·0	148·0	196·0

[a] Values in parantheses indicate monotropy.

6·7–7·1 (m, 2H at C-3′ and C-5′), 7·1–7·6 (m, 4H at C-3, C-5, C-2 and C-6), 7·6–8·3 (m, 9H, 6H of naphthalene ring system; 2H at C-2′, C-6′ and 1H of –CH=N–).

2.5. *Calorimetry*

The calorimetric study of series II and series III n-dodecyl derivatives was carried out on the Mettler TA-4000 DSC apparatus (table 2).

Table 2. DSC data for n-dodecyl members of series II and III. All enthalpies are measured on heating only.

Series	Heating rate /°C min^{-1}	Transition	H/J g^{-1}	S/J g^{-1} K^{-1}
II	10	Cr–SmC	20·1050	0·05340
		SmC–N	0·2251	0·00053
		N–I	0·6531	0·00140
III	5	Cr–N	37·8440	0·09280
		N–I	0·4083	0·00084

3. Results

3.1. *Series I: 4-n-alkoxybenzylidene-2′-aminonaphthalenes*

The n-hexyloxy to n-decyloxy derivatives exhibit a monotropic nematic phase. The n-dodecyloxy derivative exhibits a monotropic SmA phase as well as a monotropic nematic phase. The remaining members are non-mesogenic.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain figure 2 (*a*), exhibits a tendency for rising nematic–isotropic transition temperatures in the ascending series.

3.2. *Series II: 4 (4′-n-alkoxybenzoyloxybenzylidene) 2″-aminonaphthalenes*

All the members exhibit an enantiotropic nematic phase. The SmC mesophase commences from the n-heptyloxy derivative as a monotropic phase. n-Decyloxy to n-hexadecyloxy members exhibit an enantiotropic SmC phase.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain figure 2 (*b*), shows a steady fall in the temperature of nematic–isotropic transitions and exhibits a marked odd–even effect. It also exhibits a tendency for rising smectic–nematic transition temperatures in the ascending series, which levels off slightly in the higher homologues.

Series III: 4 (4′-n-Alkoxybenzoyloxybenzylidene) 2″-aminonaphthalene-1″-thiols

All the members exhibit an enantiotropic nematic phase. The SmC mesophase appears from the n-dodecyloxy derivative as a monotropic phase, and the n-tetradecyloxy and the n-hexadecyloxy homologues exhibit enantiotropic SmC phases.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain figure 2 (*c*), shows a steady fall in the nematic–isotropic transition temperature and exhibits a marked odd–even effect. It also exhibits a tendency for rising smectic–nematic transition temperatures in the ascending series.

Smectic phases were characterized by textures as well as by the contact method.

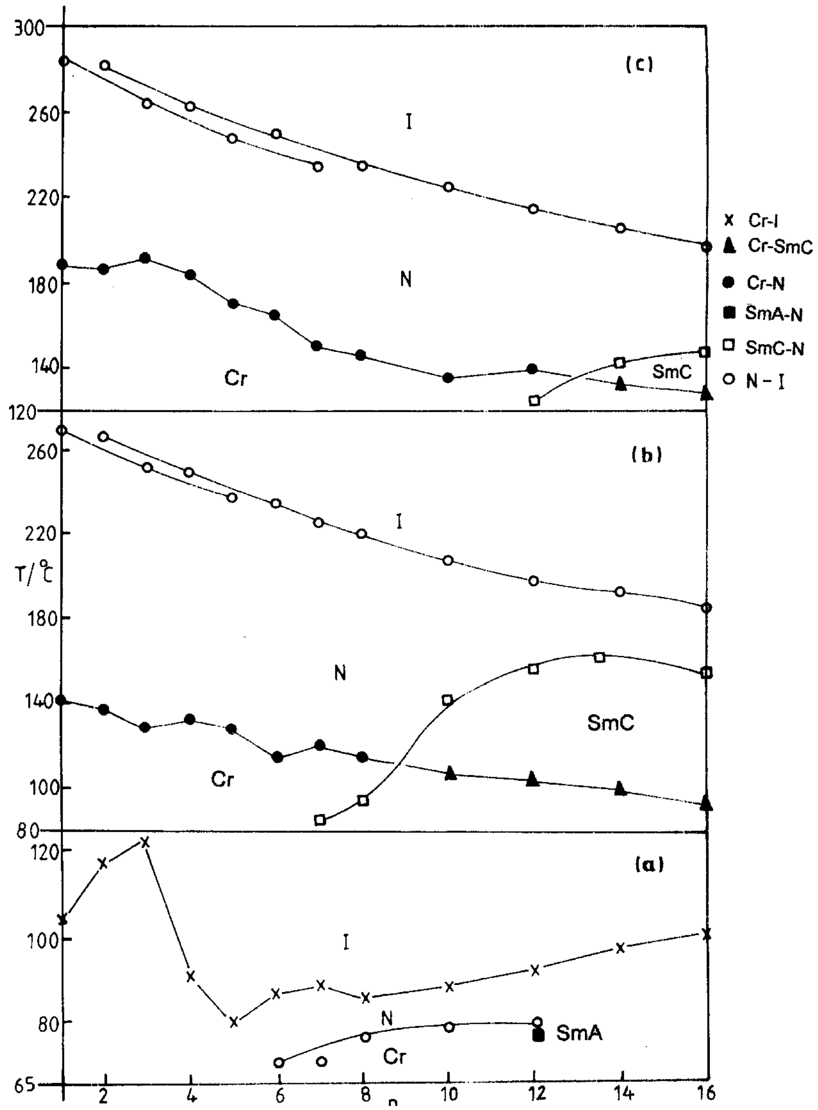


Figure 2. The phase behaviour for the series I–III.

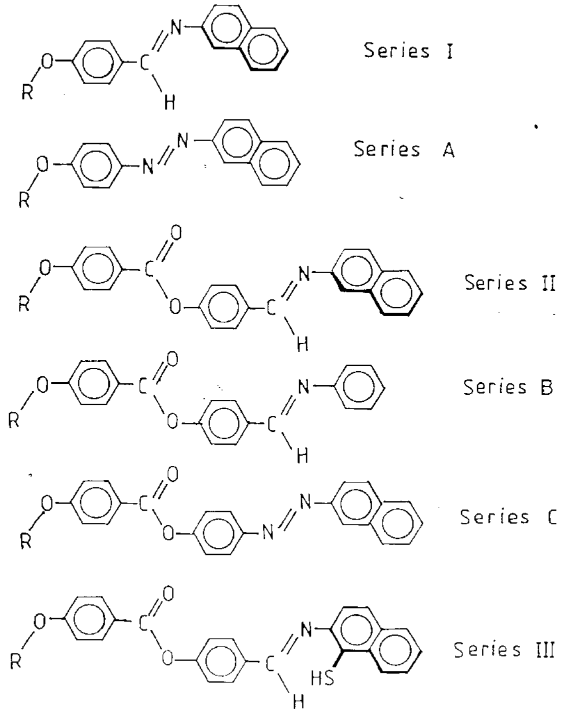
4. Discussion

Table 3 summarizes the average thermal stabilities and comparative geometry of the present series I, II, III and the structurally related series A [26], B [27] and C [26]. Series I exhibits monotropic phases whereas series A is non-mesogenic even though its molecules possess a similar structure except for the central linkage. This indicates that the azomethine linkage –CH=N– is more conducive to mesomorphism than the azo –N=N– central linkage. The smectic as well as nematic thermal stabilities of series I are much lower than those of series II. This can be attributed to the greater length and higher polarizability of series II molecules.

Reference to table 3 indicates that the smectic and nematic thermal stabilities of series II compounds are higher than those of series B. Compared with molecules of series B the molecules of series II are a little longer and more polarizable, but have increased breadth due to the naphthalene moiety. Gray [21] has explained that the increase in the breadth of the molecules reduces both nematic and smectic thermal stabilities. In the present series II, the effect of increase in breadth is not so prominent, due to 2-substitution in the naphthalene nucleus of the molecules, making them linear. Therefore, probably both the smectic and nematic thermal stabilities are higher in the present series II. The nematic thermal stabilities of series II and series C are almost the same. This is understandable as there is little difference in the geometry of the two series, the central linkage being changed from –CH=N– to –N=N–. However, the smectic thermal stabilities of the present series II are higher compared with those of series C. In series II, due to azomethine linkage the molecules become acoplanar. Probably this acoplanarity gives such a packing to the

Table 3. Average thermal stabilities.

Series	I	II	III	A	B	C
N–I (C_1–C_{14})	86·9 ($C_6 - C_{12}$)	231·73	254·8		154·8	229·18
SmC–N or I (C_{12}–C_{16})	79·0 (C_{12})	156·7	138·7	Non-mesogenic	134·2	133·0
Commencement of smectic phase	For only C_{12}	C_7	C_{12}		C_7	C_{10}



Comparative geometry of series I, II, III, A, B and C.

molecules that the smectic thermal stabilities of series II become higher than for series C. This is also reflected in series I and series A where series I exhibits monotropic mesophases and series A is non-mesogenic.

Table 3 shows that the average smectic thermal stabilities of series III are lower, and the average nematic thermal stabilities are higher, in comparison with series II. In series III the thiol group is present at the *ortho* position of the azomethine central linkage, leading to intramolecular hydrogen bonding. The decreased smectic thermal stabilities and increased nematic thermal stabilities indicate that the presence of intramolecular hydrogen bonding favours the nematic mesophase, but that the smectic mesophase is adversely affected. Vora and Gupta [20] have observed just the opposite effects in their study of mesogenic homologous series containing a lateral phenolic group. It is difficult to explain such an opposite trend in thermal stabilities as molecules of the series have different terminal aromatic rings and the type of lateral substituent also differs. Data for more of such series would help in understanding such trends.

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References

[1] Dave, J. S., Kurian, G., Prajapati, A. P., and Vora, R. A., 1971, *Mol. Cryst. liq. Cryst.*, **14,** 307; Dave, J. S., Kurian, G., Prajapati, A. P., and Vora, R. A., 1972, *Curr. Sci.*, **41,** 415; Dave, J. S., Kurian, G., Prajapati, A. P., and Vora, R. A., 1972, *Indian J. Chem.*, **10,** 754.
[2] Dave, J. S., and Prajapati, A. P., 1975, *Pramana*, Suppl. No. 1, 435; Dave, J. S., and Prajapati, A. P., 1976, *Curr. Sci.*, **45,** 95.
[3] Wiegand, C., 1954, *Z. Naturforsch. (b)*, **9,** 516.
[4] Lauk, U., Skrabal, P., and Zollinger, H., 1981, *Helv. chim. Acta.*, **64,** 1847.
[5] Coates, D., 1987, *Mol. Cryst. liq. Cryst.*, **41,** 119.

[6] Wedler, W., Demus, D., Zaschke, H., Mohr, K., Schafter, K. W., and Weissflog, W., 1991, *J. mater. Chem.*, **1,** 347.

[7] Mochizuki, A., Motoyoshi, K., and Nakatsuka, M., 1991, *Ferroelectrics*, **122,** 37.

[8] Sierra, T., Serrano, J. L., Ros, M. B., Ezcurra, A., and Zubia, J., 1992, *J. Am. chem. Soc.*, **114,** 7645.

[9] Marcos, M., Omenat, A., Serrano, J. L., Sierra, T., and Ezcurra, A., 1992, *Adv. Mater.*, **4,** 285.

[10] Hird, M., Toyne, K. J., and Gray, G. W., 1993, *Liq. Cryst.*, **14,** 741.

[11] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., and McDonnell, D. G., 1993, *Liq. Cryst.*, **15,** 123.

[12] Calundann, G., Jaffe, M., Jones, R. S., and Yoon, H., 1988, in *Fibre Reinforcements for Composite Materials*, edited by A. R. Bunsell (Amsterdam), p. 211.

[13] Vorlander, D., 1923, *Z. phys. Chem.*, **105,** 211; Vorlander, D., 1927, *Z. phys. Chem.*, **126,** 470.

[14] Steinstrasser, R., 1972, *Angew., Chem. int. Ed. Engl.*, **11,** 633.

[15] Culling, P., Gray, G. W., and Lewis, D., 1960, *J. chem. Soc.*, 2699.

[16] Berdague, P., Bayle, J. P., Ho, M. S., and Fung, B. M., 1993, *Liq. Cryst.*, **14,** 667.

[17] Schroeder, D. C., and Schroeder, J. P., 1974, *J. Am. chem. Soc.*, **96,** 4347; Schroeder, D. C., and Schroeder, J. P., 1976, *J. org. Chem.*, **41,** 2566.

[18] Goldmacher, J. E., and McCaffrey, M. T., 1970, in *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum Press), p. 375.

[19] MacMillan, J. H., and Labes, M. M., 1979, *Mol. Cryst. liq. Cryst.*, **55,** 61.

[20] Vora, R. A., and Gupta, R., 1979, *Mol. Cryst. liq. Cryst. Lett.*, **56,** 31; Vora, R. A., and Gupta, R., 1980, in *Liquid Crystals*, edited by S. Chandrasekhar (Heyden Verlag), p. 589.

[21] Gray, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals* (London: Academic Press).

[22] Gray, G. W., and Jones, B., 1954, *J. chem. Soc.*, 1467.

[23] Dave, J. S., and Vora, R. A., 1970, in *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum Press), p. 477.

[24] Dave, J. S., and Kurian, G., 1975, *J. Phys.*, **C1,** 403.

[25] Valeria, A., Giuliano, G., Luana, P., and Cario, R., 1992, *Synthesis*, 656.

[26] Vora, R. A., and Prajapati, A. K., 1996, Presented at the National Liquid Crystal Conference, Patiala, India.

[27] Dave, J. S., Kurian, G., and Patel, N. R., 1980, *Indian J. Chem.*, **19A,** 1161.