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Effect of a lateral methyl group on azo-mesogens containing the naphthalene moiety

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Two mesogenic homologous series, 2-[4-(4-*n*-alkoxybenzoyloxy)-2-methylphenylazo]-naphthalenes (I) and 2-[4-(4-*n*-alkoxybenzoyloxy)-3-methylphenylazo]naphthalenes (II) with a lateral methyl group have been synthesized. Both series are purely nematogenic. The mesomorphic properties of both series are compared with each other and also with the properties of other structurally related series to evaluate the effect of the lateral methyl group on mesomorphism. The chiral nematic (N*) mesophase was induced in the system by doping with a derivative of naturally occurring chiral menthol.

1. Introduction

To establish the correlation between liquid crystal (LC) molecular core width and its effect on mesomorphism, Dave *et al.* [1, 2] synthesized a number of schiff's base homologous series having the naphthalene moiety in the molecular core. The effect of chemical composition on 1,4-, 1,5- and 2,6-substituted naphthalene derivatives has also been studied [3–5]. Interest in naphthalene LC cores has revived in the last decade, as indicated by a significant number of research papers [6–15]. Polymeric liquid crystals [16] and ferroelectric liquid crystals [17] have also been studied extensively.

In continuation of our work on 2-aminonapthalenes [18, 19], two new naphthalene-based mesogenic homologous series have been synthesized in the present study. Recently, a number of researchers have tried to induce chirality in the achiral mesogens by doping with naturally occuring chiral compounds or their derivatives [20–22]. The use of optically active dopants may induce ferroelectric chiral nematic phases. With this in mind it was planned to incorporate derivatives of natural menthol, a readily available chiral compound.

2. Experimental

4-Hydroxybenzoic acid, the appropriate *n*-alkyl halides, 2-aminonaphthalene, *o*-cresol and *m*-cresol were used as received. Solvents were dried and distilled prior to use. Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyser. UV spectra were recorded on a Hitachi U-2000 spectrophotometer. IR spectra were recorded on a Shimadzu IR-408. NMR spectra were measured on a Perkin-Elmer R-32 spectrometer. Liquid crystalline properties were investigated on a Leitz Labolux 12 POL microscope provided with a heating stage. DSC was performed on a Mettler TA-4000 system.

The synthetic routes of both series is shown in the scheme. 2-(4-Hydroxy-2-methylphenylazo)naphthalene and 2-(4-hydroxy-3-methylphenylazo)naphthalene were prepared by known methods [23]. 4-*n*-Alkoybenzoic acids and 4-*n*-alkoxybenzoyl chlorides were synthesized by the modified method of Dave and Vora [24].

2-(4-Hydroxy-2-methylphenylazo)naphthalene (for series I) or 2-(4-hydroxy-3-methylphenylazo)naphthalene (for series II) (0.02 mol) was dissolved in dry pyridine (5 ml) and a cold solution of a 4-*n*-alkoxybenzoyl chloride (0.02 mol) in dry pyridine (5 ml) was added slowly with constant stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with 1 dilute hydrochloric acid. The separated solid was filtered off and recrystallized from acetic acid until constant transition temperatures were obtained. The observed transition temperatures are recorded in table 1. The elemental analysis of all the compounds was found to be satisfactory.

UV ($CHCl_3$): *Series I* λ_{max} 263, 338 nm; *Series II* λ_{max} 262, 334 nm.

IR (KBr): *Series I* 2900, 1740 (−COO−), 1610 (−N=N−), 1600, 1520, 1475, 1410, 1360, 1205, 890, 850, 760 cm^{-1}; *Series II* 2900, 1735 (−COO−), 1610 (−N−N−), 1600, 1520, 1470, 1410, 1350, 1200, 890, 855, 760 cm^{-1}.

NMR: (solvent $CDCl_3$, standard TMS, 90 MHz). *Series I*, δ 0.95 (t, 3H of terminal methyl group in the

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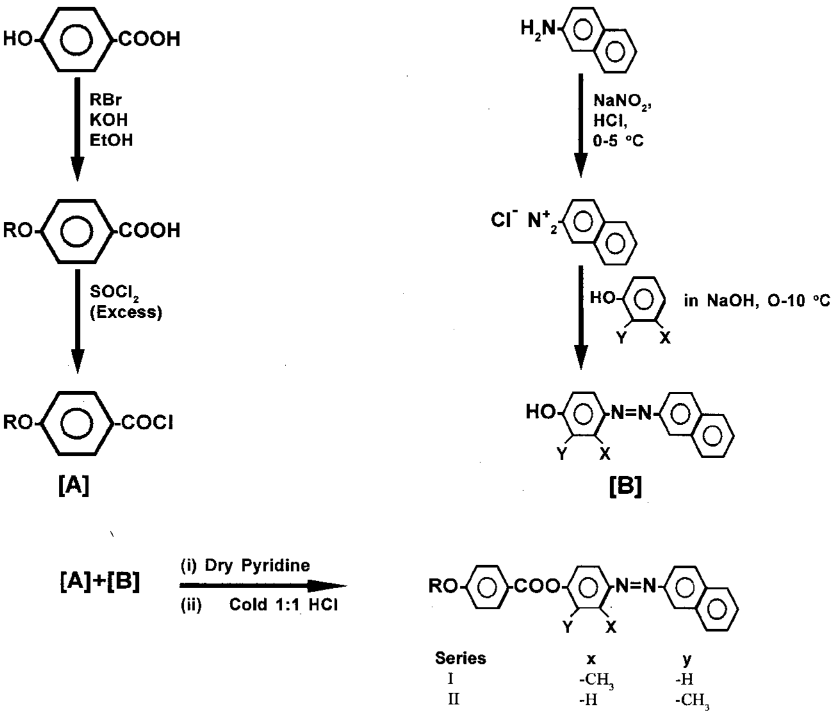


Scheme. Synthetic route for the preparation of series I and II compounds.

Table 1.

$R = C_nH_{2n+1}$, $n =$	Transition Temperatures °C N	I
Series I		
1	131.0	198.0
2	123.0	195.0
3	118.0	171.0
4	114.0	178.0
5	112.0	154.0
6	106.0	158.0
7	86.0	147.0
8	114.0	148.0
10	106.0	146.0
12	102.0	143.0
14	108.0	138.0
16	85.0	130.0
Series II		
1	147.0	218.0
2	142.0	215.0
3	126.0	198.0
4	126.0	197.0
5	115.0	176.0
6	116.0	172.0
7	112.0	160.0
8	104.0	158.0
10	108.0	153.0
12	110.0	152.0
14	107.0	151.0
16	97.0	146.0

alkoxy chain at C-4′), 1.3–2.1 (BS, 12H of six methylene protons in the alkoxy chain), 2.7 (s, 3H, ArCH_3 at C-2), 4.0 (t, 2H of ArOCH_2– at C-4′), 7.0 (d, $J = 9$ Hz, 2H at C-3′ and C-5′), 7.2 (d, $J = 9$ Hz, 2H at C-3 and C-5), 7.5–8.0 (m, 8H, 7H of naphthalene ring system and 1H at C-6), 8.3 (d, $J = 9$ Hz, 2H at C-2′ and C-6′). *Series II*, δ 0.90 (t, 3H of terminal methyl group in the alkoxy chain at C-4′), 1.3–2.1 (BS, 12H of six methylene protons in the alkoxy chain at C-4′), 2.4 (s, 3H, ArCH_3 at C-2), 4.1 (t, 2H of ArOCH_2– at C-4′), 7.0 (d, $J = 9$ Hz, 2H at C-3′ and C-5′), 7.3 (d, $J = 9$ Hz, 1H at C-5), 7.5–8.1 (m, 9H, 7H of naphthalene ring system and 2H at C-2 and C-6), 8.3 (d, $J = 9$ Hz, 2H at C-2′ and C-6′).

DSC data are given in table 2.

The chiral dopant (1*R*, 2*S*, 5*R*)-(−)-menthyl 4-nitrobenzoate was synthesized by condensing 4-nitrobenzoyl chloride with (1*R*, 2*S*, 5*R*)-(−)-menthol using pyridine as solvent [22]. Binary mixtures of the chiral dopant with

Table 2. DSC data, average results.

Series	Heating rate/°C min^{-1}	Transition	H/J g^{-1}	S/J g^{-1} K^{-1}
I	5	Cr–N	22.514	0.0585
		N–I	1.117	0.0027
II	5	Cr–N	24.501	0.0641
		N–I	0.448	0.0011

the octyl derivatives of series I and II were prepared by a standard method [25]. Transition temperatures are recorded in table 3.

3. Results and discussion

3.1. *Series I and II*

All the members of both series I and series II compounds exhibit an enantiotropic nematic mesophase. In the figure the plot of transition temperatures against the number of carbon atoms in the alkoxy chain for series I (*a*) and series II (*b*) shows a steady fall in nematic–isotropic transition temperature and exhibits the usual odd–even effect.

Table 3. Transition temperatures (°C) for binary systems of the *n*-octyl derivatives of series I and II with the chiral dopant.

Mol % of chiral dopant	Series I		Series II	
	N*	I	N*	I
15.25	113.0	130.0	104.0	137.0
28.80	(71.0)[a]	118.0	(79.0)[a]	123.0
39.49	—	109.0	—	116.

[a] Values in parentheses indicate monotropy.

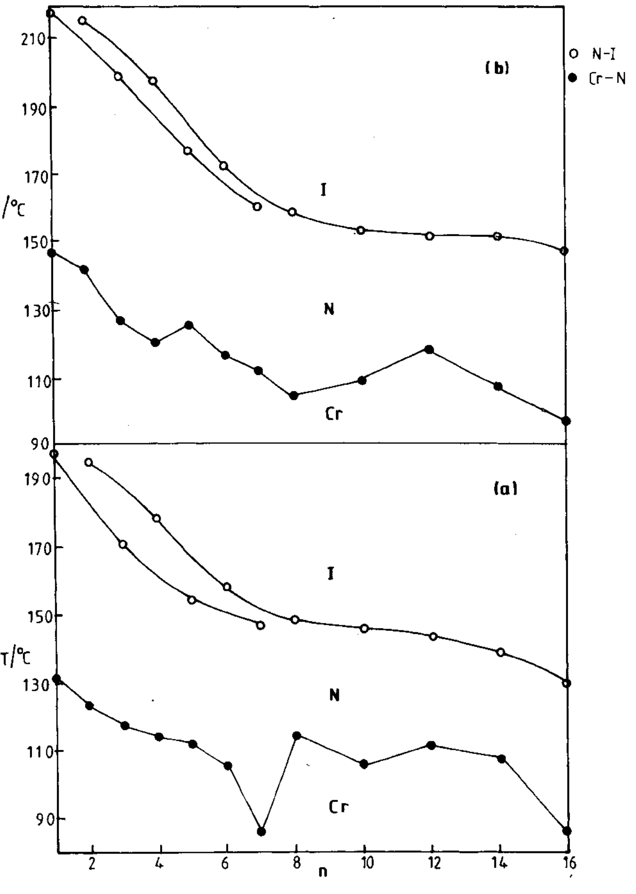


Figure. The phase behaviour for series I (*a*) and II (*b*) compounds.

Table 4 summarizes the average thermal stabilities and comparative geometry of the present series I and II and series A [18]. The average nematic thermal stabilities of both the present series are lower than those of series A. Compared with the molecules of series A, the molecules of present series I and II have increased breadth due to the lateral methyl group on the central benzene ring. Gray [3] has explained that the increase in the breadth of the molecules reduces both nematic and smectic thermal stabilities. It seems that the lateral methyl group not only increases the breadth of the molecules of series I and II, but also increases the acoplanarity in the system due to steric interaction. Both these factors would tend to eliminate the smectogenic tendencies from the present series I and II whereas, in series A the smectic C mesophase appears in the *n*-decyloxy derivative as a monotropic phase.

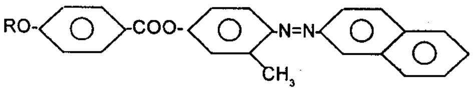
Reference to table 3 indicates that the average nematic thermal stabilities of series II are higher than those of series I. The difference in molecular geometry is only in the position of the lateral methyl group on the central benzene nucleus. In series I, the lateral methyl group is ortho to the $-N{=}N-$ central linkage whereas in series II, it is ortho to the $-COO-$ central linkage. Probably the flexibility of the $-COO-$ compensates the steric hindrance and enables a more compact packing of the molecules to stabilize the nematic.

3.2. *Binary systems*

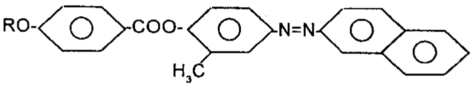
A non-mesogenic optically active menthyl-4-nitrobenzoate was doped up to a level of about 40 mol % into the *n*-octyl derivatives of series I and II (table 3).

Table 4. Average thermal stabilities (°).

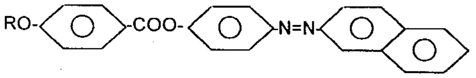
Series	N–I (C_1–C_{16})	Commencement of smectic phase
I	158.83	—
II	174.67	—
A	224.83	C_{10}



Series I



Series II



Series A

Comparative geometry of series I, II and A

In both the systems the chiral nematic was mesophase induced, lowering transition temperatures and persisting up to about 28.8 mol % of chiral dopant. The induced chiral nematic mesophase is shown by the observation of oily streaks and brilliant colours. The study provides a means to induce the chiral nematic mesophase (N*) in the system by doping it with the derivative of naturally occurring chiral menthol.

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