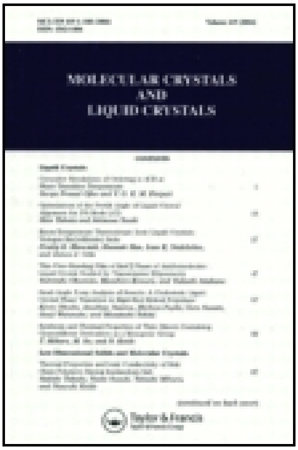

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AZOMESOGENS CONTAINING TWO FUSED RING MOIETIES: SYNTHESIS AND CHARACTERIZATION

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AZOMESOGENS CONTAINING TWO FUSED RING MOIETIES: SYNTHESIS AND CHARACTERIZATION

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Several liquid crystalline compounds derived from 2-aminonaphthalene have been synthesized. The molecules are designed to accommodate two napthalene moieties. The molecular structures of these new compounds have been characterized by element analysis, FTIR, and NMR spectral studies. The mesomorphic behavior has been studied using mainly polarized microscope and in some cases differential scanning calorimeter as well. Our investigation reveals that all the compounds exhibit enantiotropic nematic phase. The mesomorphic behaviors of these new compounds have been compared with those of structurally related materials.

Keywords: naphthalene moieties; nematogens

INTRODUCTION

Naphthalene derivatives exhibiting liquid crystalline properties have been well known for a few decades and extensive literature exists [1–4]. Dave et al. [5] and Dave and Prajapati [6] synthesized a number of schiff's base homologous series having the naphthalene moiety to establish the relation between the width of the aromatic core and mesomorphic behavior. The chemical composition on 1,4-, 1,5-, 2,6-substituted naphthalene derivatives have also been studied [7–10]. Malthete et al. [11] reported mesogenic 1,4,5,8-tetrasubstituted naphthalene derivatives. However, the mesogenic homologous series containing two naphthalene moieties are very few. Dave et al. [12,13] synthesized two extensive mesogenic homologous series of schiff's base containing two naphthalene moieties. Cotes and Gray [14] and

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*Corresponding author.

also Schafer et al. [15] have reported few mesogenic compounds accommodating two naphthalene nucleus having an ester central linkage.

Earlier we have reported few mesogenic homologous series derived from 2-aminonaphthalene containing only one naphthalene nucleus [16,17]. In continuation of our work on 2-aminonaphthalene–based mesogens, here we report the synthesis and characterization of a new homologous series accommodating two naphthalene moieties.

EXPERIMENTAL

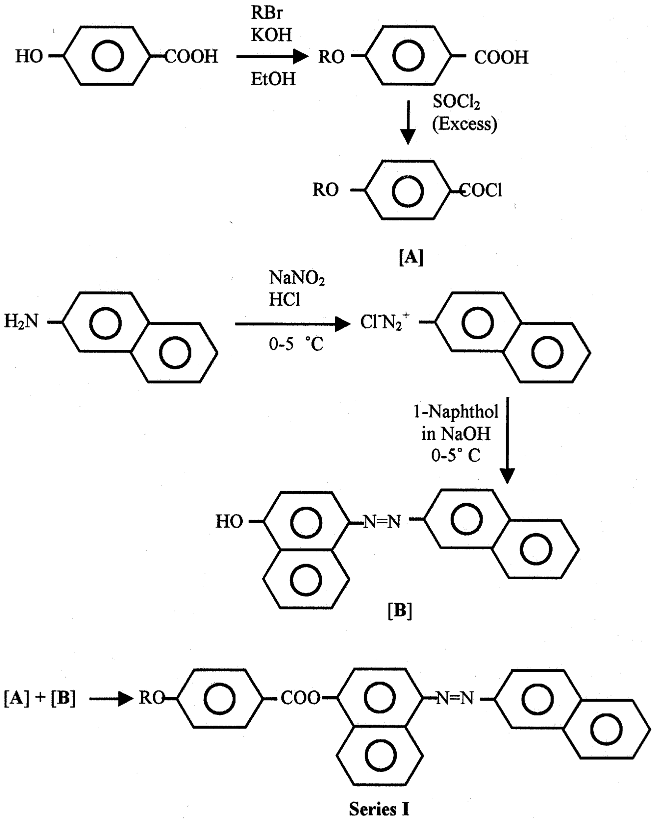
General Information

4-Hydroxybenzoic acid, n-alkylhalides, 2-aminonaphthalene, and 1-naphthol were used as received. Solvents were dried and distilled prior to use. Microanalyses of the compounds were performed on a Coleman carbon-hydrogen analyzer, and IR spectra were recorded on Shimadzu IR-408 using KBr pellets. ^{1}H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer using TMS as an internal standard. Liquid crystalline properties were investigated on a Leitz Labourlux 12POL microscope provided with a heating stage. The calorimetric studies were carried out on a Mettler TA 4000 DSC apparatus by adopting a scanning rate of 5°C/min. UV spectra were recorded on a Hitachi U-2000 spectrophotometer.

The synthetic route to series-I is illustrated in Scheme 1. 4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides [**A**] were synthesized by the modified method of Dave and Vora [18].

*Synthesis of 4-hydroxynaphthylazo 2'-naphthalene [**B**] [19]*

A well-stirred mixture of 2-aminonaphthalene (14.3 g, 0.1 mol)and 16% HCL (50 ml) was cooled below 5°C and a solution of $NaNO_2$ (7.6 g, 0.11 mol) in water (20 ml) was added dropwise in such a way that the temperature of the mixture was in the range 0–5°C. The cold, dark solution was added dropwise to a cold mixture of 1-naphthol(14.4 g, 0.1 mol), NaOH (20 g, 0.5 mol) and water (50 ml), during which the temperature of the mixture was maintained below 5°C. Acidification with aqueous HCl furnished the crude product which was collected by filtration, dried in air, and crystallized several times form alcohol; yield 23.8 g, 80%; m.p: ; UVλ_{max}: 405&539 (aromatic ring), 575 (N=N) and 662 (OH); IR ν_{max}/cm^{-1}: 3290(OH), 2950, 1610(N=N), 1585, 1500, 1460, 1385, 860, 825, and 755; ^{1}H NMR ($CDCl_3$): 7.0–7.9(m, 13H of naphthalene ring system) and 10.10(s, 1H, OH); Elemental analysis (%): calc. for $C_{20}H_{14}N_2O$; C 80.54, H 4.70, N 9.40; found: C 80.32, H 4.56, N 9.47.



R= $-C_nH_{2n+1}$;

1: n = 1
2: n = 4
3: n = 6
4: n = 7
5: n = 8
6: n = 10
7: n = 12
8: n = 16

SCHEME 1 Synthetic route to series-I compounds.

General Procedure for the Synthesis of Series-I

Dye **B** (10 mmol) was dissolved in dry pyridine (15 ml) and added slowly into acid chloride **A** (10 mmol) in dry pyridine (15 ml) below 15°C. The mixture was then heated on water bath for 1 h and was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid. The solid separated was stirred with 10% aqueous sodium hydroxide solution for 30 min. The insoluble product was collected by filtration and was washed with water for several times. Finally the crude product was recrystallized from dimethylformamide till constant transition

TABLE 1 Micronanalytical Data of Series-I

			Required (%)			Found (%)		
Compound	n	Formula	C	H	N	C	H	N
1	1	$C_{28}H_{20}N_2O_3$	77.78	4.63	6.48	77.43	4.64	6.32
2	4	$C_{31}H_{26}N_2O_3$	78.48	5.49	5.91	78.71	5.63	5.86
3	6	$C_{33}H_{30}N_2O_3$	78.88	5.98	5.58	78.47	5.85	5.69
4	7	$C_{34}H_{32}N_2O_3$	79.07	6.20	5.43	78.95	5.88	5.69
5	8	$C_{35}H_{34}N_2O_3$	79.24	6.41	5.28	79.51	6.83	5.46
6	10	$C_{37}H_{38}N_2O_3$	79.57	6.81	5.02	79.23	6.71	4.95
7	12	$C_{39}H_{42}N_2O_3$	79.86	7.13	4.78	79.66	7.40	4.62
8	16	$C_{43}H_{50}N_2O_3$	80.37	7.79	4.36	79.98	8.00	4.34

temperature. The elemental analysis of all the compounds were found to be satisfactory and have been mentioned in Table 1. The UV, IR, and ^{1}H NMR spectral data of all the compounds were found to be inconsistent with the proposed structure. As a representative case we provide spectral data for the compound **8**: UV λ_{max}: 402&569 (aromatic ring), 615 (N=N), 641 (OOC); IR $\nu_{\mathrm{max}}/\mathrm{cm}^{-1}$: 2950, 1740 (COO), 1650 (N=N), 1515, 1456, 1380, 1260, 1225, 1160, 1080, 850, 820, and 770 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.9(t, 3H, CH_3), 1.1–1.6(m, 28H, $14 \times CH_2$), 4.1(t, 2H, OCH_2), 6.45(d, 2H of benzene ring at C3' and C5'), 7.0–7.7(m, 12H of naphthalene ring system), 7.85(s, 1H of naphthalene ring system at C-1″), and 8.0(d, 2H of benzene ring at C2' and C6').

RESULTS AND DISCUSSION

The transition temperatures of the compounds of series-I are summarized in Table 2. All the members exhibit an enantiotropic nematic (N) mesophase. Figure 1 shows the plot of transition temperatures against the number of carbon atoms in the alkoxy chain, from which it can be noticed that crystal melting transition temperatures decrease with the increase in the length of terminal alkoxy tail, with the exception in the case of compounds 3 and 4. The nematic-isotropic (N-Iso) transition temperatures also decrease with increase in the transition temperature, which is in agreement with the observation reported for such homologous series.

Table 3 shows the comparison of N-Iso transition temperature and range (width) of nematic phase between a representative compound **5** (n = 8) of the present series-I and structurally related compounds **A** [16], **B** [16], and **C** [20] reported in the literature. The neamtic range of compound **5** is about 41°C, whereas that of compound **A** is 75°C. However, the N-Iso transition temperature for the compound **5** is much lower when compared with that

TABLE 2 Transition Temperatures(°C)[a] of the Present Series-I

Compound	n	Cr		N		Iso
1	1	•	195	•	214	•
2	4	•	132	•	203	•
3	6	•	138	•	177	•
4[b]	7	•	135	•	170	•
			[$\Delta H/Jg^{-1} = 24.48$]		[$\Delta H/Jg^{-1} = 0.52$]	
			[$\Delta S/Jg^{-1}k^{-1} = 0.0595$]		[$\Delta S/Jg^{-1}k^{-1} = 0.0.0012$]	
5	8	•	123	•	164	•
6	10	•	116	•	154	•
7	12	•	111	•	144	•
8[b]	16	•	95	•	135	•
			[$\Delta H/Jg^{-1} = 60.96$]		[$\Delta H/Jg^{-1} = 0.98$]	
			[$\Delta S/Jg^{-1}k^{-1} = 0.1656$]		[$\Delta S/Jg^{-1}k^{-1} = 0.0024$]	

[a] Determined by optical microscopic observation.

[b] The calorimetric studies have been performed on this sample and therefore enthalpy and entropy values have been mentioned. Cr, Crystal; N, nematic phase; Iso, Isotropic liquid state.

of compound **A**. The molecular structure of **5** differs from compound **A** only at the central aromatic core; compound **5** has naphthalene at the center, whereas in compound **A** the central core is benzene nucleus.

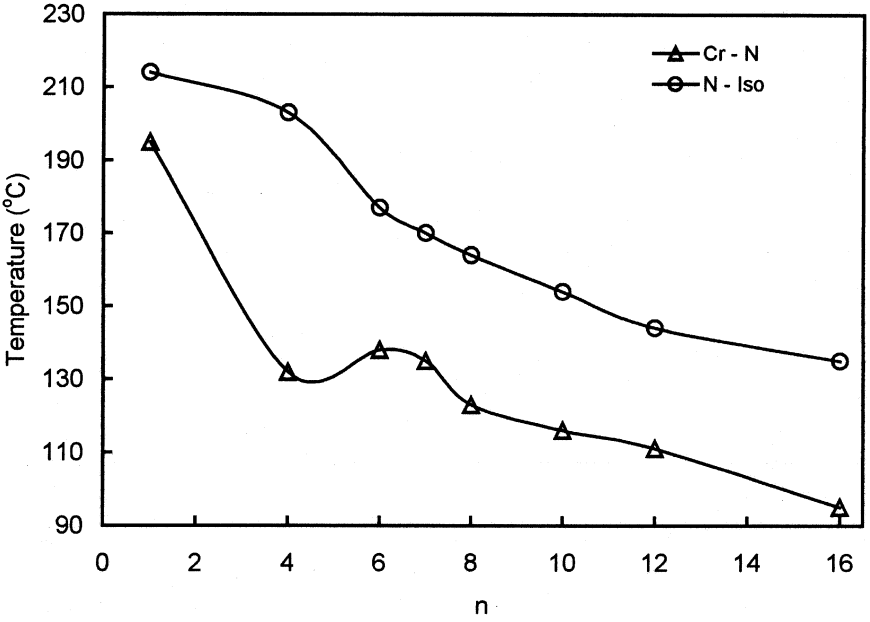
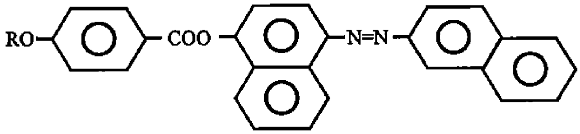


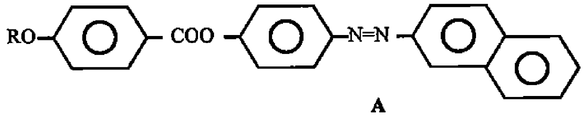
FIGURE 1 The phase behavior of series-I.

TABLE 3 The Comparison of N-Iso Transition Temperatures and the Range of Nematic Phase Between a Representative Compound **5** (C_8-homologue) of Series Structurally Related Compounds and I Reported in the Literature

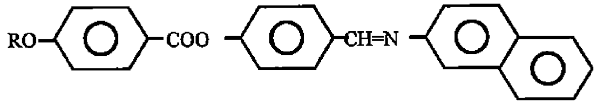
Compound	Transition temperatures (°C) N	I	Mesophase range	Commencement of smectic phase
5	123	164	41	—
A	138	213	75	C_{10}
B	115	220	105	C_7
C	152	178	26	C_{12}



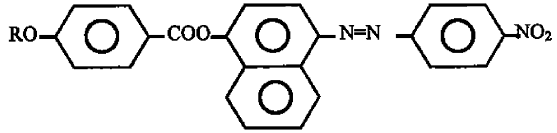
5



A



B



C

Where $R = -C_8H_{17}$

The presence of naphthalene nucleus at the center increases the breadth of the molecules of compound **I**. Gray [3] has explained that increase in the breadth of molecules reduces both nematic and smectic mesophase stability. It seems that the naphthalene nucleus at the center not only increase the breadth of the molecules but also weakens the lateral attraction. Both of these factors would tend to eliminate the smectogenic tendencies as well as decrease the mesophase range and N-Iso transition temperature for compounds reported in the present investigation. The molecular structural difference between compounds **5** and **B** lies both in central aromatic core and the linkage. This difference has significant influence on the mesophase range as well as N-Iso transition temperature, as can be seen in the Table 3. The stabilization of nematic phase in case of compound **B** is wide (over 100°C temperature range), and perhaps the foregoing discussion would hold good for this behavior.

In case of compound **C**, the width of the nematic phase is just 26°C. Gray [3] has explained that the compound, which required more thermal energy to disorganize the parallel molecular arrangement of the nematic melt, is thermally more stable. As can be seen in Table 3, more thermal energy has to be supplied to disorganize the parallel molecular arrangement of the nematic melt of compound of **C**, evidenced by the fact that the N-Iso transition temperature is higher by 14°C than that for the compound **5**. The higher nematic-isotropic transition temperatures of compound **C** may be due to the polar nature of the terminal nitro group which increases the overall polarizability of the molecules of compound **C** compared to compound **5**. The range and thermal stability of the mesophase is a more important factor in relating mesomorphic behavior to chemical constitution since the chemical grouping gives rise to intermolecular attractions which in turn determine the mesophase range and thermal stability. One should remember too that the length of the mesophase is determined partly by the CrN transition temperatures.

CONCLUSION

In this article we have presented the synthesis and characterization of eight new mesogens in which two naphthalene cores have been joined together through azo linkage. All compounds of the series exhibit enantiotropic nematic phase. However, the range of nematic phase and N-Iso transition temperatures of the present series I is lower than those of structurally related compounds that have been attributed to the presence of central naphthalene ring.

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