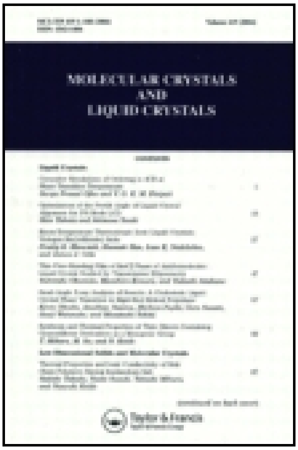

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Effect of a Lateral Chloro Group on Azomesogens Containing the Naphthalene Moiety

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EFFECT OF A LATERAL CHLORO GROUP ON AZOMESOGENS CONTAINING THE NAPHTHALENE MOIETY

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A homologous series of azomesomesogens, 2″[4-(4′-n-alkoxybenzoyloxy)-3-chloro phenylazo] naphthalene, with lateral chloro group was synthesized. All twelve homologues of the series synthesized exhibit enantiotropic nematic mesophase. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain shows a steady fall in nematic-isotropic transition temperature. The mesogenic behavior of the present series is compared with other structurally related series to evaluate the effect of lateral chloro group on mesomorphism.

Keywords: azobenzene derivative; lateral chloro group; nematic mesophase

INTRODUCTION

A vast number of mesogenic compounds showing nematic or other mesophases are reported [1–3] containing naphthalene moiety as core system. Wiegand [4] reported few mesogenic Schiff base of 2,6-, 1,5- and 1,4-diaminonaphthalenes. Gray and Jones [5] investigated liquid crystalline properties of different alkoxy naphthoic acids. Coates and Gray [6] synthesized 4-n-alkyl/alkoxy phenyl esters of 6-n-alkyl/alkoxy naphthalene 2-carboxylic acid. Dave and coworkers studied a variety of liquid crystalline compounds exhibiting smectic, nematic, and choleseric mesomorphism

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*Corresponding author. E-mail: akprajapati@yahoo.co.uk containing naphthalene moiety, such as alkozybenzoates of 1,5- and 1,4-dihydroxynaphthalene [7], esters of cholesterol [8] and alkoxy naphthylidene Schiff's bases [9–11]. Malthete et al. [12] synthesized tetra-acylated 1,4,5,8-tetrahydroxynaphthalene derivatives, which may be looked upon as "conjoined twin" mesogens. In the last decade significant number of research papers on naphthalene LC cores appeared in the literature [13–21]. Previously we have reported [22,23] the mesogenic homologous series of Schiff's base esters containing naphthalene moiety and studied the effect of lateral thiol and methoxy substituent on mesomorphism. We have also reported mesogenic homologous series of azomesogens without lateral substituent [25] as well as lateral methyl group [25] and evaluated the effect of lateral methyl group on mesomorphism. As an extension of this work, we have replaced lateral methyl group by a polar chloro group and prepared a homologous series of 2″[4(4′-n-alkoxybenzoyloxy) 3′-chloro phenylazo] naphthalenes to investigate the influence of the lateral chloro group on mesomorphism.

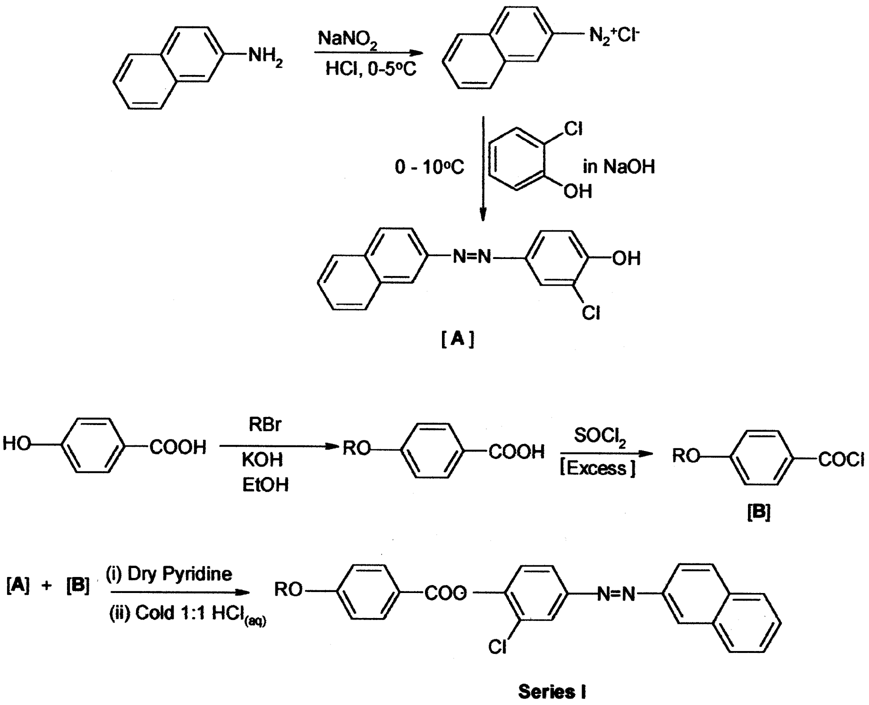
EXPERIMENTAL

4-Hydroxy benxoic acid, the appropriate n-alkylhalides, o-chlorophenol, and 2-aminonaphthalene were used as received. Solvents were dried and distilled prior to use. Microanalysis of the compounds were performed on a Coleman carbon-hydrogen analyzer. Infrared (IR) spectra were determined via KBr pellets, using a Schimadzu IR-408 spectrophotometer. ^{1}H NMR spectra were obtained with a Perking-Elmer R-32 spectrometer using tetramethylsiland (TMS) as an internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference. $CDCl_3$ was used as solvant. UV spectra were recorded on a Hitachi U-2000 spectrophotometer. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with heating stage. The enthalpies of transitions reported as J/g were determined from thermograms obtained on a Mettler TA-400 system, adopting a scanning rate of 5°C/min.

The synthetic route to series I is illustrated in scheme 1. Using a conventional method of diazotization and coupling [26], 2(4-Hydroxy-3-chlorophenylazo)naphthalene(A) was synthesized. Also 4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides(B) were synthesized by the modified method of Dave and Vora [27].

Synthesis of Series I Compounds

First 2(4-Hydroxy-3-chlorophenylazo)naphthalene (0.02 mol)was dissolved in dry pyridine (5 ml), and a cold solution of a 4-n-alkoxybenzoyl chloride



SCHEME 1 Synthetic route to series I compounds.

(0.02 mol) in dry pyridine was added slowly with constant stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 dilute hydrochloric acid. The solid obtained was separated, dried, and triturated by stirring for 30 min with 10% aqueous sodium hydroxide, and was then washed with water.

The insoluble product was thus separated from the reactants; finally, all the compounds of series I were crystallized from acetic acid until constant transition temperatures were obtained. The elemental analysis of all the compounds were found to be satisfactory and have been mentioned in Table I. The ultraviolet (UV), IR, and ^{1}H NMR spectral data of all the compounds were found to be consistent with the proposed structure. As a representative case we provide spectral data for compound 8 UV(CHCL$_3$) λ_{max}: 263, 338 nm; (KBr) ν_{max}/cm^{-1}: 2900, 1740 ((-COO-), 1610)-N=N-), 1600, 1520, 1475, 1410, 1360, 1205, 890, 850, 760, 680 (-C-Cl); :^{1}H NMR CDCl$_3$: δ 0.95(t, 3H, -CH$_3$), 1.35–1.7(m, 12H, 6 x -CH$_2$-), 4.1(t, 2H, -OCH$_2$-), 6.9(d, J = 9 Hz, 2H at C-3′ and C-5′), 7.25(s, 1H at C-2), 7.40–8.30 (m, 9H, 7H of naphthalene ring and 2H at C-5 and C-6), 8.5 (d, J = 9 Hz, 2H at C-2′ and C-6′).

TABLE I Elemental Analysis for Series I Compounds

Compound	$R = \text{-}C_nH_{2n+1}$ n =	Formula	% Required (%found) C	H	N
1	1	$C_{24}H_{17}N_2O_3Cl$	69.15(69.28)	4.08(4.28)	6.72(6.55)
2	2	$C_{25}H_{19}N_2O_3Cl$	69.69(69.58)	4.41(4.48)	6.50(6.58)
3	3	$C_{26}H_{21}N_2O_3Cl$	70.19(70.06)	4.72(4.92)	6.30(6.21)
4	4	$C_{27}H_{23}N_2O_3Cl$	70.67(70.55)	5.02(4.86)	6.12(6.37)
5	5	$C_{28}H_{25}N_2O_3Cl$	71.11(71.42)	5.29(5.38)	5.93(6.06)
6	6	$C_{29}H_{27}N_2O_3Cl$	71.53(71.26)	5.55(5.58)	5.75(5.92)
7	7	$C_{30}H_{29}N_2O_3Cl$	71.93(72.17)	5.79(5.84)	5.59(5.54)
8	8	$C_{31}H_{31}N_2O_3Cl$	72.30(71.95)	6.02(6.37)	5.44(5.24)
9	10	$C_{33}H_{35}N_2O_3Cl$	72.99(72.73)	6.45(6.66)	5.16(5.18)
10	12	$C_{35}H_{39}N_2O_3Cl$	73.62(73.46)	6.84(6.85)	4.91(4.82)
11	14	$C_{37}H_{43}N_2O_3Cl$	74.18(74.28)	7.18(7.26)	4.68(4.77)
12	16	$C_{39}H_{47}N_2O_3Cl$	74.70(74.60)	7.50(7.25)	4.47(4.42)

RESULTS AND DISCUSSION

The transition temperature of the compounds of series I are summarized in Table II. Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results, therefore we may draw conclusions concerning the nature of the phases which occur during the transitions. In the present study, enthalpies of n-decyloxy and n-tetradecyloxy derivatives were measured by differential scanning calorimetry. Data are recorded in Table II. Enthalpy values of the nematic phase transitions agree well with the literature value [28] which has helped in further confirmation of mesophase type.

All the twelve members of series I synthesized exhibit 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 chain with the exception in the case of compounds 5, 7, and 10. The nematic-isotropic (N-Iso) transition temperatures also decrease with increase in terminal alkoxy tail and exhibit the usual odd-even effect which is in agreement with the observation reported for such homologues series.

Table III shows the comparison of N-Iso transition temperature and range (width) of nematic phase between a representative compound **7**(n = 7) of the present series I and structurally related compounds **A** [24], **B** [25], and **C** [23] reported in the literature. The nematic range of compound **7** is about 75°C, where as that of compound **A** is 83°C. However the

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

Compound	n	Cr		N		Iso
1	1	●	202	●	224	●
2	2	●	167	●	218	●
3	3	●	137	●	207	●
4	4	●	122	●	209	●
5	5	●	179	●	196	●
6	6	●	99.5	●	197	●
7	7	●	111	●	186	●
8	8	●	100	●	181	●
9[b]	10	●	96	●	170	●
			$[\Delta H/Jg^{-1} = 44.30]$		$[\Delta H/Jg^{-1} = 0.89]$	●
			$[\Delta S/Jg^{-1}K^{-1} = 0.1201]$		$[\Delta S/Jg^{-1}K^{-1} = 0.0020]$	
10	12	●	116	●	159	●
11[b]	14	●	94	●	149	
			$[\Delta H/Jg^{-1} = 68.04]$		$[\Delta H/Jg^{-1} = 0.92]$	●
			$[\Delta S/Jg^{-1}K^{-1} = 0.1854]$		$[\Delta S/Jg^{-1}K^{-1} = 0.0022]$	
12	16	●	86	●	136	●

[a] Determined by optical microscopic observation.

[b] The calorimetric studies have performed on this sample and therefore enthalpy and entropy values have been mentioned.

Cr, Crystal; N, nematic phase; Iso, isotropic liquid state; n, number of carbon atoms in the alkoxy chain.

N-Iso transition temperature for the compound **7** is much lower when compared with that of compound **A**. The molecular structure of **7** differs from compound **A** only at the central aromatic core; compound **7** has a lateral chloro group at the central benzene nucleus, whereas compound **A** has no lateral substituent at the central benzene nucleus. The presence of lateral chloro group on the central benzene ring increases the breadth of the molecules of compound of series I. Gray [29] has explained that increase in the breadth of the molecules reduces both nematic and smectic mesophase stability. It seems that the lateral chloro group not only increases the breadth of the molecules of series I but also increases the acoplanarity in the system due to steric interaction. Both these factors would eliminate the smectogenic tendencies as well as decrease the mesophase range and N-Iso transition temperature for compounds reported in the present investigation.

Reference to Table III indicates that the nematic mesophase range and N-Iso transition temperature of compound **7** are higher by 27°C and 26°C, respectively, when compared with that of compound **B**. the difference in the molecular structure of both the compounds is only in the type of lateral substituent on the central benzene nucleus. Compound **7** has lateral chloro group, whereas compound **B** has lateral methyl group. Probably the

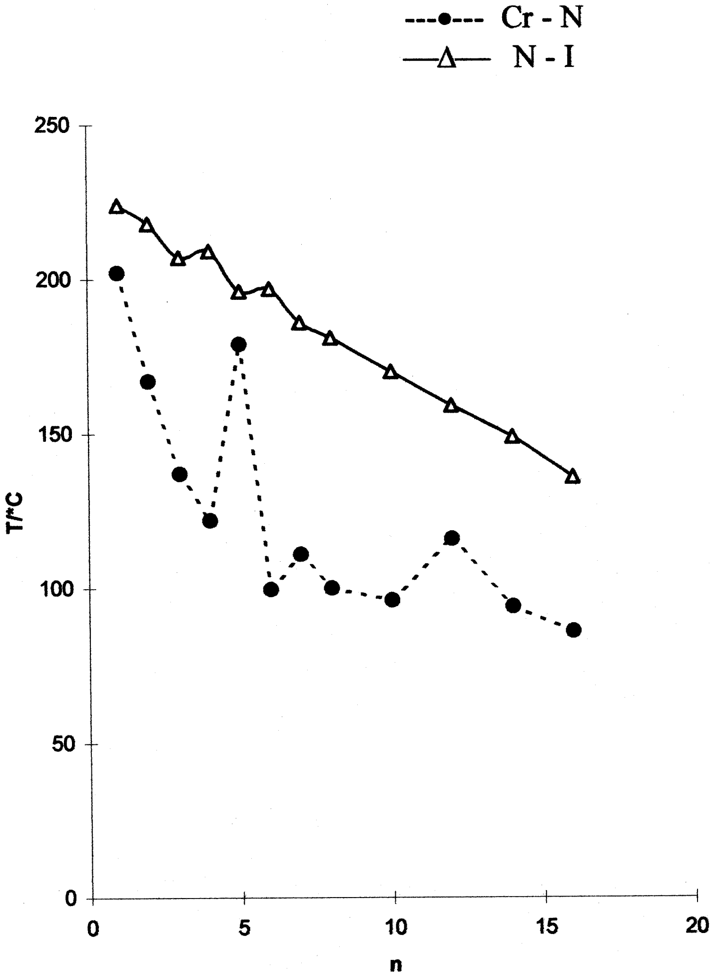


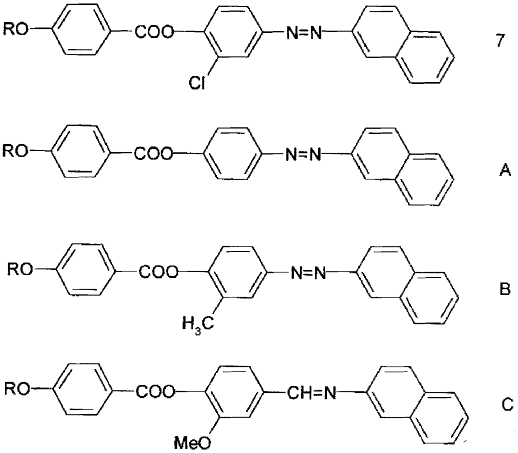
FIGURE 1 The phase behavior of series I.

increase in the polarizability of the compound **7** due to polar chloro group slightly overcomes the increase molecular separation caused by the lateral substituent and therefore the width of the nematic mesophase, as well as N-Iso transition temperature of compound **7** becoming a little higher than that of compound **B**.

The molecular structural difference between compounds **7** and **C** again lies in the lateral substituent at the central benzene nucleus. Compound **7** has lateral chloro group, whereas compound **C** has lateral methoxy group. This difference has significant influence on the nematic mesophase range

TABLE III The Comparison of N-Iso Transition Temperatures (°C) and the Range of Nematic Phase Between a Representative Compound **7** (C_7 homologue) of the Present Series I and Structurally Related Compounds Reported in the Literature

	Transition Temperatures(°C)						
Compound	Cr		N		Iso	Mesophase Range	Commencement of Smectic Phase
7	•	111	•	186	•	75	—
A	•	135	•	218	•	83	C_{10}
B	•	112	•	160	•	48	—
C	•	98	•	118	•	20	—



Where $R = -C_7H_{15}$

Comparative molecular structure of the compounds 7, A, B, and C.

as well as N-Iso transition temperature, as can be seen in Table III. The destabilization of nematic phase in the case of compound **C** is even more compared to compound **B**, and perhaps the foregoing discussion would hold good for this behavior.

From the above discussion the lateral group efficiency order for the nematic phase thermal stability can be derived for the compounds as under:

$$-H > -Cl > -CH_3 > -OCH_3.$$

It agrees well with the lateral efficiency order for the nematic phase obtained by Gray [29] for pure nematogenic rod-shaped molecules.

CONCLUSION

New mesogenic homologous series of naphthalene derivative with lateral chloro group was synthesized. The study indicated that the lateral chloro group adversely affects mesophase thermal stabilities. However, due to the polar nature of the chloro substituent, the effect is less pronounced compared to the lateral methyl and methoxy substituents.

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