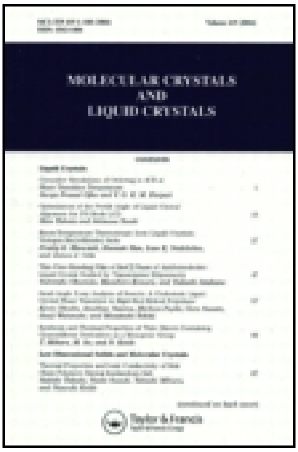

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Synthesis and Mesomorphism of Novel Liquid Crystalline: 4-(4′-*n*-Alkoxy Benzoyloxy)-Naphthylazo-4″-Chlorobenzenes

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A new azoester homologous series 4-(4′-n-alkoxy benzoyloxy)-naphthylazo-4″-chlorobenzenes is synthesized. Its first and second homologues are nonmesomorphic, while the rest of the homologues are mesomorphic, showing enantiotropic nematic behavior. Smectic character is totally absent. An odd–even effect is observed in the nematic–isotropic transition curve with alternation in transition temperatures. The average thermal stability and liquid crystal behavior for the nematic mesophase are compared with structurally similar homologous series. Analytical data support the structures of the molecules. The texture of the nematic mesophase is of threaded type. Transition temperatures are observed through hot-stage polarizing microscope. Analytical data support the structures.

Keywords Azomesogens; mesomorphism; nematic; smectic

Introduction

The present work involves the synthesis and evaluation of an azoester homologous series with –Cl as the right terminal end group and a naphthyl unit bridged through —COO— and —N=N— linking groups as the rigid core. The mesomorphic behavior of a substance depends on the magnitude of its molecular rigidity and flexibility, conducive to intermolecular forces of attraction. Variation in molecular rigidity is carried out by changing the rigid core of a molecule and by varying the central bridge or bridges and the number of phenyl rings in the molecular structure. The flexible part of the molecule is varied through the terminal groups on either side of the molecule or by lateral substitution at the phenyl ring. Thus, for this work, a naphthyl moiety was selected to vary the rigidity of the core structure by broadening the molecule. Azo and ester groups linking to the phenyl rings and a chloro (—Cl) unit as the terminal end group were also included. This study will discuss the structure–property relationships in terms of the influence of molecular breadth, and molecular polarity and polarizability on mesomorphism.

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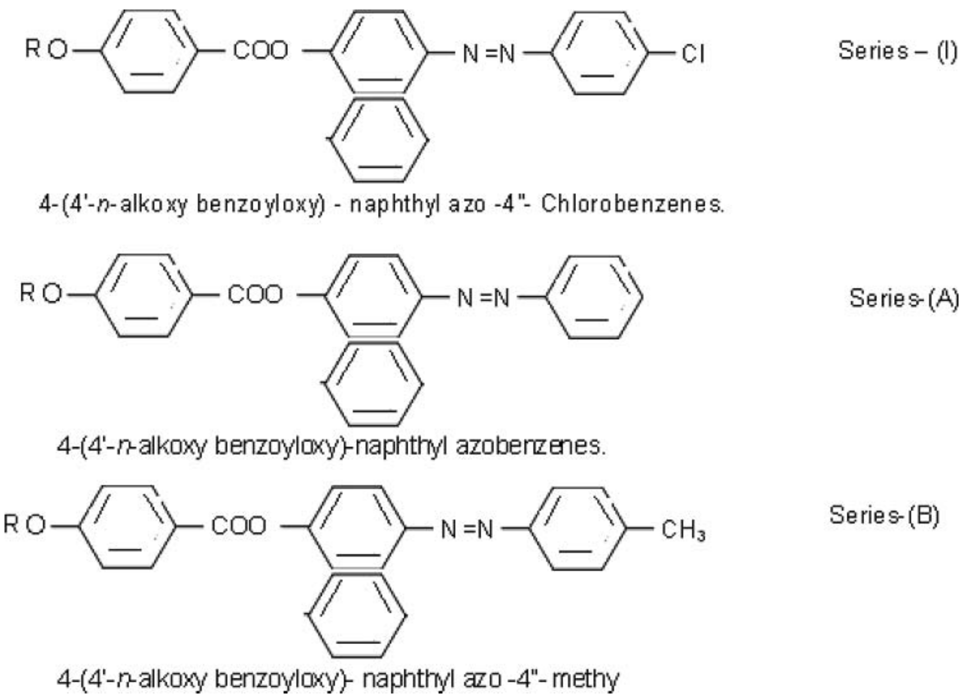


Figure 1.

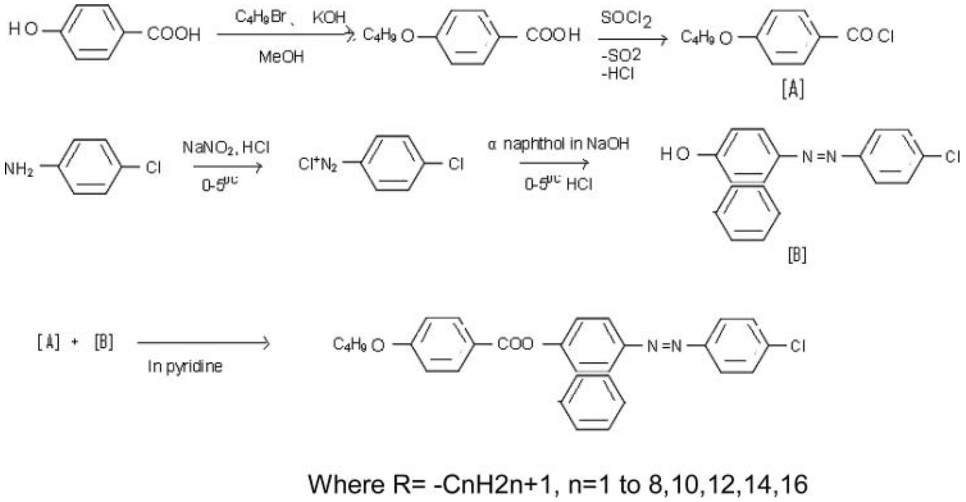
Experimental

Characterization

Some representative homologues of the series were selected for characterization of the structures by elemental analysis, infrared (IR), and ^{1}H NMR (nuclear magnetic resonance) techniques. Microanalysis was performed on a Perkin Elmer PE 2400 CHN analyzer. IR spectra were recorded on a Perkin Elmer Spectrum GX, and ^{1}H NMR was recorded on a Bruker using $CDCl_3$ as a solvent. Liquid crystalline properties were investigated using a LeitzLabourlux 12 POL hot-stage polarizing microscope. Enthalpy (ΔH) and entropy (ΔS) changes are discussed qualitatively instead of through differential scanning calorimeter (DSC) scan.

Synthesis

4-chloroaniline, sodium nitrite, α-naphthol, pyridine, thionylchloride (GSC), 4-hydroxy benzoic acid, and *n*-alkyl halides (SRL, Lancaster) were used as received. The synthetic route to the present homologous series is outlined in Scheme 1. 4-*n*-alkoxy benzoic acid and corresponding 4-*n*-alkoxy benzoyl chloride [A] were synthesized by the modified method of Dave and Vora [7]. 4-hydroxy-naphthyl azo-4′-chlorobenzene [B] was prepared by the known method of Furnis et al. [8]. 4-(4′-*n*-alkoxy benzoyloxy)-naphthylazo-4″-chlorobenzenes were synthesized by condensing 4-*n*-alkoxy benzoyl chloride [A] with 4-hydroxy-naphthyl azo-4′-chlorobenzene [B] in pyridine [9]. The azoesters were crystallized from alcohol until constant transition temperatures were obtained. The elemental analysis of the compounds was found to be satisfactory and is presented in Table 1.



Scheme 1. Synthetic route to series 1.

Results and Discussion

Transition temperatures and melting temperatures of the homologues of the titled homologous series are relatively lower compared with the corresponding alkoxy benzoic acid, and the molecular length and width are increased by fusing a phenyl ring, i.e., a naphthyl unit linked between two phenyl rings. The azo-dye, 4-hydroxy naphthyl azo-4′-chlorobenzene, is nonmesomorphic, but on linking it with *n*-alkoxy benzoyl chloride, the resulting novel products are mesomorphic from the propyl to the hexadecyl derivative. The methyl and ethyl homologues of the series are nonmesomorphic in behavior. The propyl-to-hexadecyl derivatives are enantiotropicnematic, without exhibiting any smectic property.

Transition temperatures as recorded in Table 2 are plotted versus the number of carbon atoms in the *n*-alkyl chain of the left *n*-alkoxy terminal of the homologues. Smooth curves are drawn through the like or related transition points and the phase diagram thus obtained is shown in Fig. 2. From the phase diagram, it can be seen that the solid–isotropic or the solid–nematic transition curve gradually falls from the methyl to the octyl derivative, without following a zigzag path, up to the octyl homologue. However, a zigzag path is followed from and beyond the octyl homologue. The nematic–isotropic transition curve shows an overall descending tendency as the series is ascended and behaves with negligible abnormality from the octyl to the hexadecyl homologue. An odd–even effect is observed in the nematic–isotropic transition curve, wherein both the nematic and the isotropic curve merge

Table 1. Elemental analysis for the hexyloxy and octyloxy derivatives

	Element % found (compared with % calculated)		
Molecular formula	C	H	N
$C_{27}H_{23}N_2O_3Cl$	70.45 (70.66)	4.89 (5.01)	6.18 (6.10)
$C_{29}H_{27}N_2O_3Cl$	71.38 (71.53)	5.36 (5,54)	5.87 (5.75)

IR for Butoxy Derivative

V_{max}/cm^{-1} 2929, 2871, 1429 (—C—H, aliphatic), 1722, 1253 (ester group), 1423 (—N=N—group), 1540, 1470 (—C—C aromatic stretch), 1061 (ether group), 844 (p-substituted benzene ring), 1120.5 (C—Cl aromatic).

IR for Decyloxy Derivative

V_{max}/cm^{-1}2922, 2852, (—C—H aliphatic), 1679, 1296, (ester group), 1429 (—N=N—group), 1583.4 (—C=C aromatic stretch), 1066 (ether group), 848 (p-substituted benzene ring), 1115.6 (C—Cl aromatic).

Analytical data.

into each other at the eighth homologue. The nematic mesophase exhibits a threaded type of texture, as determined by the miscibility method using optical polarizing microscopy. The nematic–isotropic transition temperatures are between 141.0°C and 101.0°C, with the nematogenic range varying from a minimum of 31.0°C at the 14th derivative to a maximum of 50.0°C at the 12th derivative of the series. Thus, the mesomorphic temperature range is fairly wide. Thus, the series under discussion is entirely nematogenic, without exhibiting smectic character. The statement that liquid crystals containing a naphthyl unit of moderate-chain length yield only nematogenic homologues [10,11] is well supported by the present investigation. The lowering of transition and melting temperatures of dimeric 4-*n*-alkoxy benzoic acids is attributed to the elimination of dimerization by esterification due to the removal of hydrogen bonding. The nonmesomorphic behavior of the azo-dye and methyl and ethyl homologues of the homologous series is due to their high crystallizing tendency, arising because the net intermolecular forces of attractions are neither anisotropic nor of suitable magnitude to maintain molecular alignment in molecules as a consequence of molecular rigidity [1–6]. Thus, the azo-dye and methyl and ethyl homologues of the titled

Table 2. Transition temperatures of the series

Compound no.	n (for R = $-C_nH_{2n+1}$)	Nematic (°C)	Isotropic (°C)
1	1	—	166.0
2	2	—	154.0
3	3	101.0	141.0
4	4	91.0	139.0
5	5	85.0	130.0
6	6	82.0	128.0
7	7	76.0	118.0
8	8	69.0	116.0
9	10	84.0	119.0
10	12	65.0	115.0
11	14	78.0	112.0
12	16	70.0	101.0

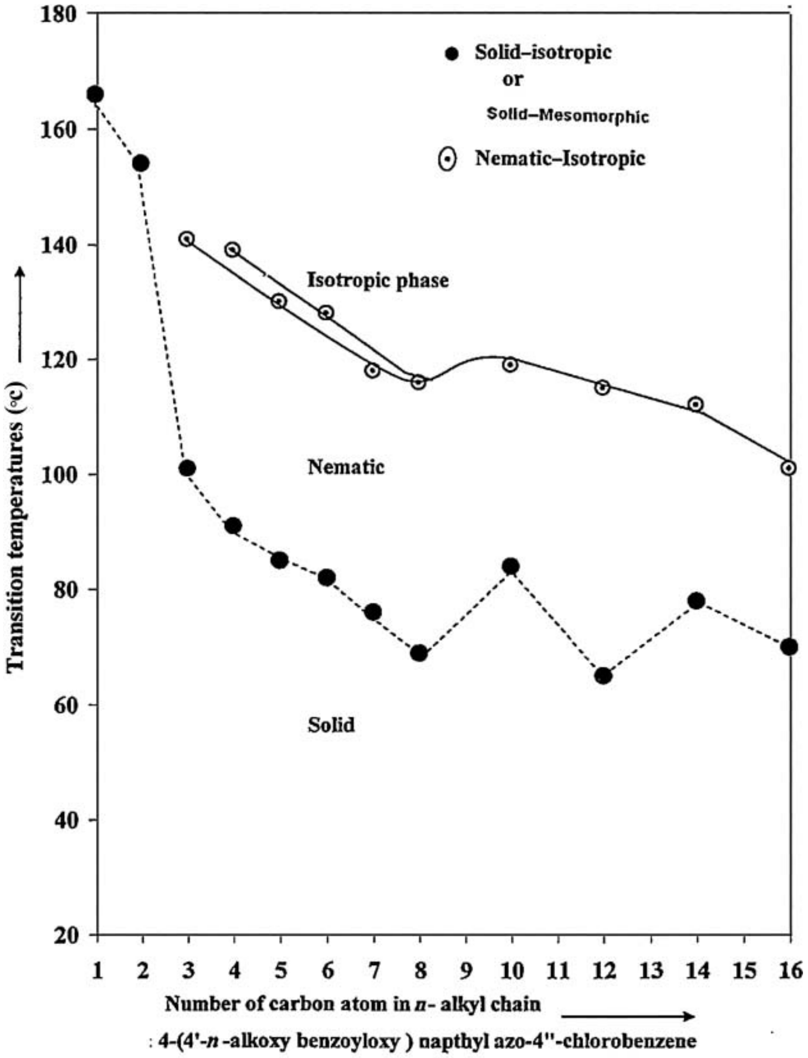


Figure 2. Phase behavior of the series.

homologous series show nonmesomorphic behavior. The exhibition of nematogenic behavior by propyl-to-hexadecyl homologues is attributed to the properly aligned molecules, in which intermolecular adhesion forces pertaining to molecular polarizability and end-to-end and lateral attractions are anisotropic and of suitable magnitude as a consequence of their molecular rigidity, flexibility, and bending, which can withstand or resist thermal vibrations exposed upon them. Thus, statistically parallel orientations of the molecules in floating condition are not restricted, which causes the nematic mesophase. The absence of a smectic mesophase is due to the lack of lamellar packing of the molecules caused by the broad core. Thus, only the nematic mesophase is exhibited by the homologous series under discussion.

The appearance of the odd–even effect in the nematic–isotropic transition curve and the alternation in transition temperatures are attributed to the sequentially added number

Table 3. Average thermal stability in (°C)

Series	1	A	B
Nematic–isotropic	129.9 (C_3—C_{16})	140.45 (C_1—C_{14})	128.63 (C_1—C_{14})
Commencement of nematic mesophase	C_3	C_1	C_1

of methylene units linked through the oxygen atom in the *n*-alkyl chain of the left *n*-alkoxy terminal end group. This effect diminishes as the series is ascended from and beyond the eighth homologue, because longer *n*-alkyl chains coil and bend. Thus, the nematic–isotropic transition curve follows a smooth trend for both odd and even homologues of longer chains. Negligible abnormality observed for higher members of the series is attributed to the presence of a polarizable —Cl end group positioned at 4″ carbon of the third phenyl ring linked through the —N=N— central bridge of the homologues.

The liquid crystal properties of the titled homologous series 1 are compared with structurally similar homologous series (A) and (B) (Fig. 2) in terms of molecular characteristics and average thermal stability of the nematic mesophase, as shown in Table 3.

Homologous series (1), (A), and (B) [12] are geometrically identical and consist of a left *n*-alkoxy terminal linked at *para* position to the first phenyl ring. The central naphthyl unit is bridged through —COO— and —N=N— central groups. Another phenyl ring is linked through the —N=N— group to the naphthyl unit. This phenyl ring possesses a varying functional group substituted at *para* position, i.e., terminal end groups —Cl, —H, and —CH_3 (without any lateral substitution) in series (1), (A), and (B), respectively. Thus, the uncommon part of the series under comparison is the right-side terminal end group. Therefore, variation in liquid crystal properties, thermal stabilities, and degree of mesomorphism exhibited from series to series depends upon variation in polarity, size, polarizability, arrangement of atom in space, etc., of the right-side terminal end groups [17] —Cl, —H, and —CH_3. Similarly, variation in liquid crystal properties and degree of mesomorphism exhibited in the same series depends upon the number of methylene units linked in the varying *n*-alkyl chain of the *n*-alkoxy terminal end group, keeping the right-side terminal intact. Thus, variation in liquid crystal properties or degree of mesomorphism arises due to uncommon features of the molecules from series to series or in the same series. The uncommon part of the molecule causes varying effects on shape, size, polarity, polarizability, aromaticity, π-electron density, electron–electron interactions, planarity of molecule, etc., and the resulting effect contributes to intermolecular forces of attractions of desired or undesired magnitude affecting mesogenic characteristics of the molecule.

All the homologous series under comparison are only nematogenic in character. However, the nematogenic character of the titled homologous series starts from the third member of series (1), while it starts from the very first member of series (A) and (B). This variation may be attributed to the difference in polarity, presence of electron clouds, and steric hindrance associated with end groups —Cl, —H, and —CH_3. Moreover, the length-to-breadth ratio and extent of non-coplanarity caused by the molecules differ more or less for series (1), (A), and (B). Hence, the polarity of the end groups affecting the end-to-end intermolecular forces of attractions undergoes variation, which in turn causes variation in the commencement of the nematic mesophase, degree of nematogenic character, and average thermal stability of the smectic (zero) and nematic mesophase.

The average thermal stabilities of the nematic mesophase for series (1) and (B) are almost equal, with negligible difference, because the —Cl and $-CH_3$ functional groups are equipolar [13]. A considerable difference in average thermal stability is observed for series (A), which has the highest value of thermal stability among the series under comparison. This may be attributed to the resultant force of intermolecular attractions arising from two opposing effects operating at a time due to the broadening of the molecule by the fusion of the other phenyl ring with the middle phenyl ring (i.e., naphthyl ring). Two opposing effects operate: one that reduces the intermolecular forces of attractions due to the broadening of the molecule, and thus increasing the intermolecular distance, and one that increases the intermolecular forces of attractions due to the increase in molecular polarizability and molecular dipolarity caused by the broadening of the molecule. Thus, the resultant intermolecular forces of attractions [14–16] are a direct result of the two opposing effects, which operate equally, but the predominating resultant effect is due to the polarity difference and other related differences in the terminal end groups —Cl, —H, and $-CH_3$. In the case of homologous series (A) without end group (—H), the second effect operates as the predominating effect, increasing intermolecular forces of attractions, as compared with series (1) and (B). The additional phenyl ring fused with the middle phenyl ring (i.e., naphthyl ring) in series (1), (A), and (B) (Fig. 1) not only increases the breadth of the molecules but also increases the extent of non-coplanarity in the system due to electron–electron interaction and steric interactions. Both these factors would eliminate the smectogenic property of all series under comparison, including the titled homologous series. According to Gray's [14,16] view, an increase in molecular breadth or the broadening of a molecule reduces both the nematic and the smectic mesophase thermal stability, and it is well supported by the present investigation.

Thus, from the above discussion, the nematic group efficiency order derived on the basis of thermal stability with respect to the terminal end group is:

Nematic group efficiency:	—H >	—Cl >	$-CH_3$
Order:	(series-A)	(series-1)	(series-B)

Conclusion

In conclusion, the study highlights that:

(i) Broadening of a molecule by fusing a phenyl ring and extending the molecular length by adding a third phenyl ring bridged through the —N=N— group are enough to induce mesophase formation in the absence of a terminal end group.

(ii) Introduction of a flexible —Cl moiety as the terminal end group by replacement of —H in series (1) reduces the nematic mesophase thermal stability.

(iii) Widening of the molecular breadth in combination with the presence of the terminal end group —Cl reduces the nematic and smectic mesophase thermal stability, and a homologous series having a naphthyl unit as part of the molecule is generally nematogenic in character, without exhibiting any smectogenic character.

(iv) The presence of a naphthyl unit in a mesogenic molecule restricts lamellar packing of molecules.

(v) Intermolecular anisotropic forces of attractions strongly favor statistically parallel orientational order in mesogenic molecules in floating condition in the presence of a naphthyl unit and a polarizable —Cl terminal.

Hence, the present investigation supports the early views of Gray [10,13] very well and raises the credibility of conclusions drawn in past.

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