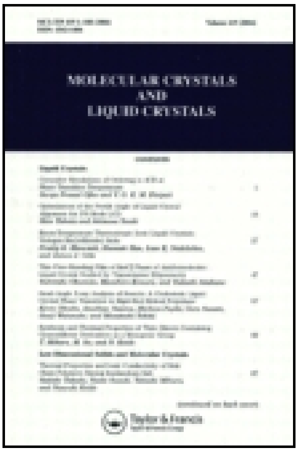

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Synthesis and Study of a Novel Azoester Mesogenic Homologous Series: 4-[4′-n-Alkoxy Benzoyloxy]-Naphthylazo-4″-Acetyl Benzenes

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The synthesis and mesomorphic properties of a novel azoester homologous series consisting of 12 members is reported. The methyl to butyl derivatives of the series are non-mesogenic, and the others are enantiotropically smectogenic and/or nematogenic. The nematic mesophase shows a threaded or Schlieren texture and smectic mesophase shows a focal conic fan-shaped texture of the SmA or the SmC. The smectic and nematic thermal stabilities are 137.4° and 166.6° respectively. Analytical data support the molecular structures. The transition temperatures of the homologues are determined using optical polarizing microscopy. An odd–even effect is observed for the nematic-isotropic transition curve and the series is equally smectogenic and nematogenic over a wide temperature range, and the melting points are in the middle order. The mesogenic properties of the present series are compared with a structurally similar homologous series.

Keywords Azoester; liquid crystal; mesogen; mesomorphism; nematic; smectic

Introduction

The synthesis of this novel azoester homologous series enables a better understanding of structure–property relationships in respect of the influence of flexibility and rigidity changes on melting point, transition temperatures, and mesophase morphology. The novel molecular structure consists of a naphthyl unit at the center and two phenyl rings linked to it by linking groups (–COO– and –N=N–) with n- alkoxy and –$COCH_3$ terminal groups. The core units provide molecular rigidity, the linking groups can maintain rigidity, but also facilitate some flexibility, and the terminal groups provide some flexible nature to the molecular structure. Thus, mesogenic characteristics and the degree of mesomorphism are varied by changing molecular moieties, which affect flexibility and rigidity, molecular breadth, and hence polarizability. The mesomorphic properties of the novel homologous series are compared with a known homologous series where a lateral chloro substituent on a phenyl ring features in place of the naphthyl core [1–5].

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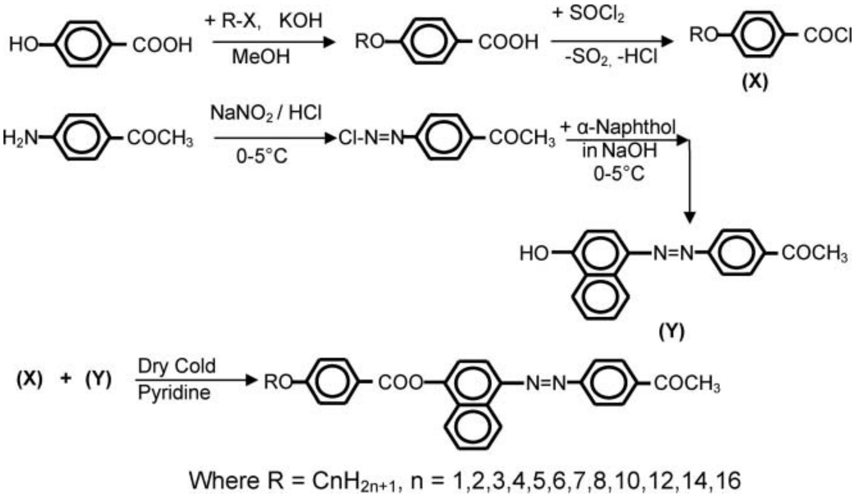
Experimental

Characterization

Some selected members of the titled series were characterized by elemental analysis, ^{1}HNMR and IR spectra. The textures of mesophases were characterized by the miscibility method. Microanalysis was performed on a Perkin Elmer PE 2400 analyzer (Table 1). ^{1}HNMR spectra were obtained on a Bruker spectrometer using $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer GX spectrometer. The transition temperatures and liquid crystal properties were investigated using optical polarizing microscope with heating stage. Thermodynamic quantities, viz. enthalpy (ΔH) and entropy (ΔS) are discussed qualitatively.

Synthesis

The 4-n-alkoxybenzoic acids were synthesized from 4-hydroxybenzoic acid using the corresponding suitable alkyl halide by the modified method of Dave and Vora [5]. The 4-n-alkoxybenzoic acids were converted to the corresponding 4-n-alkoxybenzoyl chloride (X) using freshly distilled thionyl chloride. The 4-hydroxy naphthylazo-4′-acetyl benzene (Y) was prepared by the known method of Furnis et al. [6]. Final products 4-[4′-n-Alkoxy benzoyloxy] naphthylazo 4″-acetyl benzenes were prepared by condensing components (X) and (Y) in ice-cooled pyridine. Each product (XY) was filtered, washed, dried, and finally recrystallized from alcohol until constant transition temperatures were obtained. 4-Hydroxy benzoic acid, alkyl halides, thionyl chloride, pyridine, and other chemicals required for synthesis were used as received. The synthetic route to the series is outlined in Scheme 1.



Scheme 1. Synthetic route to series-1.

Analytical Data

Nuclear Magnetic Resonance (NMR)

Decyl, 1.28 (alkyl group of $-OC_{10}H_{21}$), 2.61 ($-CH_3$ of $-CH_3CO$), 1.84 ($-OCH_2-\underline{CH_2}$ of $-OC_{10}H_{21}$), 4.09 ($-OCH_2$ of $-OC_{10}H_{21}$), 6.90 & 7.03 & 8.99 & 8.31 (aromatic).

Table 1. Elemental analysis for the hexyloxy and octyloxy derivatives

	Elemental% found (Compared with % calculated)		
Molecular formula	C	H	N
$C_{33}H_{34}N_2O_4$	75.86 (75.01)	6.51 (6.18)	5.36 (5.53)
$C_{35}H_{38}N_2O_4$	76.36 (76.98)	6.91 (6.58)	5.09 (5.15)

Tetradecyl, 1.26 (alkyl group of $-OC_{10}H_{21}$), 2.69 ($-CH_3$ of $-CH_3CO$), 4.118 ($-OCH_2-\underline{CH_2}$ of $-OC_{10}H_{21}$), 6.933 & 7.024 & 8.99 & 8.26 (aromatic).

Infrared (IR)

Decyl, V_{max}/cm^{-1} 817.8 & 846.7 (aromatic), 1066, 1151, 1732 (–COO– group), 1421(–N = N–), 1359 & 2850 (alkyl), 1168(–C–O of ether group), 1678 & 1226 (>C = 0 group).

Tetradecyl, V_{max}/cm^{-1} 808 & 835 (aromatic), 1064, 1259 & 1672 (–COO– group), 1409 (–N = N– group), 1128 (–C–O of ether group), 719 (polymethylene of alkyl group), 1357 & 2850 (alkyl group), 1668 (>C = 0 group).

Texture

Confirmed by the miscibility method.

1. Pentyloxy and hexyloxy nematic threaded or schlieren type texture.
2. Decyloxy and dodecyloxy smectic-A.
3. Hexadecyloxy homologue smectic-C.

Judged directly by microscopic observation.

Results and Discussion

The novel homologous series, 4-[4′-n-Alkoxy benzoyloxy] naphthylazo 4″-acetyl benzoates, consists of 12 members. The methyl to butyl members of the series are non-mesogenic, The pentyl and hexyl members are only enantiotropic nematogenic, the heptyl to dodecyl members are enantiotropically smectogenic in addition to enantiotropic nematogenic character, while the tetradecyl and hexadecyl members of the series are only enantiotropic smectogenic. A phase diagram (Fig. 1) plots the transition temperatures determined on a hot stage optical polarizing microscope as recorded in Table 2 versus the number of carbon atoms present in n-alkyl chain. The phase diagram indicates that the solid to isotropic or mesophase transition curve follows a zigzag path of rising and falling values from and beyond the butyloxy homologue. The smectic to nematic or isotropic transition curve initially rises, passes through a maxima and then smoothly falls as series is ascended without the exhibition of an odd-even effect. The nematic to isotropic transition curve initially rises and adopts descending tendency as the series is ascended with the exhibition of an odd–even effect and an alternation of transition temperatures. The nematic to isotropic transition curve is extrapolated to the tetradecyloxy homologue from the dodecyloxy homologue and the curve merges into the smectic to isotropic point for the tetradecyloxy homologue. These trends show that beyond the tetradecyloxy homologue only smectogenic mesophase appears and the nematogenic mesophase formation ceases to appear. The smectic to nematic or isotropic transition curve is extrapolated to the hexyloxy

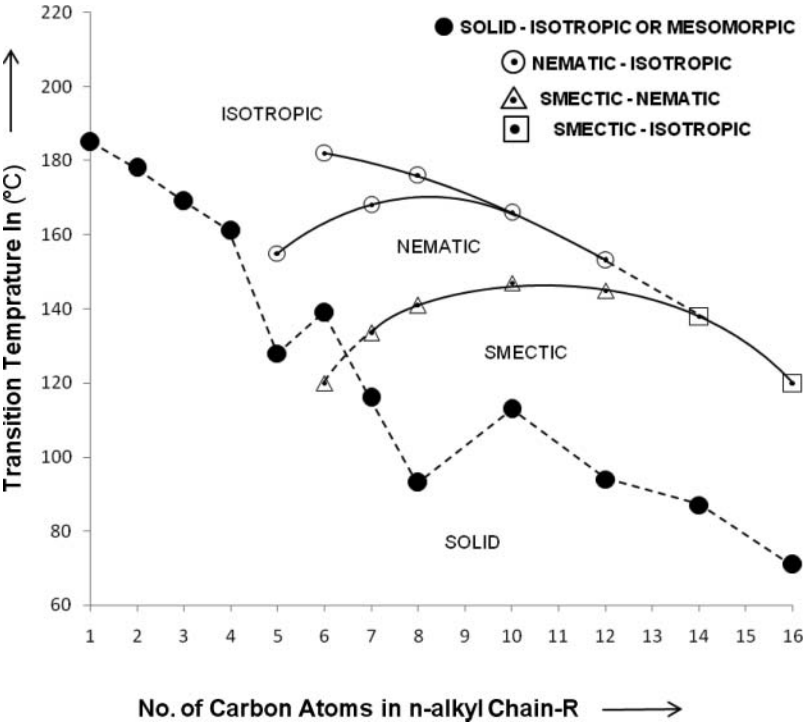


Figure 1. Two-phase behavior of series 4- [4′-n-Alkoxy benzoyloxy] naphthyl azo 4″-acetyl benzenes.

homologue following the trend of the curve to predict the probable latent transition temperature (LTT) for smectic mesophase temperature in the hexyl derivative, which is 119.0°C, and is not realizable due to the high melting point. Thus all the transition curves behave in the expected manner. The zigzag path of solid to isotropic or mesomorphic transition curve is attributed to the sequential and progressive addition of a methylene unit in the

Table 2. Transition temperatures in °C

Compound No.	n (for R = $-C_nH_{2n+1}$)	Smectic	Nematic	Isotropic
1.	1	–	–	185.0
2.	2	–	–	178.0
3.	3	–	–	169.0
4.	4	–	–	161.0
5.	5	–	128.0	155.0
6.	6	–	139.0	182.0
7.	7	116.0	133.5	168.0
8.	8	93.0	141.0	176.0
9.	10	113.0	147.0	166.0
10.	12	94.0	145.0	153.0
11.	14	87.0	–	138.0
12.	16	71.0	–	120.0

n-alkoxy chain. This causes the difference in molecular rigidity and flexibility [1–4], which is directly related to suitable or unsuitable magnitudes of anisotropic intermolecular forces of attraction. Thus, the overall end-to-end intermolecular anisotropic forces of cohesion are altered from homologue to homologue from and beyond the fourth member of the series. The absence of smectic or nematic or any sort of mesophase in methyl to butyl derivatives of the series is due to their high crystallizing tendency, which arises from resultant net unstable magnitude of anisotropic intermolecular forces of attraction as a consequence of molecular rigidity. The solid to isotropic transition curve does show an irregular trend for odd and even members up to the butyl homologue. The nematic to isotropic transition for odd and even homologues follows a smooth gradual falling tendency from the hexyloxy to dodecyloxy homologue of the series in expected manner. Both curves for odd and even members of the series merge with each other and to the main stream of the nematic to isotropic transition curve at the decyloxy homologue indicating that from and beyond decyloxy homologue there is a single curve with descending tendency. The odd–even effect diminished for higher homologues because the longer n-alkyl terminal chain may coil or bend, or flex to lie in the line with major axis of core [7,8]. Thus, the end-to-end contact would be the same for odd and even homologues of the series. The occurrence of the nematic mesophase from the pentyloxy to decyloxy homologues is attributed to the misalignment of molecules at an angle less than 90° with the plane of the surface under the influence of heat to maintain a statistically parallel orientational order or two-dimensional array of molecules in a floating condition. The absence of an odd–even effect in the smectic to nematic or isotropic transition curve arises because the smectogenic character is exhibited by almost all even numbered homologues except the heptyloxy homologue. The molecules of the heptyloxy to hexadecyloxy homologues show smectogenic character because of the lamellar packing of the molecules in a layered arrangement.

The mesogenic characteristics of the novel homologous series-1 are compared with a structurally similar series-A [9] (Fig. 2).

The novel homologous series-1 is polymesomorphic, i.e. it exhibits smectic and nematic mesophases, but homologous series-A selected for comparison is only nematogenic without the exhibition of smectogenic character. Average phase thermal stability values are shown in Table 3, with average clearing points from series 1 and A of 166.6°C and 122.8°C respectively.

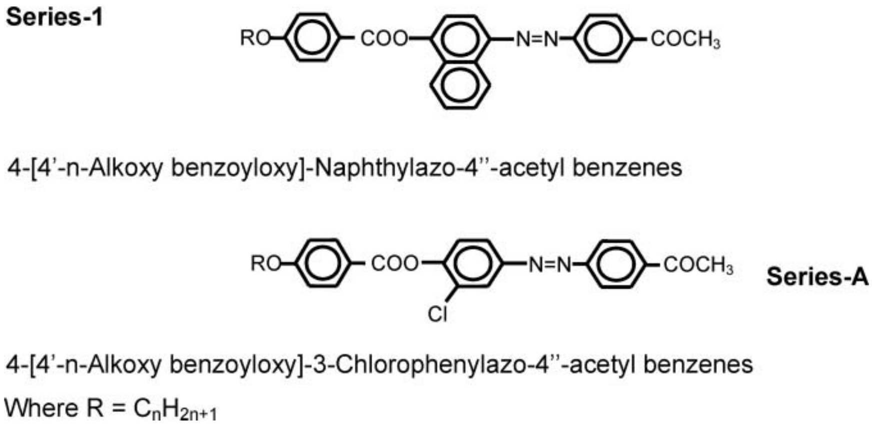


Figure 2. Two structurally similar homologous series for comparison.

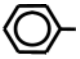
Table 3. Average thermal stability in °C

Series	1	A
Smectic–nematic or smectic–isotropic	137.4 (C_7–C_{16})	–
Commencement of smectic phase	C_7	–
Nematic-isotropic	166.6 (C_5–C_{12})	122.8 (C_6–C_{14})
Commencement of nematic phase	C_5	C_6

Thus, smectic and nematic thermal stabilities of series-1 are higher than that of series-A under comparison. The smectic mesophase commences from the heptyloxy homologue in case of series-1, while it does not commence in case of series-A until the hexadecyloxy homologue. The mesomorphic phase temperature range varies from a minimum of 49°C for hexadecyloxy homologue to a maximum of 83°C for the octyloxy homologue in series-1, while in series-A, such ranges varies from 22°C to 48°C for the tetradecyloxy homologue and the decyloxy homologue respectively. The observed differences in mesogenic properties between series 1 and A are attributed to difference in their molecular structures (Fig. 2). The terminal units and the linking groups are identical in each case, but middle part is naphthyl ring (series-1) and a chloro substituted phenyl ring in series-A. Thus, the molecular structure of series-1 differs from series-A in respect of lateral substitution. Series-1 incorporates a naphthyl unit, while series-A involves a phenyl ring with a lateral Cl group substituted at an ortho position to –COO– linking group in a central molecular location. The molecules of series-1 are broadened by a fused phenyl ring, while the molecules of series-A are broadened by a larteral chloro substituent. The difference in molecular rigidity and flexibility causes variations in aromaticity, polarity, and polarizability, and hence magnitudes of anisotropic intermolecular forces of attraction determine the presence or absence of smectic and/or nematic mesomorphism, and homologue at which the phases commence. Broadening of a molecule increases intermolecular distance and hence decreases intermolecular attractions on one hand, and it increases molecular polarizability, which increases intermolecular attraction, on the other. Thus, two opposing effects [7,8] are operating, with the observed net effect in case of series-1 causing end-to-end intermolecular attractions relatively more for series-1 as compared to series-A. Therefore, degree of nematogenic character in terms of longer nematic phase length in combination with the presence of smectogenic character is observed for series-1, while the nematogenic phase length is relatively shorter with absence of smectogenic character in series-A. This observation is attributed to weaker intermolecular attractions arising by poorer aromaticity and lateral attractions of the Cl unit as compared to lateral attractions caused by a fused phenyl ring. The commencement of smectogenic mesophase formation takes place earlier in the case of series-1 than in series-A because of the extent of coplanarity caused by the molecular structure [10,11]. The presence of a fused phenyl ring (series-1) induces higher magnitude of mesogenic character as compared to chloro unit (series-A).

Thus, the group efficiency order derived for the fused phenyl ring and a Cl unit in terms of their thermal stability is as follows.

Smectic and nematic
group efficiency order



> −Cl

Conclusion

1. Generally, the members of the naphthyl ring containing homologous series are nematogenic; however smectogenic character is also seen in several homologues.
2. The novel series is of middle ordered melting type with clearing points varying between 120°C and 182°C.
3. The presence of the naphthyl moiety invariably induces nematogenic character in the series.
4. Increasing molecular rigidity by fused phenyl ring at the middle part of a molecule induces smectogenic character in the mesophase.

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