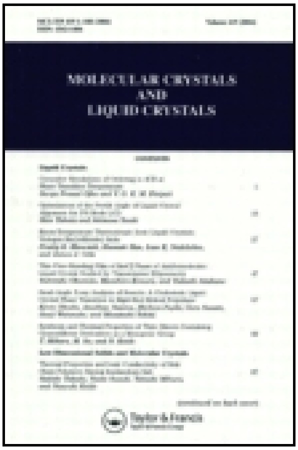

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Study of Homologous Series of Azomesogens with Lateral Aromatic Branch

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Study of Homologous Series of Azomesogens with Lateral Aromatic Branch

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A homologous series 4-acetyl-2′,4′-bis (4-n-alkoxybenzoyloxy) azobenzenes of eleven homologues has been synthesized by fixing 4-acetyl phenyl azo group to resorcinol moiety. Both the terminal and lateral hydroxyl group were esterified by 4-n-alkoxy groups. All the members of the series are monotropic/enantiotropic nematogens with the exception of the first member. The members of the series were characterized by standard spectroscopic methods, DSC, and optical microscopy. The mesomorphic properties of the present series are compared with other structurally related series.

Keywords: enantiopropy; liquid crystal; monotropy; nematic

INTRODUCTION

The vast majority of liquid crystals consists of rod- like molecules comprising of two or more aromatic and/or aliphatic rings and a small polar substituent at the lateral or terminal position and a fairly long straight hydrocarbon chain (usually alkyl or alkoxy) [1]. It is well known that the lateral substitution in the mesogenic core of the molecules causes a significant depression in the clearing point and hence diminishing the liquid crystal range, but the effect of lateral aromatic branch on the type of liquid crystals formed is quite different [2]. A number of homologous series containing aromatic branch at the lateral position of the mesogenic core have been reported in literature [3–5].

In the present study, a homologous series containing three rings in the main core linked through ester and azo central linkages and substituted by a lateral aromatic branch on the central benzene ring

Address correspondence to K. J. Ganatra, M. V. M. Science and Home Sc. College, Kalawad Road Under Bridge, Rajkot 360005, Gujarat, India. E-mail: kj_ganatra@yahoo.co.in has been synthesized in order to investigate the influence of the lateral aromatic branch on mesomorphism.

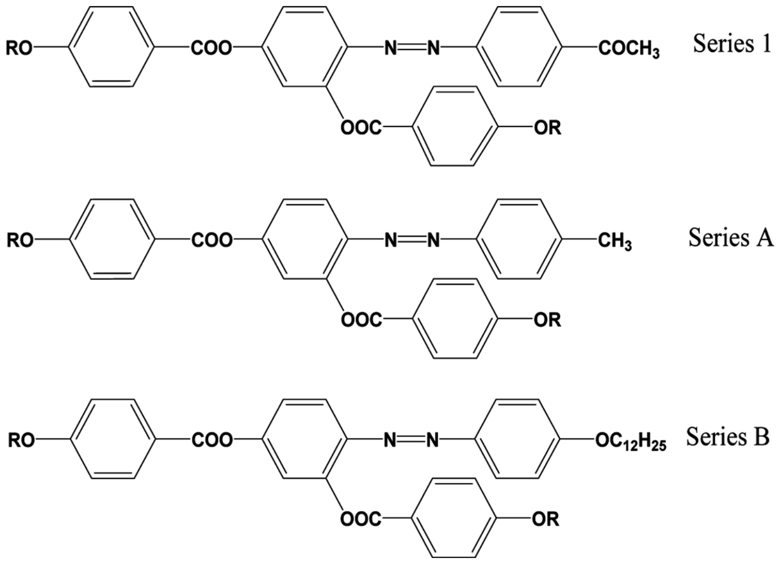
EXPERIMENTAL

Characterization

Some representative homologues of the series were selected for characterization of the structures by elemental, FT-IR, and ^{1}H-NMR techniques. Microanalysis was performed on Perkin Elmer PE 2400 CHN Analyzer. IR spectra were recorded on Perkin Elmer Spectrum GX and ^{1}H-NMR was recorded on Bruker using $CDCl_3$ as solvent. The calorimetric study was carried out DSC 2920 TA Instrument adopting a scanning rate of 5 °C/min. Liquid crystalline properties were investigated using Leitz Labourlux 12 POL Polarising Microscope with a heating stage.

Synthesis

4-Aminoacetophenone (Lancaster), sodium nitrite, resorcinol, pyridine, thionyl chloride (GSC), 4-hydroxybenzoic acid, n-alkyl halides (SRL, Lancaster) were used as received. The synthetic route to the present series is outlined in Scheme 1.



SCHEME 1 ■.

4-Acetyl 2′-4′-dihydroxyazobenzene (A) was synthesized by using conventional method of diazotization and coupling [6]. 4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoylchlorides were synthesized by the modified method Dave and Vora [7]. The eleven diesters of the series were synthesized by condensing two moles of 4-n-alkoxybenzoyl chlorides with one mole of the dye (A) in pyridine. The diesters were crystallized from alcohol till constant transition temperatures were obtained.

Data

IR for Dodceyloxy Derivative

ν max/cm^{-1}: 2921, 2852(−C−H aliphatic), 1738(−C=O ester), 1686(−C=O ketone), 1603(−N=N−), 1510, 1470(arom. −C=C−), 1251(−C−O− ester), 1168, 1052, 845, 760.

^{1}H-NMR ($CDCl_3$, Standard TMS, 400 MHz) for Decyloxy Derivative

δ 0.92 (t, 6H, 2 × $-CH_3$), 1.3–2.6 (m, 32H, 2 × $-CH_2$), 2.7 (s, 3H $-COCH_3$), 4.1 (t, 4H, 2 × $-OCH_2$), 7.3–8.2 (m, 15H, Ar−H).

RESULTS AND DISCUSSION

In the present study, 11 homologues the series 4-acetyl-2′, 4′ bis(4-n-alkoxybenzoyloxy) azo benzenes were synthesised and evaluated for their mesomorphic characteristics. The transition temperatures of the homologous series are recorded in Table 2. All the compounds of the series, except the first homologue, showed threaded or schlieren texture on heating the crystalline solid or cooling the isotropic liquid when viewed under a hot stage polarizing microscope. Ethyl to hexyl derivatives exhibited nematic mesophase in the monotropic forms while nematic enantiotropy condition commenced from the octyl derivative and continued upto the hexadecyl derivative. Figure 1 shows the dependence of the transition temperatures on the number of carbon atoms in the terminal substitutions. The solid-mesomorphic

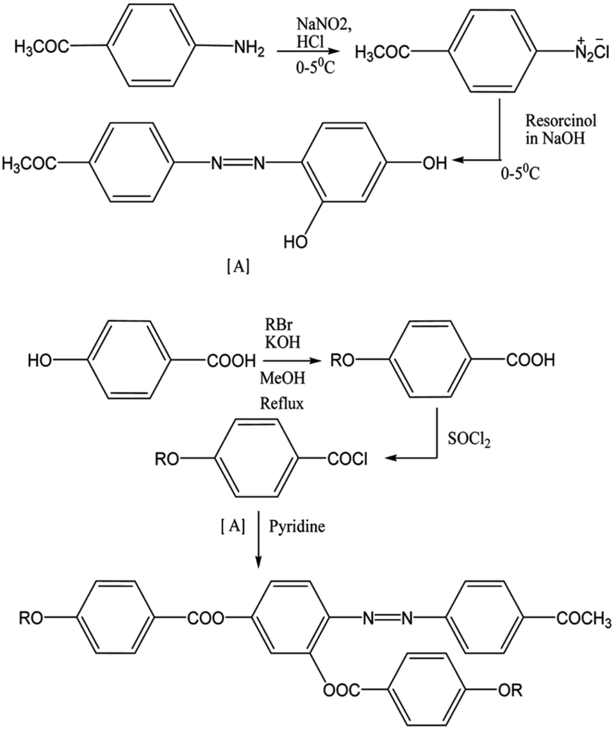
TABLE 1 Elemental Analysis for Butyloxy and Octyloxy Derivatives

	Elements % found (% calculated)		
Molecular formula	C	H	N
$C_{36}H_{36}N_2O_7$	69.98 (71.05)	5.30 (5.92)	4.10 (4.60)
$C_{44}H_{52}N_2O_7$	72.79 (73.33)	6.95 (7.22)	3.45 (3.88)

TABLE 2 Transition Temperatures of the Series

Compound No.	R = $-C_nH_{2n+1}$ n	Sm	N	I
1	1	–	□	156
2	2	–	(130)[a]	145
3	3	–	(89)	126
4	4	–	(104)	123
5	5	–	(87)	101
6	6	–	(92)	102
7	8	–	85	97
8	10	–	89	103
9	12	–	78	102
10	14	–	110	118
11	16	–	105	116

[a] Values in parenthesis indicate monotropy.



R = $-C_nH_{2n+1}$, n = 1 to 6, 8, 10, 12, 14, 16

SERIES 1

FIGURE 1 Synthetic route to the series.

TABLE 3 DSC Data for Dodecyloxy Derivative

Transition	Peak temp.°C (microscopic temp.)	$\Delta H/Jg^{-1}$	Entropy change $Jg^{-1}k^{-1}$
Cr→N	79.40 (78.0)	42.83	0.1215
N→I	103.0 (102.0)	The enthalpy value was not obtained.	

or isotropic transition curve follows a zig-zag path of rising and falling tendency as the series is ascended. The plot shows slight odd–even effect in the nematic–isotropic transition curve up to the fifth homologue, then rises upto the fourteenth homologue with a negligible decline at the twelfth homologue, and finally falls off at the sixteenth homologue.

In the present study, the enthalpy change of the dodecyloxy derivative was measured by differential scanning calorimetry; the data is recorded in Table 3. Table 4 summarizes the average thermal stabilities and molecular structure of the present series and other structurally related series A [4] and series B [5] chosen for comparative study.

The molecular geometry of all the homologous series under comparison consists of three phenyl rings linked through an $-COO-$ and $-N{=}N-$ central linkage with n-alkoxy group at the left terminal and flexible lateral aromatic branch. The right-end terminal groups are $-COCH_3$, $-CH_3$, and $-OC_{12}H_{25}$ for series 1, A, and B respectively. The variation in the mesomorphic characteristics can be attributed to the presence of different right terminal groups which have different polarity and polarizability for the formation of mesophase.

Comparing the mesomorphic characteristics of series 1 with series A, it is observed that the homologues of the entire series are monotropic or enantiotropic nematogens, while in the case of series A, the members of the series exhibit smectic phase monotropically. Molecules of Series 1 and A differ only in the right terminal groups. In general,

TABLE 4 Average Thermal Stabilities in °C

Series	1	A	B
Smectic □ nematic or isotropic	–	47.5 (C_4–C_{16})	54.05 (C_{12}–C_{16})
Nematic □ isotropic	88.09	–	71.55 (C_4,C_8,C_{12}, C_{16})
Commencement of smectic phase	–	C_4	C_{12}

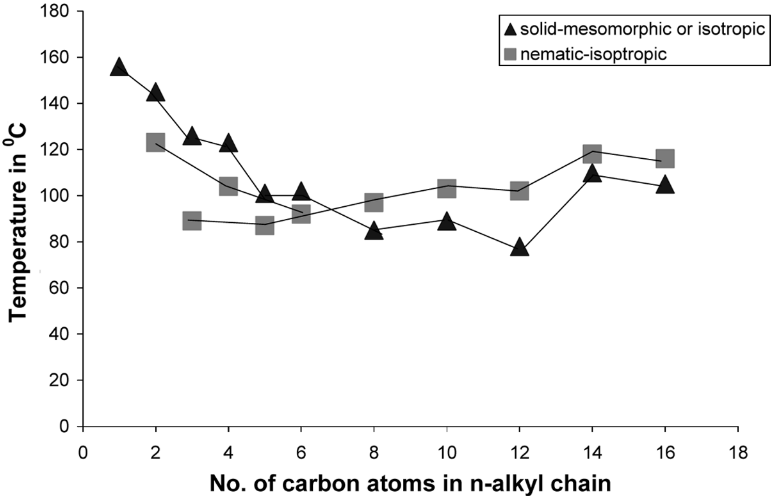


FIGURE 2 Phase behavior of the series.

large lateral substituents hinder the packing of layered structure; however, the short methyl group at the terminal position in series A along with lateral aromatic branch seems to facilitate lamellar packing required for the generation of the smectic phase. Introduction of polar acetyl group at the terminal position in series 1 enables considerable and significant forces of attraction which serve to stabilize parallel orientation by end-to-end molecular attractions which are conducive to the formation of nematic mesophase. This effect persists even in the homologues with long alkoxy groups. Comparison of the molecular geometry of the series 1 and series B indicates that series 1 has an acetyl group at the right terminal, while series B has n-dodecyloxy terminal group. The long flexible n-dodecyloxy group in series B aids the formation of smectic mesophase due to enhanced lateral attraction as compared with terminal attraction, which facilitates lamellar packing required for the formation of the smectic mesophase [8]. Thus series B exhibits smectogenic tendency along with the nematic characteristics. The nematic thermal stability of series A being marginally higher than series B is understandable because of the differences in terminal attractions arising due to the acetyl and dodecyloxy groups.

CONCLUSION

A new homologous series of mesogen 4-acetyl 2′, 4′ bis (4-n-alkoxybenzoyloxy) azobenzenes with a lateral aromatic branch has been synthesized for the study of mesomorphic characteristic. All the members of the series, except the first homologue, exhibit nematic phase under monotropic or enantiotropic condition. The study suggests that in spite of a large lateral flexible substituent; a polar substituent at the terminal position in homologous series with such geometry gives way for the exhibition of nematic phase.

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