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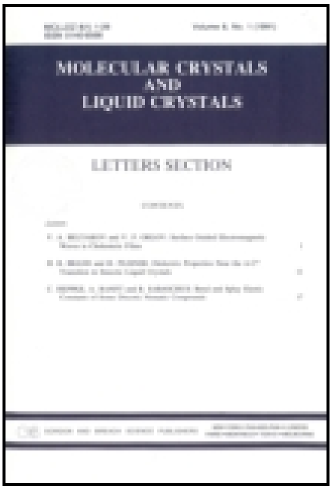

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The Mesogenic Behavior of Isomeric and Nonisomeric Series of Novel Azoesters. 4-(4′-n-Alkoxy Benzoyloxy) Phenylazo-2″-Bromobenzenes

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The Mesogenic Behavior of Isomeric and Nonisomeric Series of Novel Azoesters. 4-(4′-n-Alkoxy Benzoyloxy) Phenylazo-2″-Bromobenzenes

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A novel homologous series: 4-(4′-n-alkoxy benzoyloxy) phenylazo-2″-bromobenzenes is synthesized and studied with a view to understanding and establishing the effects of molecular structure on mesogenic behavior in a series. The mesogenic property commences from fifth homologue to the last homologue. The transition temperatures of the series are relatively low ranging between 68°C and 143°C. The mesogenic range varies between 6°C and 22°C. The novel azoester series is nematogenic without exhibition of any smectogenic property and an average thermal stability of 89.4°C. The mesogenic behavior of the novel series is compared with structurally similar isomeric/nonisomeric other known series.

Keywords Liquid crystal; mesogen; mesomorphism; nematic; smectic

Introduction

Molecular rigidity and flexibility [1–3] are important factors related to intermolecular forces of attractions. Suitable magnitudes of anisotropic forces [4] of intermolecular attractions can induce mesogenic characteristics in a molecule. Thus, introduction of proper rigidity by two or more phenyl rings bridged through central groups as well as substitution of suitable lateral or terminal functional groups positioned properly at phenyl ring or rings as flexible molecular part can yield liquid crystal substances [5–7] of desired range of temperature. The present investigation concerns a molecular geometry constructed with three phenyl rings bridged through –COO– and –N=N– central groups as the rigid core and n-alkoxy (terminal) and –Br (lateral) group as flexible part of a molecule, with a view to understanding and establishing the effect of molecular structure on liquid crystal behavior.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents by the modified method of Dave and Vora [8]. *n*-Alkoxy benzoic acids were converted to corresponding *n*-alkoxy

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Table 1. Elemental analysis for (1) propyloxy, (2) hexyloxy, and (3) dodecyloxy derivatives

		Elements% found	Elements% calculated				
Sr. no.	Molecular formula	C	H	N	C	H	N
1	$C_{22}H_{19}BrN_2O_3$	60.01	4.25	6.31	60.15	4.36	6.38
2	$C_{25}H_{25}BrN_2O_3$	62.25	5.11	5.76	62.38	5.23	5.82
3	$C_{31}H_{37}BrN_2O_3$	65.65	6.46	4.89	65.84	6.59	4.95

benzoyl chlorides (A) using thionyl chloride by the usual established method [9]. Azo dye, 4-hydroxy phenyl azo-2′-bromobenzene (B) (M.P. = 93 °C) was prepared by usual method [10] of diazotization. Components (A) and (B) were condensed in dry cold pyridine by known method [11–13]. The final novel azoester homologues were decomposed, filtered, washed, dried, and purified until they gave constant transition temperatures. Transition temperatures were determined on an optical polarizing microscope, equipped with a heating stage. The chemicals required for the synthesis, viz., 4-hydroxy benzoic acid, alkylating agents R-X, *ortho*-bromo aniline, phenol, thionyl chloride, KOH, methanol, ethanol, etc., were used as received except solvents that were purified prior to use.

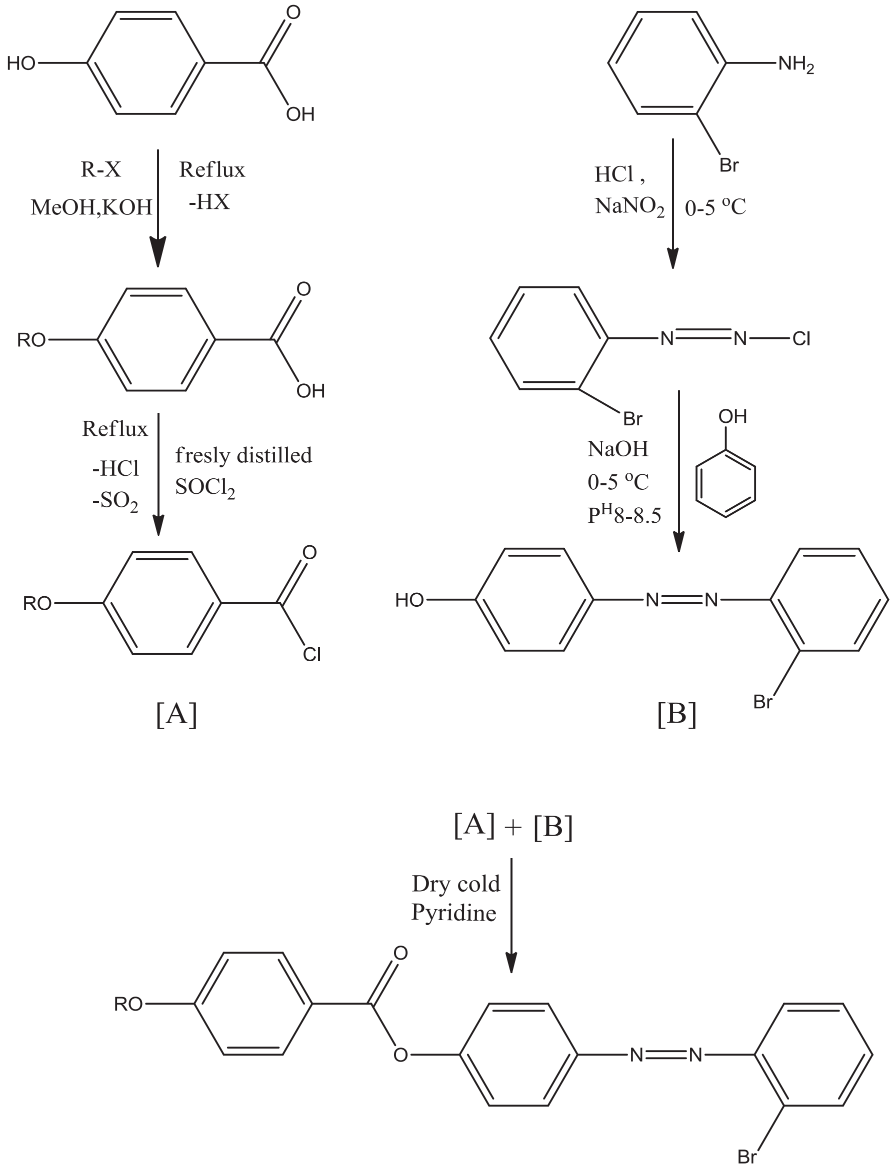
Synthetic route to the series is outlined in Scheme 1.

Characterization

Representative members of a novel series were characterized by elemental analysis (Table 1), Infrared spectroscopy, ^{1}H NMR spectroscopy, and mass spectroscopy. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer (Waltham, Massachusetts, USA). IR spectra were recorded on Shimadzu FTIR-8400 (Nishinokyou Kuwabara-cho, Nakagyo-Ku Kyoto, Japan), ^{1}H NMR spectra were recorded on Bruker spectrometer (Billerica, Massachusetts, USA) using DMSO-d_6 as solvent, and mass spectra were recorded on Shimadzu GC-MS Model No. QP-2010 (Nishinokyou Kuwabara-cho, Nakagyo-Ku Kyoto, Japan). The mesogenic behavior of the homologue derivatives was observed through polarizing microscopy. The textures of nematogenic mesophase were determined by miscibility method. Entropy(ΔS) and enthalpy(ΔH) are qualitatively discussed.

Analytical Data: Spectral Data

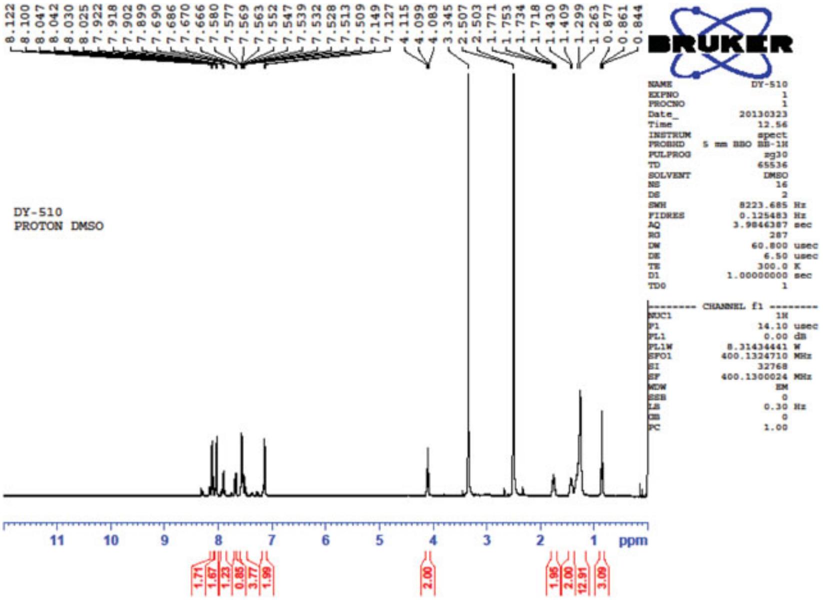
NMR in ppm for Decyloxy Derivative. 0.84–0.88 (t, 3H, -CH_3 of –$OC_{10}H_{21}$ group), 1.26–1.77 (m, 16H, -CH_3-(CH_2-)$_8$-CH_2-O-), 4.08–4.12 (t, 2H, -CH_2-O-), 7.51–7.69 (m, 7H, *o*-substituted phenyl ring), 7.90–7.92 (q, 1H, in phenyl ring *ortho* to –N=N– group), 8.03–8.12 (m, 4H, in phenyl ring *ortho* to –COO– and –N=N– group). The NMR data are reliable with the molecular structure.



4-(4'-n-Alkoxy benzoyloxy) phenylazo-2"-bromobenzenes

Where, R= C_nH_{2n+1} and n = 1 to 8 and 10,12,14,16

Scheme 1. Synthetic route to the novel series.



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RG                 287
DW              60.800 usec
DE                6.50 usec
TE               300.0 K
D1          1.00000000 sec
TD0                  1

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WDW                 EM
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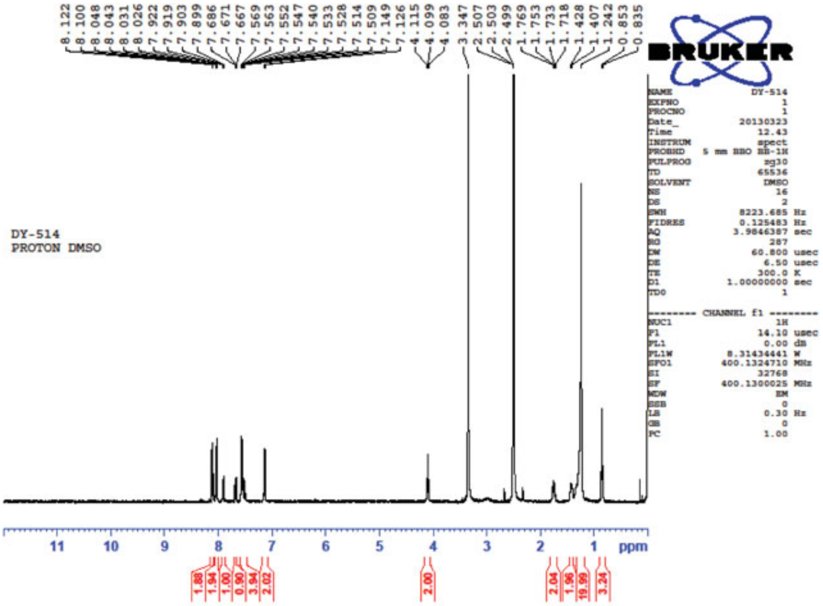
NMR of decyloxy derivative

NMR in ppm for Tetradecyloxy Derivative. 0.84–0.85 (t, 3H, -CH$_3$ of –OC$_{14}$H$_{29}$ group), 1.24–1.77 (m, 24H, -CH$_3$-(CH$_2$-)$_{12}$-CH$_2$-O-), 4.09–4.14 (t, 2H, -CH$_2$-O-), 7.12–7.69 (m, 7H, *o*-substituted phenyl ring), 7.91–7.93 (q, 1H, in phenyl ring *ortho* to –N=N– group), 8.04–8.13 (m, 4H, in phenyl ring *ortho* to –COO– and –N=N– group). The NMR data are reliable with the molecular structure.



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FIDRES        0.125483 Hz
AQ           3.9846387 sec
RG                 287
DW              60.800 usec
DE                6.50 usec
TE               300.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
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SI               32768
SF         400.1300025 MHz
WDW                 EM
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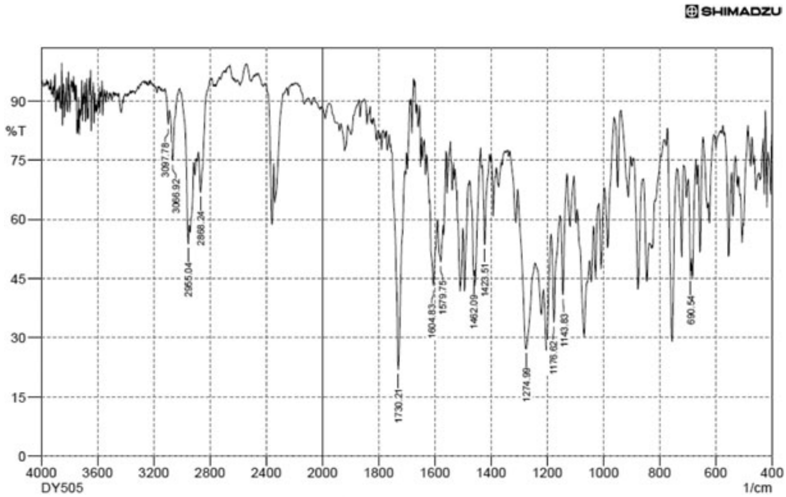
LB                0.30 Hz
GB                   0
PC                1.00
```

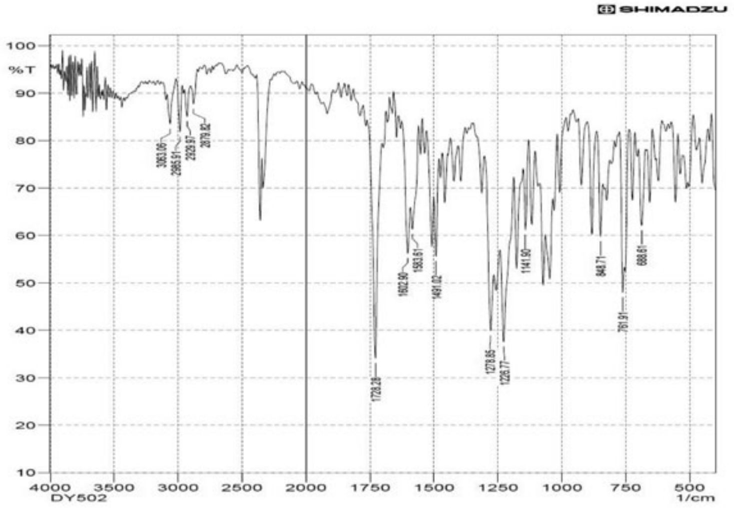
NMR of tetradecyloxy derivative

IR in cm^{-1} for Pentyloxy Derivative. 2868, 2941 (C-H Str. of (-CH$_2$-)$_n$ group of –OC$_5$H$_{11}$), 1423, 1579 (aromatic C=C Str.), 3066, 3097 (C-H Str. of aromatic ring), 1022, 1280 (C-O Str. of –COO– group), 1730 (C=O, Str. of –COO– group), 1139 (C-O-C-), 690 (C-Br Str.), 750, 848 (*para-* and *ortho*-substituted phenyl ring), 1604 (–N=N– Str.). The IR data are consistent with the molecular structure.



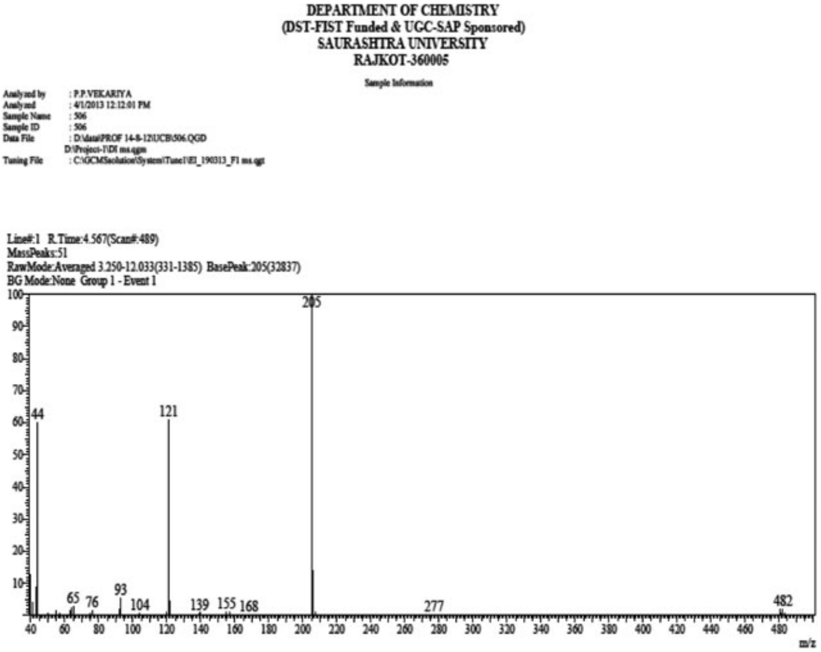
IR of Pentyloxy Derivative

IR in cm^{-1} for Ethyloxy Derivative. 2875, 2933 (C-H Str. of (-CH$_2$-)$_n$ group of –OC$_2$H$_5$), 1492, 1585 (aromatic C=C Str.), 3061, 3095 (C-H Str. of aromatic ring), 1047, 1191 (C-O Str. of –COO– group), 1732 (C=O, Str. of –COO– group), 1141 (C-O-C-), 688 (C-Br Str.), 750, 850 (*para-* and *ortho*-substituted phenyl ring), 1604 (–N=N– Str.). The IR data are consistent with the molecular structure.



IR of Ethyloxy Derivative

Mass of Hexyloxy Derivative. *m*/*z* (rel. int%): 482 $(M)^+$, 205, 121, 168, 104.



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Sample Information

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Analyzed : 4/1/2013 12:12:01 PM
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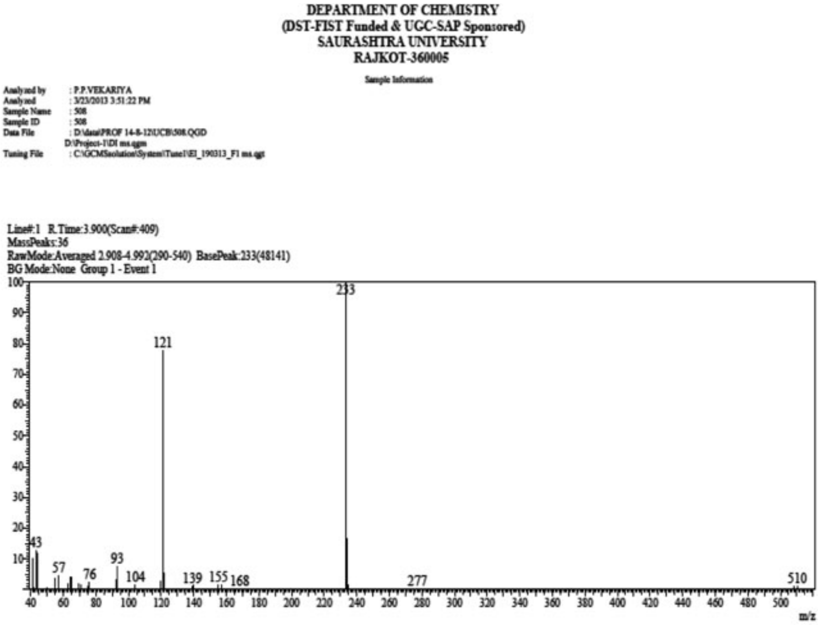
BG Mode:None Group 1 - Event 1

MASS of Hexyloxy derivative

Mass of Octyloxy Derivative. *m*/*z* (rel. int%): 510 $(M)^+$, 233, 121, 168, 104.



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Sample Information

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Analyzed : 3/23/2013 3:51:22 PM
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MASS of octyloxy derivative

Texture by Miscibility Method.

- Heptyloxy derivative-Nematic-Threaded
- Hexadecyl derivative-Nematic-Schlieren

Result and Discussion

n-Alkoxy benzoic acids are dimeric because their two molecules are bonded through hydrogen bonding. 4-Hydroxy phenyl azo-2′-bromobenzene azo dye (B) is nonmesogenic. However, mesogenic character is induced by linking it with 4-n-alkoxy benzoic acid molecule by esterification through acid chlorides of corresponding 4-n-alkoxy benzoyl chlorides. The methyl to butyl homologue derivatives of novel series are nonmesogenic, pentyl homologue derivative is monotropic nematic, and the rest of the homologue derivatives are enantiotropic nematic. None of the homologue derivatives of the novel series exhibit smectogenic mesophase formation. Transition temperatures (Table 2) of homologues as determined by polarizing microscopy are plotted versus the number of carbon atoms present in the *n*-alkyl chain of the left *n*-alkoxy terminal end group. A phase diagram (Fig. 1) shows the phase behavior of the novel series. The solid-isotropic or solid-nematic transition curve partly adopts a zigzag path of rising and falling values in an irregular manner. The nematic-isotropic (or vice versa) transition curve follows an overall falling tendency as the series is ascended, showing alternatively rising and falling behavior at the difference of every two methylene units of left *n*-alkoxy group. Thus, the nematic-isotropic transition curve appears like electromagnetic wave for even numbered mesogenic homologues. Thus, the nematic-isotropic transition curve slightly deviates from a normal behavior. An odd–even effect is observed for the nematic-isotropic (or vice versa) transition curve. Alternation of transition temperatures is also observed for the homologue derivative from the phase diagram. The odd–even effect disappears from and beyond the heptyl homologue derivative.

Table 2. Transition temperatures in °C of series-1

Compound no.	R = *n*-alkyl group C_nH_{2n+1}	Transition temperature in °C Sm	Nm	Isotropic
1	1	—	—	143
2	2	—	—	124
3	3	—	—	110
4	4	—	—	121
5	5	—	(78)	95
6	6	—	80	91
7	7	—	76	90
8	8	—	78	87
9	10	—	85	91
10	12	—	80	89
11	14	—	68	90
12	16	—	70	88

Note: () indicate monotropy.

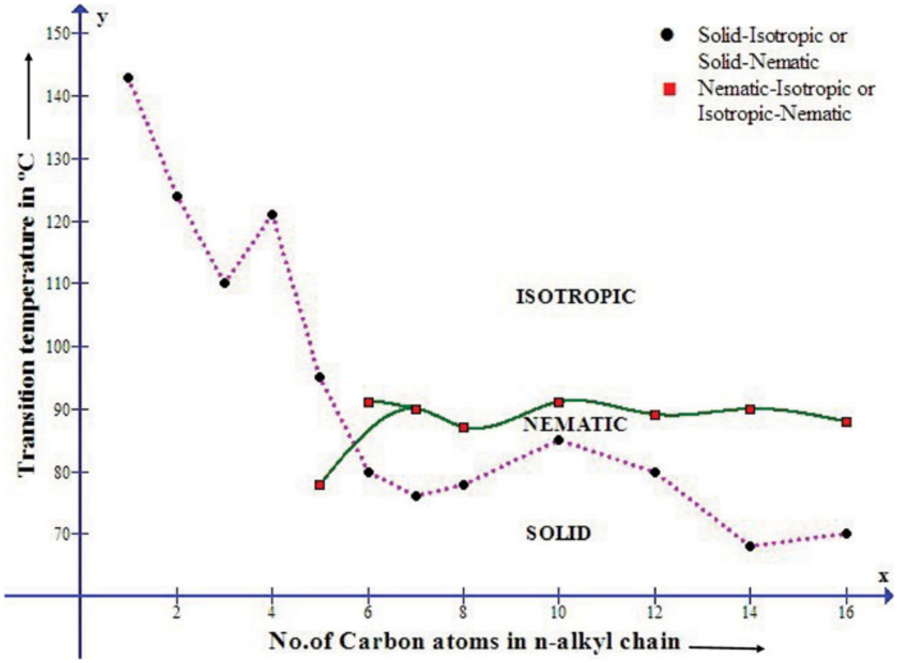

Figure 1. Phase behavior of series.

The esterification process of dimeric *n*-alkoxy benzoic acids breaks the hydrogen bonding through acid chloride formation. Azo dye (B) is nonmesogenic, however linking of one phenyl ring with *n*-alkoxy flexible terminal end group through -COO- central group balances suitable magnitudes of anisotropic forces of intermolecular attractions [4] as a result of favorable net rigidity in combination with flexibility, which commences mesogenic property from a pentyl derivative of a novel series. Nonmesogenic behavior of methyl to butyl derivatives of a series is attributed to their high crystallizing tendency and relatively shorter *n*-alkyl chain length as well as positioning of –Br functional group at the lateral position. These, three effects do not allow for suitable magnitudes of anisotropic forces of intermolecular attractions. Consequently, the crystal lattices are abruptly broken without showing up of mesophase formation. The enthalpy (ΔH) value and transition temperatures of the homologues (methyl to butyl) are raised sufficiently but melt sharply at their melting point without exhibition of any kind of mesophase. The entropy value (ΔS) suddenly reaches a value at which molecular disorder occurs to induce nonmesogenic character. Exhibition of nematogenic character by pentyl to hexadecyl derivatives of the series is attributed to the proper proportion of molecular end to end attractions that occur due to the suitable magnitudes of anisotropic forces of intermolecular adhesion, as a consequence of molecular flexibility [1–3] irrespective of *ortho*-substituted –Br end group. The laterally *ortho*-substituted –Br end group increases intermolecular distance and may cause reduction in the magnitudes of anisotropic forces of attractions. However, increased molecular width may cause an opposing force, which operates at a time for the reason of increased polarizability due to the laterally substituted –Br group [4]. Thus, the net effect of intermolecular adhesion from two opposing forces operating at a time depends upon the major effect, out of two opposing effects. The net magnitudes of intermolecular attractions as a consequence of molecular rigidity in combinations with molecular flexibility is sufficient to maintain statistically parallel orientational order of molecules in floating condition to occur nematogenic mesophase formation, but it is insufficient to prolong nematic mesophase for longer range of liquid crystallinity. Moreover, the magnitudes of net intermolecular forces of attractions are insufficient to cause lamellar packing of molecules in their crystal lattices. Therefore, none of the homologues showed smectogenic character prior to nematogenic mesophase formation. Thus, absence of lamellar packing of molecules has hindered smectogenic mesophase formation. An odd–even effect observed for nematic-isotropic transition curve is attributed to the presence of odd and even numbered of methylene units in *n*-alkyl chain of left *n*-alkoxy terminal end group. Disappearance of odd–even effect from and beyond the heptyl homologue derivative is due to the flexing or bending or coupling of the *n*-alkyl chain to the main axis of the core. The wave-like appearance of a nematic-isotropic transition curve may be due to the alternative variations of molecular rigidity and flexibility at the interval of every two methylene units. The average thermal stability is 89.4 °C and mesophase length varies from a minimum of 6 °C at the decyl homologue derivative to a maximum of 22 °C at the tetradecyl homologue derivative. Thus, homologue derivatives of the novel series are nematogenic only, without exhibition of any smectic property, and of a low melting type and relatively shorter range of liquid crystallinity.

The mesogenic properties of the novel homologous series are compared with structurally similar other known isomeric and nonisomeric series [14,15] X and Y as shown in Fig. 2.

Novel homologous series-1 and series X and Y are similar or identical with respect to their molecular structures, consisting of three phenyl rings bonded through –COO– and –N=N– central bridges, which contributes to the molecular rigidity [1–3]. Series-1 and X are isomeric, but they differ from each other by positional substitution of flexible –Br group bonded to third phenyl ring keeping –OR terminal end group unchanged, which contributes to the molecular flexibility. Series-1 and Y are identical with respect to molecular rigidity

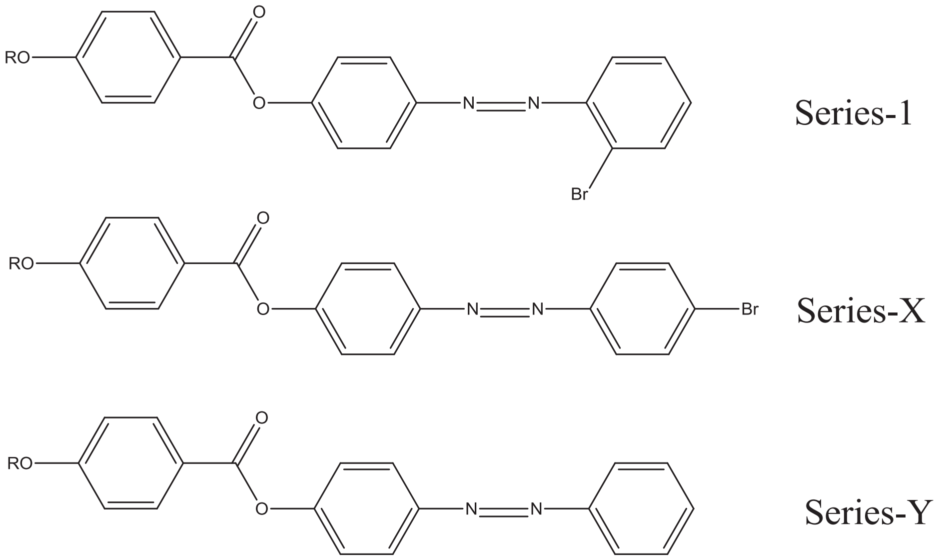

Figure 2. Structurally similar isomeric/nonisomeric series.

Table 3. Average thermal stability in °C

Series	[1]	[X]	[Y]
Smectic-isotropic or smectic-nematic	—	149.7 $[C_6–C_{16}]$	114.0 $[C_{10}–C_{16}]$
commencement of smectic phase	—	C_6	C_{10}
Nematic–isotropic	89.4	231.2	145.0
commencement of nematic phase	$[C_6–C_{16}]$ C_5	$[C_1–C_{10}]$ C_1	$[C_1–C_8]$ C_1

but differ with respect to molecular flexibility due to replacement of –H (series Y) by –Br (series-1). The difference of overall molecular rigidity in combination with molecular flexibility in series-1, X, and Y causes difference in the suitable magnitudes of anisotropic forces of intermolecular attraction, which are reflecting in the mesogenic behaviors from series to series and homologue to homologue in the same series. The positional difference of –Br in series-1 and X causes difference in length to breadth ratio of the molecular polarity to polarizability. Hence, the exhibition of type of mesophase or mesophases, degree of mesomorphism, commencement of mesophase, extent of mesophase length, mesophase thermal stability, etc., and many other properties related to mesophase formation and behaviors have sensitively direct relation with even minute variations of molecular structure. Table 3 represents average thermal stabilities for mesophase for the series-1, X, and Y.

From Table 3, it clearly indicates that

- Novel series-1, exhibits only nematogenic character with absence of smectic property.
- Series X and Y under comparison exhibited smectic and nematic mesophases within definite range of temperature.
- Nematic mesophase commences from pentyl homologue of series-1, while it commences from first member, i.e., methyl homologue of series X and Y.
- Nematic–isotropic thermal stability of series-1 is the lowest (89.4) and of series X is the highest (231.2) among the series under comparison.
- Nematic thermal stability of series Y is more than a series-1 and less than series X.
- Mesogenic phase length of series X and Y selected for comparison is relatively wider than a novel series-1.

Homologous series X and Y selected for comparison are linear and lath-like, while novel series-1 is nonlinear. Hence, intermolecular end-to-end attractions and lateral attraction of series X and Y are more than a series-1. The bromo functional group substituted as lateral position widens the molecule, while same bromo functional group positioned as terminal end group in isomeric series X increases the length to breadth ratio. Of course, molecular polarizability factor operating in series-1 is weaker than the series X. Hence, length to breadth ratio for series X has exceeded to cause relatively stronger intermolecular anisotropic forces of attraction as a consequence of molecular rigidity and flexibility, this is also the case with series Y and series-1, but the magnitudes of intermolecular adhesion for series Y is a little bit less than for series X and more than for series-1. Moreover, suitable magnitudes of anisotropic forces of intermolecular adhesion are sufficient to cause lamellar packing of molecules within the crystal lattices of the molecules facilitated belonging to series X and Y causing formation of smectic phase for particular temperature range, and then intermolecular forces of adhesion cause formation of statistically parallel orientational order of molecules in floating condition. Thus, smectic mesophase formation in addition to nematic mesophase is facilitated to occur. But, such intermolecular force of adhesion among the molecules of novel series-1 is insufficient to form smectic mesophase in addition to nematic mesophase. Smectic mesophase commences from hexyloxy and decyloxy homologue derivatives for series X and Y, respectively, while it does not commences till the last hexadecyloxy homologue derivative of a series-1, because early or late commencement of smectic phase depends upon the extent of noncoplanarity caused by a molecule [13]. The variations of mesogenic properties from homologue to homologue in the same series are attributed to the sequential addition of methylene unit, keeping right terminal or lateral end group unchanged. Similarly, mesogenic properties vary from series to series for same homologue (same –OR group) are attributed to the varying right terminal/lateral end group of different polarities keeping left terminal end group unchanged of a molecule [4,10,13].

Conclusions

- Titled novel homologous series is nematogenic without exhibition of any smectogenic character; even in the monotropic condition.
- Presently investigated series is of short range of liquid crystallinity and low-ordered melting type.
- A suitable magnitude of anisotropic forces of intermolecular attractions as a consequence of favorable molecular rigidity and flexibility governs the formation of liquid crystal mesophase.
- Absence of smectogenic character indicates absence of lamellar packing of molecules.
- Slight variation in molecular shape, size, rigidity, flexibility, position of same or different functional groups and their polarity, molecular length or/and breadth, and ratio of the molecular polarity to polarizability can change the degree of mesomorphism and mesogenic behavior to a very large extent.
- Group efficiency order derived on the basis of thermal stability for smectic and nematic is as under.
  Smectic : *para*-Br > —H > *ortho*-Br.
  Nematic : *para*-Br > —H > *ortho*-Br.
- Group efficiency order derived on the basis of early commencement of smectic and nematic mesophase is as under.
  Smectic : *para*-Br > —H > *ortho*-Br.
  Nematic : *para*-Br = —H > *ortho*-Br.

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