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The Relation Between Mesomorphism and Molecular Structure of a Novel Azoester Series Involving Laterally Substituted Chloro Groups

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A novel azoester homologous series 4-(4′-n-alkoxy benzoyloxy) phenyl azo 2″,6″-dichloro benzene is synthesized and studied with a view to understand and establish the effects of molecular structure on liquid crystal behavior of a substance with reference to steric hindrance. The novel homologous series consists of twelve homologues. Mesomorphism commences from the heptyloxy homologue and continues up to the hexadecyloxy homologue as a monotropic nematic without the exhibition of any smectogenic characteristics. Transition temperatures were determined by an optical polarizing microscopy equipped with a heating stage. Transition curves of the phase diagram behave in a normal manner. The isotropic-nematic transition curve shows an odd-even effect in the very short range of temperature. The texture of nematic mesophase is threaded. Analytical and spectral data support the molecular structures of the homologues. Thermal stability is very low and the degree of mesomorphism is poor. Thus novel series is of low melting type and nematogenic only in a monotropic manner. Mesomorphic properties of the present, novel series are compared with structurally similar other known series.

Keywords Liquid crystal; mesomorphism; monotropy; nematic; sematic

Introduction

Benzoic and cinnamic acid derivatives are bioactive molecules [1] used for pharmaceutical and medicinal [2, 3] preparations. Their derivatives of a liquid crystal nature are useful in a variety of applications [4, 5]. Azoester types of mesomorphic substances are useful to manufacture decorative articles which change their colors with frequencies of exposed radiations and are sensitive to visible light [6]. The present investigation is planned with a view to understanding and establishing the effects of molecular structure on liquid crystal prosperities, [7–9] particularly in the isomeric homologous series of a mesogenic nature. The presently proposed molecules of the azoester series consist of three phenyl rings bridged through −COO− and −N=N− groups, which will act as the rigid core of molecule, and an −OR terminal end group and two laterally substituted chloro groups closet to the −N=N− central group, which will act the flexible [10–12] part of molecule. Thus, the effects of

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molecular structure, and in particular the steric hindrance of two chloro groups, on liquid crystal behavior can be studied.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents by the modified method of Dave and Vora [13]. *n*-Alkoxy benzoic acids were converted to the corresponding *n*-alkoxy benzoyl chlorides (A) using thionyl chloride by an established method [14]. Azo dye, 4-hydroxy phenyl azo-2′6′-dichlorobenzene (B) (M.P. = 76°C) was prepared by a diazotization method [14]. Components (A) and (B) were condensed in dry cold pyridine by a known method [15]. The final azo-ester homologues of the novel series 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, 2,6-dichloro aniline, phenol, thionyl chloride, KOH, methanol, ethanol, etc. were used as received except solvents which 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}HNMR spectroscopy, and mass spectroscopy. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer. IR spectra were recorded on Shimadzu FTIR-8400, ^{1}HNMR spectra were recorded on Bruker spectrometer using DMSO-d_6 as solvent and Mass spectra were recorded on Shimadzu GC-MS Model No. QP-2010. The mesogenic behavior of the homologue derivatives were observed through polarizing microscopy. The textures of nematogenic mesophase were determined by a miscibility method.

Analytical Data

Spectral Data

^{1}H NMR in ppm for Methyloxy Derivative

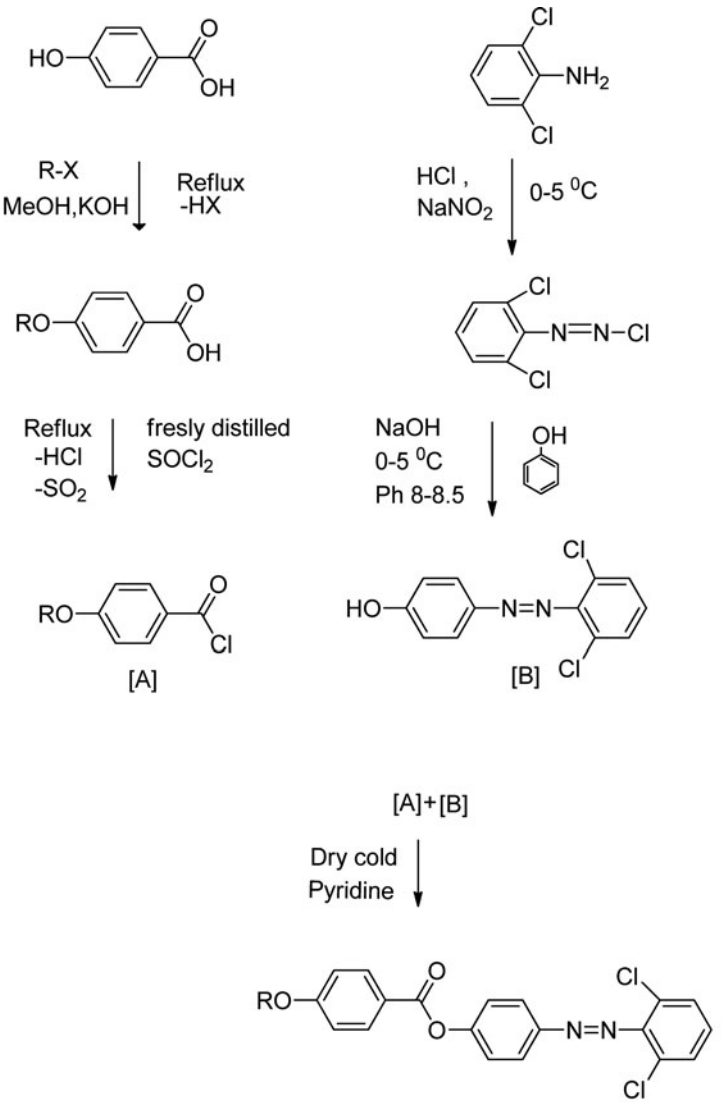
4.17 (s, 3H, $-OCH_3$), 7.15–7.17 (d, 2H, Ar−H), 7.44–7.48 (t, 1H, Ar−H), 7.57–7.59 (d, 2H, Ar−H), 7.66–7.68 (q, 2H, Ar−H), 8.04–8.06 (d, 2H, Ar−H), and 8.06–8.13 (d, 2H, Ar−H).

^{1}H NMR in ppm for Propyloxy Derivative

0.79–0.82 (t, 3H, $-CH_3$), 1.77–1.80 (m, 2H, $-CH_2$), 3.94–3.97 (t, 2H, $-OCH_2$), 6.91–6.94 (d, 2H, Ar−H), 7.11–7.15 (t, 1H, Ar−H), 7.33–7.36 (m, 4H, Ar−H), 7.97–7.98 (d, 2H, A-H), and 7.99–8.00 (d, 2H, Ar−H).

^{1}H NMR in ppm for Octayloxy Derivative

0.81–0.84 (t, 3H, $-CH_3$), 1.18–1.28 (m, 10H, 5 $-CH_2$), 2.10–2.25 (q, 2H $-CH_2$),3.97–4.00 (t, 2H, $-OCH_2$), 6.91–6.93 (d, 2H, Ar−H), 7.11–7.13 (t, 1H, Ar−H), 7.33–7.36 (m, 4H, Ar−H), 7.98–8.00 (d, 2H, Ar−H), and 8.09–8.11 (d, 2H, Ar−H).



4-(4′-n-alkoxy benzoyloxy) phenyl azo 2″, 6″- dichloro benzene

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

Scheme 1. Synthetic route to the novel series.

IR in cm^{-1} for Pentyloxy Derivative

2874, 2960 (C−H Str. of $(-CH_2-)_n$ group of $-OC_5H_{11}$), 3080 (C−H str. Of Ar. ring), 1726 (C=O str. Of −COO− gp), 1606 (−N=N− str.), 1427, 1510 (C=C str. Of Ar. ring), 1168 (C−O str. of −COO− gp), 1143 (C−O−C str.), and 761 (C−Cl Str. m-disub. Ar. ring).

Table 1. Elemental analysis for (1) butyloxy, (2) decyloxy, and (3) tetradecyloxy derivatives

		Elements % found			Elements % calculated		
Sr. no.	Molecular formula	C	H	N	C	H	N
1	$C_{23}H_{20}Cl_2N_2O_3$	62.20	4.48	6.28	62.31	4.55	6.32
2	$C_{29}H_{32}Cl_2N_2O_3$	65.98	6.06	5.16	66.03	6.11	5.31
3	$C_{33}H_{40}Cl_2N_2O_3$	67.84	6.71	4.72	67.92	6.91	4.80

IR in cm^{-1} for Dodecyloxy Derivative

2949 (C−H str. Of Ar. ring), 2862, 2916 (C−H str. Of $(-CH_2-)_n$ gp of $-OC_{12}H_{25}$), 1728 (C=O str. Of −COO− gp), 1604 (−N=N− str.), 1425, 1506 (C=C str. Of Ar. ring), 1166, 1199 (C−O str. Of −COO− gp), 1072 (C−O−C str.), and 761 (C−Cl Str. m-disub. Ar. ring).

IR in cm^{-1} for Hexadecyloxy Derivative

3076 (C−H str. Of Ar. ring), 2860, 2916 (C−H str. Of $(-CH_2-)_n$ gp of $-OC_{16}H_{33}$), 1735 (C=O str. Of −COO− gp), 1608 (−N=N− str.), 1427, 1506 (C=C str. Of Ar. ring), 1166, 1197 (C−O str. Of −COO gp), 1145 (C−O−C str.), and 684 (C−Cl Str. m-disub. Ar. ring).

Mass of Ethyloxy Derivative

m/z (rel.int%): 414 $(M)^+$, 149, 121, 93, 65, and 44.

Mass of Hexyloxy Derivative

m/z (rel.int%): 470 $(M)^+$, 205, 121, 93, 65, 44

Mass of Heptyloxy Derivative

m/z (rel.int%): 484 $(M)^+$, 219, 121, 93, 57, 43

Texture by Miscibility Method

- Octyloxy derivative-nematic-threaded
- Tetradecyl derivative-nematic-Schlieren

Result and Discussion

Azo dye 4-hydroxy phenyl azo 2′, 6′-dichlorobenzene is a nonliquid crystal (NLC) compound (m.p. 76°C). The mesomorphic property is induced on linking it with 4-*n*-alkoxy benzoic acid individually through their acid chlorides in pyridine at low temperature. The azo ester derivatives formed exhibit mesomorphism as a monotropic nematic phase from the heptyloxy homologue. A phase diagram showing phase behavior is shown (Fig. 1) for the transition and melting temperatures (Table 2) as determined from a polarizing microscope equipped with a heating stage, versus the number of carbon atoms present in *n*-alkyl

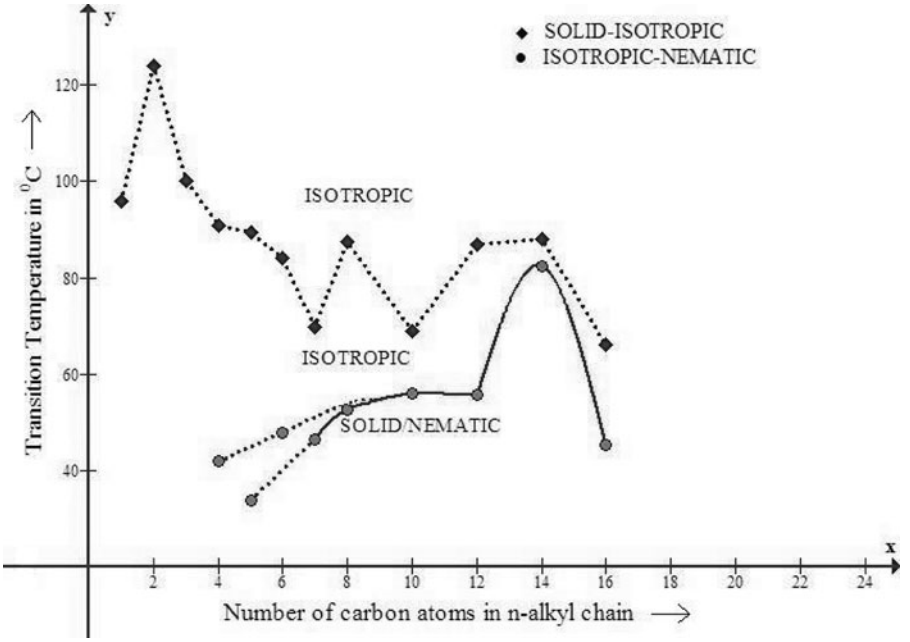


Figure 1. Phase behavior of series.

chain of the left *n*-alkoxy terminal end group. The phase diagram consists of two transition curves, a solid-isotropic transition curve and an isotropic-nematic transition curve. The solid-isotropic transition curve follows a zigzag path of rising and falling values in a normal manner. An isotropic-nematic transition curve rises from the heptyloxy to the

Table 2. Transition temperatures in °C

		Transition temperature in °C		
Compound no.	R = n-alkyl group C_nH_{2n+1}	Sm	N	Isotropic
1	1	—	—	95.8
2	2	—	—	123.9
3	3	—	—	100.0
4	4	—	—	90.8
5	5	—	—	89.6
6	6	—	—	84.2
7	7	—	(46.4)	69.7
8	8	—	(52.7)	84.1
9	10	—	(56.0)	69.0
10	12	—	(55.8)	86.9
11	14	—	(82.4)	88.1
12	16	—	(45.4)	66.1

() indicate monotropy.

tetradecyloxy homologue and then descends as series is ascended until the hexadecyloxy homologue, which reveals a very narrow and shorter odd-even effect. The curves for odd and even homologues are extrapolated [16–18]. Keeping in view the trend of curvature of a transition curve to magnify the odd-even effect and to predict the hypothetical monotropic transition temperature for the butyloxy (42°C), the pentyloxy (34°C), and the hexyloxy (48°C) homologues, which are actually not liquid crystalline. Transition curves for odd and even members of the series merge into each other at the nonyloxy homologue and then a single curve prolongs for higher homologues and beyond the nonyloxy homologue. Analytical and spectral data confirmed the structures of molecules. The textures of the nematic mesophase are of the threaded type. The nematogenic phase length below the isotropic temperature is relatively very short (1–2°C) depending upon the rate of cooling. Smectogenic character is totally absent. Thus the novel homologous series 4-(4′-*n*-alkoxy benzoyloxy) phenylazo-2″, 6″-dichloro benzenes is nematogenic only with a low thermal stability and transition temperatures as well as a late commencement of mesomorphism. The mesomorphism of the series from homologue to homologue varies with changing number of carbons in the *n*-alkyl chain. The odd-even effect diminishes as the series is ascended. The nonmesomorphic behavior of methoxy to hexyloxy homologues is attributed to their inability to resist exposed thermal vibrations and their inner high crystalline tendency, which depends upon the unsuitable magnitudes of anisotropic forces of attraction as a consequence of unfavorable molecular rigidity and flexibility from the steric hindrance of the laterally substituted two chloro groups. Thus, the methoxy to hexyloxy homologues of the presently investigated novel homologous series undergo abrupt breaking of their crystal lattices which sharply transforms into isotropic liquid without passing through anisotropic liquid state or mesomorphic state. Exhibition of mesomorphic behavior from and beyond the heptyloxy homologue is attributed to the disalignment of azoester molecules at an angle less than 90° with the plane of a floating surface; under the influence of externally applied heat, resisting exposed thermal vibrations. Thus, suitable magnitudes of anisotropic forces of intermolecular end to end attractions as a consequence of favorable molecular rigidity and flexibility, which leads to the molecular floating tendency on the surface irreversibly below isotropic temperature with statistically parallel orientational order, depend upon the combined effects of the polarizabiltiy and intermolecular closeness. Hence, nematogenic mesophase formation occurs monotropically for very few degrees of temperature based on the rate of cooling. The missing of smectogenic character is attributed to the absence of lamellar packing molecules and unsuitable magnitudes of extent of molecular noncoplanarity, which hinders the sliding layered arrangement of molecules on heating the sample substance to induce smectogenic mesophase either reversibly or irreversibly. The variation of mesogenic behavior from homolog to homologue in the same series is attributed to the sequentially added methylene units to the left *n*-alkoxy terminal end group. Low thermal stability of few degrees of nematogenic monotropic mesophase formation indicates that steric hindrance caused by the two lateral chloro groups do not facilitate parallel orientational order of the molecules to prolong the appearance of nematogenic mesophase. The diminishing of odd-even effect in isotropic-nematic transition curve for higher homologues is attributed to coiling or bending or flexing or coupling of *n*-alkyl chain with the major axis of core structure [19]. The mesomorphic properties of presently investigated novel homologues series 1 are compared with the structurally similar other known homologues series X [20] and series Y [21] as shown in Figure 2.

It is clear from Figure 2, that homologues series 1, X and Y are isomeric with respect to their molecular structure. The molecular rigidity induced by three phenyl rings and two central bridges viz. —COO— and —N=N— is identical for all the homologues series 1, X

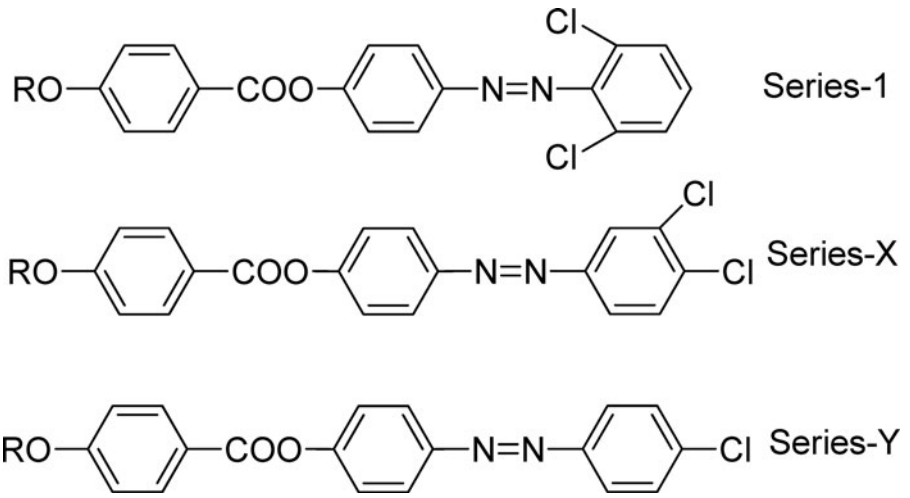


Figure 2. Structurally similar homologous series.

and Y. Moreover the flexibility contribution by −OR flexible terminal end group for the same homologue of present series and each series (X and Y) chosen for comparison is also identical. However, the molecular flexibility contributed by same two chloro groups present in molecules of each series differs due to their positions of substitution on same (series 1 and X) phenyl ring or different (series Y) phenyl rings which bears variations. Thus, the combined effects of molecular rigidity and flexibility, which governs a phenomena of mesomorphism will differ from series to series for the same homologue for the varied suitable magnitudes of anisotropic forces of intermolecular end to end terminal and lateral attractions irrespective of unchanged polarity of chloro group. Hence, mesomorphic properties and the degree of mesomorphism vary from series to series under comparison. Table 3 represents some properties like thermal stability, commencement of mesophase or mesophases, exhibition of type of mesophase, early or late occurrence of the mesophase, mesophase length, etc. as shown below.

Table 3 indicates the following.

Table 3. Average thermal stability in °C

Series	1	X	Y
Smectic-nematic or Smetic-isotrepic	—	106.0 (C_6–C_{16})	75.75 (C_{10}–C_{16})
commencement of smectic phase	—	C_6	C_{10}
Nematic-isotropic or Isotropic-nematic	Few degrees 1–2 (C_7–C_{16})	156.25 (C_1–C_{16})	149.4 (C_3–C_{16})
commencement of nematic phase	C_7	C_1	C_3

- Isomeric series X and Y exhibit smectogenic character, while the present series1 does not.
- Homologous series 1, X and Y all exhibit nematogenic property.
- The present novel series 1 is monotropic nematic while series X and Y are enantiotropic nematic.
- Smectic mesophase commence from the sixth and tenth carbon of *n*-alkyl chain in X and Y series respectively, while it does not occur at all in series 1.
- The nematogenic mesophase commences from the very first member of series X, form third member of series Y and from seventh member of series 1 of present investigation.
- Series X and Y are predominantly nematogenic and partly smectogenic, while, present series is only nematogenic.

In homologues series X and Y one of the chloro groups occupies the position as a right handed terminal end group. The group polarity and polarizibility of -Cl is more than -H. Moreover two -Cl groups of series 1 as 2′,6′-dichloro restricts the molecular flexibility due to the positional status on the third phenyl ring as the closet neighbor of the —N=N— central bridge, as compared to the positional status of two chloro groups in case of series X and Y. Thus, the molecules of series X and Y strongly resist exposed thermal vibrations to float on the surface with the sliding layered arrangement as well as with the statistically parallel orientational, two-dimensional orders within definite range of temperature in enantiotropic manner. Thus, molecules of series X and Y exert relatively stronger intermolecular end to end attractions and facilitate lamellar packing of molecules in their crystal lattices. However relatively weaker magnitudes of anisotropic forces of intermolecular end to end and lateral attractions by steric hindrance induces only monotropic nematic mesophase formation for very small range of temperature for series 1. Early or late commencement of smectic or nematic depends upon the extend of noncoplanarity [22] caused by the molecule due to a differing positional status of the two chloro groups, either on the same or different phenyl ring or rings. Thus, the varying molecular rigidity and/or molecular flexibility causes varying thermal stabilization energies and hence, thermal stability for smectic and nematic mesophase acquires variations. The variations of mesomorphic behavior from series to series for the same homologue arises by changing part of a molecule either in number of phenyl rings, central group or groups linking phenyl ring, or terminal or lateral group or groups or the positional status of substitution of same functional group or groups on either of the phenyl ring.

Conclusions

- The group efficiency order for smectic and nematic on the basis of (i) thermal stability and (ii) early commencement of mesophase are as under.
  i. Smectic: 3′, 4′-dichloro > 3-chloro, 4′-chloro > 2′, 6′-dichloro
     Nematic: 3′, 4′-dichloro > 3-chloro, 4′-chloro > 2′, 6′-dichloro
  ii. Smectic: 3′, 4′-dichloro > 3-chloro, 4′-chloro > 2′, 6′-dichloro
     Nematic: 3′, 4′-dichloro > 3-chloro, 4′-chloro > 2′, 6′-dichloro
- Suitable magnitudes of molecular rigidity and flexibility inducing favorable magnitudes of molecular entropy ($\Delta S = \frac{\Delta H}{T}$) or restricted molecular randomness can induce thermotropic mesomorphism.
- Slight variation in the molecular structure can alter a great deal of mesomorphic behavior.

- Phenomina of mesomorphism is very sensitive and susceptible to a molecular structure of substance.
- Present novel homologous series is monotropic nematic and low melting type. Such homologues on mixing with other suitable component, forming binary system can yield LC material, useful at desired low or room temperature for the manufacture of LC devices.

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