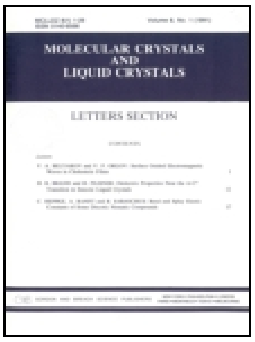

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Mesomorphic Behavior of Chloro Substituted Azoesters. A Novel Homologous Series, 4-(4′-*n*-Alkoxy Benzoyloxy) Phenyl Azo-3″,4″-dichlorobenzenes

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The titled novel homologous series consists of 12 members. Mesomorphic behavior as a nematic phase commences from the first member of the series to the hexadecyloxy homologue. The smectogenic mesophase commences from the hexyloxy homologue to the hexadecyloxy homologue with nematogenic mesophase formation in an enantiotropic manner. The textures of the nematic phase are Schileren or threaded and those of the smectic phase are focal conic fan shaped. Analytical and spectral data matched with the molecular structure of the homologues. A phase diagram shows the phase behavior, and consists of solid-mesomorphic, nematic–isotropic, smectic-nematic transition curves that behave in a normal manner with the exhibition of an odd–even effect. The thermal stabilities for smectic and nematic are 106.0°C and 156.8°C respectively. Smectogenic and nematogenic mesophase temperature ranges vary from 07°C to 24°C, 26°C to 88°C respectively. Isotropic transition temperatures vary between 110°C and 205°C. Thus, the present novel series is predominantly nematogenic and partly smectogenic whose mesomorphic behavior ranges from 34°C to 88°C. Thus, it is middle ordered melting type series.

Keywords Enantiotropy; liquid crystals; mesomorphism; nematic; smectic

Introduction

Azoester homologous series with a lath-like, linear and nonlinear geometrical shapes, and different sizes are reported [1–6] with exhibition of mesomorphic behavior. Varying molecular shapes and sizes of molecules induces different magnitudes of thermal resistivity in thermotropic liquid crystals depending upon suitable magnitudes of anisotropic forces of intermolecular attractions [7, 8] as a consequence of resultant molecular rigidity and flexibility [9, 10, 11], to generate mesomorphism in a monotropic or enantiotropic manner. The present investigation is planned with view to understanding and establishing the relationship between mesomorphism and the molecular srtucture by linking three phenyl rings, bridged through $-$COO$-$, and $-$N$=$N$-$ central groups which contribute to molecular rigidity and the rest of the molecular part ($-$OR, $-$Cl, $-$Cl) as functional groups attached at the terminal

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Table 1. Elemental analysis for methyloxy, ethyloxy and propyloxy derivatives

Sr. Reply No.	Molecular formula	Elements % found (% calculated) C Found	C Calculate	H Found	H Calculate	N Found	N Calculate
1	$C_{20}H_{14}N_2O_3Cl_2$	60.11	59.85	4.06	3.49	7.08	6.98
2	$C_{21}H_{16}N_2O_3Cl_2$	60.66	60.72	3.76	3.85	6.52	6.74
3	$C_{22}H_{18}N_2O_3Cl_2$	61.29	61.53	4.45	4.19	6.68	6.52

and/or lateral position of same or different polarity at para and meta positions which act as flexible parts of the molecule.

Experimental Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agent (R–X) to form 4-n-alkoxy benzoic acids by a modified method of Dave and Vora [12]. Azodye 4-hydroxy phenyl azo 3′,4′ dichlorobenzene was prepared by the usual established method [13, 14] of diazotization. The 4-n-alkoxy benzoic acids and an azodye were condensed in dry cold pyridine through the corresponding acid chloride formation using thionyl chloride [15, 16]. The final azoester products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures obtained. The synthetic route to the series is shown below in scheme 1.

Where $R = C_nH_{2n+1}$ Where $n = 1,2,3,4,5,6,7,8,10,12,14,16$

4-Hydroxy benzoic acid, alkyl halide (R–X). methanol, ethanol, $NaNO_2$, phenol, HCl, 3,4,-dichloro aniline, thionyl chloride, pyridine, KOH, etc. required for synthesis were used as received, except solvents which were dried and purified prior to use.

Characterization

The compounds of the novel azoester homologous series were examined under an optical polarizing microscope equipped with a heating stage to determine their melting and transition temperatures. Some selected members were characterized by elemental analysis, infrared spectroscopy, ^{1}H NMR spectroscopy and mass spectrometry.

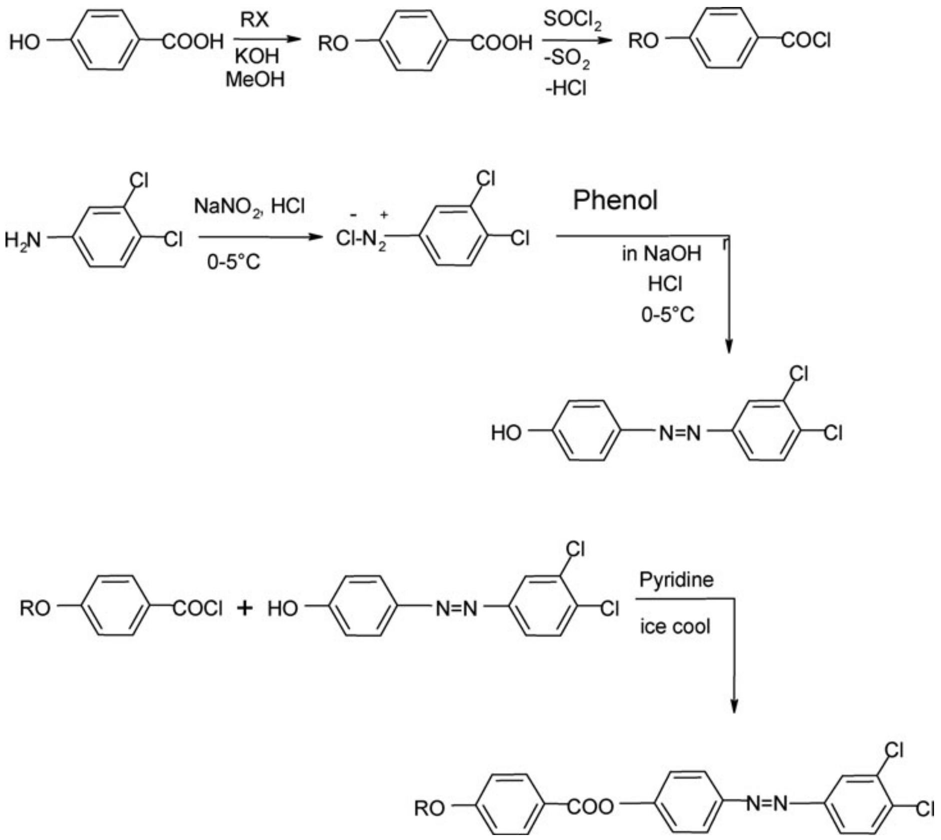
Analytical Data

Spectral Data

^{1}HNMR in ppm for the hexyloxy derivative: 0.921 [s,$-(CH_2)_n$ of $-OC_6H_{13}$], 4.052 (t, $-O-CH_2-CH_2-$ of $-OC_6H_{13}$), 7.573 and 7.615 (dd, p.sub phenyl ring),

*^{1}HNMR in ppm for the dodecyloxy derivative:*0.882 [s,$-(CH_2)_n$ of $-OC_{12}H_{25}$], 4.019 (t, $-O-CH_2–CH_2-$ of $-OC_{12}H_{25}$), 8.028, 8.071, 6.904, and 6.948 (dd, p. substituted phenyl ring).

IR in cm^{-1} for pentyloxy derivative: 3433.1 H—bonded —OH, 2929.7, 2856.4 confirms alkyl group, 1730, 1218.4, 1172.6 confirms —COO—, 1070.4 C—O of ether, 1421.4 confirms —N=N— group, 1026.1 Ar-Cl linkage, 885.3 and 823.5 confirms 1,2,4 tri. Sub aromatic ring, 840.9 confirms p-sub benzene ring.



Scheme 1. Synthetic route for the series-1.

IR in cm^{-1} for hexyloxy derivative: 3433.1 H-bonded –OH, 2927.7, 2854.5 confirms alkyl group, 1730, 1218.5, 1172.6 confirms −COO−, 1143 C–O of ether, 1421.4 confirms −N=N− group, 887.2 and 823.5 confirms 1,2,4 tri. Sub aromatic ring, 844.8 confirms p-sub benzene ring.

Mass Spectra

Mass spectra for pentyloxy derivative:

Molecular formula $C_{24}H_{22}N_2O_3Cl_2$. Calculated molecular weight 457. Practical mass observed by Mass spectroscopy 457.

Texture of the Nematic Phase by Miscibility Method

Propyloxy derivative ——————→Threaded nematic
Pentyloxy derivative ————→Schlieren nematic
Heptyloxy derivative————- Smectic-A
Tetradecyloxy derivative ———— Smectic-C

Table 2. Transition temperatures of series in °C

		Transition temperature in °C		
Compound no.	n-alkyl group ($-C_nH_{2n+1}$) (n)	Sm	N	Isotropic
1	1	—	117.0	205.0
2	2	—	162.0	199.0
3	3	—	141.0	182.0
4	4	—	152.0	174.0
5	5	—	112.0	160.0
6	6	96.0	109.0	159.0
7	7	92.0	115.0	149.0
8	8	98.0	122.0	150.0
9	10	82.0	114.0	140.0
10	12	87.0	105.0	133.0
11	14	79.0	94.0	121.0
12	16	76.0	83.0	110.0

Sm = Smectic, N = Nematic.

Results and Discussion

The novel homologous series 4-(4′-*n*-alkoxybenzoyloxy)phenyl azo-3″,4″-dichlorobenzenes consists of 12 homologues. Azo dye, 4-hydroxy phenyl azo 3′,4′ dichlorobenzene is non-mesomorphic, but on linking it with 4-n-alkoxy benzoic acid through their acid chloride yielded mesomorphic homologues from very first member of a novel series to the last hexadecyloxy member of the series. The transition temperatures are not much lower than the corresponding 4-n-alkoxy acids, but addition of a phenyl ring has raised the transition temperatures of the corresponding homologues. However, table 2 indicates that the transition temperatures of the novel homologues in some cases are lower than the corresponding n-alkoxy acids by esterification process. All the members of a series exhibit the nematic mesophase. However, the smectic mesophase formation commences from the hexyloxy homologue and continues to the hexadecyloxy homologue. Thus, the methoxy to pentyloxy homologues are only nematogenic and the hexyloxy to hexadecyloxy homologues are nematogenic, in addition to smectogenic in an enantiotropic manner. A phase diagram of the series (Fig. 1) is plotted for transition temperatures of the homologues versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal end group. Smooth curves are drawn by linking like or related points to give the solid-mesomorphic, smectic–nematic, and nematic–isotropic transition curves. The smectic–nematic and nematic–isotropic transition curves exhibit an odd–even effect up to the ninth homologue and then, from and beyond ninth homologue, the curves for odd and even merge into each other. The solid-mesomorphic transition curve adopts a zigzag path of rising and falling values and finally descend as series is ascended. Thus, the smectic–nematic and nematic–isotropic transition curves behave in a normal expected manner. The smectic–nematic transition curve is extrapolated [17, 18] for the pentyloxy homologue to determine and predict the latent transition temperatures (LTT) for the smectic phase (99.0°C), which is actually not realizable due to high crystallization tendency of the homologue concerned. The odd–even effect for the smectic and nematic transition curves disappears from and beyond the nonyloxy homologue

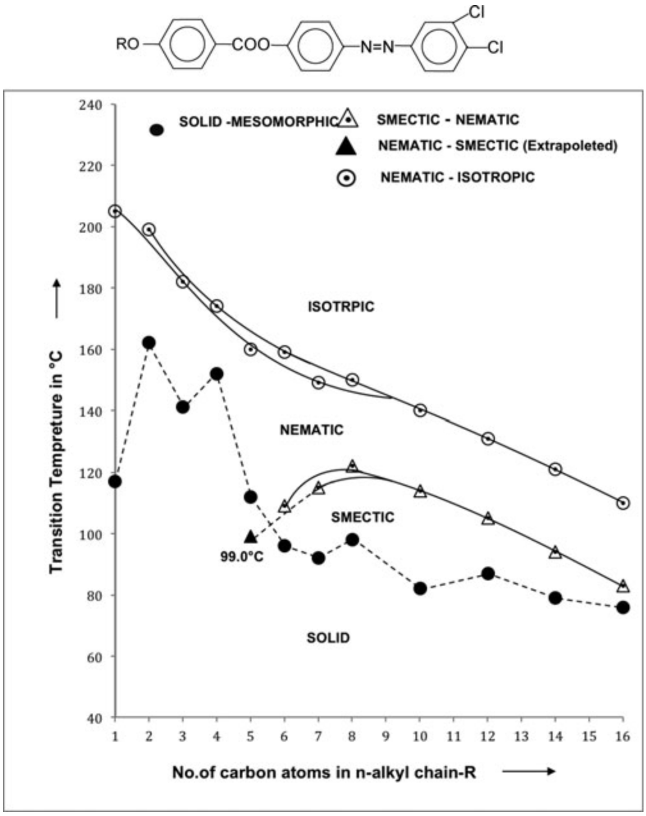


Figure 1. Phase behavior of series.

derivative. The mesomorphic behaviors and properties of the nobel series vary from homologue to homologue by extending the n-alkyl chain length in n-alkoxy terminal end group. The smectogenic and nematogenic mesophase length varies between 7°C to 24°C and 26°C to 88°C respectively with variation of isotropic temperatures between 110°C to 205°C. The thermal stabilities for smectic and nematic are 106.0°C and 156.8°C respectively with overall mesophase length varying from a minimum of 34°C at the hexadecyloxy homologue to a maximum of 88°C at the methoxy homologue. The series is fully nematogenic and partly smectogenic with middle ordered melting type and relatively wide mesophase length.

Disappearance of dimerization of 4-n-alkoxy benzoic acids by esterification is attributed to the breaking of hydrogen bonding by chemical reaction to form ester through acid chloride. The intermolecular anisotropic forces of attractions are suitable and favorably adhere as a consequence of molecular rigidity and flexibility by molecular polarity and polarizability so that all the homologues of the novel series exhibit liquid crystalline phases. The homologue derivatives from methyloxy to pentyloxy exhibit only statistically parallel orientational order of molecules to generate a nematic mesophase. Homologue derivatives from hexyloxy to hexadecyloxy additionally exhibit a smectic mesophase due to the presence of lamellar packing of molecules in their crystal lattices which causes interlinked sliding layers of molecules.

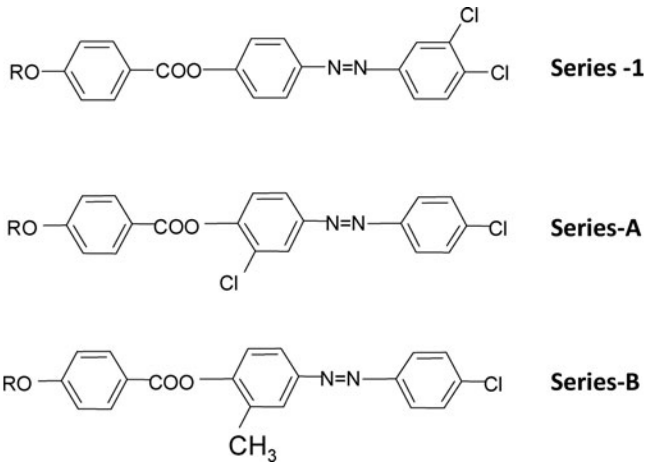


Figure 2. Structurally similar homologous series.

The exhibition of an odd–even effect, alternation of transition temperatures and variation in mesomorphic behavior from homologue to homologue of a novel series under discussion are attributed to the sequential and progressive addition of methylene unit of the left n-alkoxy terminal end group. The disappearance of the odd–even effect for higher homologues from and beyond nonyloxy homologue for smectic–nematic and nematic–isotropic transition curves is due to the coiling or bending or flexing or coupling of longer n-alkyl chain. Induced molecular polarizability by the meta substituted chloro group with a favorable length to breadth ratio, as well as end to end intermolecular attractions favorably strengthens the intermolecular adhesion which resulted in the formation of mesophases and a long range of mesomorphism as a consequence of favorable magnitudes of molecular rigidity and flexibility. The mesomorphic behavior of the novel series-1 is compared with that of two other structurally similar known series A [19] and B [20] as shown below in Fig. 2.

The molecules of homologous series 1, A, and B identically consist of three phenyl rings, bridged through $-\mathrm{COO}-$ and $-\mathrm{N}{=}\mathrm{N}-$ central group and exactly same terminal end groups viz. $-\mathrm{OR}$ and $-\mathrm{Cl}$. However, all the homologous series 1, A, and B under comparison differ with respect to their lateral substitution of the middle phenyl ring of series A and B as well as at the meta position of third phenyl ring of series-1. Therefore, the observed difference of mesomorphic behaviors and degree of mesomorphism as a consequence of differing molecular rigidity and flexibility can be assigned to the differing part of the molecular structures of series1, A, and B. Table 3 shows the average thermal stabilities for the smectic and nematic phases.

From Fig. 2 and Table 3, it is clearly seen that:

- Homologous series 1 and A are isomeric, and differ through the location of the lateral substitution of the chloro group (see Fig. 2).
- Homologous series 1 and B differ with respect to the type of lateral group ($-\mathrm{Cl}$ and $-\mathrm{CH_3}$) at third and middle phenyl rings respectively (see Fig. 2).
- The smectic–nematic or smectic–isotropic thermal stability of series A (75.75°C) is lower than the almost equal thermal stabilities of series 1 and B (≈106°C).

Table 3. Average thermal stabilities in °C

Series→	Series 1	Series A	Series B
Smectic–nematic Or Smectic-isotropic	106.0 (C_6–C_{16})	75.75 (C_{10}–C_{16})	106.6 (C_{12}–C_{16})
Commencement of smectic phase	C_6	C_{10}	C_{12}
Nematic–isotropic	156.8 (C_1–C_{16})	149.4 (C_3–C_{16})	161.5 (C_1–C_{16})
Commencement of nematic phase	C_1	C_3	C_1

- The nematic–isotropic thermal stabilities increase by 6°C or 7°C from series A to 1 to B. The nematic–isotropic, thermal stability of series 1 is lower than series B and higher than series A.
- The smectic mesophase commences earliest from the sixth member of series 1, but it commences much later from the tenth and 12th member of series A and B respectively.
- The nematic mesophase commences from the first member of series 1 and B, but it commences later from the third member of a series A.
- The mesophase length varies for the same homologue from series to series under present comparison.

Any homologous series with lateral substitution faces two opposing forces because a laterally substituted group increases intermolecular distance and decreases molecular closeness, which reduces magnitudes of intermolecular anisotropic forces of attractions, whereas, the same factor increases molecular polarizability and enhances intermolecular anisotropic forces of attractions. Thus, the net effectiveness of two opposing forces will have a significant effect on mesomorphism. The thermal stability for the smectic and nematic of series A are relatively lower than for series B and series 1. This indicates that the net effect of intermolecular adhesive forces among the molecules of series 1 is greater than a series A, i.e., the second factor due to induced polarizability predominates in series 1 while first factor predominates in case of series A out of two opposing effects. Not only thermal stabilities, but also commencement of the smectic and nematic mesophases as well as their mesophase length are also affected. Thus, only a substitution of the chloro lateral group on the middle or the third phenyl ring makes a lot of differences in lamellar packing of molecules in their crystal lattices and causes early or late emergence of sliding layered or/and statically parallel orientational arrangement of molecules in floating condition. On comparing smectogenic thermal stabilities of present series 1 and B which is almost equal or equivalent ($\approx$106°C) indicates that $-CH_3$ and $-Cl$ group polarity is almost equivalent. Therefore, though in spite of the equivalency of group polarities, the net effect of intermolecular adhesion matches with the predominancy of series 1, but it does not match with series A. Such a similarity may be attributed to differing steric effect between $-Cl$ and $-CH_3$, but their commencement of smectic mesophase may be attributed to the difference of the extent of noncoplanarity caused by the molecules due to differing molecular steric hindrance offered by tetra atomic $-CH_3$ and monoatomic $-Cl$, laterally substituted groups at the middle phenyl ring on identical position. The minor difference of nematic thermal stability between the series 1 and B, may be attributed to the individual flexibility contribution difference by $-Cl$ and

$-CH_3$ to the total molecular flexibility which shares to the overall magnitudes of anisotropic forces of intermolecular attractions and the extent of molecular noncoplanarity difference caused by $-Cl$ and $-CH_3$, i.e., lamellar packing of molecules in their crystal lattices are hindered relatively more for the molecules of series B than series1. Thus, on account of above differences among the homologous series 1, A, and B causes differences in degree of mesomorphism, commencement of smectic phase and other liquid crystal properties for the same homologue from series to series.

Conclusions

Group efficiency order derived on the basis of (i) thermal stabilities and the (ii) early commencement of mesophases. Viz. smectic and nematic for lateral substitution are as under.

1. Smectic : $-Cl$ on $\approx$ $-CH_3$ on $>$ $-Cl$ on
   Third phenyl middle phenyl middle phenyl
   Ring ring ring
   Nematic : $-CH_3$ on $>$ $-Cl$ on $>$ $-Cl$ on
   middle phenyl third phenyl middle phenyl
   Ring ring ring

2. Smectic : $-Cl$ on $>$ $-Cl$ on $>$ $-CH_3$ on
   Third phenyl middle phenyl middle phenyl
   Ring ring ring
   Nematic : $-Cl$ on $=$ $-CH_3$on $>$ $-Cl$ on
   Third phenyl middle phenyl middle phenyl
   Ring ring ring

- The presently investigated series is fully nematogenic and partly smectogenic with middle ordered melting type and relatively higher degree of mesomorphism.
- Liquid crystal behaviors of the isomeric homologous series depend upon the substitution of a same functional group on different phenyl rings or on the differing positions (ortho-meta-para) of phenyl ring or rings with respect to central group.
- Early or late commencement of smectic mesophase depends upon the extent of noncoplanarity of a molecule and the presence of lamellar packing of molecules in its crystal lattice.
- Commencement of nematic mesophase depends upon the suitable magnitudes of anisotropic forces of intermolecular end to end attractions.
- Favorable magnitudes of molecular rigidity and flexibility can induce mesomorphism.
- Liquid crystal behaviors of a substance is very sensitive and susceptible to the molecular rigidity and flexibility resulted from molecular structure of a substance.

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