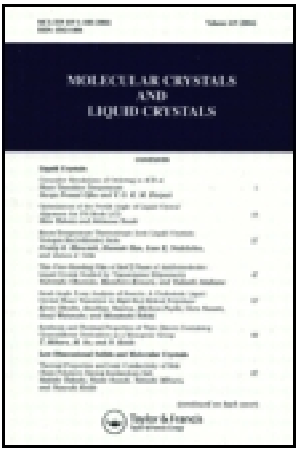

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Synthesis and Study of Novel Liquid Crystalline Homologous Series: 4-(4′-*n*-Alkoxy Benzoyloxy)-3-Methoxy Phenyl azo-3″, 4″ Dichlorobenzenes

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*The synthesis and mesomorphic properties of a new homologous series of azomesogens, 4-(4′-*n-*alkoxy benzoyloxy)-3-methoxy phenyl azo-3″,4″ dichlorobenzene is detailed. The first four members of the series are nonmesomorphic, and the other eight members are smectogenic in character. The smectic mesophase, which is exhibited montropically, commences from the pentyl to the hexadecyl derivatives. The usual odd-even effect is observed in the isotropic-smectic transition curve. The isotropic-smectic transition curve behaves in a normal manner. The smectic mesophase shows a focal conic fan shaped texture of the smectic A type. An important feature of the series is the absence of the nematic property. The thermal stability and mesomorphic characteristic are compared with two structurally similar homologous series.*

Keywords Liquid crystal; mesogens; mesomorphism; nematic; smectic

Introduction

This research of novel liquid crystal materials is aimed at enhancing the understanding of the effect of molecular structure on liquid crystal behavior of a substance depending upon molecular rigidity and flexibility [1–3]. The molecular structure in which three phenyl rings are linked through –COO– and –N=N– central bridges, to which the middle and third phenyl rings are laterally substituted by –OCH_3 and –Cl moieties in addition to a terminal n-alkoxy chain and a terminal –Cl unit. Thus, three phenyl rings bridged through two central linking groups serve as a rigid core and the remaining molecular part acts as flexible units. Therefore, liquid crystal behavior of a homologous series and its relation with molecular rigidity and flexibility of molecular structure can be correlated and discussed with reference to molecular length to breadth ratio, polarity, and polarisability.

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Experimental

Characterization

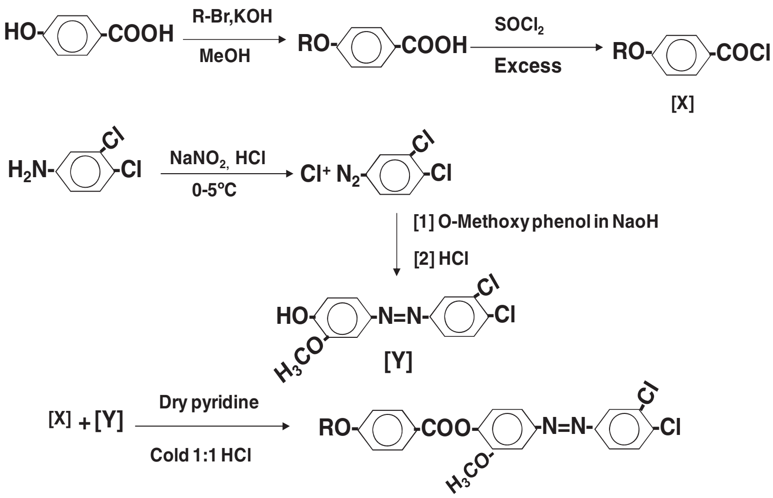
Some representative homologues of the series were selected for characterization of the structures by elemental analysis, IR, and ^{1}H-NMR techniques. Microanalysis was performed on Perkin Elmer PE 2400 CHN analyzer. IR spectra were recorded on Perkin Elmer Spectrum GX spectrometer and ^{1}H-NMR was recorded on a Bruker instrument using $CDCl_3$ as the solvent. The liquid crystalline properties were investigated using a Leitz Labourlux 12 POL polarizing microscope with a heating stage. The textures of the mesophases were determined by a miscibility method.

Synthesis

The 3,4-Dichloroaniline, sodium nitrite, 2-methoxyphenol, pyridine, thionyl chloride (GSC), 4-hydroxybenzoic acid, and n-alkyl halides (SRL, Lancaster) were used as received. The synthetic route to the novel homologous series is outlined in Scheme 1. The 4-n-Alkoxybenzoic acids and corresponding acid chlorides [x] were synthesized by a modified method of Dave and Vora [4]. The 4-Hydroxy-3-methoxy phenyl azo-3′, 4′-dichlorobenzene [y] was prepared by a known method [5]. The 4-(4′-n-Alkoxy benzoyloxy)-3-methoxy phenyl azo-3″, 4″-dichlorobenzenes were synthesized by condensing the acid chlorides [x] with 4-hydroxy-3-methoxy phenyl azo-3′, 4′-dichlorobenzene [y] in pyridine [6,7]. The azoesters were individually crystallized from alcohol until constant transition temperatures were obtained. The elemental analysis of compounds was found to be satisfactory and have been listed in Table 1.

Analytical Data

IR (cm^{-1}) for Heptyloxy Derivative. 2922, 2856.4 (–C–H aliphatic), 1732, 1255, 1166 (ester group), 1407 (–N=N–group), 1540, 1470 (–C=C– aromatic), 1107, 1203 (ether group), 842 (p-sub. benzene ring), 1066.6 (C–Cl aromatic).



Scheme 1. Synthetic route to Series 1.

Table 1. Elemental analysis for butoxy, pentyloxy, and octyloxy derivatives

		Calculated%			Observed%		
Sr. no.	Molecular formula	C	H	N	C	H	N
1	$C_{24}H_{22}N_2O_4Cl_2$	60.88	4.65	5.91	60.68	4.87	5.95
2	$C_{25}H_{24}N_2O_4Cl_2$	61.60	4.92	5.74	61.78	5.06	5.48
3	$C_{26}H_{26}N_2O_4Cl_2$	62.27	5.18	5.58	62.31	5.73	5.56

IR (cm^{-1}) for Dodecyloxy Derivative. 2920, 2850 (–C–H aliphatic), 1683, 1255, 1166 (ester group), 1419.5 (–N=N– group), 1583.4 (–C=C– aromatic), 1201, 1105 (ether group), 842 (p-sub. benzene ring), 1022 (C–Cl aromatic).

^{1}H-NMR ($CDCl_3$, Standard TMS, 400 MHz) for Heptyloxy Derivative. δppm: 0.91 (t, 3H,–CH_3) 1.33(m, 2H, –OCH_2–$\underline{CH_2}$–), 4.050 (t, 2H, –OCH_2–), 3.912 (s,–OCH_3), 6.9–8.188 (m,11H, Ar-H).

^{1}H-NMR ($CDCl_3$, Standard TMS, 400 MHz) for Decyloxy Derivatives. δppm: 0.91(t, 3H,–CH_3) 1.28(s, 2H, –OCH_2–$\underline{CH_2}$–), 4.05(t, 2H, –OCH_2–), 4.01 (s,-OCH_3), 6.898-8.186(m,11H, Ar-H).

Results and Discussion

The transition temperatures and the degree of mesomorphism are lowered by linking dimerized 4-n-alkoxybenzoic acids through their corresponding acid chlorides with 4-hydroxy-3-methoxy phenyl azo-3′,4′-dichlorobenzene by breaking of hydrogen bonding of dimerised n-alkoxy acids. The reduction in mesomorphic properties is attributed to the odd geometrical shape, which reduces the intermolecular attractions. The methoxy to butoxy homologues are nonmesomorphic while the pentyloxy to hexadecyloxy homologues are monotropic smectogenic without the exhibition of any nematogenic character. The transition temperatures of the homologues were determined by hot stage optical polarizing microscopy as recorded in Table 2, which are plotted versus the number of carbon atoms present in the n-alkoxy terminal chain. A phase diagram (Fig. 1) for the novel homologous series is obtained by joining the related points of a plot. the solid-isotropic transition curve adopts a zig-zag path of rising and falling values as the series is ascended with an overall descending tendency. The isotropic-smectic transition curve initially rises, passes through a maxima and then smoothly descends as the series is ascended up to the decyloxy homologue, but further it adopts rising tendency of about 17.0°C from and beyond the decyloxy to the hexadecyloxy derivative. The isotropic-smectic transition curve showed an odd–even effect and both curves merge into each other at the octyloxy homologue. Nematogenic character is totally absent. The mesomorphic properties varying from homologue to homologue in the same series due to the sequential addition of a methylene unit in the n-alkoxy terminal chain. The nonmesomorphic behavior of the methoxy to the butoxy homologues is due to their high crystallizing tendency because molecules are unable to withstand exposed thermal vibrations and sharply melt directly to the isotropic liquid state. The molecules of the homologues from the pentyloxy to the hexadecyloxy derivatives also melt directly to the isotropic liquid, but on supercooling, the molecules adopt a

Table 2. Transition temperatures of the homologous series: 4-(4′-n-alkoxy benzoyloxy)-3-methoxyphenyl azo-3″,4″-Dichlorobenzenes

No.	R=n-alkyl group	Transition temperatures in °C Smectic	Nematic	Isotropic
1	Methyl	–	–	171.0
2	Ethyl	–	–	136.0
3	Propyl	–	–	107.0
4	Butyl	–	–	94.0
5	Pentyl	(47.0)*	–	121.0
6	Hexyl	(57.0)*	–	88.0
7	Heptyl	(61.0)*	–	98.0
8	Octyl	(68.0)*	–	138.0
9	Decyl	(62.0)*	–	101.0
10	Dodecyl	(66.0)*	–	116.0
11	Tetradecyl	(72.0)*	–	109.0
12	Hexadecyl	(79.0)*	–	89.0

( )*Monotropic.

sliding layered molecular arrangement in a floating condition monotropically and showed smectogenic character. Thus, the magnitude of the anisotropic intermolecular forces of attraction happens to be favorable to display smectogenic character, but not for nematogenic behavior. The mesomorphic properties of the novel homologous series-1 are compared with structurally similar homologous series [A] [8] and series [B] [9] as shown in Fig. 2.

Homologous series 1, A, and B are identical with respect to three phenyl rings, molecular linearity, n-alkoxy terminal chains, the lateral –OCH_3 group, and the –COO– and –N=N– linking groups. However, they differ in that the lateral –Cl unit is missing in series A and B, and the terminal –Cl unit of series 1 is replaced with ethanoyl and methyl in series A and B respectively. Therefore, variations in mesomorphic properties, that is, extent of mesomorphism exhibited, mesophase range, commencement of mesophase formation, thermal stability, extent of noncoplanarity, and end to end intermolecular attractions are attributed to the varying end groups of fixed polarity for the homologous series 1, A, [8] or B [9]. The geometrical shape of all the series under comparison and discussion (Fig. 2) is rod-like and linear. The different structural units in series 1, A, and B will cause variation in molecular rigidity and flexibility [1–3], the length to breadth ratio, the ratio of the polarity to polarisability, the magnitude of anisotropic intermolecular forces of attraction, which will affect mesophase formation and the commencement of the mesophase or mesophases. The variation of mesomorphic properties can then be linked to the molecular structural changes [10]. Table 3 represents the average thermal stabilities of the mesophase and the commencement of the mesophase for series under comparison.

The average thermal stability of titled series 1 is the lowest and that of series A is the highest amongst the three series under comparison. The –$COCH_3$ end group more highly polar than the dichloro and –CH_3 units, this also affects the molecular rigidity and flexibility, [1–3] which are directly related to magnitudes of aniosotropic intermolecular forces of attraction. Thus, molecules of series A can resist the exposed thermal vibrations

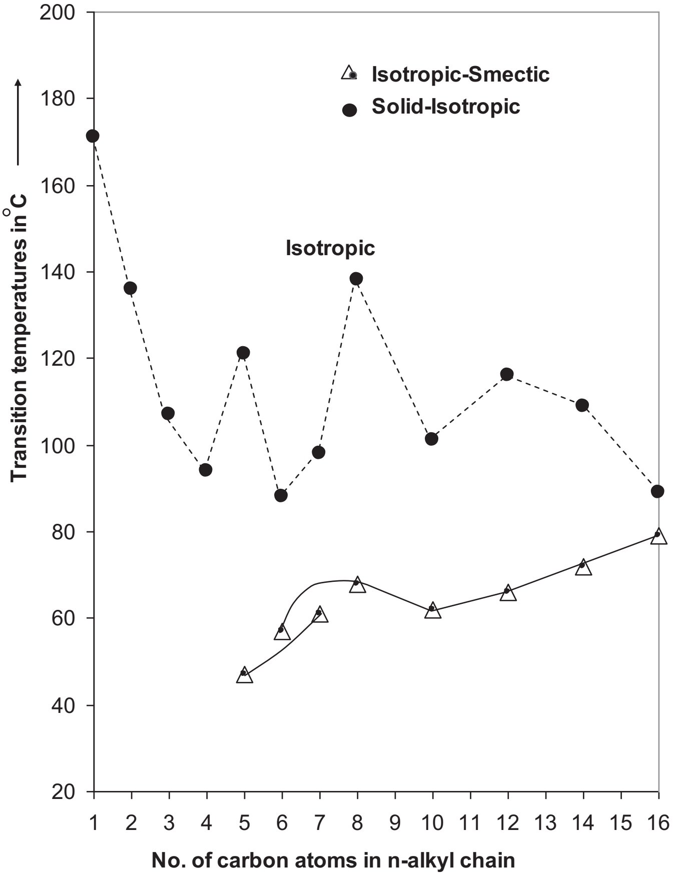
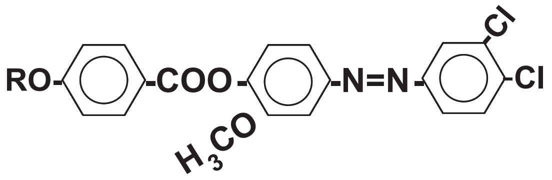


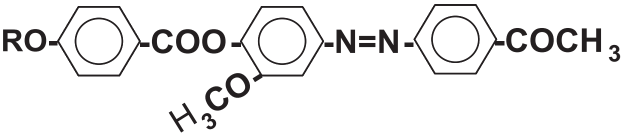
Figure 1. Phase behavior of the series.

relatively more efficiently causing end to end attractions and attractions due to lamellar packing as compared to the series 1 and B. Homologous series 1 and B individually are only smectogenic and only nematogenic respectively while series A exhibits smectogenic mesophase before the nematogenic mesophase. The nematic thermal stability of series B is highest amongst the series under comparison. However, the total mesophase range (i.e., smectic + nematic) of series A exceeds the mesophase range of series B. The commencement of the smectic mesophase takes place in series 1 from the pentyloxy homologue while it commences from the dodecyloxy homologue in series A and, it does not occur until the final homologue of series B. The extent of molecular noncoplanarity caused by the –$COCH_3$ terminal end group and dichloro group differs appreciably due to penta atomic –$COCH_3$ group and monoatomic –Cl group. Thus, early or late commencement of smectic phase depends upon the extent of noncoplanarity caused by a molecule. The molecular noncoplanarity caused by the common presence of –COO–, and –N=N–, central bridges including the common –OCH_3 and n-alkoxy terminal end group for the same homologue which remains unaltered for all the three series under comparison. However, variation arises due to right handed terminal end group –Cl, –$COCH_3$, and –CH_3 of fixed polarities. In all other respects except the central bridges which are azo –N=N– and carboxy



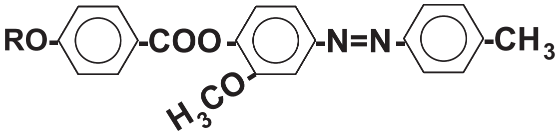
Series 1

4-(4’-n-alkoxy benzoyloxy)-3- methoxy phenyl azo- 3”,4”- dichlorobenzene.



Series-A

4-(4’-n-alkoxy benzoyloxy) -3-Methoxyphenylazo - 4”-Acetylbenzenes.



Series-B

4-(4’-n-alkoxy benzoyloxy) -3-Methoxyphenylazo - 4”-Methylbenzenes

Figure 2. Structurally similar homologous series.

–COO– for the series under comparison are closely similar to each other. The oxygen atom of the central –COO– group bump into the nonbonded sides of the adjacent hydrogen atom of the aromatic phenyl ring which will cause considerable strain on the molecule. Consequently, a twist around the C–O bond will occur forcing the phenyl ring out of the plane of the molecule. Thus, the coplanarity of the molecule is reduced to some extent making them broader. The other central bridge –N=N– present on the major axis of the core certainly endows the molecules with co-planarity. Moreover, the extent of coplanarity variation caused by the varying –Cl, $–COCH_3$, and $–CH_3$ as right terminal end groups of fixed polarities. On account of these differences the smectic–isotropic or vice versa thermal stabilities and the commencement of smectic phase differs. The isotropic–smectic transition temperatures range between 47°C and 79°C from the pentyloxy homologue to the hexadecyloxy homologue. These irreversible transition temperatures gradually decreases from the pentyloxy derivatives to the decyloxy derivatives and then smoothly increases from the dodecyloxy to the hexadecyloxy homologue below the melting point on cooling. The melting point of the mesophase lies between 121°C and 89°C. Thus, the novel series 1 is a low melting type series whose mesomorphic character starts to appear between 47°C and 79°C.

Table 3. Average thermal stabilities in °C

Series	I	A	B
Smectic—isotropic or isotropic—smectic	1.0 to 2.0	112.0	–
smectic—nematic	(few degrees)		
	(C_5–C_{16})	(C_{12}–C_{16})	
	(C_5–C_{16})		
Commencement of smectic phase	C_5	C_{12}	–
Nematic–isotropic or isotropic–nematic		124.8	134.73
	–	(C_6–C_{16})	(C_5–C_{14})
Commencement of nematic phase	–	C_6	C_5

Conclusions

(1) The novel series exhibits only smectogenic character below isotropic temperature irreversibly.

(2) Molecular rigidity and flexibility tend to create a favorable anisotropic environment to induce smectogenic character for the molecules of odd fitting shaped geometry like the dichloro end group.

(3) End to end attractions are not favored comfortably at any temperature below the melting point.

(4) The novel series is of the low melting type. Widening or broadening of a molecule through lateral substitution can reduce transition temperatures and the degree of mesomorphism, if the molecular polarisability is poorly effective.

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