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Homologous Series of Azomesogens: 4-(4′-n-Alkoxy Benzoyloxy)-3-Chloro Phenylazo-2′′-Chlorobenzenes

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The increasing demand of liquid crystalline materials in various fields of applications has inspired the present investigation. A mesogenic homologous series, 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2′′-chlorobenzenes, of twelve homologues has been synthesized. All the members of the series are either monotropically or enantiotropically mesogenic except the first member of the series. The nematic mesophase commences from the ethyl derivative and goes to the dodecyl derivative of the series. Tetradecyl and hexadecyl derivatives show a monotropic smectic phase. The nematic mesophase shows a threaded texture, while the smectic mesophase shows a focal-conic-fan-shaped texture. Polymesomorphism is not displayed by any member of the series. The solid-isotropic or solid-mesomorphic transition curve follows a zigzag path of falling and rising tendency as the series is ascended. The usual odd–even effect is observed in the nematic–isotropic transition curve with alternation of transition temperature. Transition temperatures are observed through a polarizing microscope with a heating stage. Analytical data support the structure of the molecules. The average thermal stability and mesomorphic properties of the series are compared with structurally similar other homologous series. Group efficiency order for the smectic and the nematic phases is suggested.

Keywords Azoester; liquid crystal; nematic; smectic

Introduction

A vast number of new homologous series have been reported in the literature. Terminal or lateral substituents play an important role in promoting or depressing mesomorphic properties in mesogens. Generally the terminal or lateral substituent comprise of either a homologue alkoxy or alkyl group or a compact unit such as nitro, cyano, and halogen. A number of homologous series that have a rod-like linear molecular structure were synthesized by researchers [1–14]. In the present study, a new homologous series containing three phenyl rings in the main core linked through azoester central linkages in addition to n-alkoxy and chloro terminals, respectively, and substituted by a lateral chloro substituent on the middle phenyl ring has been synthesized in order to study their effect on mesomorphic properties.

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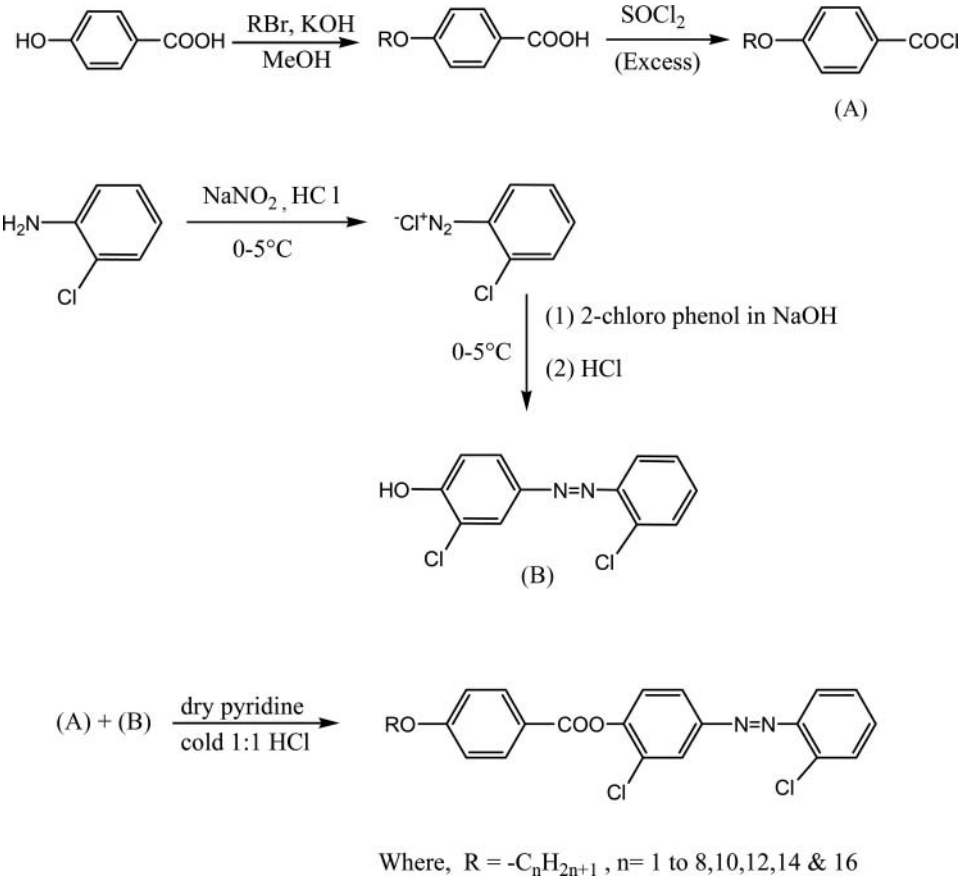
Experimental

Characterization

Microanalysis of the compound was performed on Perkin Elmer PE 2400 CHN analyzer, IR spectra were recorded on Perkin Elmer spectrum, and ^{1}H-NMR spectra were obtained with Bruker spectrometer using CDCl3 as solvent. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL Polarizing microscope with a heating stage.

Synthesis

2-Chlorophenol, 2-chloroaniline, sodium nitrate, pyridine, thionyl chloride, 4-hydroxy benzoic acid, and n-alkyl halides were used directly as received. The solvents were dried and distilled before use. The synthetic route to the present series is illustrated in the Scheme 1. 4-n-alkoxy benzoic acid and corresponding 4-n-alkoxy benzoyl chloride (A) was synthesized by the modified method of Dave et al. [15]. 4-Hydroxy-3-chloro phenylazo-2′-chlorobenzenes (B) were prepared by a known method [16]. 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2″-chlorobenzenes were synthesized by condensing 4-n-alkoxy benzoyl



Scheme 1. Synthetic route to series (1) compounds.

Table 1. Elemental analysis for 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2′′-chlorobenzenes

Sr. no.	R = n-alkyl chain	Molecular formula	Calculated %			Observed %		
			C	H	N	C	H	N
1	Methyl	$C_{20}H_{14}N_2O_3Cl_2$	59.85	3.49	6.98	59.72	3.41	6.90
2	Ethyl	$C_{21}H_{16}N_2O_3Cl_2$	60.72	3.85	6.75	60.68	3.80	6.72
3	Propyl	$C_{22}H_{18}N_2O_3Cl_2$	61.54	4.19	6.53	61.59	4.10	6.59
4	Butyl	$C_{23}H_{20}N_2O_3Cl_2$	62.30	4.51	6.32	62.38	4.58	6.38
5	Pentyl	$C_{24}H_{22}N_2O_3Cl_2$	63.02	4.81	6.13	63.11	4.80	6.19
6	Hexyl	$C_{25}H_{24}N_2O_3Cl_2$	63.69	5.09	5.94	63.60	5.19	5.88
7	Heptyl	$C_{26}H_{26}N_2O_3Cl_2$	64.33	5.36	5.77	64.30	5.22	5.70
8	Octyl	$C_{27}H_{28}N_2O_3Cl_2$	64.93	5.61	5.61	64.88	5.60	5.68
9	Decyl	$C_{29}H_{32}N_2O_3Cl_2$	66.03	6.07	5.31	66.18	6.10	5.35
10	Dodecyl	$C_{31}H_{36}N_2O_3Cl_2$	67.03	6.49	5.04	67.11	6.40	5.18
11	Tetradecyl	$C_{33}H_{40}N_2O_3Cl_2$	67.92	6.86	4.80	67.99	6.81	4.69
12	Hexadecyl	$C_{35}H_{44}N_2O_3Cl_2$	68.73	7.20	4.58	68.66	7.90	4.50

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chlorides (A) with 4-hydroxy-3-chloro phenylazo-2′-chlorobenzene (B) in pyridine [8]. The azoesters were crystallized from alcohol until constant transition temperatures were obtained.

Data

The elemental analysis of compounds found to be satisfactory (see Table 1).

IR for n-pentyloxy derivative (vmax · cm^{-1}): 3066 (−C−H aromatic stre.), 2945, 2878, 1464.8, 1385 (alkyl group), 1729.1, 1226.6 (ester group), 1600 (−N=N− group), 1579.6 (−C=C−aromatic stre.), 1063 (ether group), 846.7 (p-sub. benzene ring), 763.8 (tri sub.benzene ring), 1120.6 (C−Cl aromatic).

IR for n-Decyloxy derivative (vmax · cm^{-1}): 3066 (−C−H aromatic stre.), 2933, 2856, 1468.7, 1351 (alkyl group), 1733.9, 1230.5 (−COO− group), 1605 (−N=N− group), 1583.4 (−C=C− aromatic stre.), 1066.6 (−O− ether group), 838 (p-sub. benzene ring), 757 (tri sub. benzene ring), 1118.6 (C−Cl aromatic).

^{1}H-NMR ($CDCl_3$, standard tetramethylsilane [TMS]) for n-propyloxy derivative, δ ppm: 1.07 (t, 3H, $-CH_3$), 1.88 (m, 2H, $-OCH_2-\underline{CH_2}-$), 4.03 (t, 2H, $-OCH_2-$), 6.98–8.36 (m, 11H, Ar−H).

^{1}H-NMR ($CDCl_3$, standard TMS) for n-butyloxy derivative, δ ppm: 1.0 (t, 3H, $-CH_3$), 1.54 (m, 2H, $-CH_2-$), 1.82 (m, 2H, $-OCH_2-\underline{CH_2}-$), 4.07 (t, 2H, $-OCH_2-$), 6.97–8.22 (m, 11H, Ar−H).

Results and Discussion

4-Hydroxy-3-chloro phenylazo-2′-chlorobenzene is not a liquid crystalline substance but the linking of a phenyl ring bridged through −COO− and an n-alkoxy terminal chain increases the length of the molecules favoring lateral intermolecular attractions and

Table 2. Transition temperatures for 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2″-chlorobenzenes

Sr. no.	R = n-alkyl chain	Transition temperature (°C)		
		Smectic	Nematic	Isotropic
1	Methyl	—	—	152.0
2	Ethyl	—	138.0	260.0 (d)
3	Propyl	—	87.0	141.0
4	Butyl	—	(84.0)	117.0
5	Pentyl	—	(90.0)	102.0
6	Hexyl	—	(76.0)	104.0
7	Heptyl	—	(74.0)	76.0
8	Octyl	—	70.0	72.0
9	Decyl	—	(73.0)	83.0
10	Dodecyl	—	55.0	73.0
11	Tetradecyl	(52.0)	—	69.0
12	Hexadecyl	(64.0)	—	66.0

Note: Values in parenthesis indicate monotropy.

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polarizability. This results in the molecules of the series, 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2″-chlorobenzenes, exhibiting mesomorphic characteristics. Twelve homologues of the series were synthesized and evaluated for their mesomorphic properties. The transition temperatures of the present homologous series are recorded in Table 2. All the members of the series are mesomorphic except the first member of the series, which is nonmesogenic. The second to the twelfth homologue of the series display a nematic mesophase, while the tetradecyl and the hexadecyl derivatives of the series display only a smectic mesophase. The ethyl, propyl, octyl, and dodecyl derivatives are enantiotropic nematic, while the butyl to the heptyl and the decyl derivatives are monotropic nematic. The tetradecyl and the hexadecyl derivatives are monotropic smectic. Polymesomorphism is not displayed by any member of the series. The second member of the series does not melt sharply at a definite temperature but decomposes at higher temperature. The transition temperatures are plotted versus the number of carbon atoms in the n-alkoxy chain of the homologues. The phase diagram is shown in Fig. 1. The solid-mesomorphic or solid-isotropic transition curve follows a zigzag path of falling and rising tendency as the series is ascended. The solid-isotropic or solid-mesomorphic transition curve steeply falls from the first to the third member and rises to the fourth homologue. Thereafter the level to the fifth homologue again falls up to the eighth homologue with negligible rise at the sixth homologue and then rises at the tenth homologue of the series. Then it falls at the twelfth homologue with a rise at the fourteenth homologue. Thereafter it falls to the sixteenth homologue of the series. The zigzag path of the solid-isotropic or solid-mesomorphic curve is due to the sequential addition of methylene units in the n-alkoxy chain. This causes differences in the length and linearity of the molecules and hence the difference in end-to-end intermolecular forces of attractions. It is directly related to the magnitude of cohesive forces arising out of odd and even numbers of carbon atoms in the n-alkoxy terminal chain. Thus overall end-to-end intermolecular forces of attractions are altered from homologue to homologue in the same series for odd and even member of the series. The nematic–isotropic

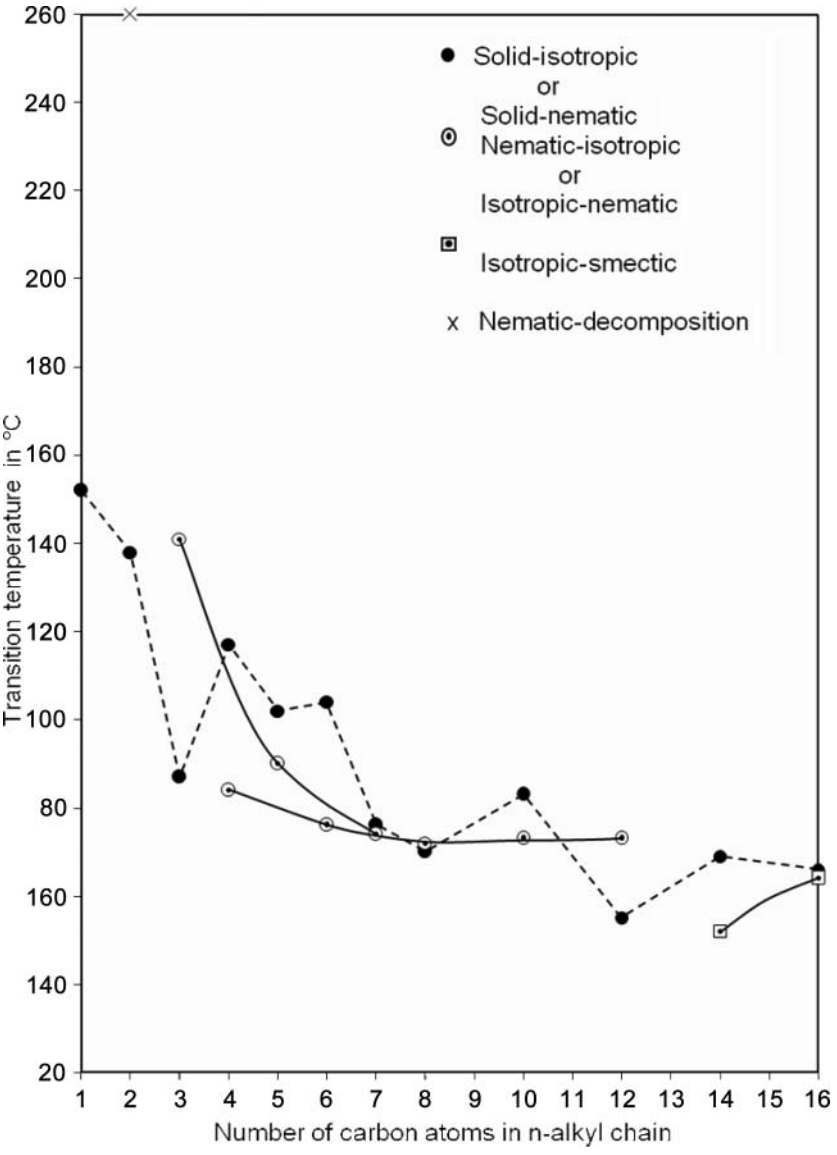

Figure 1. 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2′′-chlorobenzenes.

(or vice versa) transition curve for odd and even members follows a smooth gradual falling tendency from the third to the twelfth homologue of the series in the usual manner. Both curves (odd and even) merge to the main stream of the nematic–isotropic (or vice versa) transition curve at the eighth homologue. Thus the usual odd–even effect is observed in the nematic–isotropic (or vice versa) transition curve. The isotropic–smectic transition curve rises steeply as the series ascended. The nematic phase appeared as a threaded type of texture as judged directly by visualizing the sample of the homologues in a field of view of the hot-stage polarizing microscope. The texture of the smectic mesophase is focal conic fan shaped. Thus the homologous series under present investigation can be considered a middle ordered melting type with a mesophase range minimum of 2°C at the eighth

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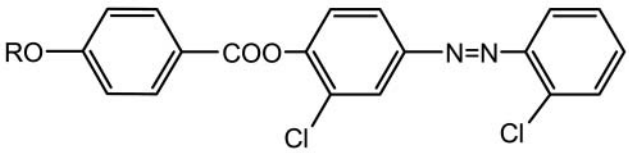
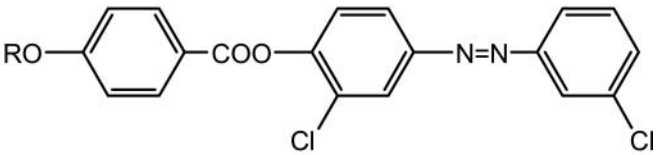
member and maximum of 122°C at the second member for the series. The first member of the homologous series is nonmesogenic because of its high crystallizing tendency and the incapability of intermolecular cohesion forces to maintain a statistically parallel orientation or to form an ordered layered arrangement of molecules. Enantiotropic or monotropic nematic mesomorphism is exhibited by the remaining members of the series due to the statistically parallel orientations of molecules with end-to-end attractions. Late or early commencement of the smectic mesophase in the series is related to the extent noncoplanarity caused by the molecule. Thus, the commencement of the smectic mesophase takes place later at tetradecyl and hexadecyl derivatives. The nematic–isotropic (or vice versa) transition curve shows alternation of transition temperatures from the third to the seventh homologue but alternation diminishes as the series ascended because higher homologues are of even number, and in the case of higher homologues, the longer n-alkoxy chain may be coiled or coupled to lie in the line with major axis of the core. Thus, end-to-end contact would then ultimately be the same for odd and even homologues.

The mesomorphic characteristics of the homologous series (1) are compared with the structurally similar homologous series (A) and (B) (see Fig. 2). The homologous series (1), (A), and (B) possess three phenyl rings linked through —COO— and —N=N— central bridges, and an n-alkoxy terminal chain at the para position, with chloro unit at the ortho position to —COO— group at the middle phenyl ring as common identical features, with the only uncommon part being another —Cl unit, which is positioned at ortho, meta, and para with respect to —N=N— at the third phenyl ring in the series (1), (A), and (B), respectively. Therefore, mesogenic behavior and degree of mesomorphism of the series under comparison is varied due to the variation in the position of the —Cl unit at the third

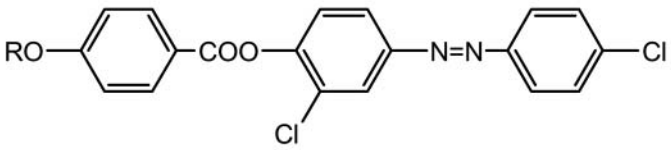
(1) 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-2″-chlorobenzenes



(A) 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-3′-chlorobenzenes [04]



(B) 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenylazo-4′-chlorobenzenes [05]



where, R = $-C_nH_{2n+1}$, n = 1--8, 10, 12, 14, & 16.

Figure 2. Relative characteristic of series.

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Table 3. Average thermal stabilities in °C

Series	1	A	B
Smectic–Isotropic or Smectic–Nematic	67.5 (C_{14}-C_{16})	—	75.75 (C_{10}-C_{16})
Commencement of smectic phase	C_{14}	—	C_{10}
Nematic–Isotropic or Isotropic–Nematic	114.22 (C_2-C_{12})	130.6 (C_6-C_{14})	149.4 (C_3-C_{16})
Commencement of nematic phase	C_2	C_6	C_3

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phenyl ring. The average thermal stabilities of the series (1), (A), and (B) are given in Table 3. The nematic–isotropic average thermal stability of the homologous series (B) is the highest amongst the group of the homologous series (1), (A), and (B) (see Table 3). On comparing the nematic–isotropic average thermal stabilities for the series (1) and (A), the meta-substituted derivative has stronger intermolecular forces of attractions than the ortho-substituted derivative, though length to breadth ratio being same. This may be due to the distance of location of −Cl unit at the third phenyl ring from the −N=N− central bridge. Thus group efficiency order derived for smectic and nematic for the −Cl group with respect to its position is as follows.

Smectic group efficiency order (Terminal substitution): −Cl (para) > −Cl (ortho) > −Cl (meta)

Nematic group efficiency order (Terminal substitution): −Cl (para) > −Cl (meta) > −Cl (ortho)

Conclusion

A new homologous series of azoester mesogens with a terminal −Cl (ortho) unit has been synthesized for the study of their mesomorphic properties. The study indicated that the position of lateral −Cl (ortho) unit adversely affects the mesophase thermal stabilities. Meta-substituted −Cl unit does not allow formation of smectic mesophase even in the monotropic condition.

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