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Synthesis and Characterization of a Novel Azoester Homologous Series

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An azoester homologous series of 4-(4′-n-alkoxybenzoyloxy) 3-methylphenyl azo-2′′-chloro-3′′-methyl benzenes consisting of 12 homologues was synthesized. The methoxy to pentyloxy homologues are nonmesogenic, the hexyloxy to dodecyloxy homologues are monotropic nematic and the tetradecyloxy to hexadecyloxy homologues are enantiotropic nematic. The textures of the nemetic phase are of the threaded or schlieren type. Transition curves showing phase behavior in a phase diagram behave in normal manner, with the exception of the last enantiotropic homologue. An odd–even effect is observed for the nematic-isotropic transition curve. Thermal phase transitions were observed through an optical polarizing microscope equipped with a heating stage. Analytical and spectral data support the molecular structures of the homologue molecules. Smectogenic character is totally absent from all the novel homologues. The average thermal stability for the nematic phase is 121.5 °C. Mesogenic properties of the present novel series are compared with other structurally similar known series.

Keywords Liquid crystal; mesogens; monotropy; nematic; smectic

Introduction

Substances with long linear narrow lath like shapes and appropriately substituted polar end groups or/and laterally substituted group or groups have [1] the potential to exhibit mesogenic behavior as a consequence of favorable molecular rigidity and flexibility [2–4]. The present investigation is aimed at understanding and establishing the influence of molecular structure on mesogenic behavior of a substance by constructing a molecular architecture, which consists of three phenyl rings bonded through −COO− and −N=N− central bridges as the rigid core, and the left n-alkoxy terminal end group and laterally substituted methyl and chloro units to act as the flexible section of the azoester [5] molecule.

Experimental

Synthesis

Dimerized 4-n-alkoxy benzoic acids were synthesized by reacting suitable alkyl halides (R–X) with 4-hydroxy benzoic acid in methanol by a modified method of Dave and Vora [6].

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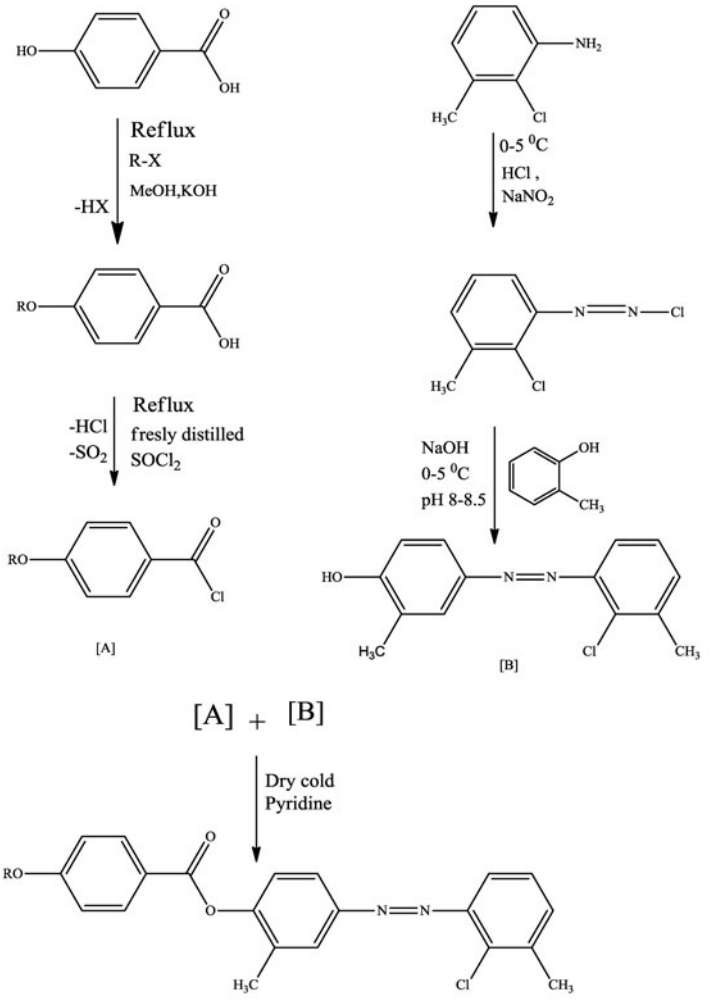

4-(4'-n-Alkoxy benzoyloxy)3-methyl phenylazo-2"-chloro-3"-methyl benzenes

Where, R= C_nH_{2n+1} and n= 1to8,10,12,14and 16.

Scheme 1. Synthetic route to the series.

4-Hydroxy 3-methyl phenyl azo-2′-chloro-3′-methyl benzene as the azo dye was prepared by the diazotization of 4-hydroxy 3-methyl benzene with 2-chloro-3-methyl aniline by the usual established method [7]. 4-n-Alkoxy benzoic acid and the azo dye were condensed in dry cold pyridine [8, 9]. The final product azoesters were individually decomposed, filtered, washed, dried, and crystallized until constant transition temperature obtained. The synthetic route to the series is shown in Scheme. 1.

4-Hydroxy benzoic acid, alkyl halides, thionyl chloride, methanol, ortho-cresol, 2-chloro-3-methyl aniline, pyridine, ethanol, KOH, NaOH, and glacial acetic acid required for synthesis were used as received, except solvents which were purified and dried prior to use.

Table 1. Elemental analysis for (1) Methyloxy (2) Butyloxy (3) Heptyloxy derivatives.

		Elements % found			Elements % calculated		
Sr. no.	Molecular formula	C	H	N	C	H	N
1	$C_{22}H_{19}ClN_2O_3$	66.85	4.80	7.15	66.92	4.85	7.09
2	$C_{25}H_{25}ClN_2O_3$	68.80	5.82	6.40	68.72	5.77	6.41
3	$C_{28}H_{31}ClN_2O_3$	65.65	6.40	5.92	70.21	6.52	5.85

Characterization

The structures of compounds of this series were identified using various analytical techniques such as ^{1}HNMR, mass spectrometry, IR spectroscopy, and Elemental analysis. All analytical data supported the novel structures. Elemental analysis data was obtained using a EuroEA Elemental Analyser, and as shown in Table 1 are in good agreement with the theoretical values. IR data were determined using a SIMADZU-FTIR-8400 spectrometer. ^{1}HNMR spectra were recorded using a BRUKER spectrometer instrument in DMSO-d_6 solvent. The molecular ion peak obtained from the experimental EI-MS data matched with the molecular mass using a SHIMADZU-GC-MS, Model No.QP-2010 spectrometer.

Elemental Analysis

Spectral Data

NMR in ppm for the Ethyloxy Derivative. 1.36–1.39 Triplet, (3H,$-CH_3$ of $-OC_2H_5$ group), 2.29 Singlet (3H$-CH_3$ of phenyl ring ortho to $-COO-$ group), 2.73 singlet, ($-CH_3$ of phenyl ring meta to $-N{=}N-$ group), 4.17 Triplet ($-OCH_2$ of $-OC_2H_5$), 7.13–;8.14 (10 Aromatic proton in substituted phenyl ring) (Table 1). The NMR data support the molecular structure.

NMR in ppm for the Octyloxy Derivative. 0.85–0.88 Triplet, (3H,$-CH_3$ of $-OC_8H_{17}$ group), 1.23–1.77 $(-CH_2-)_6$ group of OC_8H_{17}, 2.28 Singlet(3H$-CH_3$ of phenyl ring ortho to $-COO-$ group), 2.71–2.76 multiplet, ($-CH_3$ of phenyl ring meta to $-N{=}N-$ group), 4.09–4.12 Triplet ($-OCH_2$ of $-OC_8H_{17}$), 7.13–8.18 (10 Aromatic proton in substituted phenyl ring). The NMR data support the molecular structure.

NMR in ppm for the Dodecyloxy Derivative. 0.86, Triplet, (3H,$-CH_3$ of $-OC_{12}H_{25}$ group), 1.26–1.45 $(-CH_2-)_9$ group of $-OC_{12}H_{25}$, 2.28 Singlet (3H$-CH_3$ of phenyl ring ortho to $-COO-$ group), 2.67 multiplet, ($-CH_3$ of phenyl ring meta to$-N{=}N-$ group), 4.11 Triplet, ($-OCH_2$ of$-OC_{12}H_{25}$), 7.13–8.15 (10 Aromatic proton in substituted phenyl ring). The NMR data support the molecular structure.

IR in cm^{-1} for the Propyloxy Derivative. 628 and 763 $(-CH_2-)_n$ group of $-OC_3H_7$), 810 (1,2 disubstituted phenyl ring), 848 (p-substituted phenyl ring), 1165 (C$-$O of $-OC_3H_7$), 1236, 1263&1643 ($-COO-$ ester group), 1602 ($-N{=}N-$), 2870 and 2933 (C$-$H Str. of $(-CH_2-)_n$ group), 3076 (C$-$H Str. of phenyl ring), 1728 (>C =O group), 692 (C$-$Cl), 717&848 (para, ortho and meta substituted phenyl ring). The IR data support the molecular structure.

IR in cm^{-1} for Tetradecyloxy Derivative. 650 and 771,($-CH_2-$)$_n$ group of $-OC_{14}H_{29}$, 810 (1, 2 disubstituted phenyl ring), 850 (p-substituted phenyl ring), 1166 (C−O of $-OC_{14}H_{29}$), 1257, 1280&1643,(−COO− ester group), 1604 (−N=N−), 2848 and 2916 (C−H Str. of ($-CH_2-$)$_n$ group), 3068 (C−H Str. of phenyl ring), 1730 (>C =O group), 694 (C−Cl), 720 and 844 (para, ortho, and meta substituted phenyl ring). The IR data support the molecular structure.

IR in cm^{-1} for the Hexadecyloxy Derivative. 719 and 617,($-CH_2-$)$_n$ group of$-OC_{16}H_{33}$, 820 (1,2 disubstituted phenyl ring), 848 (p-substituted phenyl ring), 1166 (C−O of$-OC_{16}H_{33}$), 1253, 1288 and 1643 (−COO− ester group), 1604 (−N=N−), 2848 and 2918 (C−H Str. of ($-CH_2-$)$_n$ group), 3061 (C−H Str. of phenyl ring), 1730 (>C=O group), 646 (C−Cl), 769, 848 and 692 (para, ortho, and meta substituted phenyl ring). The IR data support the molecular structure.

Mass Spectra of the Pentyloxy Derivative. m/z (rel.int%): 450$(M)^+$

Mass Spectra of the Hexyloxy Derivative. m/z (rel.int%): 464 $(M)^+$

Mass Spectra of the Decyloxy Derivative. m/z (rel.int%): 521$(M)^+$

Results and Discussion

4-n-Alkoxy benzoic acids are dimeric, which on condensation with 4-hydroxy-3-methyl azo 2′-chloro-3′-methyl benzene yielded 4-(4′-n-alkoxy benzoyloxy)-3-methyl phenyl azo-2′′-chloro-3′′-methyl benzene homologue derivatives through the appropriate acid chlorides. The transition temperatures were determined by an optical polarizing microscope equipped with a heating stage (Table 2). The homologous series consists of 12 homologues

Table 2. Transition Temperatures in °C

		Transition temperature in °C		
Compound no.	n-alkyl C_nH_{2n+1} chain (n)	Sm	N	Isotropic
1	Methyl	—	—	146.0
2	Ethyl	—	—	126.0
3	Propyl	—	—	113.0
4	Butyl	—	—	105.0
5	Pentyl	—	—	101.0
6	Hexyl	—	(74.0)	96.0
7	Heptyl	—	(72.0)	90.0
8	Octyl	—	(79.0)	84.0
9	Decyl	—	(83.0)	86.0
10	Dodecyl	—	(71.0)	83.0
11	Tetradecyl	—	96.0	118.0
12	Hexadecyl		94.0	125.0

( ) indicate monotropy.
Sm – Smectic, N – Nematic.

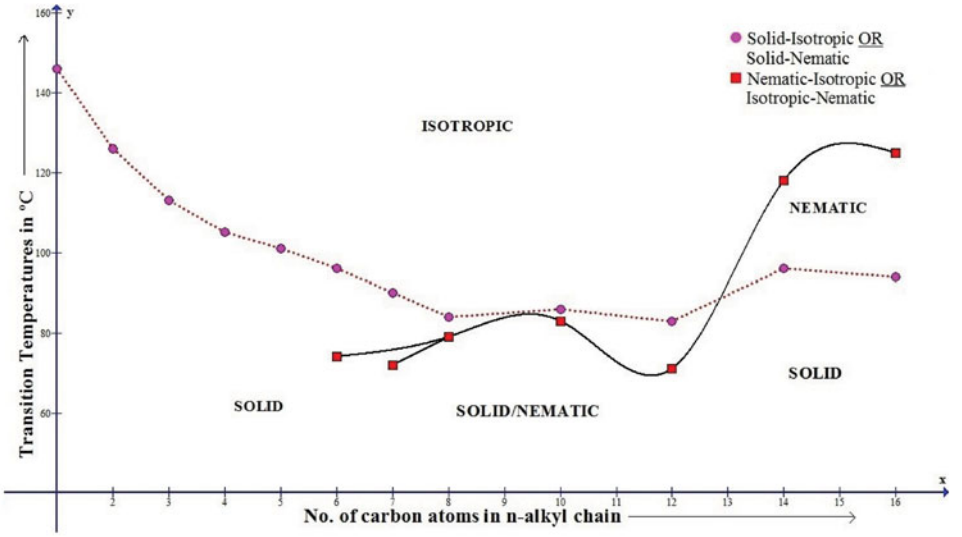

Figure 1. Phase behavior of series.

whose mesogenic property commences from the hexyloxy homologue and continued as a monotropic nematic phase up to the dodecyloxy homologue. Then, enantiotropic nematic mesophase formation is exhibited by the tetradecyloxy and hexadecyloxy homologues. None of the homologues exhibit smectogenic behavior. The methoxy to pentyloxy homologues are nonmesogenic. The textures of the nematic mesophase are of the threaded or schlieren type. Transition temperatures of homologues were plotted against the number of carbon atoms present in n-alkyl chain of a left n-alkoxy terminal end group. A phase diagram [Fig. 1] is obtained by smooth linking of like or related points forming the solid-isotropic or nematic and nematic-isotropic (isotropic-nematic) transition curves. An odd–even effect is observed for the nematic-isotropic transition curve. The mesogenic behavior of the novel series varies from homologue to homologue. The average nematic-isotropic thermal stability for the novel series is 121.5°C. Thus, the present novel series is mainly monotropic nematogenic without exhibition of smectogenic character. The solid-isotropic or nematic transition curve continuously descends up to the octyloxy homologue without adopting a zigzag path of rising and falling values. However, a zigzag path of rising and falling is adopted from and beyond the octyloxy homologue. The nematic-isotropic (or vice versa) transition curve initially rises and then descends for the monotropic homologues up to the dodecyloxy homologues, but, then it suddenly rises for the enantiotropic tetradecyloxy and hexadecyloxy homologues. Analytical and spectral data support the molecular structures.

4-Hydroxy –2-methyl phenyl azo 2′-chloro-3′-methyl benzene azodye is a non-mesogenic, but on extending the molecular length of the 4-n-alkoxy benzoic acids through their corresponding acid chlorides, the length to breadth ratio is enhanced to yield azoester products with relatively lower transition temperatures, due to the breaking of the hydrogen bonding between two molecules of the n-alkoxy acids. The suitable magnitudes of anisotropic forces of intermolecular attractions commences from the hexyloxy homologue on cooling the isotropic melt which shows nematic phase below the melting point irreversibly. The homologues from hexyl to dodecyl of the novel series arrange themselves to disalign perpendicular or at an angle less than ninety degree on the plane of a floating

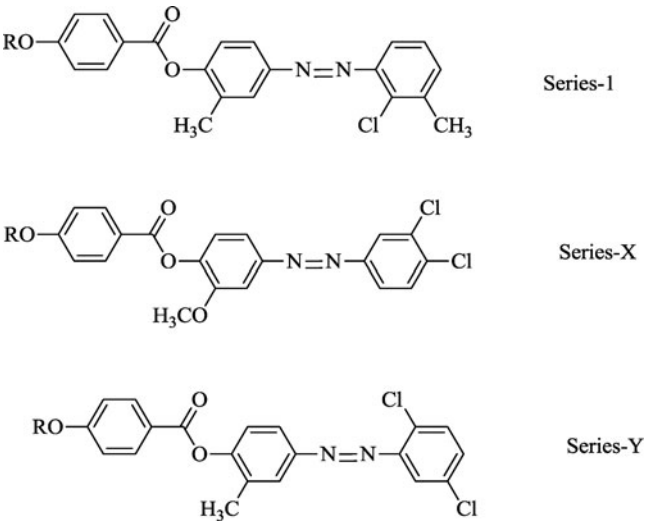

Figure 2. Structurally similar homologous series.

surfaces, resisting thermal vibration at the monotropic temperature under the influence of thermal energy and then immediately transform into solid state. Thus, statically parallel orientational order of molecules requires suitable magnitudes of anisotropic forces of end to end attractions to maintain the nematic mesophase for few degrees of temperature difference. However, the mesophase of monotropic homologues is difficult to detect accurately due to the high crystallizing tendency. Enantiotropic nemetogenic mesophase formation is exhibited by the tetradecyloxy and hexadecyloxy homologues and is attributed to their longer n-alkoxy chain of a terminal end group which has strengthened the intermolecular anisotropic forces to maintain a statistically parallel orientational order of molecules in a floating condition in a reversible manner for detectable accurate range of temperature. The absence of a smectogenic phase in the novel series indicates absence of lamellar packing of molecules. The lateral chloro and methyl groups increase the molecular width and intermolecular distance, which causes a reduction in the intermolecular attractions, however, the intermolecular attraction is enhanced by increased polarizability of the molecule by the three lateral almost equally polar functional groups. Therefore, the resultant net effective intermolecular attractions depend upon the dominant effect from the two opposing effects. Hence, absence of smectogenic property, poor range of nemetogenic phase length, late commencement of the mesogenic phase (from sixth homologue), exhibition of nemetogenic phase in monotropic manner and low melting type behavior, suggests that the first effect of reduced intermolecular attractions by increasing molecular width surpasses the second effect related to molecular polarizability. The absence of a mesophase in the methoxy to pentyloxy homologues is attributed to their high crystallizing tendency arising from unsuitable magnitudes of anisotropic forces of intermolecular end to end attractions. Variations in mesogenic behavior from homologue to homologue in the novel series is attributed to sequentially added methylene unit to the left n-alkoxy terminal end group. The mesogenic behaviors of the present series-1 are compared with the structurally similar other known series X [10] and Y [11]; as shown in Fig. 2.

The presently investigated homologus series-1 and series-X and series-Y selected for comparison from series to series are identical with respect to left n-alkoxy terminal end

Table 3. Average thermal stability in °C

Series →	[1]	[X]	[Y]
smectic – nematic or smectic- isotropic or isotropic-smectic	—	1.0 to 2.0 few degrees (C_5−C_{16})	—
commencement of smectic phase	—	C_5	—
nematic –isotropic or isotropic-Nematic	121.5 [C_{14}−C_{16}]	—	125.57 [C_6−C_{16}]
commencement of nematic phase	C_6	—	C_6

group (-OR), and three phenyl rings bonded through –COO– and –N =N– central bridges. However, they differ with respect to the lateral and/or terminal end groups, which of course causes differences in liquid crystal behavior and the degree of mesomorphism as a result of varying molecular rigidity and flexibility [2–4]. Thus, variations in phase behavior or mesogenic properties from series to series can be correlated with the molecular structure of a substance. Table 3 shows the average thermal stabilities for the series 1, X, and Y.

Table 3 indicates that (i) the present novel homologous series 1 is, predominantly monotropic nematic and partly enantiotropically nematogenic only, whereas, series X is monotropically smectogenic only, and homologous series Y is enantiotropically nematogenic without exhibition of any smectogenic character; (ii) the nematogenic mesophase commences from the hexyloxy homologue equally in series 1 and Y, without the exhibition of smectogenic character, however, the smectogenic mesophase commences from the pentyloxy homologue without exhibition of nemetogenic character in series X. Thus, the initial four or five members of each series (Fig. 2) under comparison are nonmesogenic; and mesophase exhibition commences from the fifth to sixth member of the series. Homologous series 1 and X are only nematogenic or only smectogenic respectively. Homologous series-1 has three laterally substituted groups with absence of right sided terminal end group; whereas homologous series X bears two laterally substituted groups and one terminally substituted right handed end group. Moreover, the $-OCH_3$ is more polar than $-CH_3$ substituted to the middle phenyl ring. On account of these differences the molecular polarity and polarizability differs for the series-1 and X. Accountability of such differences makes possible to induce inter layered lamellar packing of molecules with favorable extent of molecular co-planarity including end to end anisotropic forces of intermolecular attractions to induced smectogenic character monotropically below the melting point from the pentyloxy homologue, without the exhibition of a nematogenic mesophase in series-X. However, in case of series-1, only parallel orientational order of molecules by end to end attractions are maintained in floating condition without formation of lamellar packing of molecules. On comparing the homologous series 1 and series Y, they are perfectly identical including $-CH_3$ group at middle phenyl ring and −;Cl group bonded to the ortho position to −N=N− central group with rest of the unchanged molecular part. Thus, series 1 and Y differ only by $-CH_3$ and −Cl as laterally substituted flexible groups. Therefore, whatever the difference observed for mesogenic properties between the series 1 and Y is attributed

to the positional deference of $-CH_3$ and $-Cl$ and to their individual group polarity difference. The individual group polarity of $-CH_3$ and $-Cl$ are almost equal [1] for the nematic mesophase formation. Hence, the mesogenic difference between series 1 and Y is attributed to the position of lateral substitution at the third phenyl ring of $-CH_3$ and $-Cl$ for series 1 and Y. Thus, the novel aeries 1 and series Y exhibit only a nemetogenic mesophase, but their average thermal stabilities are 121.5°C and 125.57°C with equal commencement of nematic mesophase formation from the hexyloxy homologue. The positional difference of $-CH_3$ and $-Cl$ also created differing magnitudes of anisotropic forces of intermolecular end to end attractions to stabilize the statistically parallel orientational order of molecule to cause nematogenic mesophase. Variations in mesogenic behavior from series to series for the same homologue is attributed to the varying ratio of molecular polarity to polarizability, varying the length to breadth ratio etc. as a consequence of individual effective molecular rigidity and flexibility [2–4] of the novel series 1 and the series X and Y chosen for comparison.

Conclusions

- The group efficiency order derived on the basis of

  (i) Thermal stability and
  (ii) The commencement of mesophase formations

- are as under for smectic and nematic mesophases

  (i) Smectic: series X > series Y = series 1
  Nematic: series Y > series 1 > series X
  (ii) Smectic: series X > series Y = series 1
  Nematic: series 1 = series Y > series X

- Variations in mesogenic properties from homologue to homologue in the same series are due to the varying methylene units at the left n-alkoxy terminal end group.
- Variations in mesogenic properties for the same homologue, from series to series is due to changing molecular rigidity and flexibility by either changing ortho, meta and pera position of same functional group or different functional group or groups of dissimilar polarities keeping rest of the molecular part intact.
- Mesogenic behavior of a substance is the most sensitive and susceptible to its molecular structure.
- Present novel series is nematogenic without exhibition of smectogenic character low melting behavior.

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