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Synthesis and Evaluation of Liquid Crystal Behavior of a Novel Homologous Series: 4-(4′-n-Alkoxy benzoyloxy) Phenylazo-2″, 6″-dimethylbenzenes

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A novel homologous series entitled 4-(4′-n-alkoxy benzoyloxy) phenyl azo 2″, 6″-dimethyl benzenes consisting of 12 members is reported. Liquid crystal behavior as a nematogenic mesophase commences from the pentyloxy homologue monotropically and then continues enantiotropically until the last hexadecyloxy homologue without exhibition of any smectogenic behavior. An odd-even effect is observed for nematic-isotropic transition curve of the phase diagram. The textures of the nematic mesophase are of the threaded or Schlieren type. Analytical and spectral data support the molecular structure of the homologues. Transition temperatures of the novel homologues were determined by an optical polarizing microscopy. Liquid crystal properties of a novel homologous series are compared with other known homologous series. The average thermal stability for the nematic phase is 77.1°C.

Keyword Liquid crystal; mesogen; monotropy; nematic; smectic

Introduction

Suitable molecular rigidity from the rigid core of a molecule and the flexibility from units such as the terminal alkyl chains [1–3] play an important role in generating favorable magnitudes of anisotropic forces of intermolecular attractions, which induces liquid crystal properties [4] in a substance. Thus, liquid crystalline behavior of a substance is directly related to its molecular structure, that is, molecular shape, size, aromaticity, polarity and polarizability, and position of functional groups. The structure of the novel molecules reported here consist of three phenyl rings bridged through −COO− and −N=N− functional groups which act as the rigid core and the left n-alkoxy (−OR) terminal end group on first phenyl ring as well as the two lateral methyl groups substituted at ortho position of the −N=N− on third phenyl ring act as a flexible units of the molecule. Thus, liquid crystal behavior of a molecule can be correlated with its molecular structure.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agent by the modified method Dave and Vora [5]. The azodye, 4-hydroxy phenyl azo 2′, 6′ dimethyl benzene was prepared

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Table 1. Elemental analysis for (1) Ethyloxy (2) Pentyloxy (3) Heptyloxy derivatives

Sr. no.	Molecular formula	Elements %Found			Elements %Calculated		
		C	H	N	C	H	N
1	$C_{23}H_{22}N_2O_3$	73.72	5.95	7.40	73.78	5.92	7.48
2	$C_{26}H_{28}N_2O_3$	74.90	6.81	6.70	74.97	6.78	6.73
3	$C_{28}H_{32}N_2O_3$	75.61	7.22	6.22	75.65	7.26	6.30

by the well-known method of diazotization [6]. 4-n-Alkoxy benzoic acids were converted to the corresponding acid chlorides using freshly distilled thionyl chloride and condensed with an ice cold solution of azodye in pyridine [7]. The final azoester products were individually decomposed in 1:1 hydrochloric acid aqueous solution, filtered, washed, dried, and purified until a homologue gave constant transition temperatures.

4-Hydroxy benzoic acid, alkyl halides, KOH, thionyl chloride, methanol, ethanol, pyridine, 2, 6, dimethyl aniline, and phenol were used as received except solvents which were dried and purified prior to use. The synthetic route to the azoester homologue is shown in Scheme 1.

Characterization

Selected member of a series were characterized by elemental analysis (Table 1), ^{1}HNMR spectroscopy, infrared spectroscopy, mass spectrometry, and textural identification. Microanalysis was performed using a EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR-8400 spectrometer, ^{1}HNMR spectra were recorded on Bruker spectrometer using DMSO-d_6 as the solvent and mass spectra were recorded on Shimadzu GC-MS Model No. QP-2010 instrument. The type of textures of liquid crystal phases were determined by a miscibility process, and liquid crystal properties were determined by optical polarizing microscopy equipped with heating stage.

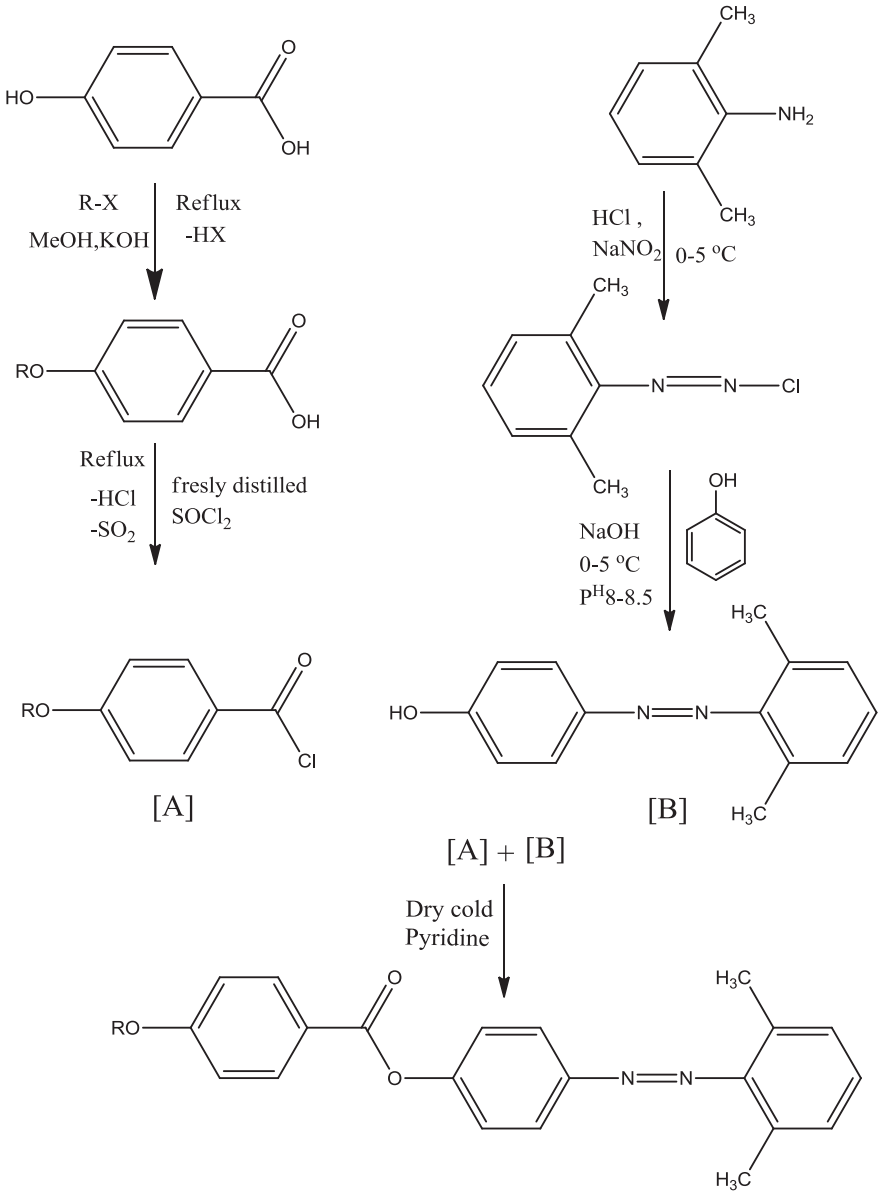
Analytical Data

Elemental Analysis (Table 1).

Spectral Data

NMR in ppm for the Hexayloxy Derivative. 0.873–0.908 (t, 3H, $-CH_3$ of $-OC_6H_{13}$ group), 1.31–1.45 (6H, m, polymethylene group of $-OC_6H_{13}$), 1.74–1.77 (t, 2H, $-CH_2-CH_2-O-$), 2.317 (6H, s, $-CH_3$ of phenyl ring). 4.08–4.12 (t, 2H, $-CH_2$-O-), 7.12–8.12 (m, 11H, substituted phenyl ring). The NMR data are consistent with the molecular structure.

NMR in ppm for the Octyloxy Derivative. 0.87–0.88 (t, 3H,-CH_3 of $-OC_8H_{17}$ group), 1.27–1.45 (10H, m, polymethylene group of $-OC_8H_{17}$), 1.72–1.79 (t, 2H,$-CH_2-CH_2-O-$), 2.31 (6H, s, $-CH_3$ of phenyl ring). 4.08–4.11 (t, 2H, $-CH_2-O-$), 7.12–8.11 (m, 11H, substituted phenyl ring). The NMR data are consistent with the molecular structure.



4-(4'-n-Alkoxy benzoyloxy) phenylazo-2"-6"-dimethyl benzenes

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

Scheme 1. Synthetic route to the series.

IR in cm^{-1} for the Hexadecyloxy Derivative. 636 (polymethylene (−CH_2-)$_n$ group of −$OC_{16}H_{33}$), 740, 771 (para & ortho substituted phenyl ring), 835 (1,6 disubstituted phenyl ring), 1170 (>C=O group), 1259 (−COO ester group), 1606 (−N=N− Str.), 1753 (C=O, Str. of −COO− group), 2847, 2916 (Aromatic phenyl ring). The IR data are consistent with the molecular structure.

Table 2. Transition temperatures in °C of series-1

Compound no.	n-Alkyl group $n = C_nH_{2n+1}$	Transition temperature in °C		
		Sm	N	Isotropic
1	1	—	—	104.0
2	2	—	—	111.2
3	3	—	—	102.0
4	4	—	—	100.0
5	5	—	(71.9)	82.3
6	6	—	80.6	83.2
7	7	—	51.5	78.3
8	8	—	60.3	79.7
9	10	—	49.8	76.6
10	12	—	57.9	74.0
11	14	—	59.7	71.3
12	16	—	86.9	130.0

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

IR in cm^{-1} for the Dodecyloxy Derivative. 650 (polymethylene $(-CH_2-)_n$ group of $-OC_{12}H_{24}$), 742, 761 (para & ortho substituted phenyl ring), 840 (1,6 disubstituted phenyl ring), 1175 (>C−O group), 1026, 1261 (−COO ester group), 1606 (−N=N− Str.), 1730 (C=O, Str. of −COO– group), 2845, 2937 (Aromatic phenyl ring). The IR data are consistent with the molecular structure.

Mass Spectra of the Decyloxy Derivative. m/z (rel. int.%): 486 $(M)^+$

Mass Spectra of the Tetradecyloxy Derivative. m/z (rel. int.%): 542 $(M)^+$

Texture Determination by Miscibility Method.

- Hexyloxy homologue: Threaded nematic
- Tetradecyloxy homologue: Schlieren nematic

Result and Discussion

The azodye, 4-hydroxy phenyl azo-2′,6′dimethyl benzene(M.P. 144.5°C) is nonmesomorphic, but on condensing it with dimerized n-alkoxy benzoic acids through their acid chlorides, mesomorphic derivatives of a novel homologous series 4-(4′-n-alkoxy benzoyloxy)phenylazo 2″,6″-dimethyl benzenes are generated. Nemetogenic mesophase formation commences from the pentyloxy homologue monotropically and then enantiotropically from the hexyloxy to hexadecyloxy homologue without exhibition of a smectogenic mesophase even in the monotropic condition. Transition temperatures (Table 2) of the novel homologues, as determined by an optical polarizing microscope with heating stage, are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group, to give a phase diagram showing phase behavior (Fig. 1). The solid-isotropic or nematic transition curve follows a zigzag path of rising and falling values and behaves in a

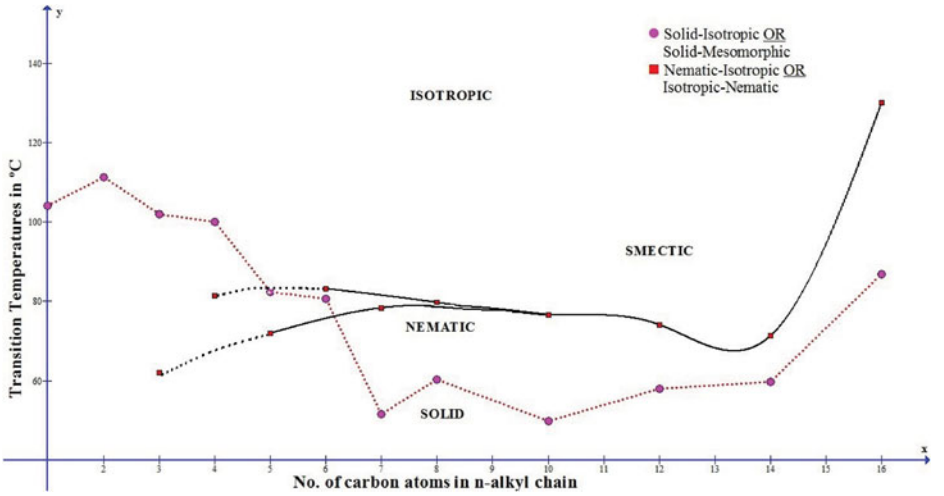


Figure 1. Phase behavior of series.

normal manner. The nematic-isotropic transition curve slightly rises and then descends as the series is ascended up to the tetradecyloxy homologue and then drastically ascends for the hexadecyloxy homologue. Thus, the nematic-isotropic transition curve behaves in a usual established manner up to the tetadecyloxy homologue and then a somewhat unexpected behavior is shown by the hexadecyloxy homologue. The nematic-isotropic transition curve is extrapolated [8], following the trend of a nematic-isotropic transition curve for third [odd] and fourth (even) nonmesomorphic members of the novel homologous series to predict their latent ability to exhibit mesomorphism. The predicted latent transition temperature (LTT) for the propoxy and butoxy homologues are below their melting points at 61.5°C and 82.0°C respectively. An odd–even effect is observed for nematic-isotropic transition curve and the effect is magnified by extrapolating the nematic-isotropic transition curve. Mesomorphic (nematic) phase length varies from 11.6°C to 43.1°C. The average thermal stability (Table 3) is 77.1°C. The series under discussion is nematogenic only with lower ordered melting type and without exhibition of smectic character. The odd–even effect diminishes and disappears from and beyond the nonyloxy homologue. Mesomorphic properties vary from homologue to homologue in the same novel series.

Table 3. Average thermal stability in °C

Series	[1]	[X]	[Y]
Smectic—nematic or Smectic-isotropic	—	—	114.0 C_{10}–C_{16}
commencement of smectic phase	—	—	C_{10}
Nematic-isotropic	77.1	113.0	138.54
Commencement of nematic phase	[C_6–C_{14}] C_5	[C_{10}–C_{16}] C_3	[C_1–C_8] C_1

The disappearance of dimerisation of 4-n-alkoxy benzoic acids is attributed to the breaking of hydrogen bonding by the esterification process. Addition of a phenyl ring linking through a −N=N− central bridge to a 4-n-alkoxy acid (via acid chloride) increases the molecular rigidity and aromaticity, and the two methyl groups increase molecular flexibility and length to breadth ratio; which enables liquid crystal properties as a consequence of suitable magnitudes of anisotropic forces of intermolecular attractions from the pentyloxy to hexadecyloxy homologues. However, liquid crystal properties are not induced for methoxy to butoxy homologues because of the absence of suitable magnitudes of anisotropic forces of intermolecular attractions in terms of a high tendency towards the crystal state. Relatively shorter n-alkyl chain lengths from methyl to n-butyl induces lower molecular flexibility and higher crystallizing tendency in a molecule which hinders disalignment of molecules at an angle less than 90 degrees. Molecules from pentyloxy to hexadecyloxy homologues disalign at an angle of less than 90 degree for a definite range of temperature against the externally exposed thermal vibrations and float on the surface with a statistically parallel orientational order for a particular temperature range with suitable magnitudes of anisotropic forces of end to end intermolecular attractions. Thus, the nematic mesophase formation is exhibited by the pentyloxy to hexadecyloxy homologues of the present series. Absence of smectogenic behavior of the present series is attributed to the absence of lamellar packing [4,9] of molecules in their crystal lattices due to inadequate ability of intermolecular attractions to maintain a sliding layered arrangement of molecules in a floating condition under the influence of heat by resultant molecular polarity and polarizability. An odd-even effect of alternation of transition temperatures as well as changing mesomorphic behavior from homologue to homologue in the present series are attributed to the sequential change in the number of methylene units in the n-alkoxy terminal end group. The disappearance of the odd–even effect for higher homologues from and beyond the nonyl homologue is attributed to the flexing, bending, coiling, or coupling of n-alkyl chain with major axis of the core. The mesomorphic nematogenic phase length varies from a minimum of 11.6°C at the tetradecyloxy homologue to a maximum of 43.1°C at the hexadecyloxy homologue. Thus, present novel series is predominantly nematogenic without exhibition of smectogenic character. The average thermal stability for nematic of the series is 77.1°C. Thus, series is considered as low melting type and medium ranged liquid crystallinity. The mesomorphic properties of the present series-1 are compared with the structurally similar other known homologous series X [10] and Y [11] shown in Fig. 2.

The average thermal stabilities and other information for series-1 and series-X and series-Y chosen for comparison are shown in Table 3.

Table 3 shows the thermal stabilities for the smectic phase and/or the nematic phase, the commencement of the nematic and/or the smectic mesophase for the novel series-1, and series-X and series-Y chosen for comparing mesomorphic properties. Homologous series-1, series-X, and series-Y (Fig. 2) are identical with respect to their molecular rigidity formed by three phenyl rings bonded through −COO− and −N=N− central bridges as well as left handed flexible n-alkoxy (–OR) terminal end group for the same homologue from series to series. However, they differ with respect to the presence or absence of methyl groups substituted at different positions with respect to the −N=N− or −COO− functional groups and the changing n-alkoxy terminal end group from homologue to homologue in the same series. Thus, series-1, series-X, and series-Y are identically similar in their molecular rigidity but differ in their molecular flexibility. The generation of mesomorphic properties and the degree of mesomorphism depend upon the combined effects of the magnitudes of molecular rigidity and flexibility. Therefore, observed variations in mesomorphic behavior of series-1, series-X, and series-Y can be attributed and correlated with the variation of

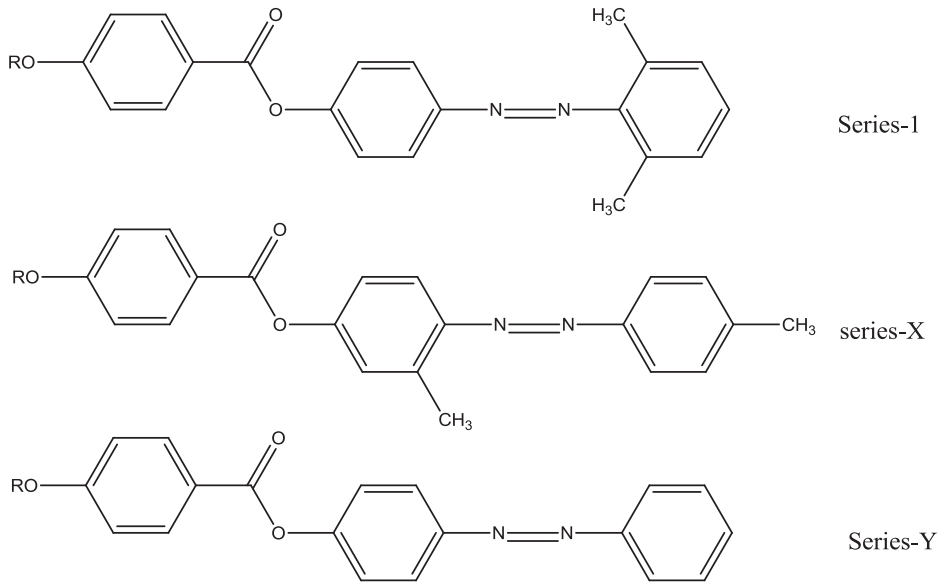


Figure 2. Structurally similar homologous series.

molecular structures (Fig. 2). Homologous series-1 and series-X are isomeric with each other containing two methyl groups with identical molecular rigidity but with different molecular flexibility caused by two methyl groups linked at different position of same (i.e., ortho position to −N=N−) and different phenyl rings. Steric hindrance to protect the −N=N− central group by two methyl groups in series-1 is relatively more as compared to series-X. Moreover the length to breadth ratio and hence the ratio of the molecular polarity to polarizability varies between series-1 and series-X. Thus, polarizability is the predominant factor out of two opposing effects [9] concerning anisotropic forces of intermolecular attractions [4] for series-Y as compared to series-1. Hence, series-1 shows only the nematic mesophase while, series-Y additionally shows a smectic mesophase. Homologous series-1 and series-X show only the nematogenic mesophase without the exhibition of a smectic phase, but their commencement of nematic mesophase formation differs (series-1 from fifth and series-X from third member), which indicates difference in magnitudes of anisotropic forces of intermolecular attractions. Absence of smectogenic character in isomeric series-1 and series-X indicates the absence of lamellar packing of molecules in their crystal lattices due to inappropriate magnitudes of anisotropic forces disturbing an extent of molecular coplanarity and hinders layered arrangement of molecules perpendicular to the plane of a surface in floating condition to form smectic mesophase. Intermolecular adhesive end to end forces are sufficient to maintain a statistically parallel orientational order of molecules in floating condition from very first member of a series-Y and the same nematogenic mesophase commences relatively late from fifth and third member of a series-1 and series-X respectively due to poorer end to end attractions. The variations in mesomorphic behavior from homologue to homologue in the same series and series to series for same homologue are attributed to the sequentially added methylene unit and the changing position of the same functional groups [12] respectively. The increasing order of thermal stability for the nematic phase is attributed to the energy stored by a molecule (ΔH) based on the combined

effect of molecular rigidity and flexibility to stabilize the mesophase formed within definite range of temperature.

Conclusions

The following conclusions are drawn for the novel homologous series.

1. The novel homologous series is only nematogenic without exhibition of any smectogenic property.
2. The novel homologous series is a relatively low melting type with considerable mesophase length.
3. Group efficiency order derived on the basis of thermal stability for nematic is, Series − Y > Series − X > Series − 1
4. Group efficiency order derived on the basis of early commencement of nematic phase is, Series − Y > Series − X > Series − 1
5. Group efficiency order derived on the basis of thermal stability and the early commencement of smectic mesophase is as under. Series − Y > Series − X > Series − 1
6. Liquid crystal property in a substance is induced only by favorable and suitable magnitudes of molecular rigidity and flexibility.
7. Mesomorphic behavior of a series from homologue in the same series varies with the sequentially added methylene unit, keeping right terminal or lateral end group unchanged.
8. Mesomorphic behavior for the same homologue from series to series depend upon (i) varying right sided lateral or/and terminal end group or groups or (ii) varying position of the same functional group or groups present on right side of isomeric series, keeping n-alkyl chain of left n-alkoxy group unchanged.
9. Suitable magnitude of molecular rigidity and flexibility, that is, molecular structure has direct relation to induce liquid crystal property in a substance or fittest molecular rigidity and flexibility operates liquid crystal behavior of a substance with respect to its molecular structure.

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