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ABSTRACT

A novel azoester homologous series, $RO-C_6H_4-COO-C_6H_4-N =$ $N-C_6H_4-OC_7H_{15}(n)$ (para) has been synthesized and studied with a view to understanding and establishing the effects of molecular structure on mesomorphic properties with reference to tthe flexible terminal chain. The novel azoester series consists of thirteen (C1-C18) members. Mesomorphism commences from C_5 homologue. $C_1 - C_4$ homologues are nonmesomorphic, C₅ homologue is only nematogenic and C₆-C₁₈ homologues are smectogenic and nematogenic. All mesogenic homologues are enantiotropically mesomorphic. Transition temperatures and textures were determined by polarizing optical microscopy (POM) and a heating stage. Cr-M/I transition curve follows a zigzag path of rising and falling values and behaves in a normal manner. The Sm-N and N-I transition curves of a phase diagram behave in the normal established manner except for a small deviation for the higher homologues (C₁₄ and C₁₆). An odd-even effect is exhibited by Sm-N and N-I transition curves. Analytical spectral and thermal data support the molecular structures. Smectic and nematic thermal stabilities are 93.62°C and 114.3°C, respectively. Smectic and nematic mesophas elengths range from 12.0°C to 18.0°C and 11.0°C to 31.0°C. The series is predominantly nematogenic and partly smectogenic and of middle order melting type. Group efficiency order derived for smectic and nematic. Smectic and nematic: $-OCH_3 > -OC_4H_9 > -OC_7H_{15}(n)$.

KEYWORDS

Azoester; liquid crystals; mesogenic; nematic; smectic

Introduction

This study on novel liquid crystals of the thermotropic type [1] is planned with a view to understanding and establishing the relationship between molecular structure and LC properties [2–6] by altering the moiety, geometrical shape, size, aromaticity, thermal and/or lateral functional groups or central group or groups in isomeric and/or nonisomeric molecules or by changing or exchanging place of the position or positions on same or different phenyl or alicyclic or heterocyclic ring, etc. Such information can play an important role in predicting the temperature or temperature range and the suitability for LC and other applications such as, light emitting materials, agriculture prediction, pharmaceuticals, etc. in the benefit of mankind. Azoester dyes including LC properties which are useful and applicable as equal as ordinary and other normal dyes and for many other application [7–11]. This

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investigation focuses on the synthesis of compounds with three phenyl rings bonded through -COO- and -N=N- central bridges and varying and fixed terminal end groups of -OR and $-OC_7H_{15}(n)$, respectively. Evaluated thermometric data after due characterization will be discussed and interpreted in terms of molecular rigidity and flexibility [12–15]. Many azoesters and esters have been reported to date [16–21].

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating agents (R-X) to convert it into 4-n-alkoxy benzoic acids by a modified method of Dave and Vora [22]. Alkylation of Paracetamol using an alkylating agent (R-X) is carried out to form 4-n-alkoxy acetanilide and then hydrolyzed to give 4-n-heptyloxy aniline by a reported method [23(a)], The azo dye was prepared by a known method [23(b)]. The azoesters were synthesized by a literature method [24]. Thus, the azo-ester homologue derivatives were filtered and washed with sodium bicarbonate solution following distilled water and dried and purified until constant transition temperatures obtained, using an optical polarizing microscopy equipped with a heating stage. 4-Hydroxy benzoic acid, alkyl halides, Paracetamol, dicyclohexyl carbodimide, dimethyl amino pyridine, DCM, MeOH, acetone required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is shown in Scheme 1.

Characterization

Representative homologues of the series were characterized by elemental analysis, mass spectrography, infrared spectroscopy, and ¹H NMR spectra. IR spectra were recorded on a Perkin-Elmer spectrum GX, ¹H NMR spectra were recorded on a Bruker using CDCl₃ as solvent. Microanalysis was performed on a Perkin-Elmer PE 2400 CHN analyzer (Table 1). Transition temperatures and LC properties (Textures) were determined using an optical polarizing microscopy equipped with heating stage. Texture images of nematic phase were determined by a miscibility method (Table 2).

Analytical data

IR spectra in cm⁻¹ for octyloxy and decyloxy derivatives

Octyloxy: 694 Polymethylene ($-CH_2$ -)n of $-OC_8H_{17}$, 844 (-C-H- def. m di-substituted-Para), 759 Polymethylene ($-CH_2$ -) of $-OC_7H_{15}$, 968 (-C-H- def. hydrocarbon) 1083 and 1015 (-C-O-) Str, 1168, 1246, and 1307 (-C-O str in $-(CH_2)$ n chain, 1427 and 1462 (-C-H- def. in CH_2), 1512 (-C=C-)str, 1604(N = N group) and 1728 (-COO- ester group), 2850 and 2924 (-C-H str in $-CH_3$).

Decyloxy: 640 Polymethylene ($-CH_2$ -)n of $-OC_{10}H_{21}$, 840 (-C-H- def. m di-substituted-Para), 756 Polymethylene ($-CH_2$ -) of $-OC_7H_{15}$, 968 (-C-H- def. hydrocarbon), 1083 and 1022 (-C-O-) Str, 1172,1246 and 1307 (-C-O str in $-(CH_2)$ n chain, 1458 (-C-H- def. in CH₂), 1527 (-C=C-) str, 1604 (N = N group) and 1728 (-COO- ester group), 2850 and 2924 (-C-H str in CH₃).



Scheme 1. Synthetic route to the series.

Table 1. Elemental analysis for heptyloxy, decyloxy, tetradecyloxy, and hexadecyloxy derivatives.

		%	%Elements found		%El	%Elements calculated		
Sr. no.	formula	С	Н	Ν	С	Н	N	
1	$C_{22}H_{42}O_4N_2$	74.67	7.90	5.26	74.71	7.92	5.28	
2	$C_{36}^{33}H_{48}^{42}O_{4}^{3}N_{2}^{2}$	75.60	8.35	4.78	75.52	8.39	4.89	
3	$C_{40}^{30}H_{56}^{30}O_{4}^{3}N_{2}^{2}$	76.68	8.66	4.49	76.43	8.91	4.45	
4	C ₄₂ H ₆₀ O ₄ N ₂	76.79	9.23	4.33	76.82	9.14	4.26	

1HNMR spectra in CDCl₃ in δ ppm for hexyloxy & dodecyloxy derivative

Hexyloxy: 0.86 (t,-CH₃ of $-C_6H_{13}$), 1.18–1.28(m, n-poly methylene groups of-OC₆H₁₃), 1.43 (m, n-poly methylene groups of $-OC_7H_{15}$), 3.9 (s, $-OCH_2-CH_2$ -of OC_6H_{13}), 4.0 (s, $-OCH_2-CH_2$ -of OC_7H_{15}), 6.79–7.28 (s, phenyl ring), 7.8–8.1 (s, p-disubstituted phenyl ring).

Sr. no.		Texture		
	Homologue	Smectic	Nematic	
1	C ₇	Sm-A	Threaded	
2	C ₁₀	Sm-A	Threaded	
3	C ₁₄	Sm–C	Schlieren	
4	C ₁₈	Sm–C	Schlieren	

Table 2. Texture of smectic and r	ematic phase of C_7 , C_{10}	0, C14, C18 by	y miscibility method.
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 α -4-(4'-n-alkoxybenzoyloxy) phenyl azo-4'- heptyloxy benzene

Dodecyloxy: 0.898 (t,-CH₃ of $-C_{12}H_{25}$), 1.09–1.34 (m, n-poly methylene groups of $-OC_{12}H_{25}$), 1.48 (m, n-poly methylene groups of $-OC_7H_{15}$), 3.51 (s,-OCH₂-CH₂-of $OC_{12}H_{25}$), 4.16 (s,-OCH₂-CH₂-of OC_7H_{15}), 6.9-7.4 (s,phenyl ring), 7.9–8.1 (s, p-disubstituted phenyl ring).

Results and discussion

Novel homologous series of azoesters was synthesized by condensation of dimeric 4-n-Alkoxy benzoic acids and 4-hydroxy phenyl azo-4⁷- heptyloxy benzene (m.p. -89°C, yield 81.22%). Dimerization of 4-n-alkoxy benzoic acids disappears on esterification and mesomorphism commences from C₅ homologue in enantiotropic manner. C₅ homologue is only nematogenic and the rest of the LC homologues are (C_6-C_{18}) smectogenic plus nematogenic. Transition temperatures including textures were determined by polarizing optical microscopy equipped with a heating stage (POM). Transition temperatures (Table 3) were plotted versus the number of carbon atom present in n-alkyl chain '-R-' of -OR terminal group and on linking, like or related points, the transition curves Cr-M/I, Sm-N, and N-I are obtained as shown in a phase diagram (Fig. 1) showing phase behaviors of series. Cr-M/I transition curve follows a zigzag path of rising and falling values with overall descending tendency. Sm-N transition curve initially rises passes through maxima at C₁₀ homologue and then descended up to last homologue of a series with exhibition of sharp narrow and shorter odd-even effect. N-I transition curve descended as series is ascended with exhibition of sharp and short odd-even effect, with negligible deviation at C₁₄ and C₁₆ and overall descending tendency. Thus, all the transition curves of a phase diagram behaved in normal manner except negligible deviation in N-I

	R = n-alkyl group	Transition temperatures in°C			
Sr. no		Smectic	Nematic	lsotropic	
1	C1	_	_	137.0	
2	C2	_	_	134.0	
3	C3	_		125.0	
4	C4	_		127.0	
5	C5	_	91.0	118.0	
6	C6	79.0	92.0	123.0	
7	C7	84.0	96.0	126.0	
8	C8	86.0	98.0	122.0	
9	C10	89.0	100.0	112.0	
10	C12	80.0	93.0	104.0	
11	C14	78.0	90.0	106.0	
12	C16	77.0	92.0	110.0	
13	C18	70.0	88.0	108.0	

Table 3. Transition temperature table in°C.



Figure 1. Phase behaviors of series.

curve for C_{14} and C_{16} homologue. Analytical, thermal and spectral data supported molecular structure of homologues. Thermal stabilities for smectic and nematic are 93.62°C and 114.33°C with total mesophase length varying from 23.0°C to 44.0°C. Mesomorphic properties and behaviors vary from homologue to homologue in a same series including textures of homologues.

Disappearances of dimerization of n-Alkoxy benzoic acids and the lowering of transition temperatures of corresponding azoester homologues are due to the breaking of hydrogen bondings between two molecules of n-alkoxy benzoic acids by esterification process. In exhibition of mesomorphism, either in reversible or irreversible manner by C_1 , C_2 , C_3 , and C_4 homologues is attributed to their high crystallizing tendency which arises from unsuitable magnitudes of anisotropic forces of intermolecular end to end or lateral cohesion as a consequence of unfavorable molecular rigidity and flexibility, due to low magnitudes of dispersion forces and low magnitudes of dipole-dipole interactions, which hinders the disalignments of molecule under the influence of exposed thermal vibrations as a result of their low thermal resistivity. Exhibition of mesomorphism by C_5 to C_{18} homologues either as enantiotropic nematic and/or smectic is attributed to the disalignments of molecules at an angle ninety



Figure 2. Structurally similar analogous series.

degree or/and less than ninety degree with the plane of the floating surface, which resisted exposed thermal vibrations to float with statistically parallel orientational order excluding or including sliding layered molecular arrangement for definite range or ranges of temperature in reversible manner. The exhibition of odd-even effect by Sm-N and N-I transition curves of a phase diagram is due to the sequentially added methylene unit or units at n-alkyl chain '-R-' of -OR group up to C_8 or C_9 homologue respectively. Beyond that (C_8 or C_9), a single transition curve is followed, i.e. odd-even effect disappears from and beyond merging of transition curves indicating odd-even effect for higher homologues of longer n-alkyl chain 'R' of left-OR group. Because, longer n-alkyl chain may coil or bend or flex or couple to lye with major axis of core structures of a molecule. The negligible deviation in N-I transition curve observed for C₁₄ and C₁₆ homologues is attributed to the unpredictable and unexpected or unusual status of left and right -R and $-OC_7H_{15}(n)$ hydrocarbon chains of -OR and $-OC_7H_{15}(n)$ terminally situated end groups. The extrapolation of Sm-N transition curve at C_5 [25] predicts a value (LTT) at 83°C but it is unrealizable due to high crystalline tendency. The variations in mesogenic properties and behaviors from homologue to homologue in the same series is attributed to the variations of number of carbon atoms or -CH₂unit, which causes variations in the length to breadth ratio, ratio of the molecular polarity to polarizability, permanent dipole moment across the long molecular axis, magnitudes of the molecular rigidity and flexibility, intermolecular dispersion forces, etc. required to facilitate and stabilize a phenomena of mesomorphism as smectic and/or nematic in either reversible or irreversible manner. The mesogenic (some) properties of presently investigated novel series-1 are compared with structurally similar analogous series-X [26] and Y [27] as mentioned in Fig. 2.

Above Fig. 2 indicates that, homologous series-1 of present investigation and the homologous series X and Y chosen for comparative study are identical with respect to molecular rigidity through aromaticity of three phenyl rings and the identically same central bridges -COO- and -N=N- from series to series as well as homologue to homologue in the same series. Left flexible n-alkoxy terminal end group are identical for the same homologue from series to series but, varies from homologue to homologue in the same series. Tailed terminal end groups $-OC_7H_{15}$ (n) and $-OCH_3$ which differ in the magnitudes of thermal property for the same homologue from series to series but, remains unaltered for, all the members of each same series. Thus, variations in mesomorphic properties and their magnitudes depend upon

Series	Series-1(–OC ₇ H ₁₅ (n))	Series-X ($-OC_4H_9$ (n))	Series-Y (–OCH ₃)
Sm-N or Sm-I Commencement of Smectic phase	93.62 (C ₆ -C ₁₈) C ₆	111.3 (C ₈ -C ₁₈) C ₈	137.0 (C ₁₄ -C ₁₆) C ₁₄
N-I Commencement of Nematic phase	114.33 (C ₅ -C ₁₈) C ₅	124.7 (C ₆ -C ₁₈) C ₆	251.7 (C ₁ -C ₁₄) C ₁
Total mesophase length range in°C	23.0°C to 44.0°C C ₁₀ C ₆	7.0°C to 40.0°C C ₆ C ₁₄	70.0°C to 170.0°C C ₃ C ₄

Table 4. Relative thermal stability in°C.

the varying combined effects of molecular rigidity plus flexibility or upon the differing features of individual molecular structure for the same homologue from series to series and from homologue to homologue in the same series. Following Table 4 represents some thermometric properties of series 1, X and Y in comparative manner.

Careful observation of Table 4 suggest that,

- All the homologues of series 1, X and Y under comparative study are enantitropically smectogenic plus nematogenic.
- Thermal stabilities foe smectic and nematic are in increasing order from series-1 to series-X to series-Y.
- Early commencement of smectic phase is in decreasing order from series-1 to series-X to series-Y.
- Early commencement of nematic phase is the highest for series-1 (C₁) and the lowest for series-X (C₆) and intermittent for series-1 (C₅).
- Upper and lower total mesophase lengths increases from series-X to series-1 to series-Y.

Exhibition of smectic plus nematic mesophase formations are obvious, because of the presence of varying $-OC_7H_{15}$ (n), $-OC_4H_9$ (n) and $-OCH_3$ tailed ended functional groups of linear, lath like geometrical shape, their group polarity, size, end to end as well as lateral cohesions and closeness, dispersion forces, etc. within the molecules of each same series and for the same homologue from series to series, which creates possibilities to facilitate an environmental situation to induce smectic and/or nematic phase early or late as a consequence of suitable differing magnitudes of anisotropic forces of intermolecular attractions and combined effects of differing molecular rigidity plus flexibility. The increasing order of thermal stabilities for smectic and nematic is attributed to the decreasing length of flexible tailed nalkoxy end groups $-OC_7H_{15}(n)$, $-OC_4H_9(n)$, and $-OCH_3$ which decreases possibilities of uncertainty in the status of n-alkyl chain $-C_7H_{15}(n)$, $-C_4H_9$, and $-CH_3$ commonly bonded through oxygen atom with phenyl ring which affects magnitudes of molecular flexibility in favor of increasing thermal stabilities at constant molecular rigidity. Early or late commencement of mesophase depended upon the extent of molecular noncoplanarity and the degree of uncertainty in the status of n-alkyl chain of flexible end groups. The total mesophase lengths are depended upon the thermal resistivity offered by a molecule depending upon the internal energy stored by the molecules of different characteristics of varying structures. Thus, upper and lower total mesophase lengths followed the same order of comparison as early commencement of mesophase or mesophases.

Conclusions

- Novel azoester homologous series is predominantly nematogenic and partly smectogenic with its middle ordered melting type.
- As tailed ended n-alkyl chain become shorter the early commencement of nematic mesophase and total mesophaselengths are favored positively.

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 - The group efficiency order derived for smectic and nematic on the basis of (i) thermal stabilities (ii) early commencement of mesophase and (iii) total mesophaselengths are as under.
 - (i) Smectic: $-OCH_3 > -OC_4H_9(n) > -OC_7H_{15}(n)$ Nematic: $-OCH_3 > -OC_4H_9(n) > -OC_7H_{15}(n)$
 - (ii) Smectic: $-OC_7H_{15}(n) > -OC_4H_9(n) > -OCH_3$ Nematic: $-OCH_3 > -OC_7H_{15}(n) > -OC_4H_9(n)$
 - (iii) Total mesophaselengths
 - **Upper and lower**: $-OCH_3 > -OC_7H_{15}(n) > -OC_4H_9(n)$
 - Molecular structure of a molecule is very sensitive and susceptible to mesomorphism or vice versa as a result of molecular rigidity and/or flexibility.
 - Present investigation very well supports and raises credibility to the conclusions drawn earlier.

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