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Mesomorphism dependence on central bridge and tail ended polar group

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ABSTRACT

A novel azoester homologous series of laterally and terminally substituted viz, $RO-C_6H_4-CH=CH-COO-C_6H_3-(CH_3) -N=N-C_6H_4-CI$ is synthesized, characterized and studied with a view to understand and establish the relation between molecular structure and thermotropic liquid crystalline property of its homologs. Series consists of twelve homologs. LC properties commence from very first member of a series and continue up to last homolog as enantiotropic nematic with absence of smectic property even in the monotropic condition. Transition temperatures of homologs were determined by polarizing optical microscopy equipped with a heating stage. The transition curves Cr–N and N–I behaved in normal manner. Thermal stability for nematic is 196.7 °C whose mesophaselength ranges from 35 °C to 131 °C.

KEYWORDS

Azoester; liquid crystal; nematic; smectic; thermotropic

Introduction

Azoester compound of LC variety [1] are applicable to electronic display devices, light emitting materials and useful as equal as normal dyes including changing their color with changing frequency of exposed radiation. Azoester are useful ingredients to pharmaceutical industries [2–8]. However, present investigation is planned to study the relation between molecular structure and mesomorphism with reference to central bridge and tail ended variations polar groups [9–13]. Proposed investigation involves synthesis and characterization of novel substances and the study of their relation of mesogenic property with molecular structure, excluding their applications through molecular rigidity and flexibility. Numbers of homologous series are reported till the date [14–29].

Synthesis

4-*n*-Alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with corresponding *n*-alkyl bromides (1 equiv.) in the presence of potassium carbonate (1 equiv.) and acetone as a solvent [30]. The resulting 4n-alkoxybenzaldehydes were reacted with malonic acid (1.2 equiv.) in the presence of 1–2 drops piperidine as catalyst



where $R = C_n H_{2n+1}$, n= 1-10, 12, 14, 16.

Scheme 1 Synthetic route to the novel series.

and pyridine as solvent to yield corresponding trans 4-n-alkoxy cinnamic acids (A) [31]. Azo 4-hydroxy-3-methyl phenylazo-4', chlorobenzene[B] was prepared by the usual established method of diazotization [32,33] Yield – 70.5%. Coupling of compound A and compound B is done by steglich esterification to yield [34].

		Elem	Elements %Found			Elements %Calculated		
Sr. No.	Molecular formula	С	Н	0	С	Н	0	
1	$C_{27}H_{27}CIN_2O_3$	69.98	5.83	10.36	70.05	5.88	10.37	
2	C ₂₉ H ₃₁ CIN ₂ O ₃	70.90	6.31	9.77	70.94	6.36	9.78	
3	$C_{34}H_{41}CIN_2O_3$	72.15	7.30	8.55	72.10	7.00	9.00	

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

The synthetic route to the novel homologous series is mentioned in Scheme 1.

Characterization

Some of members of a novel series as the representative member of a series were characterized by elemental analysis (Table 1), Infrared spectroscopy, ¹H NMR spectra and mass spectroscopy. Microanalysis was performed on EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR Model-IR Affinity-1S (MIRacle 10), ¹HNMR spectra were recorded on Bruker spectrometer using CDCl₃as solvent and mass spectra were recorded on Shimadzu GC–MS Model No.QP-2010.

Spectral data:

¹HNMR in ppm for ethyloxy derivative

1.32–1.40(t, 3H CH₃ of $-OC_2H_5$), 2.15(s, 1H, $-CH_3$ –Ph), 3.90–4.0(q, 2Hof $-OC_2H_5$), 6.29–6.31(d,1H of -CH=CH-COO-), 6.90–6.94(m, 2H of first phenyl ring), 7.37(s, 1H of second phenyl ring meta to $-CH_3$ group), 7.48–7.50(d, 1H of -CH=CH-COO-), 7.62–7.69(m, 4H, 2H of first phenyl ring nearer to -CH=CH-COO- and 2H of third phenyl ring nearer to -Cl), 7.78–7.83(m, 2H of second phenyl ring nearer to -N=N- group), 7.90–7.94(m, 2H of third phenyl ring nearer to -N=N- group). The NMR data are consistent with the molecular structure.

¹H NMR in ppm for propyloxy derivative

1.35–1.40(t, 3H CH₃ of $-OC_3H_7$), 1.74 (M, 2H of $-CH_3-CH_2-CH_2-O_-$),2.17(s, 1H, $-CH_3-Ph$), 3.91–4.1(t, 2Hof $-OC_3H_7$), 6.24–6.31(d,1H of $-CH=CH=COO_-$), 6.80–6.84(m, 2H of first phenyl ring), 7.33(s, 1H of second phenyl ring meta to $-CH_3$ group), 7.50–7.56(d, 1H of $-CH=CH-COO_-$), 7.60–7.65(m, 4H, 2H of first phenyl ring nearer to $-CH=CH-COO_-$ and 2H of third phenyl ring nearer to -Cl), 7.79–7.83(m, 2H of second phenyl ring nearer to -N=N- group), 7.95–7.98(m, 2H of third phenyl ring nearer to -N=N- group). The NMR data are consistent with the molecular structure.

IR in cm⁻¹ for hexyloxy derivative

3037 (=C-H str. of phenyl nucleus), 2922 & 2850 (C-H str. of $(-CH_2-)_n$ group of $-OC_6H_{13}$), 1724 (C=O str. of carbonyl carbon of ester group), 1625 (C=O str. of α,β unsaturated ketone), 1589 (C=C str. of alkene), 1510 & 1477 (C=C str. of aromatic

Compound No.	<i>n</i> -alkyl chain C _n H _{2n+1} (n)	Sm	Ν	Isotropic
1	C ₁	-	172	274
2	C ₂	-	160	263
3	C ₃	-	131	205
4	C ₄	-	91	222
5	C ₅	-	115	185
6	C ₆	-	109	201
7	C ₇	-	129	180
8	C ₈	-	111	183
9	C ₁₀	-	102	175
10	C ₁₂	-	104	167
11	C ₁₄	-	108	157
12	C ₁₆	-	114	149

Table 2. Transition temperatures in °C.

Sm=Smectic, N=Nematic.

ring), 1423 (Ar-N=N-Ar str.), 1394 (C-H bending of alkene disubstituted), 1307 (C-O str. of ether linkage), 1128 (C-O str. of ester group), 972 & 891 (C-H bending of alkene). The IR data are consistent with the molecular structure.

IR in cm⁻¹ for hepyloxy derivative

2964 (=C-H str. of phenyl nucleus), 2922 & 2850 (C-H str. of $(-CH_2-)_n$ group of $-OC_6H_{13}$), 1722 (C=O str. of carbonyl carbon of ester group), 1633 (C=O str. of α,β unsaturated ketone), 1598 (C=C str. of alkene), 1510 & 1477 (C=C str. of aromatic ring), 1421 (Ar-N=N-Ar str.), 1394 (C-H bending of alkene disubstituted), 1307 (C-O str. of ether linkage), 1132 (C-O str. of ester group), 974 & 891 (C-H bending of alkene). The IR data are consistent with the molecular structure.

Mass spectra of methyloxy derivative

m/z (rel.int%): 406 (3%, M⁺), 246 (21%, ester linkage break), 161 (100%), 107 (35%).

Results and discussion

Present azoester novel series is derived from trans *n*-alkoxy cinnamic acids and an azodye 4-hydroxy 3-methyl phenyl azo-4'-chlorobenzene. Azodye is nonliquid crystal, but on condensation with dimeric trans vinyl carboxylic acid yielded LC homologs by esterification process with alternations of transition temperatures up to C_8 derivative and then alternation disappears. Esterification process breaks the hydrogen bonding between two molecules of *n*-alkoxy aromatic cinnamic acid and lowers the transition temperatures of final azoester homologs, including showing up to odd even effect. Transition temperatures as determined by an optical polarizing optical microscopy (POM) (Table 2) were plotted versus the number of carbon atom present in *n*-alkyl chain 'R' of –OR terminal (Fig. 1). Transition curves Cr–N and N–I are obtained by linking like or related transition points as depicted in Fig. 1. Cr–N transition curve follows zigzag path of rising and falling with overall descending tendency and behaved in normal manner. N–I transition curve adopted continuous descending tendency as series is ascended with exhibition of odd–even effect



Figure 1 Phase behaviors of homologous series.

up to C_8 homolog, beyond which odd-even effect disappears for higher homologs of longer *n*-alkyl chain 'R' of -OR groups. Thus, N-I transition curve behaved in normal expected manner. Thermal, analytical and spectral data confirmed molecular structures of novel homologs. Thermal stability for nematic is 196.7 °C and mesophaselength ranges maximum 131.0 °C to minimum 35.0 °C at the C₄ and C₁₆ homolog respectively. Thus, novel series is high melting series, with sufficient degree of mesomorphism.

Esterification and diazotization process introduces conjugated double bond between two carbon atoms of vinyl group as well as double bond between two nitrogen atom which strengthens the molecular rigidity and the presence of ortho substituted lateral methyl group and para substituted polar/polarizable -OR, -Cl terminal groups raises flexibility of the molecules of each homolog to such an extent that, suitable magnitudes of anisotropic forces of intermolecular end to end attractions only, which maintains the statically parallel orientational order of molecules under floating condition on the floating surface. Thus, LC state of all the homologs of series facilitated the exhibition of nematogenic mesophase formation as observed from the heating top of POM with considerable ranges of temperature. However, smectogenic mesophase facilitation is hindered due to insufficient or inadequate suitable magnitudes of anisotropic forces of lateral to terminal intermolecular cohesion to adopt layered structure of molecules even in the monotropic condition. Thus, smectogenic mesophase formation is missing to appear. The exhibition of odd-even effect observed up to C8 homolog from very first member of present novel series is attributed to the gradual change in molecular rigidity and flexibility of the homolog molecules as depended upon their size, permanent dipole moment across the long molecular axis, aromaticity, molecular polarity and polarizibility, length to breadth attraction etc. Thus, sequential addition of methylene unit play an important role in alternation of transition temperatures causing odd-even effect in a



Figure 2 Homologous series for comparative study.

transition curve (N–I) of a series. However, disappearance of odd–even effect from and beyond C₈ homolog for higher homologs of longer *n*-alkyl chain 'R' is attributed to the coiling or bending or flexing or coupling of *n*-alkyl chain with the core structure of a molecule. Thus unusual status of *n*-alkyl chain 'R' of –OR group causes such effects. The relatively wider range of mesophaselength of nematic mesophase stabilization is attributed to the favored magnitude of molecular rigidity and flexibility from homolog to homolog in the same series, related to add –CH₂– unit or –CH₂–CH₂– unit. Some LC properties of a present novel Series 1 are compound with following structurally analogous and similar homologous Series X [35] and Y [18] as under (Fig. 2).

In above homologous series shown in Fig. 2 for comparative study,

All the series, X and Y are identically same with respect to three phenyl rings, -N=N- central bridge linking middle and third phenyl ring as a one of the central group partly contributing to the total molecular rigidity. Ortho substituted lateral -CH₃ group which substituted identically on same position and same middle phenyl ring contributing partly to the total molecular flexibility. However, they differ with respect to first central bridge linking first and middle phenyl ring with present (Series 1) and absence (Series X and Y) of -CH=CH- unit contributing partly to the molecular rigidity and changing homolog to homolog in same series at the left terminal -OR and fixed tail ended terminal -Cl (Series 1 and X) and -OCH₃ which contributes partly to the total molecular flexibility from series to series for the same homolog. Thus, molecular rigidity and flexibilities of homologs in the same series or from series to series for the same homolog vary with more or less extent, which reflects in the variations in the thermal resistivity toward exposed thermal vibrations causing difference in the mesogenic properties or LC behaviors from homolog to homolog in the same series or for the same homolog from series to series. Following Table 3 represent some variations of LC properties for the same homolog from series to Series 1, X and Y under comparison.

Above data indicate that,

Series \rightarrow	Series-1 –CH=CH–COO– and –Cl	Series-X –COO– and –Cl	Series-Y $-COO-$ and $-OCH_3$
Smectic–Nematic		106.6	118.6
Or	-	(C ₁₂ -C ₁₆)	(C ₁₂ -C ₁₆)
Smectic–Isotropic			
Commencement of Smectic phase	-	C ₁₀	C ₁₂
Nematic–Isotropic	196.7	161.5	183.0
	(C ₁ –C ₁₆)	(C ₁ -C ₁₆)	(C ₁ -C ₁₂)
Commencement of nematic phase	C ₁	C ₁	C ₁
Upper and lower total mesophase lengths	35.0-131.0	31.0-74.0	23.0-137.0
In °C	C ₁₆ C ₄	C ₁ C ₄	C ₁₄ C ₂

Table 3. Relative average thermal stabilities in °C.

- Present novel Series 1, is only nematogenic without exhibition of smectogenic property whereas, Series X and Y chosen for comparative study are predominately nematogenic and partly smectogenic.
- Mesomorphism commence from very first member of the Series 1, X and Y under comparison.
- Thermal stability for nematic is the lowest for Series X (161.5) lower for Series Y(183.0) and the highest for Series 1(196.7), whereas, thermal stability for smectic follows decreasing order from Series Y to X to 1.
- Smectogenic character commences late from C10 homolog of Series X and from C12 homolog of Series Y whereas, it does not commence even from last homolog of a present novel Series 1.
- Lower total mesophaselengths are in decreasing order from Series 1 to Series X to Series Y whereas; upper total mesophaselengths are in increasing order from Series X to Series 1 to Series Y under comparative manner.

Homologous Series 1 of present investigation and the analogous homologous Series X and Y are almost identical in all respect except the first ester central bridge which is -CH=CH-COO- in case of Series 1 and carboxylate -COO- in case of Series X and Y under comparative study. These are closely similar to each other except differing by -CH=CH- unit. Therefore, vinyl carboxylate -CH=CH-COO- has greater or longer molecular length and the permanent dipole moment across the long molecular axis, as compared to -COO- central bridge of series X and Y. Therefore, Series1 causes more non-coplanarity due to a twist obtained as the oxygen atoms of the vinyl carboxyl group bump into the non-bonded adjacent hydrogen atom of the aromatic ring. On account of these differences the thermal stability of Series1 is missing or the smectic-isotropic thermal stabilities are in a general way lower than the corresponding smectic thermal stabilities of Series X and Y. Thus, exhibition of only nematic character of Series 1 is facilitated or smectic mesophase formation is hindered as compared to Series X and Y. Early or late commencement of smectic phase is related with the extent of molecular non-coplanarity of a molecule. However, though there is no much difference except tail ended except tail ended terminal groups between the Series X and Y but much differs in case of Series 1. The commencement of nematic phase are equally facilitated from very first member of the each series, because, the suitable magnitude of anisotropic forces of intermolecular end to end attractions as a consequence of favorable molecular rigidity and flexibility which causes required environmental condition to facilitate

nematogenic mesophase formation. Thermal stabilities and the degree of mesomorphism for smectic or/and nematic mesophases depended upon the internal energy (Δ H) stored by individual molecules of each homolog of each series or substance, as a consequence of combined effect of molecular rigidity and/or flexibility and their thermal resistivity toward exposed thermal vibrations balance the suitable or unsuitable magnitudes of anisotropic or isotropic forces of intermolecular cohesion with or without adoption of LC state or none LC state with different temperature range or at isotropic temperature. Thus, variations in the thermal stabilities for mesophase or the sequential status of thermal stabilities and the extent of total mesophaselengths for smectic and/or nematic depended upon changing molecular rigidity and/or flexibilities varied through numerical values of their Δ H for the same homolog from series to series or from homolog to homolog in the same series.

Thus, present novel series is entirely nematogenic whose mesophaselength is consistently wide and considered as high melting azoester series.

Conclusions

- Novel azoester series is entirely nematogenic with absence of smectogenic character.
- Group efficiency order derived for smectic and nematic on the basis of [a] thermal stabilities [b] early commencement of mesophase and [c] total mesophaselengths are as under.

```
(a) Smectic
Series Y > Series X > Series 1
Nematic
Series 1 > Series Y > Series X
(b) Smectic
Series X > Series Y > Series 1
Nematic
Series 1=Series X=Series Y
(c) Mesophaselength
Upper
Series Y > Series 1 > Series X
Lower
Series 1 > Series X > Series Y
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- Molecular structure is very sensitive and susceptible to phenomena of mesomorphism and the degree of mesomorphism.
- Present study may be useful for the sensing deviation to be operated to control thermo processes 91.0 °C-274.0 °C.
- Favorable magnitude of molecular rigidity and flexibility operates mesomorphic tendancy of a substance and its magnitude of stabilization.
- Present investigation supports and raises the credibility to the conclusions drawn earlier.

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