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Mesomorphism dependence on the combined effect of molecular rigidity and flexibility

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ABSTRACT

A novel liquid crystalline (LC) homologous series of azoesters with a laterally substituted methoxy group RO-C_6H_4-COO-C_6H_3-(-OCH_3)-N=N-C_6H_4-COO-$C_4H_{9(n)}$ has been synthesized and studied with a view to understanding the effect of molecular structure on thermotropic mesomorphism. The novel homologous series consists of thirteen homologues (C_1–C_{18}). The C_1–C_5 homologues are nonliquid crystals. The C_6 and C_7 homologues are only enantiotropically nematogenic and the rest of the mesomorphic homologues (C_8–C_{18}) are enantiotropically smectogenic and nematogenic. Transition temperatures and the textures of the mesophases were determined using an optical polarizing microscope (POM) equipped with a heating stage. The novel azoester homologues were characterised and confirmed using their analytical, spectral and thermometric data. Transition curves Cr-M/I, Sm-N and N-I behaved in normal manner without (Sm-N) and with (N-I) exhibition of odd-even effect respectively in a phase diagram. Thermal stabilities for smectic and nematic are 100.0°C and 127.7°C whose, mesomorphic phase length vary from 13.0°C to 24.0°C and 11.0°C to 33.0°C, respectively. The mesomorpism is compared with other known series.

KEYWORDS
Azoester; enantiotropy; liquid crystals; smectic; nematic

Introduction

The technological importance of the liquid crystalline (LC) [1] state and its utility have attracted scientists from many disciplines [2–9]. The ester central group is biologically active as antibacterial and antifungal and useful in the growth of agricultural plants like flowers and fruit forming plants. Also they are used in light emitting and to manufacture display devices to be operated at desired temperature. Therefore, the present investigation is planned with a view to studying, understanding and establishing the relation between LC properties and the molecular structure of substances by synthesizing novel LC azoesters [10–14]. The target homologous series consist of three phenyl rings and two central bridges, viz., —COO— and —N=N—, left —OR group and tailed ended —$COOC_4H_{9(n)}$ group, whose LC behaviors will be interpreted and discussed on the basis of molecular rigidity and flexibility [15–18] after due characterization through thermal analytical and spectral data. Group efficiency order will be derived from the comparative study of present homologous series with structurally similar analogous series. Several homologous series with ester group are reported to date [19–25].

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Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating agent (R-X) to convert it into 4-n-alkoxy benzoic acids (A) by a modified method of Dave and Vora [26]. 4- amino butyl benzoate ester (B) was prepared by a usual establish method [27]. Azo dye (C) 4-hydroxy 3-methoxy phenyl azo 4′-butyl benzoates (m.p. 121°C, yield 74%) was prepared by a well-known azotization method [28], Final azoester [D] products were synthesized by condensation of (A) and (C) [29]. Thus, the azo-ester homologue derivatives were filtered, washed with sodium bicarbonate solution followed by distilled water, dried and purified until constant transition temperatures obtained, using an optical polarising microscope equipped with a heating stage. 4-Hydroxy benzoic acid, Alkyl halides, O-Cresol, $NaNO_2$, $SOCl_2$, 1-Butanol, MeOH, 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

Some selected representative homologues of the series were characterized by infrared [IR], ^{1}HNMR technique and elemental analysis. IR spectra were recorded on Perkin Elmer spectrum GX. ^{1}HNMR spectra were recorded on brucker using $CDCl_3$ as solvent. Elemental analysis was performed on Perkin Elmer PE 2400 CHN analyzer (Table 1). Liquid Crystal properties, i.e., transition and melting temperatures of homologues were investigated by an optical polarizing microscopy equipped with heating stage. Textures of the novel homologues were determined by miscibility method. Thermodynamic quantities enthalpy (ΔH) and entropy (ΔS) are qualitatively discussed.

Analytical data

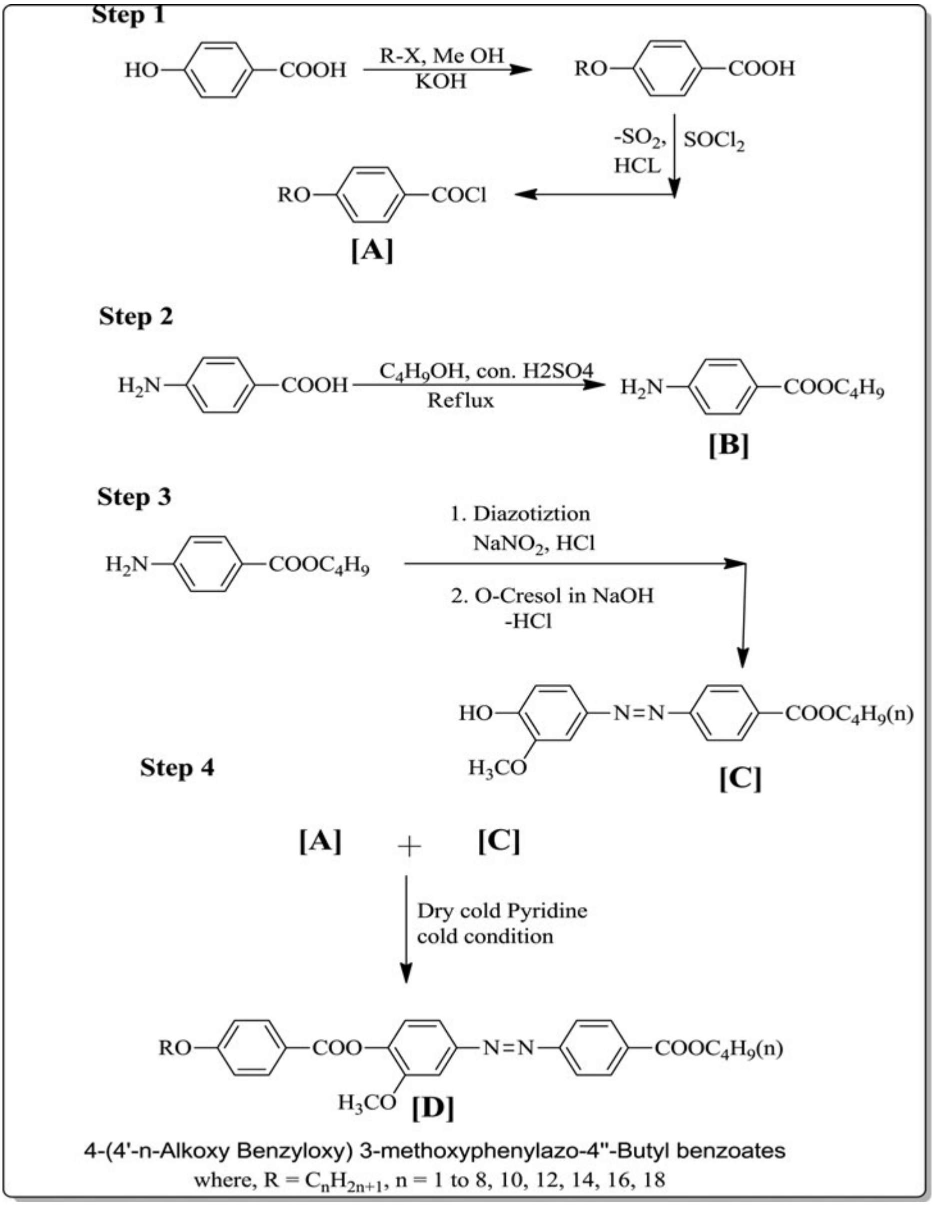
IR Spectra (KBr) in cm^{-1} for Heptyloxy, Hexadecyloxy Derivatives

Hexyloxy: 760 Poly methylene ($-CH_2-$)n of $-OC_7H_{15}$, 883($-$C-H- def. di-substituted-Para), 690 Polymethylene ($-CH_2-$) of $-OC_7H_{15}$, 989 ($-$C$-$H$-$ def. hydrocarbon), 1060 and 1105($-$C$-$O$-$) Str, 1296 and 1321 and 1423, 1494 ($-$C$-$O str in $-$ (CH_2)n chain), 1579 ($-$C$-$H$-$ def. in CH_2), 1390 ($-$N=N$-$)str, 1641 ($-$C=O group), 1735 (-COO- ester group), 2872 and 3272 and ($-$C$-$H str in CH_3). IR confirms the molecular structure.

Hexadecyloxy: 759 and796 Polymethylene ($-CH_2-$)n of $-OC_{16}H_{33}$, 883($-$C$-$H$-$ def. m di-substituted-Para), 989 ($-$C$-$H$-$ def. hydrocarbon), 1008, 1056, ($-$C$-$O$-$) Str, of $-C_4H_9$,1276 and 1392 and 1373, 1246($-$C$-$O str in $-(CH_2)$n chain, 1496($-$C$-$H$-$ def. in CH_2),1512 and 1392 ($-$N=N$-$)str, 1660 ($-$C=O group), 1737 ($-$COO$-$ ester group), 2733 and 2930 and 3084 (-C-H str in CH_3). IR confirms the molecular structure.

1H NMR spectra in $CDCl_3$ in δ ppm for Tetradecyloxy and Octyloxy Derivative

Tetradecyloxy: 0.88 (t, $-OC_{14}H_{29}$, 3H, of $-C_{14}H_{29}$), 0.93 (t, 3H, $-C_4H_9$), 1.45 (p, of $-C_4H_9$), 1.80 (p, of polymethylene $-C_4H_9$), 4.06 (t, 4H, $-OCH_2-CH_2-$ of $-OC_{14}H_{29}$), 1.43 (p, $-OC_{14}H_{29}$), 3.83 (s, 3H, $-OCH_3$), 8.25-8.11 (s, Ar-H, substituted first and third phenyl ring), 7.63, 7.62–7.45 (s, Ar-H, p-substituted second phenyl ring), 7.15 (S, Ar-H, para substituted phenyl ring), NMR confirms the molecular structure.



Scheme 1. Synthetic route to the series.

Table 1. Elemental analysis for C_5, C_6, C_8, C_{10}, C_{14}.

Sr. No.	Molecular formula	%Elements found C	%Elements found H	%Elements found N	%Elements calculated C	%Elements calculated H	%Elements calculated N
1	$C_{30}H_{34}O_6N_2$	69.26%	6.48%	5.32%	69.49%	6.56%	5.40%
2	$C_{31}H_{36}O_6N_2$	69.84%	6.70%	5.32%	69.92%	6.76%	5.26%
3	$C_{33}H_{40}O_6N_2$	70.64%	7.04%	4.86%	70.71%	7.14%	5.00%
4	$C_{35}H_{44}O_6N_2$	70.21%	7.40%	4.68%	71.42%	7.48%	4.76%
5	$C_{39}H_{53}O_6N_2$	71.04%	8.10%	4.20%	72.55%	8.21%	4.34%

Table 2. Texture of nematic phase of C_6, C_{10}, C_{14}, C_{18} by miscibility method.

Sr. no.	Homologue	Texture
1	C_6	Threaded Nematic
2	C_{10}	Schlieren nematic
3	C_{14}	Schlieren Nematic
4	C_{18}	Smectic-C

Octyloxy: 0.88 (t, $—OC_8H_{17}$, 3H, of $—C_8H_{17}$), 0.93 (t, 3H, $—C_4H_9$), 1.45 (p, of $—C_4H_9$), 1.80 (p, of polymethylene $—C_4H_9$), 4.06 (t, 4H, $—OCH_2—CH_2—$ of $—OC_8H_{17}$), 1.43 (p, $—OC_8H_{17}$), 3.83 (s, 3H, $—OCH_3$), 8.25–8.11 (s, Ar-H, substituted first and third phenyl ring), 7.63, 7.61-7.46 (s, Ar-H, p-substituted second phenyl ring), 7.14 (S, Ar-H, para substituted phenyl ring), NMR confirms the molecular structure.

Homologous Series: 4-(4′-n-alkoxy benzoyloxy)-3-methoxyphenyl azo -4′′-Butyl benzoates

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Results and discussion

A novel liquid crystalline azoester homologous series is formed by condensing dimeric n-alkoxy benzoic acids and non-mesomorphic component azo dye 4-hydroxy 3-methoxy phenyl azo-4′-n-butyl benzoate (M. P.: 121.0°C, yield: 74%). The transition temperatures of novel homologues are relatively lower than the corresponding dimeric n-alkoxy acids. Mesomorphism commences from C_6 homologue as nematic and from C_8 homologue as smectic until C_{18} member of a series in enantiotropic manner. The rest of the C_1–C_5 homologues are non-mesomorphic. Transition temperatures as determined from POM are plotted versus the number of carbon atoms present in n-alkyl chain 'R' of –OR group, and on linking the like or related points, the Cr-N/I, Sm-N and N-I transition curves are obtained showing their phase behaviours in a phase diagram (Fig.-1). A Cr-M/I transition curve follows a zigzag path of rising and falling with overall descending tendency and behaved in normal manner. A Sm-N transition curve commences from its maxima point and then descended until the last member of a series in usual manner with absence of odd-even effect. N-I transition curve initially

Table 3. Transition temperatures in°C.

Compound no.	Homologue (n-alkyl chain)	Transition temperatures in°C		
		Smectic	Nematic	Isotropic
1	C_1	—	—	156.0
2	C_2	—	—	148.0
3	C_3	—	—	151.0
4	C_4	—	—	139.0
5	C_5	—	—	136.0
6	C_6	—	132.0	144.0
7	C_7	—	122.0	136.0
8	C_8	108.0	121.0	132.0
9	C_{10}	94.0	118.0	134.0
10	C_{12}	90.0	110.0	130.0
11	C_{14}	74.0	88.0	118.0
12	C_{16}	65.0	80.0	112.0
13	C_{18}	68.0	83.0	116.0

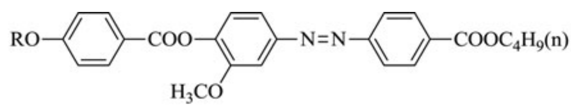
descends from C_6 to C_8 and then ascended to C_{10} and then continuously descended in normal established manner with exhibition of short and narrow odd even effect. Thus, transition curves of a phase diagram behaved in normal manner with negligible deviation at C_8 and C_{18} member of a novel series. N-I transition curves for odd and even homologues are extrapolated [30–33] to C_4 and C_3 homologue to intensify odd-even effect and to determine their latent ability for nematic and the corresponding latent transition temperatures (LTT) which merges into their (C_4 and C_3) isotropic temperatures, eliminating the possibilities of mesophase formation. Similarly Sm-N transition curve is extrapolated to C_6 homologue which predicts its LTT for smectic as121.5°C, as monotropic transition temperature. Odd-even effect for nematic merges into each other at C_8 homologue and then prolonged up to C_{18} homologue as a single transition curve for higher homologues of longer n-alkyl chain 'R' of –OR. Thermal stability for smectic and nematic are 100.0 and 127.7 with their mesophase lengths ranging from 13.0°C to 24.0°C and 11.0°C to 33.0°C, respectively. (Sm+N) mesophase length ranges from 12.0°C to 48°C at the C_6 and C_{18} homologues. Textures of nematic phase are threaded or Schlieren and that of a focal conic fan shaped of type A or C. Spectral, analytical and thermal data supported the molecular structures of homologues. The changing trend in mesomorphic properties and the degrees of mesomorphism etc. from homologue to homologue in the same present novel series undergoes variation with changing number of carbon atoms present in n-alkyl chain 'R' of –OR group at left terminal end, keeping the rest of the molecular part unchanged throughout a series.

Lowering of transition temperatures of present novel series as compared to corresponding dimeric n-alkoxy benzoic acids are attributed to the breaking of hydrogen bonding between aromatic acid molecules through esterification process. The lack of LC properties by the C_1–C_5 homologues is due to the low magnitudes of dispersion forces and the low magnitudes of dipole–dipole interactions which induces high crystallizing tendency in the molecules of nonmesomorphic homologues. Thus, the molecules of C_1 to C_5 members of a series sharply transform into isotropic state without passing through LC state and from isotropic state to crystalline solid state excluding monotropic mesophase formation as a consequence of unfavorable and unsuitable magnitudes of molecular rigidity and flexibility. The facilitation of smectic and then nematogenic or only nematic mesophase formation from C_8 or C_6 homologue members of a series is attributed to the disalignment of molecules perpendicular to the plane of floating surface or/and at an angle less than ninety degree to the plane of a floating surface, which arranges the floating of the molecules of mesogenic homologues, resisting exposed thermal vibrations; either in sliding layered molecular ordered organization and then with statistically parallel orientational ordered molecular organization (C_8–C_{18}) or with only statistically parallel orientational ordered molecular organization as depending upon magnitudes of intermolecular cohesion and closeness to facilitate either smectic plus nematic phase (C_8 to C_{18}) or only nematic phase formation for different ranges of liquid crystallinity. Thus, suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence favorable molecular rigidity and flexibility, through suitable magnitudes of dispersion forces and dipole–dipole interactions facilitate or induce to cause mesophase formation. The exhibition of odd-even effect by N-I transition curves by C_6, C_7, and C_8 homologues is due to the C_7 odd and C_6 plus C_8 even numbered homologues, whose number of carbon atoms are sequentially added in n-alkyl chain 'R' of –OR group. However, absence of odd-even effect in Sm-N transition curve of a phase diagram is attributed to the presence of none of the odd mesogenic member from the group of smectogenic homologues or alternatively one can say that, all the smectogenic homologues are even numbered. Disappearance of odd-even effect of higher homologues of longer n-alkyl chain from and beyond C_8 is attributed to the possibilities of the coiling or bending or flexing or coupling of n-alkyl chain 'R' with the major axis of core structure which may cause uncertainty in the status of longer n-alkyl chains and modifies magnitudes of molecular rigidity and flexibility as well as predominancy of intermolecular cohesions operating oppositely at a time depending upon decreasing tendency of intermolecular distance and presence of highly polar $-OCH_3$ lateral group substitution together, which increases molecular polarizability and consequently increasing intermolecular attractions. Thus, the net intermolecular cohesions, molecular rigidity and flexibility, exhibition of either smectic or/and nematic mesophase and the degree of mesomorphism are the results of Net effects of the status of n-alkyl chain 'R' of –OR under the influence of exposed thermal vibrations. The extrapolations of N-I transition curves for C_4 and C_3 eliminate the possibilities of monotropic nematic phase because, extrapolated curve matches with isotropic temperatures of C_4 and C_3 homologues but the extrapolation of Sm-N transition curve predicts monotropic transition temperature as 121.5°C. But actually it is not realizable due to its high crystallising tendency. The variations in mesogenic properties and their magnitudes from homologue to homologue in the same series is attributed to the varying number of methylene unit or units which affects the parameters, responsible and their suitable magnitudes for possibility to induce and facilitate mesophase or mesophases of their type. Following Fig. 2 represents some thermotropic azoester series-1 and the structurally similar analogous series-X [34] and Y [35] which are chosen for comparative study are as under.

Figure 2 of presently investigated series-1 and structurally similar analogous series X and Y are thermotropically mesomorphic and identical with respect to first and third phenyl rings which are liked through –COO- and –N=N- central bridges with middle phenyl ring substituted by lateral $-OCH_3$ group (series-1) or another fused phenyl ring in naphthyl unit (series-X) or –H in series-Y respectively, which constitute differing total molecular rigidity of each individual series under comparative study. Flexible –OR group is commonly and identically present as left n-alkoxy group for the same homologue which partly contributes to the total molecular flexibility in equal manner for the same homologue from series to series; but, the total molecular flexibility varied with changing tailed end groups $-COOC_4H_{9(n)}$ in which $-OC_4H_{9(n)}$ bonded through >C=O with third phenyl ring or directly bonded as $-OC_4H_{9(n)}$ and through lateral $-OCH_3$, fused phenyl ring or –H for the same homologue from series to series. Thus, facilitating mesophase and its type and magnitudes in terms of mesophase length or degree of mesomorphism depended upon the magnitudes of differing features, including combined effect of molecular rigidity and flexibility which varied for the same homologue from series to series as well as homologue to homologue in the same series. Following Table 4 represents some LC properties of series-1, X and Y in comparative manner as mentioned below.

Above comparative data of series-1, X and Y under comparison suggests that,

- Series-1, X and Y are smectogenic plus nematogenic.
- Thermal stabilities for smectic adopted increasing order from series-1 to series-Y to series-X, i.e., smectic thermal stability of series-1 is the lowest and of series-X is the highest.
- Thermal stabilities for nematic are in increasing order from series–Y to series-1 to series-X, i.e., Nematic thermal stability of series-Y is the lowest and of series-X is the highest.
- Smectogenic mesomorphism commences earliest from C_8 homologue for series-1 and Y but it commences late from C_{12} homologue from series-X.
- Nematogenic mesomorphism commences from C_6 homologue for Series-1, X and Y in equal manner.
- Lower mesophase lengths follow increasing order from series-Y to series-1 to series-X.
- Upper mesophase lengths follow increasing order from series-X to series-Y to series-1.



Homologous Series: 4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenyl azo -4"-Butyl benzoates

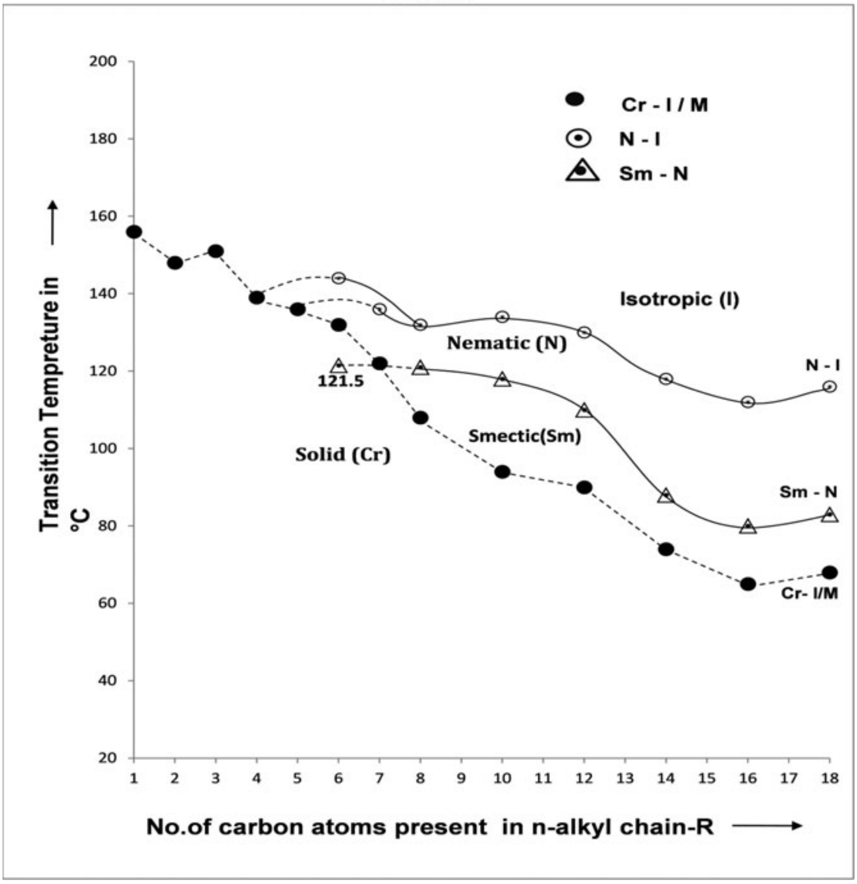


Figure 1. Phase behaviors of series.

Thermal stability of mesophase is a direct effect of the combined effect of molecular rigidity and flexibility as a consequence of internal energy stored by a thermodynamic system due to mass and characteristics at constant pressure (ΔH), or the amount of energy released or absorbed, i.e., exchanged with surroundings during its formation by breaking of old bonds (reactant) and forming of new chemical bonds (product), which constitutes the molecular rigidity and flexibility, and the magnitudes of which alters from substance to substance and from series to series depending upon respective molecular structure. Thus, suitable and favorable magnitudes of intermolecular cohesion and closeness as a consequence of combine effects of molecular rigidity and flexibility is a thermally resisting internal power of a substance or energy of mesophase stabilization under floating condition on the surface, when external heat is exposed upon a sample substance. All the homologous series-1, X and Y under comparative study are differing with respect to combined effect of molecular rigidity and flexibility for the same homologue from series to series in which molecules of a homologous series-X are comparatively more rigid in presence of common flexible end groups –OR and $–OC_4H_{9(n)}$ whose contribution to flexibility is almost identical, neglecting bonding of $–OC_4H_{9(n)}$ through

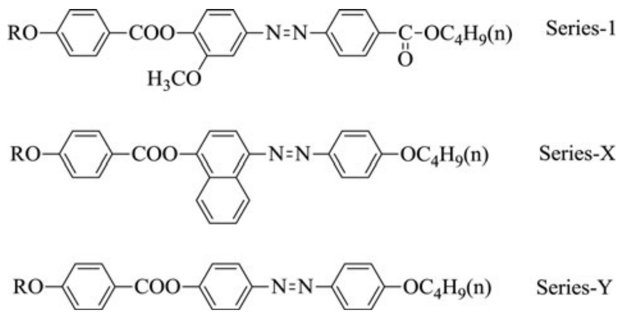


Figure 2. Structurally similar analogous series.

Table 4. Relative thermal stability in°C.

Series→	Series-1	Series-X	Series-Y
Sm-N or Sm-I Commencement of smectic phase	100.0 (C_8–C_{18}) C_8	115.5 (C_{12}–C_{18}) C_{12}	111.3 (C_8–C_{18}) C_8
N-I Commencement of nematic phase	127.7 (C_6–C_{18}) C_6	138.5 (C_6–C_{18}) C_6	124.7 (C_6–C_{18}) C_6
Total (Sm+N) mesophase length in°C	12.0 to 48.0 C_6 C_{18}	13.0 to 36.0 C_7 C_{14}	07.0 to 40.0 C_6 C_{14}

-C=O in series-1. Thus, the most rigid series-X facilitated stabilization of smectic and nematic mesophase to higher extent as compared to series -1 and Y. The lower nematic thermal stability and a little bit higher smectic thermal stability of series-Y as compared to series-1 is attributed to the absence and presence of lateral substitution in series-Y as compared to series-1 including effect due to its linking $–OC_4H_{9(n)}$ through >C=O part of tailed end, as well as difference in intermolecular distance or intermolecular closeness, of almost equally rigid but, of lower rigidity than series-X. The early or late commencement of mesophase depend upon the extent of molecular noncoplanarity. All the series-1, X and Y are almost equally planer or noncoplaner, but, fused phenyl ring at the middle part of molecules of series-X causes disturbance comparatively more than the molecules of series-1 and Y due to combined effects of effective molecular polarity and polarizability. Therefore, smectogenic mesophase formation commences late from C_{12} homologue of series-X, but it commences earlier from C_8 homologue for series-1 and Y. The commencement of nematic mesophase formation takes place in equal manner from C_6 homologue, irrespective of difference in molecular rigidity or the extent of molecular noncoplanarity, because molecular structure is loosened more under the influence of exposed thermal vibrations beyond ordered smectogenic molecular organization, which reorganizes and arrange easily in less ordered texture of nematic type at relatively higher temperature. Increasing or decreasing order of mesophase lengths depends upon the magnitudes of thermal resistivity induced during floating of molecules in LC state on the floating surface.

Conclusions

- An azoester novel homologous series of liquid crystals is predominantly nematogenic and partly smectogenic whose degree of mesomorphism is 12°C to 48°C and it is a middle ordered melting type series.
- The group efficiency order derived on the basis of (i) thermal stabilities (ii) early commencement of mesophase and (iii) mesophase length foe smectic and nematic are as under.

(i) Smectic Series-X > Series-Y > Series-1 Nematic Series-X > Series-1 > Series-Y
(ii) Smectic Series-1 = Series-Y > Series-X Nematic Series-1 = Series-X = Series-Y
(iii) (Sm±N) mesophase lengths: Lower: Series-X > Series-1 > Series-Y Upper: Series-1 > Series-Y > Series-X

- Mesomorphism is very sensitive and susceptible to molecular structure; as a result of effective molecular rigidity and/or molecular flexibility.
- Present novel LC dyes reported here are useful as equal as other dyes and other light emitting devices or devices related to thermography.
- Present investigation supports and raises the credibility to the early conclusions related to the relation between molecular structure and LC properties.

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