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Mesomorphism dependence on ortho-substituted lateral groups in isomeric and nonisomeric homologous series

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ABSTRACT

A novel monomeric homologous series of α,β-ethylene derivatives was synthesized and studied with a view to understanding and establishing the relation between molecular structure and liquid crystal properties. The series consists of 12 novel compounds. The methoxy to propyloxy derivatives are not liquid crystals, the butyloxy homologue is monotropic nematic, the pentyloxy homologue is monotropic smectic and enantiotropic nematic, and the rest of the homologues (C_6–C_{16}) are enantiotropically smectic in addition to nematic. Transition temperatures and texture were determined by an optical polarizing microscope equipped with a heating stage, and show an odd–even effect for nematic–isotropic and smectic–nematic transition curves. Analytical and spectral data confirm the molecular structures. The average smectic and nematic thermal stabilities are 84.9°C and 94.15°C, respectively. The liquid crystal properties of present series are compared with the structurally similar known series.

KEYWORDS

Liquid crystal; mesomorphic; monotropy; nematic; smectic

Introduction

A liquid crystalline state (LC) of a substance is known since 1888 [1], has proved its utility in many of science and technology [2–5]. A critical survey of literature about the synthesis and study of the LC state, it is concluded that the synthesis of novel LC substances is an interesting and important field from research point of view. Synthesis of novel LC substances [6–10] can be useful to the researchers in other fields in addition to chemistry. Thus, the present investigation is planned with a view to understanding the effects of molecular structure on liquid crystal properties [11–15] by varying terminal group or groups, central bridge or bridges, or number of phenyl ring or rings, changing the position of the functional group or changing polarity of the functional group at lateral or/and terminal position, etc. The present study is aimed to construct a nonlinear molecule of three phenyl rings bridged through -COO- and -CO-CH=CH- group and -OC_nH_{2n+1}, left terminal as well as ortho substituted –Cl group. Thus, effect of molecular rigidity/flexibility related to molecular structure can be correlated with liquid crystal properties of thermotropic LC novel substances [16–18].

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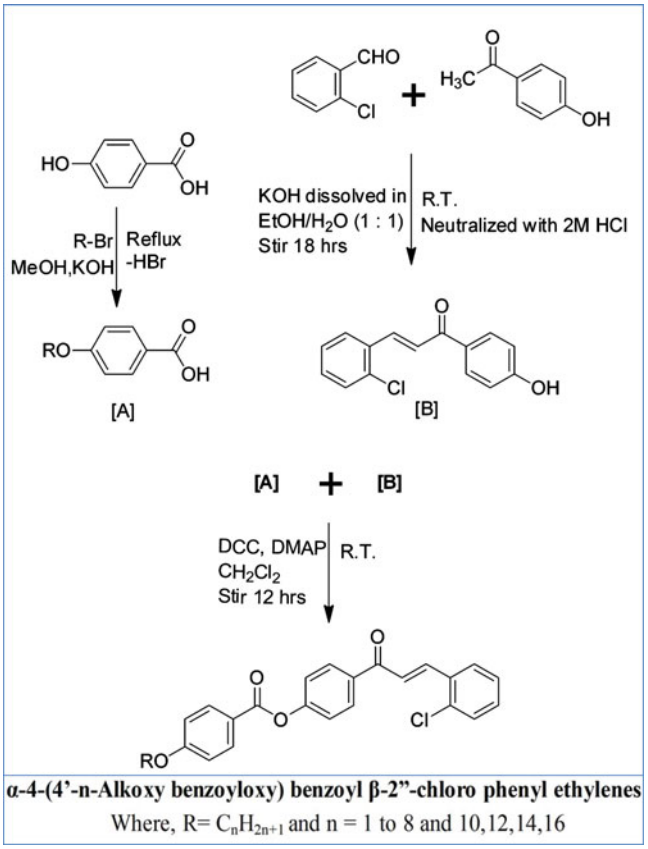

Scheme 1. Synthetic route to the novel series.

Experimental

Synthesis

n-Alkoxy benzoic acids were prepared from 4-hydroxy benzoic acid, by suitable alkylating agents by modified method of Dave and Vora [19]. α-4-Hydroxy benzoyl β-2′-chloro phenyl ethylene was prepared by usual established method [20]. 4-n-Alkoxy benzoic acids and α-4-hydroxy benzoyl-β-2′-chloro phenyl ethylene were condensed in 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) and CH_2Cl_2 [21]. Synthetic route to usual series is shown in scheme 1. Final products were individually decomposed, filtered, washed, dried and purified till the constant transition temperatures obtained.

The chemicals 4-hydroxy benzoic acid, 4-hydroxy acetophenone, 2-chloro benzaldehyde, alkyl bromide (R-Br), methanol, KOH, DCC, 4-dimethylaminopyridine, hydrochloric acid, dichloromethane, ethanol etc. were used as received except solvents, which were dried, purified and distilled prior to use.

Characterization

Some selected members of a series were characterized by elemental analysis (Table 1), IR spectra,^{1}H NMR spectra and mass spectra. Transition temperatures and textures of the

Table 1. Elemental analysis for (1) ethyloxy, (2) propyloxy, (3) dodecyloxy derivatives.

S. No.	Molecular formula	Elements %Found			Elements %Calculated		
		C	H	O	C	H	N
1	$C_{24}H_{19}ClO_4$	70.85	4.71	15.73	70.92	4.85	15.09
2	$C_{25}H_{21}ClO_4$	71.34	5.03	15.21	70.95	5.18	15.85
3	$C_{34}H_{39}ClO_{-4}$	74.64	7.18	11.70	73.20	7.01	10.85

nematic and smectic phase were determined by an optical polarizing microscope equipped with a heating stage. Microanalysis was performed on Perkin Elmer PE 2400 CHN Analyzer (Table 1). The structures of the materials were elucidated by infrared (IR) spectroscopy (SHIMATZU FTIR-8400 Spectrophotometer), proton nuclear magnetic resonance (^{1}H NMR) spectrometry (BRUKER Advance-III (400 MHz) Spectrometer using $CDCl_3$ as a solvent) and Mass spectrometry (Shimadzu GC-MS Model No.QP-2010,). The analyses of the structures of the products and intermediates by spectroscopic methods were found to be consistent with the predicted structures.

Analytical data

Elemental analysis (Table 1)

Spectral data

^{1}H NMR in ppm for tetradecyloxy derivative

0.77–0.79(t,3H,-CH_3 of –$OC_{14}H_{29}$ group), 1.51–1.36 (m,22H,(-CH_2-)$_{11}$), 1.68–1.72(t,2H,-CH_2-CH_2-O-), 3.89–3.92 (t,2H,-CH_2-O-), 6.84–6.88 (d,2H, ortho to –$OC_{14}H_{29}$ group in phenyl ring), 7.15–7.31 (s,s,s, dd 5H, ortho, pera & meta to –CO-CH=CH- & ortho to Ph-COO-),7.36–7.40(d, 1H,-CO-CH-CH-), 7.63–7.64 (d, 1H, in phenyl ring ortho to –Cl group),7.98–8.04(m,4H,ortho to–COO- & -CO-CH-CH- group in phenyl ring), 8.07–8.11(1H, d, -CO-CH-CH-)The NMR data are consistent with the molecular structure.

^{1}H NMR in ppm for hexadecyloxy derivative

0.78–0.81 (t,3H,-CH_3 of –$OC_{16}H_{33}$ group),1.17–1.39 (m,26H,(-CH_2-)$_{13}$), 1.72–1.75 (q, 2H,-CH_2-CH_2-O-), 3.94–3.97 (t,2H,-CH_2-O-), 6.86–6.90 (d,2H, ortho to -$OC_{14}H_{29}$ group in phenyl ring), 7.17–7.37 (s,s,s, dd, 5H, ortho, pera & meta to -CO-CH=CH- & ortho to Ph-COO-),7.37–7.44(d, 1H,-CO-CH-CH-), 7.67–7.69 (d, 1H, in phenyl ring ortho to –Cl group),7.98–8.07(m,4H,ortho to–COO- & -CO-CH-CH- group in phenyl ring), 8.10–8.14(1H, d, -CO-CH-CH-). The NMR data are consistent with the molecular structure.

IR in cm^{-1} for pentyloxy derivative

3074 (=C-H Str. of Phenyl nucleus), 2918 & 2848 (CH_2 sym. & asym. stra.), 1732 (Aromatic C=O Str.), 1602 (aromatic C=C str.), 1506 (C–C aromatic str.), 1413 (C–H bend alkanes), 1325 (aromatic & aliphatic C-O str.), 1168 (Ar-O str.), 850 (C-H oop. phenyl ring), 759 (C-H oop.bending of phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for heptyloxy derivative

3070 (=C-H Str. of Phenyl nucleus), 2914 & 2848 (CH_2 sym. & asym. stra.), 1730 (Aromatic C=O Str.), 1602 (aromatic C=C str.), 1508 (C-C aromatic str.), 1415 (C-H bend alkanes),

1313 (aromatic& aliphatic C–O str.), 1165 (Ar–O str.), 846 (C–H oop. phenyl ring), 758 (C–H oop.bending of phenyl ring). The IR data are consistent with the molecular structure.

Mass spectra of butyloxy derivative

m/z (rel.int%): 434 $(M)^+$, 241,193, 136, 121

Mass spectra of octyloxy derivative

m/z (rel.int%): 491$(M)^+$,377, 241,136,121,113

Results and discussion

Novel α, β ethylene derivatives of ester homologous series of liquid crystal behaviors consists of twelve homologues. C_1 to C_3 members of a series are not liquid crystals and the rest of the homologues are liquid crystals in either monotropic or enantiotropic condition. C_4 member is monotropic nematic, C_5 member is monotropic smectic and enantiotropically nematic, as well as the, rest of the homologues (C_6 to C_{16}) are enantiotropically, smectic in addition to nematic. α-4-Hydroxy benzoyl β-2'-chloro phenyl ethylene (151–153°C) is a nonliquid crystal component, however, on linking it with dimeric 4-n-alkoxy benzoic acids through their acid chlorides yielded nine homologues with liquid crystal behaviors out of twelve in either monotropic or enantiotropic manner. Transition temperatures (Table 2) as determined by an optical polarizing microscopy equipped with a heating stage (POM) are plotted against the number of carbon atoms present in n-alkyl chain (R= C_nH_{2n+1}) bonded to first phenyl ring through oxygen atom. Transition curves (Cr-I or Cr-M, Sm-N, N-I or I-N etc.) are obtained on linking like or related points, showing phase behaviors of series in a phase diagram (Fig. 1). The Cr-I or Cr-Mesomorphic transition curve adopt a zigzag path of rising and falling tendency as series is ascended. Sm-N (or vice versa) transition curve follows serpentine shaped path with exhibition of odd–even effect and deviating trend of propagation as series is ascended. Similarly N-I (or vice versa) transition curve follows parallel path to Sm-N curve in deviating manner with exhibition of odd–even effect. The curves for odd and even members (Sm-N and N-I) merged into each other at the decyloxy (C_{10}) derivative of a novel series and then from and beyond the both curves (Sm-N and N-I) are individually follow the paths as a single curve. Alternation of transition temperatures created the exhibition of odd–even effects in Sm-N and N-I transition curve. Transition curves for odd members occupied lower position than the even members of a series in case of Sm-N and N-I, both curves. Thermal

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

		Transition temperature in °C		
Compound no.	R= n-alkyl group	Sm	Nm	Isotropic
1	Methyl	—	—	101.7
2	Ethyl	—	—	105.1
3	Propyl	—	—	102.5
4	Butyl	—	(86.3)	91.8
5	Pentyl	(75.6)	84.0	86.8
6	Hexyl	84.1	86.0	94.8
7	Heptyl	56.5	79.2	87.6
8	Octyl	67.4	84.1	90.3
9	Decyl	60.5	74.8	82.8
10	Dodecyl	66.8	82.3	90.1
11	Tetradecyl	62.3	73.0	81.5
12	Hexadecyloxy	89.2	116.9	139.3

Sm- Smectic: Nm- Nematic, ( ) indicate Monotropy.

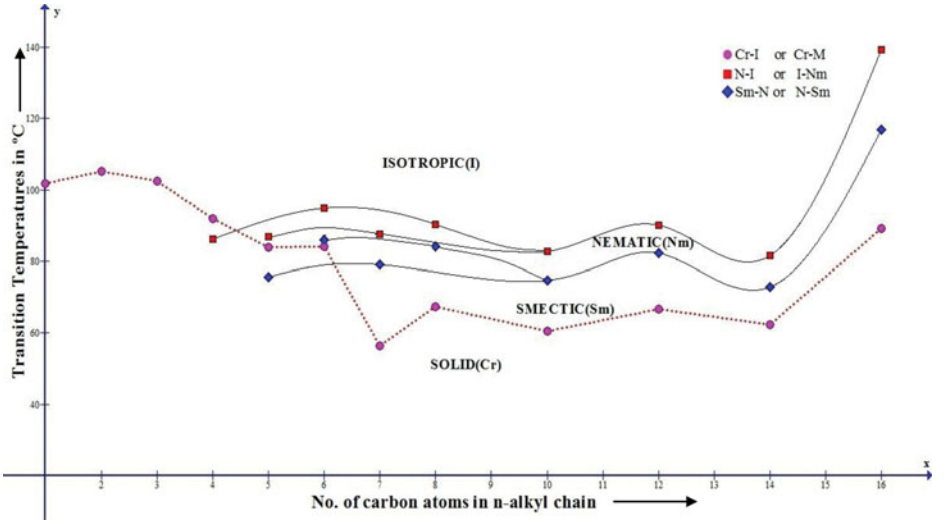

Figure 1. Phase behavior of series.

stability for smectic and nematic are 84.9°C and 94.15°C, respectively. The mesophase length for smectic and nematic ranges from 1.9°C to 27.7°C and 2.8°C to 22.4°C, respectively. Cr–Sm transition temperatures and Sm–N transition and N–I temperatures (except C_{16} homologue) of mesomorphic homologue (C_4 to C_{14}) are below hundred degree centigrade. Thus, present novel homologous series is partly smectogenic and partly nematogenic with middle ordered melting type. The liquid crystal properties are varied from homologue to homologue with changing molecular length and polarizability as well as with the changing permanent dipole moment across the long molecular axis and related cohesive intermolecular forces.

The lack of liquid crystal properties by C_1 to C_3 homologues is attributed to their high crystallizing tendency arising from their inability to withstand the exposed thermal vibrations from external source, due to unfavorable and unsuitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions; as a consequence of resultant molecular rigidity and/or flexibility, induced by low dipole–dipole interactions and dispersion forces occurring through the interactions between instantaneous dipole produced by the spontaneous oscillations of the electron clouds of molecules, leading and inducing high crystallizing tendency in a substance. Thus, liquid crystal mesophase formation is inhibits and a solid crystalline substances directly possess into isotropic liquid without passing through an intermediate state of existence between crystalline state and isotropic liquid state. Hence, the molecules of C_1 to C_3 homologues whose crystal lattices are abruptly breaking and then sharply transform into isotropic liquid under the influence of exposed thermal vibrations. Exhibition of liquid crystal state either smectic or nematic are attributed to the disalignment of molecules at an angle ninety or less than ninety degree on a floating surface depending upon suitable magnitudes of end to end or/and lateral intermolecular anisotropic forces of attractions. Molecules of homologues C_5 to C_{16} possess lamellar packing of molecules with layered structure and then, on heating the same the intermolecular attractive forces are loosened and layers of molecules slide upon each other. Thus, sliding layered arrangement of molecules from focal conic fan shaped appearance under POM of the type smectic A or C enantiotropically (C_6 to C_{16}) or monotropically (C_5) in reversible and irreversible manner respectively. All the smectogenic homologues C_5 to C_{16} reversibly and C_4 homologue irreversibly exhibited nematogenic mesophase formation. i.e. molecules of C_5 to C_{16} homologues above Sm-N

transition temperature adopt statistically parallel orientational order of molecules in floating condition, depending upon magnitudes of end to end attractions under thermal treatment with appearance of threaded or Schlieren texture of nematic phase under POM. The C_4 homologue shows nematic mesophase formation below isotropic temperature in monotropic condition. The n-alkoxy benzoic acids are dimeric but, their dimerization disappears on esterification process by breaking of hydrogen bonding into two molecules. Therefore, the transition temperatures of final ester homologues are generally lower than the corresponding n-alkoxy benzoic acids. All the members of a series either mesomorphic or nonmesomorphic from and beyond isotropic temperature shows high order of molecular disorder or high entropy ($\Delta S = \Delta H/T$) in which the molecules of a targeted substance are randomly oriented in all possible directions with irregular molecular arrangement. However, on cooling the same, the enantiotropic homologues exhibit mesophase formation from and below isotropic temperature in reversible manner and monotropic homologues (C_4 and C_5) exhibit smectic and/or nematic mesophase below isotropic temperature in irreversible manner. Nonmesomorphic homologues undergo crystallization below isotropic temperature if proper rate of cooling is maintained. The exhibition of odd–even effect by transition curves in a phase diagram is attributed to the alternations of transition temperatures of homologues up to decyloxy (C_{10}) homologue. But, alternations diminishes as series is ascended from and beyond C_{10} homologue for longer n-alkyl chains of left n-alkoxy terminal end group, because longer n-alkyl chain may coil or bend or flex or couple to lie with major axis of the core structure of molecules. Thus, uncertainty in the status of longer n-alkyl chain causes deviation in transition temperature (C_{16}) and/or transition curves which follow as single transition curve without showing odd–even effect. Odd–even effect observed in initial homologues (C_4, C_6, C_8 and C_5, C_7) is attributed to sequentially added methylene unit or units, with probable excepted status of n-alkyl chain. However, deviating effect in transition curves and temperatures may be attributed to the alternating tendency of intermolecular anisotropic forces of attractions due to laterally substituted polarizable –Cl group which may decrease intermolecular attractions due to increased molecular width or increase the intermolecular attractions due to molecular polarizability by –Cl group. Thus, two opposing forces operated at a time for the same reason, i.e. broadening of molecular width by laterally substituted –Cl group which alternates the tendency of the factors inducing mesomorphism, after decyloxy (C_{10}) homologue. The change in mesomorphic properties and the degree of mesomorphism from homologue to homologue in present (or any) homologous series is due to the progressive added methylene unit or units to the n-alkyl chain bonded to phenyl ring through oxygen atom which varies molecular flexibility and overall combined effect of molecular rigidity and flexibility to causes suitable magnitudes of anisotropic forces of intermolecular attractions to induce mesophase formation. The selected mesomorphic properties of present series are compared with the structurally similar other known series-X [22] and Y [23] shown below in Fig. 2.

Presently investigated novel homologous series-1 and a structurally similar homologous series-X are identical with respect to three phenyl ring, i.e. aromaticity, central bridges –COO–, and –CO–CH=CH– linking phenyl rings and left n-alkoxy (–OR) terminal end group which varies from homologue to homologue in same series but remains unaltered for the same homologue from series to series under comparison. Moreover homologous series 1 and X are isomeric and identical with respect to functional group –Cl; but, chloro group of same group polarity occupied at different positions (viz. ortho or para to –CO–CH=CH–). Thus, only the positional difference of chloro group which causes difference in molecular polarity, polarizability, permanent dipole moment across the long molecular axis, dipole–dipole

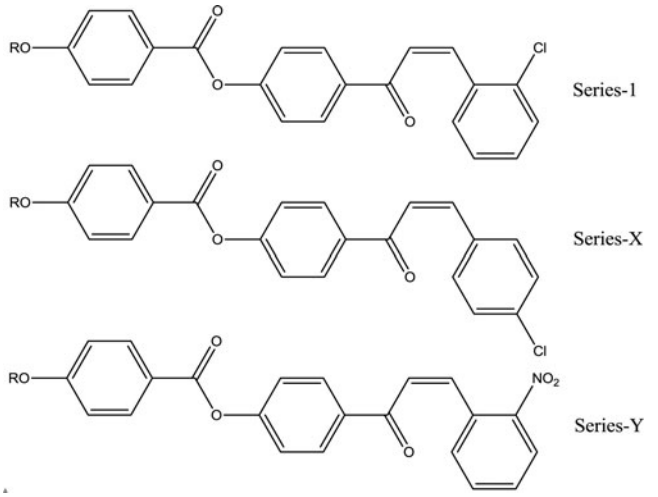

Figure 2. Structurally similar homologous series.

interactions, dispersion forces, molecular rigidity and/or flexibility, etc. can cause alteration for the same homologue from series to series in inducing mesomorphism and the degree of mesomorphism. Homologous series-1 and Y are equally identical with respect to each other as discussed earlier, except the position and group polarity of functional group on third phenyl ring. –Cl and $-NO_2$ functional groups occupy identically their substitution position (ortho to –CO–CH=CH–) and induced molecular polarizability and steric hindrance in equivalent manner but their extent of molecular rigidity–flexibility may differ for the same homologue from series to series. Thus, homologous series 1, X and Y though structurally similar in appearance, but their liquid crystal properties behaviors and the degree of liquid crystallinity may differ for the same homologue from series to series depending upon even a very small or negligible differing features of a molecular structure as a consequence of a little difference of molecular rigidity and/or flexibility. Following Table 3 represent some LC properties, viz. average thermal stability, commencement of LC state, mesophase length range exhibition of odd–even effect, etc. in comparative manner, which indicate the effect of molecular structure on liquid crystal properties and their magnitudes.

Table 3 indicates that,

- A homologous series of present investigation-1 and a homologous series-Y chosen for comparison are smectogenic in addition to nematogenic in behavior.
- Homologous series-X, chosen for comparison and isomeric with series-1 is only nematogenic without exhibition of any smectogenic character.
- Thermal stability of nematic mesophase progressively increases from series-1 to series-Y.
- Smectic thermal stability of series-1 is lower than a series-Y.
- Smectic mesophase formation commences later (C_5) than a series-Y which commences from third (C_3) homologue of series-Y.

Table 3. Average thermal stability in °C.

Series:→	[1]	[X]	[Y]
Smectic – Isotropic or Smectic - Nematic	84.9 [C_6-C_{16}]	—	138.0 [C_3-C_{14}]
Commencement of smectic phase	C_5	—	C_3
Nematic –isotropic	94.15 [C_5-C_{16}]	149.1 [C_5-C_{16}]	163.7 [C_3-C_{16}]
Commencement of nematic phase	C_4	C_5	C_3
Total mesophase length in °C (Sm + Nm)	2.8 to 50.1	14 to 25	16 to 49

- Nematic mesophase formation commences from C_4, C_5, and C_3 homologues for series-1, series-X and series-Y, respectively.
- Total mesophase length range is the highest (2.8 to 50.1) of present series-1 and the lowest for an isomeric series-X (14 to 25) and an intermittent value (16 to 49) of series-Y.
- Odd–even effects are observed for all the transition curves of series-1, X, and Y under comparative study.
- Odd membered transition curves in respective phase diagrams occupy their lower position than the corresponding transition curves of even membered homologues for the series under comparison.

Thus, mesomorphic properties and their degrees of mesomorphism for the same homologue vary from series to series, depending upon changing part of their respective molecule or changing position (o, m, p) of same substituent group.

The lack of smectic property by the molecules of series-X is attributed to the absence of lamellar packing of molecules in their crystal lattices. However, the molecules of series-1 and Y being laterally substituted by −Cl or $-NO_2$ polar groups, broadens respective molecules and intermolecular closeness as compared to series-X. Thus, the molecular polarizability factor activated and operates lamellar packing of molecules which builds two or three dimensional network of molecules to cause sliding layered molecular arrangement under the influence of exposed thermal vibrations in case of series-Y and series-1, but the same polarizability factor fails to build up sliding layered molecular arrangement under identical condition for series-X due to absence of lateral substitution. Moreover early or late commencement of smectic phase depends upon the extent of noncoplanarity of molecules. The –Cl group and $-NO_2$ group of series-1 and Y though situated on identical lateral position, but, their group polarities and atomic make up are different the molecules of series-X are linear lath like. Therefore, the extent of molecular noncoplanarity vary from series to series and smectic mesophase commences earliest (from C_3) of series Y, from C_5 for present series-1and it does not commence till the last homologue for series-X. Smectic and nematic thermal stability of series-Y are greater than the present series-1 and even a nematic thermal stability of series-X is though greater than a series-1 but it is lower than series-Y. The suitable magnitudes of anisotropic forces of intermolecular end to end attractions for the same homologue from series to series vary depending upon intermolecular closeness and thermal resistivity associated with molecular rigidity and flexibility in terms of enthalpy (ΔH) or internal energy which, vary from homologue to homologue in a same series and series to series for same homologue. The highest total mesophase length range (2.8 to 50.1) indicated for a present series is attributed to the degree of thermal resistivity against exposed thermal vibrations possessed by the molecules of respective series-1, X and Y after acquiring suitable magnitudes of anisotropic forces of intermolecular attractions and favorable enthalpy values, to cause mesomorphism. Exhibition of odd–even effect by initial members of the series are due to the expected status of the n-alkyl chain which alternates the transition temperatures as per expected manner, but alternation diminishes as series is ascended due to uncertainty in the status of flexible n-alkyl chain arising for different uncontrollable reasons.

Conclusions

- Presently investigated series is partly smectogenic and partly nematogenic whose, thermal stability and transition temperatures of mesomorphic homologues are below 100°C (except C_{16} homologue).

- Laterally substituted homologous series increases molecular polarizability and reduces transition temperatures.
- The group efficiency order derived on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) total mesophase length range (Sm + N) or for smectic and/or nematic are as under.

(i) Smectic: ortho - NO_2 > ortho –Cl > para –Cl
Nematic: ortho - NO_2 > para –Cl > ortho –Cl
(ii) Smectic: ortho - NO_2 > ortho –Cl > para –Cl
Nematic: ortho - NO_2 > ortho –Cl > para –Cl
(iii) Smectic+ Nematic : ortho –Cl > ortho - NO_2 > para–Cl

- Molecular rigidity and flexibility of suitable magnitudes are useful to induce mesomorphism.
- Phenomena of mesomorphism and the degree of mesomorphism are very sensitive and susceptible to molecular structure.
- Present investigation may be useful (i) to construct LC devices workable below 100°C or below 40°C to 46°C by binary mixture study with C_7 and C_{10} homologues (ii) to study biological activity of the novel compounds which may prove their ability as anticancer, anti-malaria, anti-inflammatory, etc. [24–28].

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