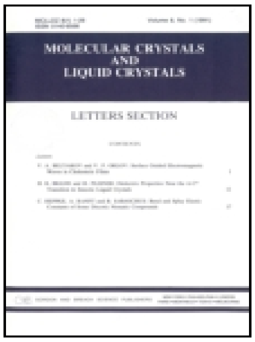

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Mesomorphism Dependence on Molecular Flexibility and Molecular Rigidity

G. N. BHOLA AND U. C. BHOYA*

Department of Chemistry, Saurashtra University, Rajkot, Gujarat, India

A novel liquid crystal (LC) homologues series of ethylene derivatives was synthesized and evaluated for mesomorphic properties. Mesomorphism commences from sixth member of the series. Textures of the nematic phase are threaded or Schlieren and those of the smectic phase are of the focal conic fan type. The N-I and Sm-N transition curves of the phase diagram exhibit odd-even effects and behave in a normal manner. The average thermal stabilities of the smectic and nematic are 113.4 °C and 123.2 °C with mesogenic phase lengths varying between 3.3°C and 8.1 °C and 4.5 °C to 13.5 °C, respectively. The LC behavior of the novel series is compared with a structurally similar known series.

Keywords Isotropic; liquid crystal; nematic; smectic; Thermotropic

Introduction

The liquid crystalline state of a substance is known since 1888 [1]. It has been utilized and studied by chemists, physicists, biologists, agriculturists, pharmacists, technologists, and many other research groups in science and technology [2–6]. Chemists have shared their research interests in producing and reporting novel thermotropic and lyotropic liquid crystal (LC) substances and other research groups studied the same LC substances with different angle of their interest [7–9]. A chemist designs and synthesizes novel LC substances, often through homologues series, and characterizes the materials for structure, purity, and mesomorphic properties. The present investigation is planned with a view to understanding and establishing the relation between LC behavior of a substance and the molecular structure [10,11] by changing flexible parts of a molecule by synthesizing a novel series of ethylene (styrene) derivatives and evaluate them with respect to molecular rigidity [12–16] and flexibility [12–15] because ethylene derivatives are useful as biological and medicinal compounds for anti-inflammatory, anticancer, antioxidant, antiangiogenic, antitumor agent, inhibitor to radiation effect, antibacterial, etc. useful to mankind and drug delivery [17,18].

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*Address correspondence to U.C. Bhoya, Department of Chemistry, Saurashtra University, Rajkot 360005, Gujarat, India. E-mail: drucbhoya@gmail.com

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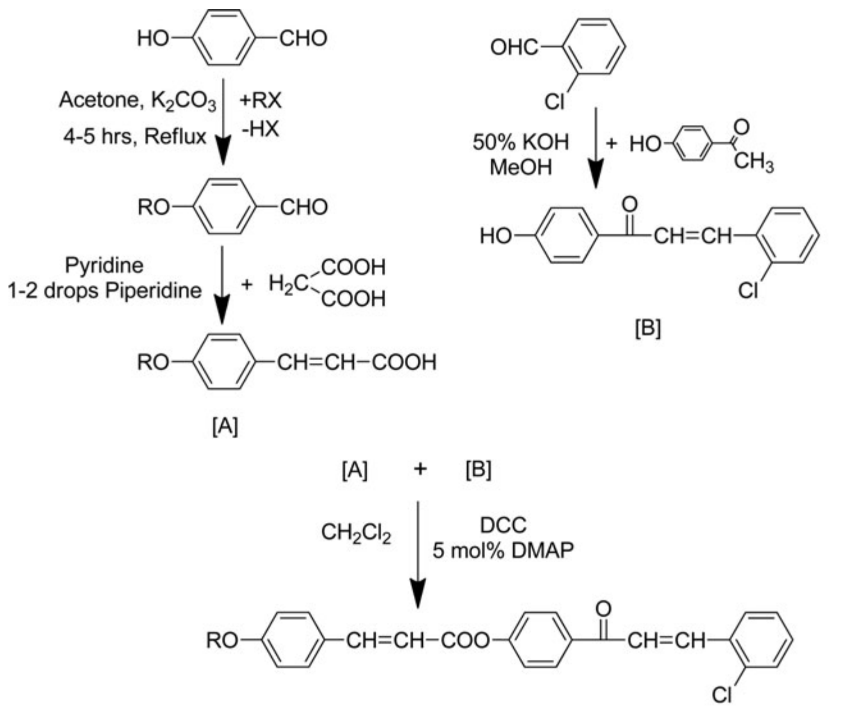
Experimental

Synthesis

4-*n*-Alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with the corresponding *n*-alkyl bromides (1 equiv.) in the presence of potassium carbonate (1 equiv.) with acetone as the solvent [19]. The resulting 4-*n*-alkoxybenzaldehydes were reacted with malonic acid (1.2 equiv.) in the presence of 1–2 drops piperidine as a catalyst and pyridine as the solvent to yield the corresponding trans 4-*n*-alkoxy cinnamic acids (A) [20]. α-4-Hydroxy benzoyl β-2′-chlorophenyl ethylene (B) was prepared by an established method [21] M.P.170.5°C, yield 67.2%. Coupling of compound A and compound B is effected by Steglich esterification to yield 4(4′-*n*-alkoxy cinnamoyloxy) benzoyl-β-2′′-chlorophenyl ethylene [22].

The synthetic route to the novel homologues series of ethylene derivatives is shown in Scheme 1.



α-4(4'-n-alkoxy cinnamoyloxy)benzoyl-β-2"-chlorophenyl ethylene
Where, R=C_nH_{2n+1}, n=1 to 8, 10, 12, 14, 16 and 18

Scheme 1. Synthetic route to the novel series.

Characterization

Some of members of a novel series were characterized by elemental analysis (Table 1), infrared spectroscopy, ^{1}H NMR spectroscopy, and mass spectrometry. Microanalysis was

Table 1. Elemental analysis for (1) propyloxy, (2) heptyloxy, and (3) tetradecyloxy derivatives

		Elements % found			Elements % calculated		
Sr. no.	Molecular formula	C	H	O	C	H	O
1	$C_{27}H_{23}ClO_4$	72.50	5.22	14.35	72.56	5.19	14.32
2	$C_{31}H_{31}ClO_4$	74.06	6.24	12.73	74.02	6.21	12.72
3	$C_{38}H_{45}ClO_4$	75.86	7.56	10.67	75.91	7.54	10.64

performed on 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 a solvent and mass spectra were recorded on Shimadzu GC-MS Model No. QP-2010 spectrometer. The LC behavior and the type of textures were determined by a miscibility method on microscopic observations.

Analytical Data

Elemental analysis (Table 1)
Spectral Data

^{1}HNMR in ppm for Hexyloxy Derivative

0.88–092 (t,3H, $-CH_3$ of $-OC_6H_{13}$ group), 1.32–1.34 (m,4H,$CH_3-CH_2-CH_2-$), 1.43–1.46 (p,2H,$-CH_2-CH_2-CH_2-O-$), 1.75–1.79 (p,2H,$-CH_2-CH_2-O-$), 3.94–3.98 (t,2H,$-CH_2-O-$), 6.44–6.48(d,1H, $-COO-CH=CH-$), 7.49–7.51(d,1H, $-COO-CH=CH-$), 7.28–7.29 (d,1H, $-CO-CH=CH-$), 7.80–7.84(d,1H, $-CO-CH=CH-$), 7.27–7.45 (4H, phenyl ring with –Cl group),7.49–7.51 and 8.17–8.21 (4H, middle phenyl ring), 6.89–6.91 and 7.72–7.74 (4H, phenyl ring with alkoxy chain). The NMR data are consistent with the molecular structure.

^{1}HNMR in ppm for Decyloxy Derivative

0.86–0.89 (t,3H,$-CH_3$ of $-OC_{10}H_{21}$ group), 1.27–1.30 (m,12H,$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$), 1.42–1.44(p,2H,$-CH_2-CH_2-CH_2-O-$), 1.74–1.79 (p, 2H, $-CH_2-CH_2-O-$), 3.95–3.98 (t,2H,$-CH_2-O-$), 6.45–6.49(d,1H, $-COO-CH=CH-$), 7.49–7.52(d,1H, $-COO-CH=CH-$), 7.28–7.29 (d,1H, $-CO-CH=CH-$), 7.81–7.85 (d,1H, $-CO-CH=CH-$), 7.27–7.45 (4H, phenyl ring with –Cl group),7.49–7.51 and 8.17–8.21 (4H, middle phenyl ring), 6.89–6.91 and 7.72–7.74 (4H, phenyl ring with alkoxy chain), The NMR data are consistent with the molecular structure.

IR in cm^{-1} for Butyloxy Derivative

3066(C$-$H str. of alkene disubstituted), 2864 and 2947 (C$-$H str. of $(-CH_2-)_n$ group of $-OC_4H_9$), 1730 (C$=$O str. of carbonyl carbon of ester group), 1664 (C$=$O str. of α,β unsaturated ketone), 1664 and 1631 (C$=$C str. of alkene), 1606, 1514, and 1471(C$=$C str. of aromatic ring), 1325 and 1290 (C$-$H bending of alkene disubstituted), 1253 (C$-$O str.

Table 2. Transition temperatures in °C

Compound no.	*n*-alkyl chain C_nH_{2n+1} (*n*)	Sm	N	Isotropic
1	1	—	—	141.2
2	2	—	—	155.4
3	3	—	—	159.8
4	4	—	—	145.4
5	5	—	—	149.7
6	6	(96.1)	117.3	121.8
7	7	(100.9)	107.0	119.4
8	8	99.3	107.2	120.7
9	10	102.6	110.7	119.5
10	12	111.3	116.2	123.4
11	14	112.6	115.9	126.1
12	16	108.0	113.6	125.2
13	18	110.6	116.8	129.9

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

of ether linkage), 1139 (C—O str. of ester group), 997, 966, and 833(C—H bending of alkene),738 (C—Cl str.). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Dodecyloxy Derivative

3061(C—H str. of alkene disubstituted), 2914 & 2847 (C—H str. of $(-CH_2-)_n$ group of $-OC_{12}H_{25}$), 1720 (C=O str. of carbonyl carbon of ester group), 1656 (C=O str. of α,β unsaturated ketone), 1631 (C=C str. of alkene), 1601, 1512, and 1465 (C=C str. of aromatic ring), 1338 and 1290 (C—H bending of alkene disubstituted), 1249 (C—O str. of ether linkage), 1130 (C—O str. of ester group), 974 and 825 (C—H bending of alkene), 750 (C—Cl str.). The IR data are consistent with the molecular structure.

Mass Spectra of Pentyloxy Derivative

m/z (rel.int%): 474 $(M)^+$,257,217,165,87

Mass Spectra of Octyloxy Derivative

m/z (rel.int%): 516$(M)^+$,275,259,147,91

Results and Discussion

The methoxy to pentyloxy novel homologues are nonliquid crystals (NLC). The rest of the homologues are LC with exhibition of smectic and nematic mesophases. The transition temperatures (Table 2) of the homologues were plotted versus the number of carbon atoms in the n-alkoxy terminal end group. A phase diagram (Fig. 1) consisting of transition curves behaves in a normal manner. Solid-isotropic or mesomorphic transition curves adopt a zigzag path of rising and falling values as the series is ascended with an overall descending tendency. The N—I transition curve initially rises and then descends with negligible

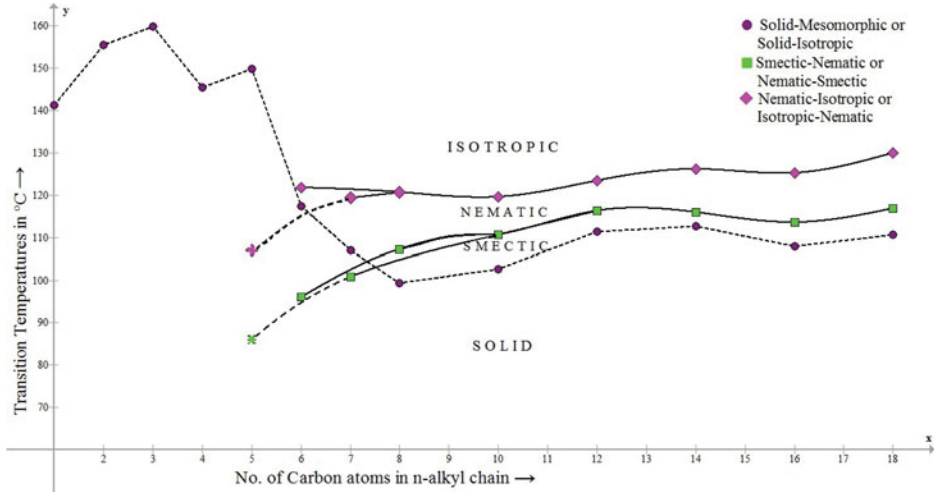


Figure 1. Phase behavior of series.

deviation from normal behavior with the exhibition of odd-even effects. The Sm—N and N—I transition curves are extrapolated [23–26] to the pentyloxy homologue to predict its isotropic-nematic and N—Sm transition temperatures, which are not actually realizable by following the trend of the corresponding transition curves respectively. The average thermal stabilities for smectic and nematic are 113.4 °C and 123.2 °C, respectively. The total mesophase length (Sm+N) varies between 4.5 °C and 21.4 °C. Thus, novel series is partly smectogenic and partly nematogenic with lower middle ordered melting type and short mesophase length. Linking of α-4-hydroxy benzoyl β-2′-chlorophenyl ethylene with trans 4-*n*-alkoxy cinnamic acid increases molecular length, width, polarity, and polarizibility, which induces LC behavior in the novel series from the sixth member of the series. The nonmesomorphic behaviors of first five members of a series is attributed to their high crystallizing tendency arising from their relatively higher magnitudes of intermolecular forces of attractions, which are not suitable to induce mesomorphism but leads to sharp melting of homologues concerned (first five). Thus suitable magnitudes of anisotropic forces of intermolecular attractions and closeness as a consequence of favorable molecular rigidity and flexibility are important to induce mesomorphism in a substance. The exhibition of smectic and nematic mesophases by the LC homologues is attributed to the misalignment of molecules at an angle less than 90° with the plane of a floating surface. All the mesomorphic homologues have a sliding layered molecular arrangement due to the presence of originally lamellar packing of molecules in their crystal lattices, facilitating smectic A or C type mesophase formation, within particular range of temperature. At higher temperature, the molecules adopt a statistically parallel orientational order of molecular arrangement. The exhibition of odd even effects of Sm—N or N—I transition curves is attributed to the sequential addition of a methylene unit in the *n*-alkoxy terminal end group. The diminishing of odd-even effect in the (Sm-N and N-I) transition curves in the phase diagram (Fig. 1) for the higher homologues of decyloxy and octyloxy derivatives is attributed to the coiling, flexing, bending, or coupling of *n*-alkyl chain with the major axis of a molecular core structure. Extrapolated values of transitions temperatures predicted for the fifth member of the series for smectic and nematic are 86 °C and 107 °C, respectively, which are not realizable due to its high crystallizing tendency. Lowering of transition temperatures, mesophase

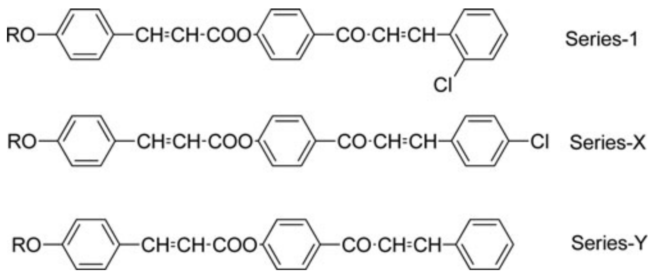


Figure 2. Structurally similar series.

length and thermal stabilities is attributed to the laterally ortho substituted chloro unit which has widened the molecule and raised the intermolecular distance. The mesomorphic behavior of the presently investigated series 1 is compared with the known structurally similar homologues series X [27] and Y [28] as shown in Fig. 2.

The presently investigated novel homologues series 1 and series X and Y chosen for comparison are structurally identical with respect to three phenyl rings and central bridges —CH=CH—COO— and —CO—CH=CH— linking three phenyl rings. Therefore, the contribution towards molecular rigidity remains almost identical for all the three series (1, X, and Y) under comparison. However, they differ with respect to the molecular flexibility from homologue to homologue in the same series due to the changing number of methylene units in the *n*-alkoxy terminal end group, as well as from series to series for the same homologue due to the changing either the polar terminal/lateral end group (series 1 and Y) on third phenyl ring or due to positional difference of equipolar same functional group (1 and X) on third phenyl ring. Thus, the combined effects of molecular rigidity and flexibility of unsuitable or suitable magnitudes of anisotropic forces of intermolecular attractions evolved by respective molecules from homologue to homologue in the same series or from series to series for the same homologue as a consequence of changing molecular rigidity plus flexibility facilitating either LC or NLC state of a novel substance under investigation. Thus, variations in LC or NLC behaviors and the extent of liquid crystallinity of a novel substance depend upon the favorable or unfavorable effective magnitudes of molecular rigidity plus flexibility which has direct relations with molecular structure. The following table-3 represents some LC behaviors presently investigated homologues series-1 and the series X and Y chosen for comparative study.

Table 3 indicates that

Table 3. Average thermal stabilities in °C

Series →	1	X	Y
Sm-N or N-Sm	113.4 (C_8-C_{18})	132.6 (C_8-C_{12})	—
Commencement of smectic mesophase	C_6	C_8	
N-I	123.2 (C_6-C_{18})	156.7 (C_5-C_{16})	155.4 (C_5-C_{16})
Commencement of nematic phase	C_6	C_5	C_5
Mesophase length range (Sm + N)	4.5 °C–21.4°C	6.0°C–76.0°C	11.0°C–48.0°C

- chloro group substituted either at ortho or para position have exhibited smectic and/or nematic mesophases individually or one after another together.
- series Y without chloro group substitution on third phenyl ring exhibited only nematic mesophase or say smectic mesophase is totally absent.
- nematic mesophase commences from sixth member (C_6) of a novel series 1, while it commences from the fifth member (C_5) of the series X and Y.
- smectic mesophase formation commences from hexyloxy or octyloxy homologue, respectively, for series 1 and X; but it does not commence till the last member of series Y.
- nematic thermal stability of present series 1 is the lowest (123.2) where as it is higher (156.7 and 155.4) for series X and Y.
- smectic thermal stability of series 1 is lower than a series X under comparison with absence of smectic property in series Y.
- total mesophase length range of present series 1 is the lowest among the series under comparison.

Suitable magnitudes of anisotropic forces of intermolecular end to end and/or lateral attractions as a consequence of favorable molecular rigidity and flexibility is more of series X, than the series 1 and Y. Series 1 and X are isomeric with each other differing only by positional difference (ortho or para) of –Cl group. Ortho-substituted chloro group increases molecular width and intermolecular distance or closeness. Therefore, increased molecular width decreased intermolecular attractions predominates or exceeds the magnitudes of intermolecular attractions due to molecular polarizibility factor in case of present series 1. However para substituted chloro group in series being its linear lath-like shape adopts relatively more intermolecular closeness than a present series 1. Such intermolecular closeness in series X, yielded relatively more and optimum intermolecular attractions to facilitates smectic and nematic mesophases together, one after another, with more (series X) or less (series 1) degree of mesomorphism and thermal stabilities. Homologues series Y dose not bear any polar group on third phenyl ring except – H. The intermolecular end to end attractions facilitated only parallel orientational order of molecules in floating condition with originally absence of lamellar packing of molecular in crystal lattices of all its homologues. Thus, series Y under comparison exhibited only nematic phase with absence of smectic character. Early or late commencement of mesophase or mesophases and the degree of mesomorphism depend upon the extant of noncoplanarity caused by a molecule and intermolecular closeness as required for smectic or/and nematic mesophase formation. Thus, the variations in mesomorphic behaviors for the same homologue from series arises due to changing either terminal/lateral functional end group or due to changing positional (ortho or para wrt –CO—CH=CH—) status of same functional group.

Conclusion

- The group efficiency order derived on the basis of (i) thermal stabilities and (ii) the early commencement of mesophase or mesophases are as under
  - (i) Smectic: para – Cl > ortho—Cl >—H
    Nematic: para – Cl>—H > ortho—Cl
  - (ii) Smectic: ortho – Cl > para—Cl >—H
    Nematic: para – Cl=—H > ortho—Cl
- Variations in mesogenic behaviors from homologue to homologue in the same series depends upon number of methylene units in *n*-alkyl chain and from series to series

for the same homologue depends upon either the changing polar terminal/lateral group or changing positional status of same functional group.

- A suitable magnitude of molecular rigidity and flexibility operates the phenomena of mesomorphism. Phenomena of mesomorphism are sensitive and susceptible to molecular structure, which operates molecular rigidity and flexibility.
- Molecular rigidity and flexibility are complimentary to each other.
- Novel homologues series is partly smectogenic and partly nematic with first five members of series nonmesomorphic (NLC).

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