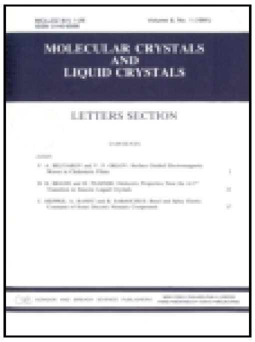

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Study of the effect of a heterocyclic ring end group and an azomethane linkage on mesomorphism

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ABSTRACT
A novel homologous series RO-C_6H_4-COO-C_6H_4-N = CH-C_5H_4N of liquid crystalline Schiff base esters has been synthesized and studied with a view to correlating molecular structure to the liquid crystal properties on the basis of molecular rigidity and flexibility. All 12 members of series are either monotropic (C_1, C_3, C_5) or enantiotropic (C_2, C_4, C_6 to C_{16}) nematic with the absence of smectogenic character throughout the series. Transition temperatures and LC behavior of the series were determined using an optical polarizing microscope equipped with a heating stage. Transition curves (Cr-N or Cr-I and N-I or I-N) behave in the normal established manner as depicted in a phase diagram. An odd–even effect is exhibited by the N-I transition curve up to the C_8 homologue.

KEYWORDS
Liquid crystal; monotropy; nematic; Schiff base; smectic

Introduction

Our continuous studies concern the effects of molecular structure on thermotropic liquid crystal (LC) [1] properties by changing various molecular aspects, such as shape, size, aromaticity, terminal, lateral, and linking groups. The LC state is very sensitive and susceptible to molecular structures [2–7] and such studies can be useful to the manufacture of display devices [8–13] and many other fields like agricultural productions and pharmaceutical preparations. The variations in mesomorphic (LC) properties is a direct result of the molecular rigidity and flexibility of the molecule [14–17] whose suitable magnitudes operate the emergence of an unique state of matter which can flow like liquid and possess optical properties like crystal. The present investigation is planned to synthesize a novel series of ester Schiff's base substances containing heterocyclic ring as terminal and its some (thermometric) LC properties are compared with the structurally similar azoester series of LC substances, to derive group efficiency order. Many ester homologous series of LCs have been reported to date [18–26]

Experimental synthesis

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agent by the modified method of Dave and Vora [27]. 4-((pyridin-2-yl) methyleneamino)phenol (B) was prepared by an

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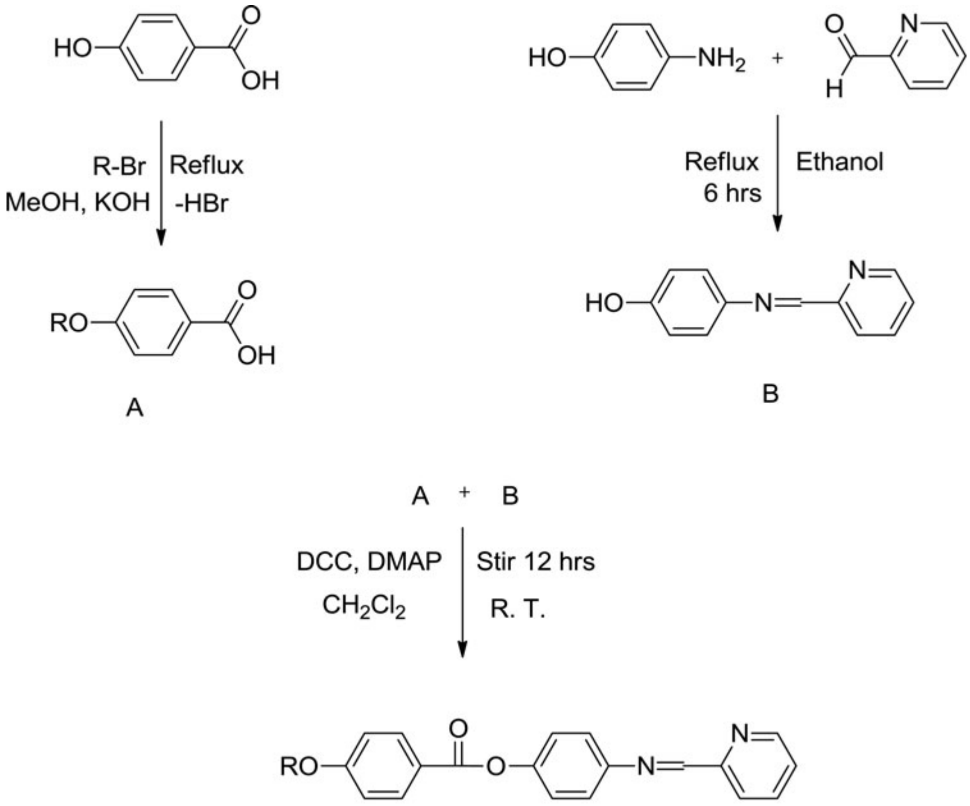


Where, R= C_nH_{2n+1} and $n = 1$ to 8 and 10,12,14,16

4(4’-n-Alkoxy benzoyloxy) phenyl amino methylene (2”-pyridin)

Scheme 1. Synthetic route to the novel series.

established method [28]. Coupling of compounds A and B was done by Steglich esterification to yield 4-(4′-n-alkoxybenzoyloxy) phenyl amino methylene (2″-pyridine) [29].

The synthetic route to the novel homologous series of azomethane derivatives is under mentioned in scheme 1.

Characterization

Representative members of a novel series were characterized by elemental analysis (Table 1), Infrared spectroscopy, ^{1}HNMR spectroscopy, and mass spectroscopy. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer. IR spectra were recorded on Shimadzu FTIR-8400, ^{1}HNMR spectra were recorded on Bruker spectrometer using DMSO as solvent

Table 1. Elemental analysis for (1)Ethyloxy(2)Pentyloxy(3)Hexadecyloxy derivatives.

Sr. No.	Molecular formula	Elements %Found	Elements %Calculated
		CHN	CHN
1	$C_{21}H_{18}N_2O_3$	72.825.248.09	72.765.288.01
2	$C_{24}H_{24}N_2O_3$	74.216.237.21	74.186.207.12
3	$C_{35}H_{46}N_2O_3$	77.458.545.16	77.408.605.12

and Mass spectra were recorded on Shimadzu GC-MS Model No.QP-2010. The mesogenic behavior of the homologue derivatives were observed through polarizing microscopy. The textures of smectogenicmesophase were determined by miscibility method.

Analytical data

1H NMR in ppm for hexyloxy derivative

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.84 – 0.91 (t, J = 7.6 Hz, 3H), 1.35 – 1.39 (tt, J = 3.3, 5.9 Hz, 4H), 1.42 – 1.52 (m, 2H), 1.77 – 1.83 (p, J = 7.7 Hz, 2H), 4.10 – 4.12 (t, J = 7.4 Hz, 2H), 7.04 – 7.11 (m, 4H), 7.38 – 7.40 (dd, J = 1.1, 4.9, 7.8 Hz, 1H), 7.44 – 7.46 (d, J = 7.5 Hz, 2H), 7.57 – 7.59 (dd, J = 1.1, 8.0 Hz, 1H), 7.63 – 7.66 (td, J = 1.2, 7.9 Hz, 1H), 8.07 – 8.13 (m, 2H), 8.22 (s, 1H), 8.66 – 8.68 (dd, J = 1.2, 5.0 Hz, 1H) ppm.

1H NMR in ppm for heptyloxy derivative

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.87 – 0.92 (t, J = 8.0 Hz, 3H), 1.20 – 1.35 (m, 8H), 1.38 – 1.48 (m, 2H), 1.71 – 1.77 (p, J = 7.7 Hz, 2H), 4.10 – 4.12 (t, J = 7.4 Hz, 2H), 7.06 – 7.09 (dq, J = 2.5, 8.5 Hz, 4H), 7.21 – 7.23 (dd, J = 1.0, 8.1 Hz, 1H), 7.36 – 7.46 (m, 3H), 7.54 – 7.58 (td, J = 1.2, 8.0 Hz, 1H), 8.07 – 8.13 (s, 2H), 8.65 – 8.66 (dd, J = 1.1, 5.0 Hz, 1H) ppm.

1H NMR in ppm for tetradecyloxy derivative

1H NMR (400 MHz, DMSO-d6) δ 0.90 – 0.98 (t, J = 7.6 Hz, 3H), 1.20 – 1.26 (m, 20H), 1.67 – 1.75 (d, J = 30.8 Hz, 2H), 3.96 – 3.98 (t, J = 6.5 Hz, 2H), 4.11 – 4.16 (t, J = 7.0 Hz, 2H), 6.89 – 6.91 (d, J = 8.4 Hz, 2H), 7.41 – 7.47 (dd, J = 8.4, 14.8 Hz, 2H), 7.78 – 7.80 (d, J = 8.1 Hz, 3H), 8.07 – 8.10 (d, J = 8.5 Hz, 2H), 8.22 (s, 1H), 8.65 – 8.67 (dd, J = 1.2, 5.1 Hz, 1H) ppm.

IR in cm^{-1} for heptyloxy derivative

IR (KBr): 3070 (Ar str.), 2946, 2852 (-CH_3 str.), 1728 (-C = O str.), 1656 (-C = C- Ar str.), 1590 (-CH = N- str.), 1560 (-C = N- str.), 1213, 1074 (-C-O str.), 844, 707 (-CH Ar bend.) cm^{-1}.

IR in cm^{-1} for butyloxy derivative

IR (KBr): 3038(Ar str.), 2930(-CH_3 str.), 1750(-C = O str.), 1670 (-C = C- Ar str.), 1588 (-CH=N- str.), 1560 (-C = N- str.), 1056(-C-O str.), 880, 742 (-CH Ar bend.) cm^{-1}.

IR in cm^{-1} for methyloxy derivative

IR (KBr): 3068 (Ar str.), 2955 (-CH_3 str.), 1719, 1728 (-C = O str.), 1690 (-C = C- Ar str.), 1595 (-CH = N- str.), 1560 (-C = N- str.), 1415, 1064 (-C-O str.), 885, 732 (-CH Ar bend.) cm^{-1}.

Mass of hexyloxy derivative

m/z (rel.int%): 402 $(M)^+$ 149, 121, 93, 65, 44

Mass of octyloxy derivative

m/z (rel.int%): 430 $(M)^+$205, 121, 93, 65, 44

Mass of dodecyloxy derivative

m/z (rel.int%): 486 $(M)^+$ 219, 121, 93, 57, 43

Table 2. Transition temperatures in °C.

Compound No.	n-alkyl chain C_nH_{2n+1} (n)	Sm	Nm	Isotropic
1	1	—	(125)	142
2	2	—	142	163
3	3	—	(113)	132
4	4	—	104	129
5	5	—	(114)	127
6	6	—	101	118
7	7	—	100	115
8	8	—	97	116
9	10	—	99	123
10	12	—	92	112
11	14	—	88	92
12	16	—	58	76

Sm = Smectic, Nm = Nematic, () indicate monotropy

Results and discussion

4-((Pyridin-2-yl) methyleneamino) phenol (m.p-108°C and yield- 88%) is a non LC component, which on linking with dimeric 4-n-alkoxy benzoic acid yielded Schiff's bases of LC substances, whose transition temperatures are relatively lower than the corresponding n-alkoxy acids. Transition and melting temperatures as determined from POM (Table 2) are plotted against the number carbon atoms present in n-alky chain 'R' of–OR end group. Transition curves Cr-N or Cr-I and N-I or I-N are obtained by linking like or related points showing phase behaviors of novel series as shown in a phase diagram (Fig. 1) Cr-N/I transition curves follows a zigzag path of rising and falling tendency in usual manner with overall descending tendency. N-I or I-N transition curve smoothly decends and rises to C_{10} homologue and again descended after passing through maxima at C_{10} derivative. Odd-even effect is observed for N-I (or vice versa) transition curve upto C_8 homologue. Then, odd-even effect disappears for higher homologues of longer n-alkyl chain from and beyond C_8 derivatives. Thus, N-I or

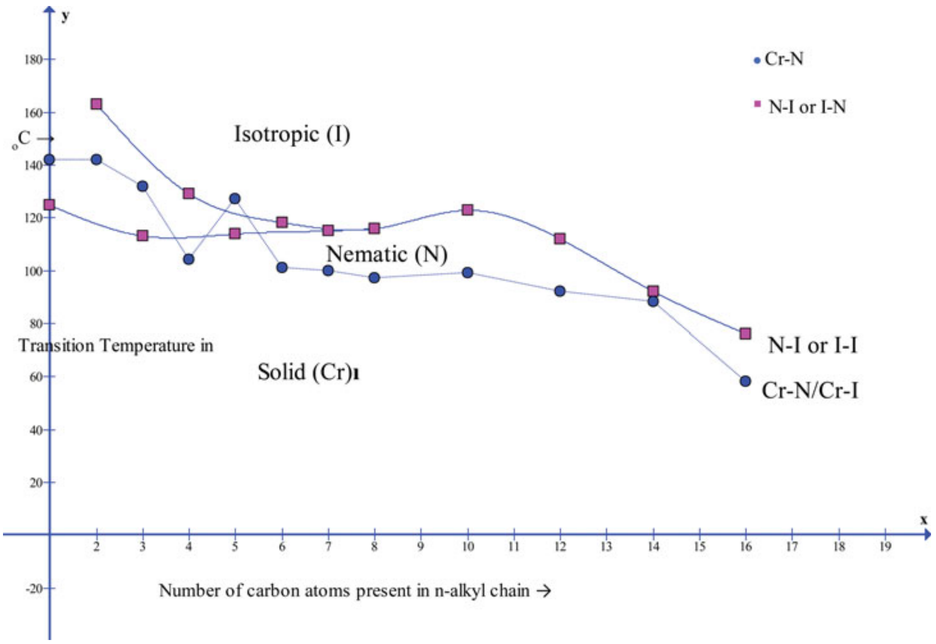


Figure 1. Phase behavior of series.

I-N transition curve behaved in normal manner. The textures of nematic phase are threaded or Schlieren. Analytical, spectral and thermal data supported molecular structures of homologue. Thermal stability for nematic is 116.0°C and mesophase length is relatively shorter. The LC properties from homologue to homologue undergo variation with changing number of carbon atom or methylene units in n-alkyl chain 'R' of–OR end group.

The lowering of transition temperatures as compared to the corresponding n-alkoxy benzoic acids is attributed to the breaking of hydrogen bonding between two molecules of benzoic acids by esterification process. The exhibition of LC property from very first member of series in either monotropic or enantiotropic manner is due to the disalignment of molecules at angle less than ninety degree centigrade under the influence of exposed thermal vibrations. The suitable magnitudes of anisotropic forces of intermolecular end to end attractions and closeness as a consequence of favorable molecular rigidity and flexibility leads to arrange and organize molecular floating on the surface maintaining statistically parallel orientation order, depending upon an angle of disalignment below ninety degree, which resists or withstands the effect of exposed thermal vibrations for some degree of temperature difference. Hence, nematogenicmesophase formation appears from C_1 to C_{16} members of a series. All the homologue molecules from and beyond their isotropic temperature randomly oriented in all possible directions with high order of disorder or randomness or high entropy $\Delta S = \Delta H/T$ in uncontrolled manner; but, on carefully cooling the same, the C_1, C_3 and C_5 homologues exhibited nematogenicmesophase formation in irreversible manner below their isotopic temperature which is termed as monotropic transition temperature and corresponding homologues are called monotropic mesomorphs. Rest of the homologues of the present novel series were similarly (C_2, C_4,C_8 and C_{16}) and careful cooling form and below isotropic temperature gave rise to reappear nematicmesophase formation exactly at a temperature at which nematicmesophase was appear on heating the same. Thus, the nematogenic homologues formed and showed nematic phase in reversible manner i.e. on heating and cooling mesophase appeared at the same temperature. Such transitions are called enantiotropic transitions and corresponding homologues area called as enantiotropic homologues. None of the nematogenic exhibited monotropicsmectic mesophase formation due to insufficient intermolecular forces of cohesion and closeness to attain sliding layered molecular arrangement in floating condition. The exhibition odd-even effect by N-I transition curve is due to the sequential addition of methylene unit at the N-alkyl chain 'R' of-OR group. The N-I curves for odd and even homologues merged into each other at C_8 homologues and then odd-even effect disappeared for the higher homologue because, longer n-alkyl chain 'R' of-OR may coil or bend or flex or couple to lie with major axis of core structure of a molecule and acquire unusual and unexpected status of n-alkyl chain disturbing intermolecular parameters related to cohesive forces and closeness. The changing trend in LC properties form homologue to homologue in the same series is attributed to the actual status of n-alkyl chain 'R' of-OR group related to effective molecular length, length to breadth ratio, ratio of the molecular polarity to polarizibility permanent dipole moment across the long molecular axis, magnitudes of dispersion forces dipole-dipole interactions, suitable magnitudes of molecular rigidity and flexibility etc. to induce mesophase of proper degree of mesomorphism. Some thermometric properties of presently investigated novel series-1 are compared with the other structurally similar analogous series-X [30] as under in Fig. 2.

Homologous series-1 of present investigation and a homologous series-X selected for comparative study are identical with respect to two phenyl rings and one central bridge-COO-as well as–N = nitrogen atom bonded to middle phenyl ring. Moreover left n-alkoxy terminal end group (-OR) is commonly present for the same homologue from series to series.

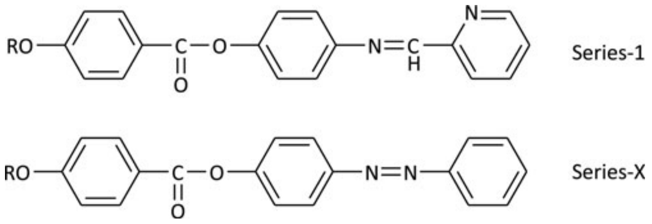


Figure 2. Structurally similar series.

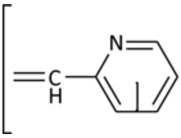
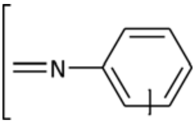
However, they differ from each other with respect to units of tailed parts i.e. = $CH-C_5H_4N$ and = $N-C_6H_5$ of series-1 and a series-X, respectively. i.e. = CH-bonded to heterocyclic ring containing nitrogen atom i.e. series-1 and = N-bonded to homocyclic phenyl ring in series-X. Thus, variation in LC properties and the degree of mesomorphism will depend upon the magnitudes of differing features of series-1 and X as mentioned above. Following Table 3 represents some thermometric properties of series-1 and X in comparative manner.

From Table 3 it is clear that,

- Presently investigated series-1 is nematogenic only but, series X under comparison is smectogenic plus nematogenic.
- Smectogenicmesophase formation commences from C_{10} homologue in series-X, but it does not commence till the last homologue of series-1. The nematicmesophase formation commences from very first member of series-1 and X under comparative study.
- Smectogenicmesophase does not stabilize at all in series-1, but it stabilizes in case of series-X whose smectic thermal stability in 114.0
- Nematogenic thermal stability is in increasing order from series-1 to X.
- Upper and the lower mesophase lengths are in increasing order from series-1 to series-X. However, the difference between upper and lower mesophase lengths are 21.0 and 22.0 for series-1 and X, respectively.

The exhibition of nematic, mesophase formation by both the series under comparison is by usual established environmental condition of suitable magnitudes of anisotropic forces of intermolecular end to end attractions, cohesions and closeness as consequence of favorable molecular rigidity and flexibility as required to exhibit nematogenic character with more or less mesophase length according to thermal resistivity of individual molecules of each homologue or for the same homologue form series to series. However, the exhibition of smectogenic character by series-X is due to trans -N = N- configuration which maintains linearity,

Table 3. Thermal stability in °C.

	1	X
Series→		
Smectic-IsotropicOrSmectic-NematicCommencement of smectic phase	—	114.0(C_{10}–C_{16})C_{10}
Nematic-IsotropicCommencement of nematic phase	116.0(C_2–C_{16})C_1	138.54(C_1–C_8)C_1
Total, upper and lower mesophase lengths in °C, t_1 to t_2	4.0 to 25.0$C_{14}C_4$	16.0 to 38.0C_1C_2

comparatively more than its comparative group -N = CH- under identical position. Moreover the bonding of -N = N- with homocyclic phenyl ring (= N-phenyl) being more polarizable and polar as compared to = CH-C = N- heterocyclic ring unit of series-1. Therefore, probability of forming lamellar packing of molecules in the crystal lattices of series-X being more favorable than in case of series-1. Thus, the layered molecular arrangement in rigid crystalline state and subsequently the sliding layered molecular arrangement of molecules from C_{10} homologue commence and continued up to C_{16} last homologue for different range of temperature persisted to show smectogenic character in addition to nematic property in case of series-X, but does not persist for smectic phase formation in case of series-1 containing heterocyclic ring in place of homocyclic phenyl ring. Early commencement of smectic phase in series-X as compared to series-1 is attributed to the extent of molecular planarity maintained as required for smectogenic character from C_{10} homologue favorably in series-X, but the extent of molecular noncoplanarity fails to adopt smectogenic molecular organization possibility till the last C_{16} homologue of series-1. The potential ability as emerging from molecular structures of both the series-1 and X are sufficient enough to maintain statistically parallel orientation order of molecules which are floating on the surface of by suitable magnitudes of anisotropic forces of end to end attractions from very first member of both the series under comparison in monotropic or enatiotropic manner, respectively. The increasing order of thermal stabilities for mesophase as well as upper and lower mesophase lengths from series-1 to X is attributed to thermodynamic quantity enthalpy (ΔH and ΔH_x) difference of series-1 and X whose values are basically depended on molecular structure and constitutional difference. Thus, when a quantum of heat energy exposed upon a homologue substance, the magnitudes of resistivity towards exposed thermal vibration vary from homologue to homologue in the same series and series to series for the same homologue, which, causes differences in transition temperature, thermal stabilization, magnitudes of end to end and lateral cohesion and closeness, dispersion forces, mesophase stabilization and the upper and lower degree of mesomorphism, thermal resistivity etc. Thus, present series is nematogenic, whose mesophase lengths are shorter and of middle ordered melting type.

Conclusions

- Homocyclic phenyl ring bonded to –N=N- central bridge is potentially more capable of inducing smectic and nematic phase of higher thermal stabilities and longer mesophase lengths as compared to heterocyclic ring bonded to-N=CH- centered bridge.
- The group efficiently order derived for smectic and nematic on the base of (a) thermal stability(b) early commencement of mesophase and (c) mesophase length, are as under
  - (a) Smectic:
    Series X > Series 1
    Nematic:
    Series X > Series 1
  - (b) Smectic:
    Series X > Series 1
    Nematic:
    Series X > Series 1
  - (c) Total mesophase length (Sm+N)
    Upper and lower
    Series X > Series 1

- Mesomorphism is very sensitive and susceptible to molecular structure; as consequence of molecular rigidity and flexibility.
- Present investigation supports and raises the credibility to the conclusions drawn earlier.

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