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Mesomorphism dependence on heterocyclic end group

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ABSTRACT

An ester homologous series containing a heterocyclic end group was synthesized and studied with a view to understanding and establishing the effect of molecular structure on liquid crystal behavior. The novel series consists of 13 homologues. All members of the series are enantiotropically smectogenic without exhibition of nematogenic character. The textures of smectogenic homologues are of the type smectic A or C. The transition temperatures were determined by an optical polarizing microscope equipped with a heating stage. The Sm-I transition curve in a phase diagram behaves partly in an abnormal manner with the exhibition of an odd-even effect. The average thermal stability for smectic is 141.45°C and the mesomorphic phase length ranges from 8.1 °C to 30.3 °C. Analytical and spectral data confirm the molecular structures. The liquid crystal properties of present series are compared with the structurally similar known homologous series.

KEYWORDS

Enantiotropy; liquid crystal; mesomorphic; nematogenic; smectic

Introduction

The study of mesomorphism has proven its importance since its discovery in 1888 [1] for its unique combination of molecular ordering in a liquid phase. Various research groups in different branches of science and technology have exploited the liquid crystal phase for the benefit of mankind [2–12]. The present investigation is planned with a view to understanding and establishing the effects of molecular structure on mesomorphism of a substance through the synthesis of novel homologous series. Several homologous series have been reported [13–20] of varying moieties by changing molecular rigidity and flexibility [21–24] through variation of the number of phenyl, heterocyclic or hydrocarbon rings, the central groups, the terminal or lateral groups, which change the shape, size, length, polarity, and polarizibility, etc. [25–27]. Mesomorphic properties were evaluated in terms of molecular rigidity and flexibility. Thus, with the knowledge of the effects of molecular structure the wider research community can benefit from this novel research.

Experimental

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

HO—CHO

HO—COCH₃

+RX

$$K_2CO_3$$

Acetone

Reflux

Reflux

HO—COCH=CH—O

Methanol

Reflux

HO—CO-CH=CH—O

Pyridine

Reflux

RO—CH=CH—COOH

[A]

DCC

5 mol% DMAP

DCM

RO—CH=CH—COO—CO-CH=CH—O

 α -4(4'-n-alkoxy cinnamoyloxy) benzoyl- β -(2-furanyl) 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.

(1 equiv.) and acetone [28]. The resulting 4-n-alkoxybenzaldehydes were reacted with malonic acid (1.2 equiv.) in the presence of 1-2 drops piperidine as catalyst and pyridine as solvent to yield corresponding trans 4-n-alkoxy cinnamic acids (A) [29]. 3-(2-furanyl)-1-(4-hydroxyphenyl) 2-propen-1-one (B) was prepared by an established method [30] M.P.: 158 °C-160 °C, Yield: 69.3%. Coupling of compound A and compound B was done by Steglich esterification to yield α -4(4'-n-alkoxy cinnamoyloxy) benzoyl- β -(2-furanyl) ethylene [31].

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

Characterization

Some of the members of novel series were characterized by elemental analysis (Table 1), infrared spectroscopy, ¹H NMR spectra, and mass spectroscopy. Microanalysis was performed using a EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR Model -IRAffinity-1S (MIRacle 10), ¹HNMR spectra were recorded on a Bruker spectrometer using CDCl₃ as a solvent, and mass spectra were recorded on Shimadzu GC-MS Model No.QP-2010. The liquid crystal behavior and the type of textures were determined by a miscibility method on microscopic observations.

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

		Elements %found			Elements %calculated		
Sr. no.	Molecular formula	С	Н	0	С	Н	0
1	C ₂₄ H ₂₀ O ₅	74.15	5.22	20.63	74.21	5.19	20.60
2	$C_{30}^{24}H_{32}^{20}O_{5}^{3}$	76.29	6.81	16.91	76.25	6.83	16.93
3	C ₃₄ H ₄₀ O ₅	77.19	7.65	15.16	77.24	7.63	15.13

Analytical data

Elemental analysis (Table 1)

Spectral data

¹HNMR in ppm for pentyloxy derivative

0.92–0.95 (t,3H,-CH₃ of $-OC_5H_{11}$ group), 1.36–1.48 (m,4H,CH₃- $\underline{CH_2}$ -CH₂-), 1.73–1.83 (p,2H,- $\underline{CH_2}$ -CH₂-O-), 3.97–3.99 (t,2H,- $\underline{CH_2}$ -O-), 7.26–7.32 (d,1H, $-\overline{CH}$ =CH-COO-), 6.46–6.52 (d,1H, -CH= \underline{CH} -COO-), 7.53–7.54 (d,1H, -CO- \underline{CH} =CH-), 7.82–7.86 (d,1H, -CO-CH= \underline{CH} -), 6.87–7.62 (3H, furfural ring),7.47–7.54 & 8.08–8.10 (4H, middle phenyl ring), 6.91–6.93 & 7.58–7.62 (4H, phenyl ring with alkoxy chain). The NMR data are reliable with the molecular structure.

¹HNMR in ppm for decyloxy derivative

0.86–0.90 (t,3H,-CH₃ of $-OC_{10}H_{21}$ group), 1.27–1.32 (m,12H,CH₃- $\underline{CH_2\text{-}$

IR in cm⁻¹ for heptyloxy derivative

3056 (C-H str. of alkene disubstituted), 2927 & 2856 [C-H str. of (-CH₂-)_n group of $-OC_4H_9$], 1720 (C=O str. of carbonyl carbon of ester group), 1653 (C=O str. of α , β unsaturated ketone), 1653 & 1629 (C=C str. of alkene), 1593, 1571, & 1504 (C=C str. of aromatic ring), 1332 & 1288 (C-H bending of alkene disubstituted), 1251 (C-O str. of ether linkage), 1130 (C-O str. of ester group), 999, 972, & 867 (C-H bending of alkene). The IR data are consistent with the molecular structure.

IR in cm⁻¹ for tetradecyloxy derivative

3052 (C-H str. of alkene disubstituted), 2918 & 2850 (C-H str. of (-CH₂-)_n group of – OC₁₂H₂₅), 1724 (C=O str. of carbonyl carbon of ester group), 1654 (C=O str. of α , β unsaturated ketone), 1629 (C=C str. of alkene), 1597, 1573, & 1514 (C=C str. of aromatic ring), 1336, 1303, & 1288 (C-H bending of alkene disubstituted), 1255 (C-O str. of ether linkage), 1132 (C-O str. of ester group), 972, 831, & 817 (C-H bending of alkene). The IR data are consistent with the molecular structure.

Mass spectra of propyloxy derivative

m/z (rel.int%): 402 (M)⁺,189, 147, 119, 91, 65

Mass spectra of hexyloxy derivative

m/z (rel.int%): 444(M)⁺, 231, 214, 147, 127, 119, 91, 65

Table 2. Transition temperatures in °C.

Compound no.	n-alkyl chain C _n H _{2n+1} (n)	Sm	N	Isotropic
1	1	132.5	_	157.5
2	2	119.3	_	149.6
3	3	141.0	_	146.1
4	4	143.4	_	158.9
5	5	140.3	_	148.5
6	6	126.6	_	142.8
7	7	128.7	_	147.2
8	8	119.4	_	140.4
9	10	115.0	_	129.1
10	12	116.3	_	135.3
11	14	115.8	_	130.8
12	16	116.0	_	127.5
13	18	117.7	_	125.8

Sm, Smectic; N, Nematic.

Results and discussion

4-n-Alkoxy cinnamic acids are dimeric, which on condensation with 3-(2-furanyl)-1-(4hydroxyphenyl) 2-propen-1-one in pyridine yielded C_1 – C_8 , C_{10} , C_{12} , C_{14} , C_{16} , and C_{18} smectogenic homologues with absence of nematogenic mesophase formation. Their transition and melting temperatures are between 115.0 °C and 158.9 °C. Dimerization of trans n-alkoxy cinnamic acids disappears on esterification. Transition temperatures (Table 2) of homologues as determined from a hot stage polarizing microscopy were plotted versus the number of carbon atoms in the n-alkoxy chain and then, like or related points were linked to draw the Cr-Sm and Sm-I transition curves of the phase diagram (Fig. 1). The Cr-Sm transition curve adopts a zigzag path of rising and falling values with an overall falling tendency as the series is ascended. The Sm-I transition curve descends with about five degrees Celsius difference in the transition temperatures of the odd and even members; and then passes through a maxima at the C_{12} homologue and finally descends through the C_{14} , C_{16} , and C_{18} homologues. The transfer sition curves for odd and even homologues merge at the nonyloxy (C₉) homologue and then continue as a single curve up to the C_{18} member. Thus, the Cr-Sm transition curve behaves in a usual established manner and the Sm-I transition curve behaves partly in normal manner. The average thermal stability for smectic is 141.45 °C and the mesophase length ranges from 8.1 °C to 30.3 °C. Thus, the present novel series is middle ordered melting type with short range of liquid crystallinity of smectic type. The mesomorphic properties commence

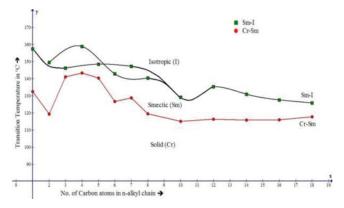


Figure 1. Phase behavior of series.

from the very first member of the novel series and vary from homologue to homologue due to the changing length of the left n-alkoxy terminal end group. None of the homologues show monotropic mesomorphism and nonmesomorphic behaviors.

The absence of nematogenic mesophase formation and the exhibition of only smectic mesophase formation from very first member of a present series is attributed to the unsuitable magnitudes of anisotropic forces of intermolecular end-to-end attractions as a consequence of combined effects of unfavorable molecular rigidity and flexibility which are not sufficiently strong enough to maintain statistically parallel orientational order of molecules in floating condition to induce nematic property. However, the favorable molecular rigidity displayed by the central bridges which link the phenyl or heterocyclic ring through at least one conjugated double or multiple bond as well as overall sufficient molecular polarizibility which favors the formation of lamellar packing of molecules in their crystal lattices from very first member (C_1) of the series to its last member (C_{18}) . Thus, the molecules of C_1-C_{18} homologues with suitable magnitudes of intermolecular anisotropic forces are sufficient to facilitate originally layered order in their crystal lattices which acquires sliding layered molecular arrangement under exposed thermal vibrations for certain definite range of temperatures; depending upon molecular resistivity toward heat or exposed thermal vibrations or the forces holding the planes of the layers together in the rigid crystal which are weakened relative to the attractions among the molecules within a given layer at solid mesomorphic transition temperature and the layers may become free to slide and rotate over one another giving rise to smectic mesophase formation and then on heating the smectic phase to a higher temperature the intermolecular forces between the slides of the molecules weakened to such an extent that resultant intermolecular forces do not permit molecules to slide out of the layer and statistically parallel orientational order is not maintained at all; but entire sample of a substance transform into isotropic liquid. Conversely on cooling the isotropic melt, the smectic phase reappears exactly at a temperature at which mesophase was disappeared in a reversible manner in case of all the homologues (C_1-C_{18}) of the present novel series. The shorter n-alkoxy terminal end group lies with the major axis of the core, and the end-to-end contact ultimately differs for odd and even homologues through C1-C8. Therefore, an odd-even effect is observed. However, the odd-even effect disappears from C₉ because the longer n-alkyl chain may coil, flex, or bend to lie with the major axis of the core structure and the end-to-end contact would then be the same for odd and even homologues. Variations in degree of mesomorphic properties from homologue to homologue in the same series is attributed to the sequentially added methylene unit to the left n-alkoxy chain. The sequential addition of a methylene unit contributes toward molecular flexibility and the resultant combined effects of molecular rigidity and flexibility, which vary from homologue to homologue causing changing trend in mesomorphic behaviors.

Some mesomorphic properties such as thermal stability, commencement of mesophase, mesophase length range, and odd-even effect of the presently investigated novel series-1 are compared with the structurally similar known homologues series-X [32] and -Y [33] as shown below in Fig. 2.

Homologous series-1, -X, and -Y are identical with respect to two or three phenyl rings and two central bridges linking three phenyl rings or two phenyl rings and a heterocyclic ring. Moreover, they are identical with respect to left n-alkoxy terminal end group for the same homologue, but they differ from homologue to homologue in the same series. However, homologous series-1 differs from series-X and -Y with respect to ring system as terminal end groups. Series-1 contain a heterocyclic five-membered furan ring system, series-X contain aromatic unsubstituted phenyl ring system and series-Y contain monoatomic chloro

Figure 2. Structurally similar series.

(para)-substituted phenyl ring. Therefore, the mesomorphic properties and the degree of mesomorphism vary with changing part of the molecular structures of series-X and -Y chosen for comparison in Fig. 2; because molecular rigidity and flexibility vary with the changing molecular structures. Table 3 shows comparative data for series-1, -X, and -Y.

From Table 3 the following points emerge:

- Presently investigated homologous series-1 is only smectogenic, series-X is only nematogenic, and series-Y is smectogenic in addition to nematogenic.
- Smectogenic property commences from very first member of a series-1, but it commences late from eighth member of a series-Y and it does not commence till the last (C₁₆) member of a series-X.
- Nematic property commences from fifth (C₅) member of the series-X and -Y, but it does not commence till the last member of a present series-1.
- Thermal stability for smectic of series-1 and -Y are 141.45 °C and 132.6 °C, respectively.
- Thermal stability for nematic for series-X and -Y are 155.4 °C and 156.7 °C, respectively.
- Total mesophase length is in increasing order from series-1 to series-X to series-Y.
- All the three homologous series under comparison exhibited odd-even effect in their transition curves of respective phase diagram.

Exhibition of mesophase formation, the type of mesophase formation, either smectic or nematic, and the total mesophase length range of a series depends upon its suitable magnitudes of anisotropic forces of intermolecular end-to-end and/or lateral attractions as a consequence of favorable molecular rigidity and/or flexibility as immerged from the permanent dipole moment across the long molecular axis, dipole-dipole and electronic interactions, dispersion forces, etc. Homologous series of present investigation contain five-membered ring with oxygen as hetero atom, which withdraws electron from carbon with absence of any flexible functional group bonded to terminal ring system, except left n-alkoxy group. Therefore, molecular rigidity of series-1 predominates over its molecular flexibility forming lamellar packing of molecules in their crystal lattices giving rise to sliding layered arrangement of molecules in floating condition under the influence of exposed thermal vibrations favorably to cause smectic phase due to heterocyclic terminal. However, on further heating the same

Table 3. Average thermal stabilities in °C.

Series →	1	X	Υ
Smectic-sotropic Commencement of smectic mesophase	141.15 (C ₁ -C ₁₈)	-	132.6 (C ₈ -C ₁₂)
Nematic-isotropic	Ч -	155.4 (C ₅ -C ₁₆)	156.7 (C ₅ -C ₁₆)
Commencement of nematic phase Total mesophase length range (Sm $+$ N)	8.1 (C ₁₈) to 30.3 (C ₂)	11.0 (C ₁₆) to 48.0 (C ₆)	6.0 (C ₁₆) to 74.0 (C ₈)

smectic phase, the end-to-end attractions are weakened to such an extent that statistically parallel orientational order of molecules is not maintained in floating condition to cause nematic phase. Series-X possesses phenyl ring as terminal instead of heterocyclic ring, but it is homocyclic ring with absence of hetero atom like oxygen. Therefore, combined effect of molecular rigidity and flexibility causes suitable magnitudes of end-to-end intermolecular attractions, which maintains only statistically parallel orientational order of molecules to cause nematic phase, but it fails to form lamellar packing of molecules and hence the sliding-layered molecular arrangement which is missing under thermal treatment; showing absence of smectic phase. Homologous series-Y contains polarizable monoatomic functional -Cl group substituted at para position of third phenyl ring, which increases molecular length, polarity and polarizibility, flexibility in addition to equivalent rigidity of series-1 and -X, the intermolecular endto-end and lateral attractions are suitable and sufficient to maintain sliding-layered molecular arrangement, and then to maintain statistically parallel orientational order of molecules beyond smectic phase under exposed thermal vibrations in floated condition. Thus, smectic phase in addition to nematic phase, one after another appeared for different ranges of temperature from homologue to homologue in the same series and for the same homologue from series to series with varying degree or range and the type (Sm or/and N) of mesomorphism which are resulted and appeared through an optical polarizing microscopy equipped with a heating stage or thermogram from differential scanning calorimeter or thermal analysis. Early commencement of smectic mesophase as compared to series-Y and -X is attributed to the less noncoplanarity of the molecules, i.e., molecules of series-1 are relatively less noncoplaner than the corresponding same homologue of series-Y and -X due to heterocyclic end. However, nematic mesophase commences from C₅ member of series-X and -Y, but it does not commence till the last member of a series-1, because the end-to-end attractions are stronger for the series-X and -Y as compared to series-1 due to chloro substitution at para position and polarizibility difference of phenyl ring and a heterocyclic ring system. The thermal stability for smectic of series-1 is greater than a series-Y under comparison is due to the variation in the molecular rigidity and flexibility associated with the respective molecular structure whose energy content (Δ H) differs. Thermal resistivity and thermal withstanding capacity of the same homologue molecules from series-1 to series-Y may be in decreasing order for smectic which reflected in facilitating the stabilization of smectic phase throughout the series-1, but partly stabilized smectic phase in case of series-Y. The highest thermal stability for nematic of series-Y as compared to series-X and -1 is attributed to the difference of end-to-end intermolecular attractions occurred due to differing permanent dipole moment across the long molecular axis, dipole-dipole and electronic interactions, etc., which hinders the stabilization of nematic phase in series-1 but favors in case of series-X and -Y. Odd-even effect is observed for transition curve or curves in the phase diagrams of series of present investigation and the series-X and -Y chosen for comparison. Thus, liquid crystal behavior and properties from homologue to homologue in the same series and for the same homologue from series to series depend upon the changing part of the molecules as a consequence of changing molecular rigidity and flexibility due to varying magnitudes of heat content (ΔH) of different molecular structures under comparative study.

Conclusions

 Presently investigated homologous series is entirely smectogenic without exhibition of nematic property with middle-ordered melting type and shorter phase length range.

It consisted with three-ring system bonded through -CH=CH-COO- central bridge between two phenyl rings and another central bridge -CO-CH=CH- linking a phenyl ring and a heterocyclic furan ring.

- Group efficiency order derived on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) total (Sm + N) mesophase length range for smectic and nematic are as under.
- (i) Smectic Nematic (ii) Smectic Nematic (iii) Smectic + Nematic
 - A molecule bearing heterocyclic ring is smectogenic irrespective of nematogenic central bridge -CH=CH-COO-.
 - A phenomenon of mesomorphism and the degree of mesomorphism are very sensitive and susceptible to the molecular structures as a consequence of favorable molecular rigidity and flexibility.
 - Present investigation of smectogenic mesophase may be useful for the study of binary systems and for the devices operated between 115.0 °C and 158.9 °C or below about 20.0 °C (i.e., 100.0 °C) or smectic LC are valuable for increasing the sensitivity of the color response of modified nematic.
 - Present homologue derivatives may be useful to act as antimalarial, anticancer, antibacterial, anti-inflammatory, antifungal, etc. if their biological or microbiological activity is properly studied by the researchers or biologists.
 - Mesomorphism depends upon molecular structure.

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