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Synthesis and Evaluation of Liquid Crystal Behavior of a Novel Homologous Series :4-(4-n-alkoxy benzoyloxy) β -Methoxy Ethyl Benzoats

Jagtap M. S.¹ and Chauhan M. L.*

¹Department of Chemistry, Shri Jagdishprasad Jhabarmal Tibrewala University, (JJT Uni.) Jhunjhunu, Rajasthan, India

*Department of Chemistry, Sheth P.T. Arts & Science College, Godhra, Gujarat

ABSTRACT

A novel homologous series of liquid crystals, viz., 4-[4'-n-alkoxy Benzoyloxy] β -Methoxy Ethyl Benzoates has been synthesized. The series consists of eleven homologs. The methyl to butyl derivatives are not liquid crystalline and the rest of the homologs are enantiotropic liquid crystals. The octyl and decyl derivatives of the series are enantiotropically smectogenic in addition to nematogenic in character, but the Pentyl, hexyl, dodecyl, tetradecyl, and hexadecyl homolog derivatives of the series are only nematogenic without the exhibition of a smectic phase. The transition temperatures of the novel substances were determined by optical polarizing microscopy equipped with a heating stage. A plot of transition temperatures versus the number of carbon atoms present in the n-alkoxy terminal chain represents the phase behavior of the series. An odd-even effect is observed for the nematic-isotropic transition curve. The textures of the nematic phase are of a threaded or Schlieren type and those of the smectic A phases are typical. Analytical and spectral data agree with the molecular structures. The smectic and nematic thermal stabilities are 179.0 °C and 196.28 °C, respectively. The smectic phase commences from the octyloxy homologue and Nematic mesophase commences Pentyl homologue. Smectogenic phase lengths vary from 15.0 °C to 17.0 °C and the nematogenic phase lengths vary from 7.0 °C to 33.0 °C. The series is predominantly nematogenic and partly smectogenic with considerable mesophase length and a middle-ordered melting type. The liquid crystal properties of the present series are compared with structurally similar homologous series.

Keywords: Liquid crystal; smectic; nematic; mesomorphic; thermotropic

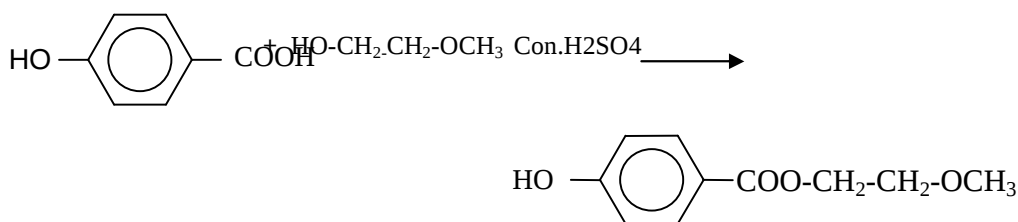
INTRODUCTION

The unique properties of the liquid crystalline state of a substance is exploited in varying fields of application in present era. Therefore, it is interesting to study the relationship between molecular structure and the liquid crystal state of a substance through homologous series, whose molecular rigidity and flexibility [1–3] dictate the formation of mesomorphism. Liquid crystal phases are formed as a consequence of suitable magnitudes of anisotropic intermolecular forces of attraction [4,5,6], and as a consequence of favorable molecular rigidity and/or flexibility. The novel series under investigation has a molecular structure based on two phenyl rings linked through –COO– central linking groups, two terminal end groups of –OR and –COOCH₂–CH₂–OCH₃, hence the structures are linear with no lateral substituents.

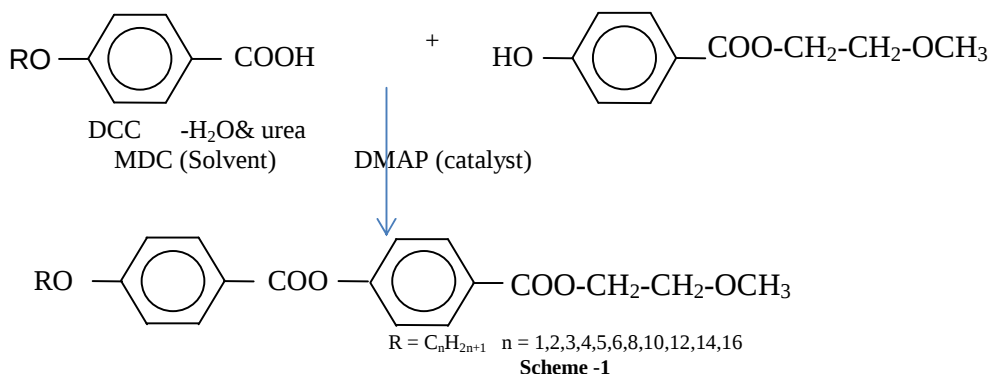
MATERIALS AND METHODS

Synthesis: p-n-alkoxy benzoic acids were prepared by the method of Gray and Winsor (6), Vora and Dave (7), Vogel (8). p-hydroxyβ-methoxy ethyl benzoate is prepared by reacting p-hydroxy benzoic acid with corresponding freshly distilled 2-methoxy ethyl alcohol in presence of concentrated sulphuric acid mixture. p-n-alkoxy benzoic acids dissolved in MDC with p-hydroxyβ-methoxy ethyl benzoate is in portions with DCC & DMAP as catalyst by stirring reaction mixture. (9-11) Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy benzoic acid, alkyl halides (R-X), tert-butanol, KOH, DCC, DMAP, MDC etc. required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below in **Scheme -1**

- (1) 4-Hydroxy -β-Methoxy Ethyl benzoate.



- (2) 4-(4'-n-alkoxy benzoyloxy) β-Methoxy Ethyl Benzoates



Characterization

Some homologs as representative members of the series were selected for characterization of their structures by IR and ¹H NMR techniques. IR spectra were recorded on Perkin Elmer spectrum GX and NMR were recorded using CDCl₃ as solvent. Microanalysis was performed on Perkin Elmer PE 2400 CHN analyzer. Transition and melting temperatures and liquid crystal properties were investigated by using optical polarizing microscopy.

Analytical Data

Spectral Data

NMR in ppm for Pentyloxy Derivative. 0.9 (CH₃ of OC₅H₁₁ group), 1.28 (CH₂)_n polymethylene group of OC₅H₁₁), 4.12 (OCH₂CH₂ of OC₅H₁₁), 3.82 (OCH₃), 6.87 to 8.18 (p substituted phenyl ring). The NMR data are consistent with the molecular structure.

NMR in ppm for Dodecyloxy Derivative. 0.88 (CH₃ of OC₁₂H₂₅ group), 1.20 (CH₂)_n polymethylene group of OC₁₂H₂₅), 4.01 (OCH₂CH₂ of OC₁₂H₂₅), 3.22 (OCH₃), 6.90 to 8.13 (p substituted phenyl ring). The NMR data are consistent with the molecular structure.

NMR in ppm for Tetradecyloxy Derivative. 0.87 (CH₃ of OC₁₄H₂₉ group), 1.25 (CH₂)_n polymethylene group of OC₁₄H₂₉), 4.01 (OCH₂CH₂ of OC₁₄H₂₉), 3.52 (OCH₃), 6.81 to 8.13 (p substituted phenyl ring). The NMR data are consistent with the molecular structure.

IR in cm^{-1} for Propoxy Derivative. 760 polymethylene (CH_2)_n group of OC_3H_7 , 885 p substituted phenyl ring, 1200, 1260 and 1700 (COO ester group), 1600, 1580 (phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Octyloxy Derivative. 770 (polymethylene (CH_2)_n group of OC_8H_{17}), 855 (p substituted phenyl ring), 1260 and 1605 (COO ester group). 1605, 1550 (phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Dodecyloxy Derivative. 740 (polymethylene (CH_2)_n group of $\text{OC}_{12}\text{H}_{25}$), 840 (p substituted phenyl ring), 1210, 1260 & 1600 (COO ester group). 1580, 1480 (phenyl ring). The NMR data are consistent with the molecular structure.

Table 1. Elemental analysis for some derivatives

Sr. No.	R = n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1	Propyl	$\text{C}_{20}\text{H}_{22}\text{O}_6$	67.03	6.14	68.99	6.50
2	Pentyl	$\text{C}_{22}\text{H}_{26}\text{O}_6$	68.39	6.73	69.23	6.90

RESULTS AND DISCUSSION

n-Alkoxy Benzoic acids and 4-Hydroxy- β -Methoxy Ethyl benzoate are nonmesomorphic. However, on condensing the two nonmesomorphic components through DCC, the resultant homologous ester derivatives from pentyloxy to hexadecyloxy give rise to mesomorphic behavior. The methyl to butyl homologs are nonmesomorphic. The octyloxy, decyloxy homologs are enantiotropically smectogenic in addition to nematogenic in character and the rest of the homologs are enantiotropic nematic only (Table 2). The transition and melting temperatures of all the homologs were determined on an optical polarizing microscope equipped with a heating stage, and are shown in Table 2. A plot of the transition temperatures versus number of carbon atoms present in n-alkoxy terminal chain shows the phase behavior of the series (Fig. 1). An odd-even effect is observed for a nematic-isotropic transition curve, but the effect is missing in the smectic-nematic transition curve. The smectic-nematic transition curve initially rises, passes through maxima and then descends as series is ascended up to the decyloxy homolog.

Table 2. Transition temperatures of series in $^{\circ}\text{C}$

Sr. No.	R = n-alkyl group	Transition temperature in $^{\circ}\text{C}$		
		Smectic	Nematic	Isotropic
1.	Methyl	-		222
2.	Ethyl	-		220
3.	Propyl	-		192
4.	Butyl	-		199
5.	Pentyl	-	177	202
6.	Hexyl	-	188	198
7.	Octyl	162	179	212
8.	Decyl	164	179	188
9.	Dodecyl	-	189	196
10.	Tetradecyl	-	174	192
11.	Hexadecyl	-	176	186

The smectic mesophase formation should occur at 162.0°C . However, practically it is a solid-nematic transition temperature, which suggests that the smectic mesophase ceases to form and only the nematic mesophase forms. The nematic-isotropic transition curve descends as the series is ascended and behaves in normal manner. The curves for the odd and the even homologs merge into one nematic-isotropic curve at the eleventh homolog. Thus, the odd-even effect diminishes as the series is ascended for higher homologs from and beyond eleventh homolog. The solid mesomorphic or isotropic curve follows a zigzag path of rising and falling values as the series is ascended with an overall falling tendency. Thus, all the three transition curves behave in normal manner. The texture of the nematic mesophase is threaded or Schlieren and that of a smectic mesophase is of the typical A or C type. The smectic mesophase varies from a minimum of 15°C at the decyloxy homolog to a maximum of 17°C at the octyloxy homolog. The nematic mesophase length varies from a minimum of 7°C at the dodecyloxy homolog and maximum of 33°C at the octyloxy homolog. The present series is predominantly nematogenic and partly smectogenic with a

middle-ordered melting type. The smectic and nematic mesophases commence from the octyl and Pentyl homolog derivatives, respectively

The Pentyl to hexadecyl homologs are mesomorphic due to their suitable magnitudes of rigidity and flexibility. The octyloxy and decyloxy homologs generate a lamellar packing of the molecules at a transition temperature t_1 , and then adopt a statistically parallel orientational order from and beyond a higher temperature t_2 . However, on further continued heating of the sample, the molecules randomly orient in all possible directions without any molecular ordering at a higher temperature t_3 . Thus, the samples under microscopic examination exhibit and show a smectic mesophase between t_1 and t_2 , and then a nematic mesophase between t_2 and t_3 , and an isotropic liquid beyond temperature t_3 . Mesomorphic molecules of homologs other than octyloxy and decyloxy exhibit only nematogenic mesomorphism. The methyl to butyl homologs of the series are unable to withstand exposed thermal vibrations due to the unsuitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of unfavorable molecular rigidity and flexibility [1–4]. The odd-even effect diminishes for higher homologs, because longer n-alkyl chain from and beyond decyloxy homolog may coil, bend, flex or couple to lie with the major axis of the core [4, 9]. The degree of mesomorphism exhibited by the series is sufficiently high, because the series under discussion has sufficient lateral and terminal end-to-end attractions by the linear shape with two central groups bearing a conjugating double bond which strengthens rigidity of a molecule. The variation in mesomorphic property from homolog to homolog is attributed to the sequentially added methylene unit of the n-alkoxy terminal chain.

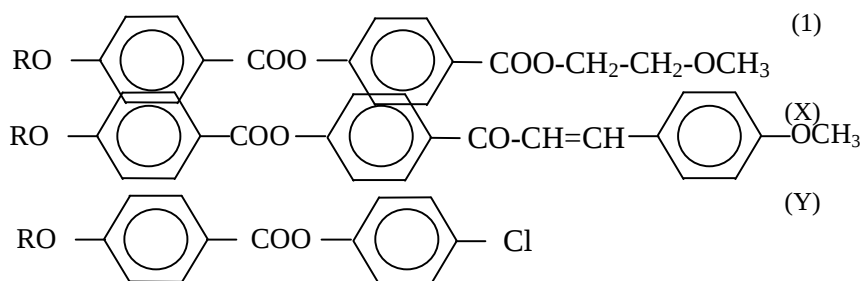


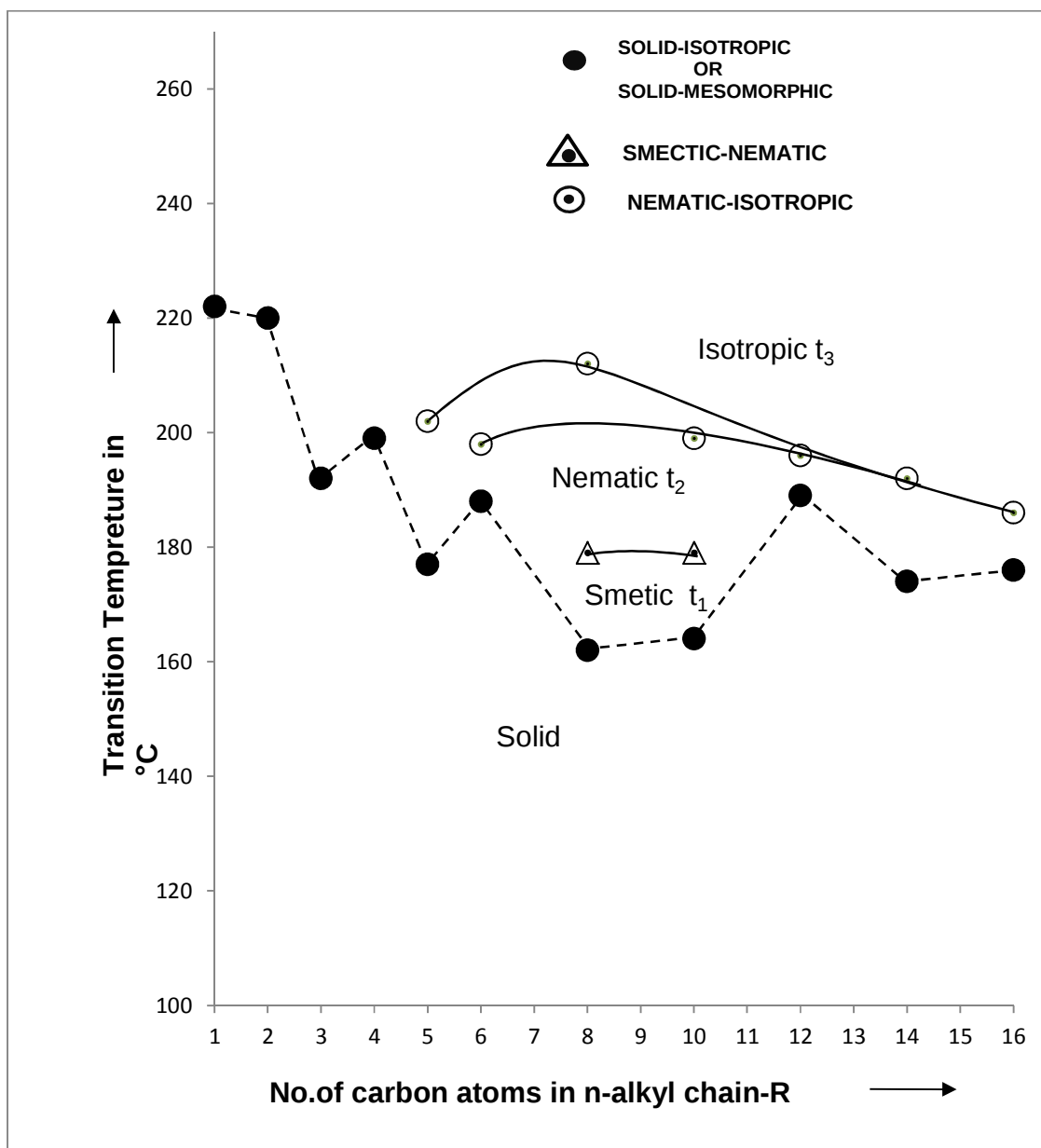
Figure 2

The variation in mesomorphic properties is compared with other structurally similar homologous series-X [12] and Y [13], as shown in Fig. 2. Figure 2 shows the structurally similar series-1 and Y are identical in respect of two phenyl rings bridged through to central groups-COO- with a common left terminal end group OR. However, the uncommon part is a right handed terminal end groups Para -Cl, and -COO-CH₂-CH₂-OCH₂. Homologous series -X is a differ by right terminal groups with the series-1.

Table-(3) Thermal stabilities in °C

Series	(1)	(X)	(Y)
Smectic-isotropic	179.0 °C (C ₈ -C ₁₀)	118.0 (C ₇ -C ₁₄)	104.7 (C ₁₂ -C ₁₈)
Commencement of Smectic phase	C ₈	C ₇	C ₇
Nematic-isotropic	196.28 °C (C ₅ -C ₁₆)	157.0 (C ₅ -C ₁₆)	-
Commencement of Nematic-phase	C ₅	C ₅	-

Therefore, the molecular Aromaticity and rigidity remains identical, but the molecular flexibility varies due to polarity and induced polarizability of laterally and right terminally group. Thus, suitable magnitudes of anisotropic forces or intermolecular adhesion as a consequence of varying molecular flexibility differ accordingly. Thus, mesomorphic properties and the degree of mesomorphism vary with changing of the terminal end groups of series 1, X, and Y respectively. Thermal stability of each series and commencement of mesophase are given in Table 3. Table 3 indicates that present series-1 and X are smectogenic in addition to nematogenic character, while series-Y chosen for comparison are smectogenic only without exhibition of any nematogenic character. The absence of nematogenic character in series- Y chosen for comparison indicates the absence of lamellar packing of molecules in their crystal lattices.



The commencement of smectogenic property takes place from the octyl homolog of series-1, but it does not commence until the last homolog of the series X and Y. This variation may be attributed to the extent of noncoplanarity [9] caused by the molecules concerned. The Cl terminal end group is more polar and monoatomic, which reduces the extent of molecular noncoplanarity than the differing end group $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{OCH}_2$ or phenyl ring. Thus, suitable and favorable extent of molecular noncoplanarity facilitates lamellar packing of the molecules from the octyloxy to decyloxy homologs of series-1 but it does not facilitate for any homolog of series X and Y. The nematic mesophase formation commences identically from the Pentyl homolog of the series-1 and X under comparison. This indicates that suitable magnitudes of anisotropic intermolecular forces of attraction, as emerging from molecular rigidity and flexibility, operate equally on end to end attractions, though the thermal stability of series-1 is higher among those under comparison. Suitable magnitudes of anisotropic intermolecular forces of attraction facilitate a statistically parallel orientational order of the molecules which commences from the fifth homolog of series 1 and X to generate the nematic mesophase. Thus the variation of mesomorphic properties for the same homolog from series to series is attributed to the unchanging terminal and/or lateral end group of each

individual homologous series. The group efficiency order derived on the basis of (a) thermal stability and (b) early commencement of the mesophase is mentioned below in the conclusion.

CONCLUSION

- (1) The novel series of 4-[4'-n-alkoxy Benzoyloxy] β -Methoxy Ethyl Benzoates is predominantly nematogenic and partly smectogenic with a middle ordered melting type.
- (2) High smectic thermal stability and the early commencement of smectogenic mesophaseforming tendency are favored more in group bonded to β carbon of $-\text{CH}_2-\text{CH}_2-$ in isomeric series.
- (3) Variations in mesomorphic properties from homologue to homologue in a same series and from series to series for same homologue is a direct result of a varying molecular rigidity and/or flexibility due to varying lateral central or/and terminal group or groups or/and varying number of aromatic phenyl ring, constituting a molecule.
- (4) Suitable magnitudes of anisotropic forces of intermolecular attractions can induce mesophase formation.

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