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Effect of a Central Group on Mesomorphism

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A novel homologous series: 4-(4'-n-alkoxy benzoxyloxy)-4''-methoxy benzyl benzoates is studied with a view to understanding the effect of a central group on the phenomenon of mesomorphism. The novel homologous series consists of eleven compounds. Mesomorphism commences from the second member of a series. All the mesogenic homologues from ethoxy to hexadecyloxy exhibit nematogenic mesomorphism without the exhibition of smectogenic character. The nematic–isotropic transition curve of the phase diagram behaves in normal manner up to the dodecyloxy homologue and then deviated for the tetradecyloxy and hexadecyloxy homologues. The solid-isotropic or nematic transition curve adopts a normal behavior in a zigzag manner. The nematic-isotropic transition curve shows an odd-even effect and continues up to the octyloxy homologue. Transition and melting temperatures including the textures of mesophases are determined by an optical polarizing microscope, equipped with a heating stage. The textures of the nematic mesophase are threaded or Schlieren in type. Analytical data and spectral data support the molecular structures. The mesomorphic behavior of the present series is compared with structurally similar other known series of differing central group (viz. $-N=N-$ and $-CO-CH=CH-$) keeping rest of a molecular part unchanged. The nematic thermal stability of the series is 236.8°C of a high melting type present series whose nematogenic mesophase length varies between 27°C and 98°C. Thus, series is only nematogenic without exhibition of a smectic mesophase.

Keywords Central bridge; mesogen; mesomorphism; nematic; smectic

Introduction

Liquid crystal materials workable at room temperature or at a desired temperature enjoy wide industrial applications in the present era [1, 2]. Liquid crystal properties can be induced in a substance if favorable and suitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions are generated by a molecular structure [3–5] depending upon combined effects of molecular rigidity and flexibility [6–9]. The construction of a molecular shape, size aromaticity, polarities of functional groups, their positions at a terminal end group or at lateral positions [10, 11] or as a central bridge or molecular polarizability contribute to the molecular rigidity and flexibility. Thus, the present investigation is planned

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with a view to understanding and establishing the molecular structure [12, 13] dependence of mesomorphism by varying the central group of a linear lath like molecule and keeping rest of the molecular structure unchanged. The proposed molecules consist of three phenyl rings bonded through two central bridges of $-\text{COO}-$ and $-\text{COO}-\text{CH}_2-$ as rigid core and n -alkoxy ($-\text{OR}$) and $-\text{OCH}_3$ groups as terminal end groups ($\text{R}=\text{C}_n\text{H}_{2n+1}$) without any lateral substitution, which will act as flexible core of a novel molecule. The study will be restricted to the synthesis of a novel homologous series, characterization of some selected homologues by elemental analysis IR, $^1\text{HNMR}$, mass spectra, and the determination of mesophase textures by a miscibility method, transition and melting temperatures by hot stage polarizing microscope, and to correlate their liquid crystal properties by comparing with azoester [14] and chalconyl [14] homologous series.

Experimental

Synthesis

4-Hydroxy benzoic acid was converted into dimeric 4- n -alkoxy benzoic acids using suitable alkylating (R-X) agents by a modified method of Dave and Vora [15]. 4-Hydroxy benzoic acid was converted to 4-hydroxy-4'-methoxy benzyl benzoate by the modified method of a European patent EP0117502B1 [16]. 4- n -alkoxy benzoic acids were individually condensed with 4-hydroxy-4'-methoxy benzyl benzoate (m.p. 180°C , yield is 33%) in pyridine through their acid chlorides in dry cold pyridine [17, 18]. Final products were individually decomposed, filtered, washed dried and purified in ethanol until constant transition temperatures obtained. Transition and melting temperatures were determined by an optical hot stage polarizing microscopy.

The chemicals 4-hydroxy benzoic acid, 4-methoxy benzyl alcohol, dibutyltin oxide, pyridine, alkyl halides, MeOH, EtOH, thionyl chloride, HCl, KOH were used as received, except solvents, which were dried and distilled prior to use. The synthetic route to the series is outlined in Scheme 1.

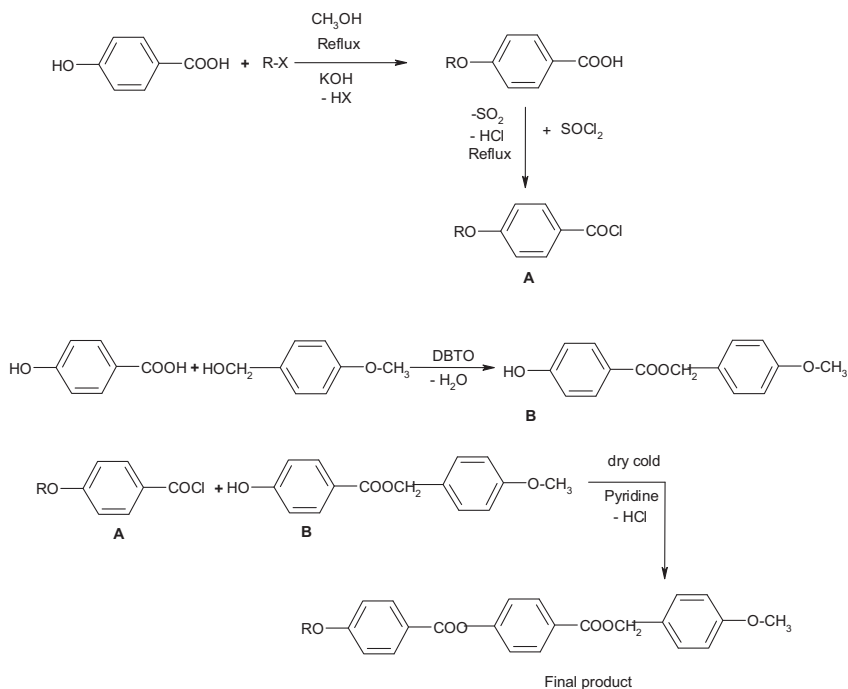
Characterization

Selected members of the novel series were characterized by elemental analysis, infra red spectra, $^1\text{HNMR}$ spectra and mass spectra. Micro analysis was performed on a Perkin-Elmer PE 2400 CHN analyzer, $^1\text{HNMR}$ spectra were recorded on Bruker spectrometer using DMSO solvent. Infra red spectra were recorded on Perkin Elmer spectrum GX spectrometer. Transition temperatures and the textures of the nematic mesophase were determined by a miscibility method using an optical polarizing microscope equipped with a heating stage. Thermodynamic quantity enthalpy change (ΔH) and entropy change ($\Delta S = \Delta H/T$) are qualitatively discussed instead of DSC scan.

Analytical Data

Spectral Data

$^1\text{HNMR}$ in ppm for the hexyloxy derivative: 0.88–1.72 (H of C_6H_{13}), 2.51 ($-\text{O}-\text{CH}_2-\text{CH}_2$ of $-\text{OC}_6\text{H}_{13}$), 3.76 ($-\text{OCH}_3$), 3.99 ($-\text{OCH}_2$ of $-\text{OC}_6\text{H}_{13}$), 5.1 ($-\text{COO}-\text{CH}_2-\text{C}_6\text{H}_4$),



Scheme 1. Synthetic route to the series. Series: 4-[4'-n-alkoxy benzoyloxy]-4''-methoxy benzyl benzoates where R = C_nH_{2n+1}; n = 1,2,3,4,5,6,8,10,12,14,16.

6.92 & 7.01 (p-substituted benzene ring), 7.34 (presence of another benzene ring), 7.89 & 8.03 (p-substituted benzene ring).

¹HNMR in ppm for the octyloxy derivative: 0.83–1.71 (H of C₈H₁₇), 3.73 (–OCH₃), 4.0 (–OCH₂ of –OC₈H₁₇), 5.0 (–COO–CH₂–C₆H₄), 6.9–7.01 (p-substituted benzene ring), 7.32 (another benzene ring), 7.86–8.03 (p-substituted benzene rings).

IR in cm^{–1} for tetradecyloxy derivative: 827 para-substituted phenyl ring, 1250 ether linkage of (–C₁₄H₂₉O–C₆H₄), 1681 & 1169 (–COO–ester group).

IR in cm^{–1} for tetradecyloxy derivative: 827 para-substituted phenyl ring, 1250 ether linkage of (–C₁₆H₃₃O–C₆H₄), 1681 & 1170 (–COO–ester group).

Mass Spectra

Mass spectra for butyloxy derivative:

Molecular formula C₂₆H₂₆O₆ calculated molecular weight 434.

Mass observed by mass spectroscopy 434.

Texture of nematic by miscibility method

Pentyloxy derivative → Threaded nematic

Decyloxy derivative → Schlieren nematic

Table 1. Elemental analysis for methoxy, ethoxy and propyloxy derivatives.

Sr. no.	Molecular formula	Elements % found (% calculated)	
		C	H
1	C ₂₃ H ₂₀ O ₆	70.22 (70.40)	5.08 (5.10)
2	C ₂₄ H ₂₂ O ₆	70.28 (70.93)	5.37 (5.41)
3	C ₂₅ H ₂₄ O ₆	71.18 (71.42)	5.47 (5.71)

Results and Discussion

The novel homologous series 4-[4'-*n*-alkoxy benzyloxy]-4''-methoxy benzyl benzoates consists of eleven members. The ethoxy to hexadecyloxy homologues are enantiotropically nematogenic and only first member of the series is non-mesogenic. The smectogenic mesophase is totally absent. The transition temperatures (Table 2) of the homologues are plotted versus the number of carbon atoms present in *n*-alkyl chain of left *n*-alkoxy terminal end group. Like or related points are joined to draw the appropriate curves of solid-mesomorphic/isotropic and nematic-isotropic to construct a phase diagram (Figure 1) showing the phase behavior of the novel homologous series. The solid-mesomorphic/isotropic transition curve follows a zigzag path of rising and falling values as series is ascended and behaved in normal manner. The nematic-isotropic transition curve initially rises and then descends as the series is ascended up to the dodecyloxy homologue, but it shows deviating behavior for the tetradecyloxy and hexadecyloxy homologues. Thus, the nematic-isotropic transition curve majorly behaved in a normal manner. An odd-even effect is observed for the nematic-isotropic transition curve. The curves for the odd and even members of a series merge into each other at the octyloxy homologue and then it propagates up to hexadecyloxy homologue in a single transition curve. Thus, the odd-even effect disappears from

Table 2. Transition temperatures of series in °C.

Compound no.	n-alkyl group (—C _n H _{2n+1}) (n)	Transition temperature in °C		
		<i>Sm</i>	<i>N</i>	Isotropic
1	1	—	—	201.0
2	2	—	202.0	240.0
3	3	—	198.0	220.0
4	4	—	205.0	229.0
5	5	—	201.0	249.0
6	6	—	181.0	255.0
7	8	—	172.0	270.0
8	10	—	188.0	220.0
9	12	—	162.0	212.0
10	14	—	215.0	242.0
11	16	—	204.0	231.0
<i>Sm</i> : Smectic		<i>N</i> : Nematic		

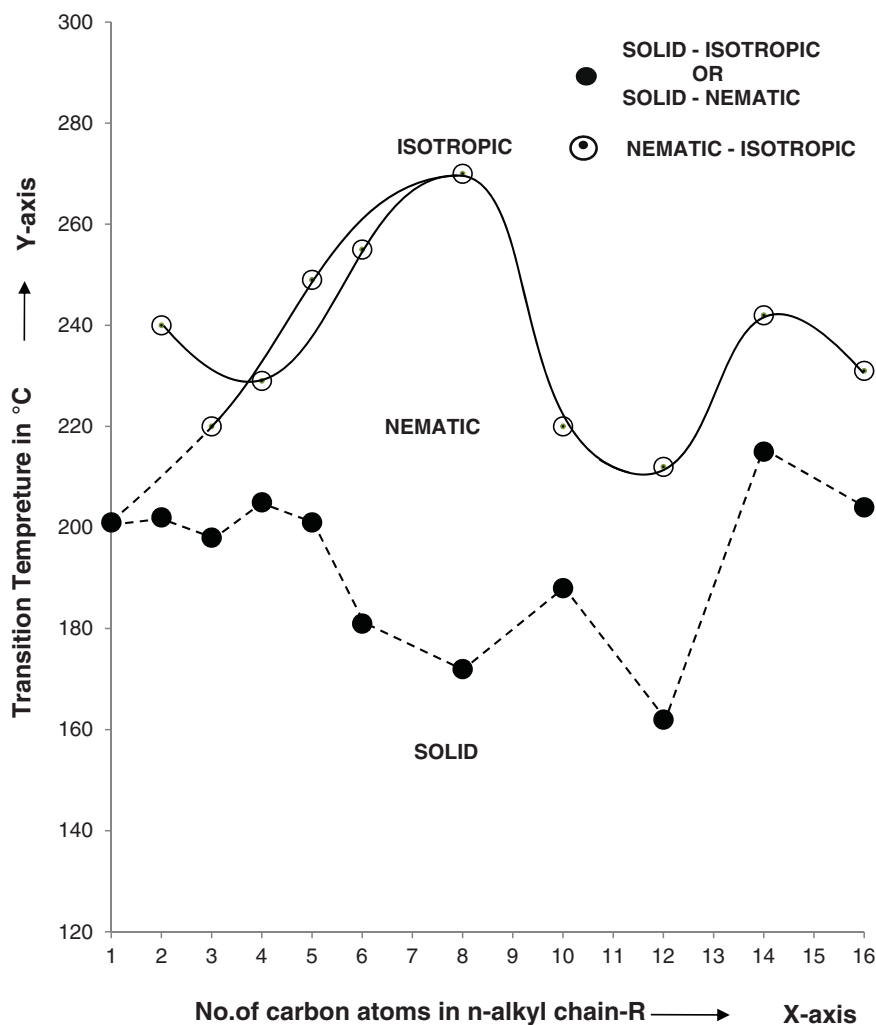


Figure 1. Phase behavior of series.

and beyond octyloxy homologue. The nematic-isotropic transition curve for the first non-mesomorphic member of the series is extrapolated [19, 20] to predict the nematic-isotropic transition temperature. Analytical and spectral data confirm the molecular structures of homologues. The mesomorphic properties vary from homologue to homologue in the present novel series. The thermal stability for the nematogenic mesophase is 236.8°C and mesomorphic phase length varies between 27°C (tetradecyloxy and hexadecyloxy homologues) and 98°C (octyloxy homologue). Thus, the present series under discussion is nematogenic and high melting type with absence of smectogenic character.

Non-mesomorphicity of first member of the series is attributed to the high crystallising tendency due to the presence of two identical polar $-\text{OCH}_3-$ end groups of the first homologue of the series. The intermolecular closeness and intermolecular attractions generated as a consequence of unfavourable molecular rigidity and flexibility against exposed thermal vibrations are relatively weaker or imbalanced to cause mesomorphism and hence sharply

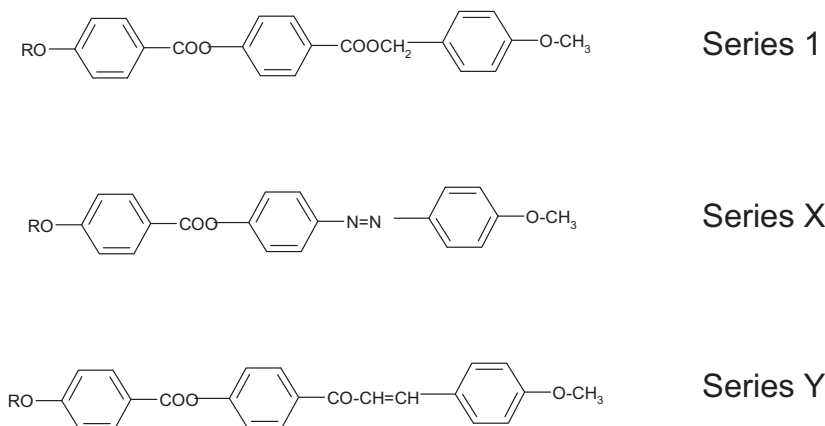


Figure 2. Structurally similar homologous series.

transforms into an isotropic liquid from the solid crystalline state without passing through anisotropic state of mesomorphism. The nematogenic mesophase formation is attributed to the disalignment of the molecules on the plane of a surface at an angle less than 90° and withstanding externally exposed thermal vibrations for definite temperature range with statistically parallel orientational order of molecules in a floating condition. As a result of suitable magnitudes of anisotropic forces of intermolecular favourable closeness and end to end attractions for some temperature difference prior to isotropic temperature. Thus, favorable quantum of molecular rigidity and flexibility facilitated nematogenic mesophase formation for the ethoxy to hexadecyloxy homologues without exhibition of smectic character. The absence of smectogenic character for all the homologues of presently investigated is attributed to the absence of lamellar packing of molecules in their crystal lattices which did not facilitate a sliding layered arrangement of molecules, prior to nematogenic mesophase formation. The ordered arrangement of molecules gradually diminishes with rising of temperature and the molecule of a sample substances under polarising microscopy are randomly oriented freely in all possible directions with high order of disorder or randomness or entropy ($\Delta S = \Delta H/T$). The reversal of mesophase reappears on cooling the isotropic melt of the mesomorphic homologue at the same temperature at which it disappears on heating if appropriate rate of heating and cooling is maintained for enantiotropic transitions. The disappearance of odd-even effect from and beyond octyloxy homologue is attributed to the effect of coiling or bending or flexing or coupling of longer n -alkyl chain, bonded through oxygen atom with core structure of a molecule. The changing trend of mesogenic properties from homologue to homologue in present series is due to the sequential addition of methylene unit or units in left n -alkoxy terminal end group keeping unaltered, polar $-\text{OCH}_3$ group at the other end of a molecule. The nematic-isotropic transition curve for odd members of a series is extrapolated [21–23] to the nonmesomorphic first member of a present series to determine and predict nematic-isotropic transition temperature of first homologue, keeping in view of the trend of the transition curve, it matches to the point at 201°C , which is a solid-isotropic temperature of first odd member of a series i.e., $201=201=0$, or mesophase length zero degree centigrade indicates or means, there is no possibility of mesophase formation beyond 201°C . The mesomorphic behaviors of a present novel series are compared with structurally similar known homologous series X [24] and Y [25] which

Table 3. Average thermal stability in °C.

Series→	Series 1	Series X	Series Y
Smectic-Nematic Or Smectic-Isotropic Commencement of Smectic phase	—	137.0 (C ₁₄ –C ₁₆) C ₁₄	118.0 (C ₇ –C ₁₄) C ₇
Nematic-Isotropic Commencement of nematic phase	236.8 (C ₂ –C ₁₆) C ₂	251.7 (C ₁ –C ₁₄) C ₁	157.0 (C ₅ –C ₁₆) C ₅

differs with respect to one of the central groups, keeping rest of the molecular part identical for the same homologue from series to series, shown as under in Fig. 2.

Homologous series-1 investigated presently and series X and Y chosen for comparative study are identical with respect to three phenyl rings and one of the central bridge linking first and middle phenyl ring. But their second central bridges linking middle and third phenyl rings are different. Therefore, series 1, X and Y differ with molecular rigidity. Moreover all the three series under comparison have same terminal end groups for the same homologue from series to series responsible to contribute identical molecular rigidity. However, combine effects of suitable magnitudes of molecular rigidity and flexibility differ from series to series and homologue to homologue in the same series. Thus, mesomorphism and the degree of mesomorphism vary from series to series and homologue to homologue in the same series. Following Table 3 represents some mesomorphic properties of the series 1, X and Y under comparison.

From Table 3, it is clear that,

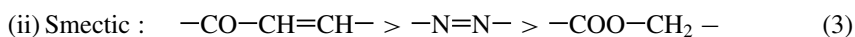
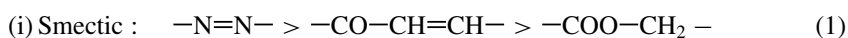
- Homologous series 1 is only nematogenic, while series X and Y are nematogenic in addition to smectogenic.
- Thermal stabilities for nematic mesophase decreases from series X to 1 to Y while smectic thermal stability decreases from X to Y to 1.
- Smectogenic mesophase stabilizes for series X and Y but it destabilized in case of series 1 until the last hexadecyloxy homologue.
- Smectic mesophase commences earliest from seventh member of a series Y, from tetradecyloxy homologue in series X, but it did not commence until the last member of series 1.
- Nematic mesophase commences from very first member of a series X, from second member of a series 1 and from fifth member of series Y.

The central group of —COO— linking first and middle phenyl ring is commonly present in all the homologous series under comparison with changing central groups ($\text{—COO—CH}_2\text{—}$, —N=N— , —CO—CH=CH—) linking middle and third phenyl rings, for the same homologue from series to series. Central groups $\text{—COO—CH}_2\text{—}$ and —N=N— in case of present series and series X are comparable to each other. The oxygen atom of central carboxy group bumps into the nonbonded sides of the adjacent hydrogen atoms of aromatic phenyl ring, which causes considerable strain on the molecule. Consequently, a twist around C-O bond occurs forcing the phenyl ring out of the plane of a molecule. Thus, molecular coplanarity is reduced to some extent making them thick. The central group —N=N—

certainly endows the molecular coplanarity in trans position. On account of these differences the smectic-Nematic and nematic-isotropic thermal stabilities of series-1 is lower than a series X. Central bridge $-\text{CO}-\text{CH}=\text{CH}-$ is relatively longer than $-\text{COO}-\text{CH}_2-$ central bridge with absence of conjugated double bond in series-1, which causes more noncoplanarity due to the twist obtained by oxygen atom of vinyl $\text{C}=\text{O}$ carbonyl group of series Y. On account of this difference the nematic-isotropic thermal stability of series Y is lower than a series 1. Smectic mesophase formation is hindered by absence of lamellar packing of molecules in the crystal lattices of series 1. Early or late commencement of the smectic or nematic mesophase also depends upon the extent of noncoplanarity caused by the molecules. Thus, the degree of molecular noncoplanarity of series 1 does not permit the lamellar packing of molecules in their crystal lattices to cause smectic mesophase formation until the last member of a series 1. The suitable magnitudes of anisotropic forces of inter molecular closeness and end to end as well as lateral attractions as a consequence of varying molecular rigidity and flexibility is attributed to varying polarity and polarizability of changing central bridges of series 1, X and Y. Thus, variations in mesophase formation and the varying degree of mesomorphism is susceptible to differing central groups of $-\text{COO}-\text{CH}_2-$, $-\text{N}=\text{N}-$, $-\text{CO}-\text{CH}=\text{CH}-$. Hence, observed variation in mesomorphic behavior for the same homologue from series to series is attributed to changing central group, keeping rest of the molecular parts unchanged.

Conclusions

- The group efficiency order derived on the basis of (i) thermal stability and (ii) the early commencement of mesophase for smectic and nematic are as under.



- The phenomena of mesomorphism and the degree of mesomorphism depend upon the polarity and polarizability of central group of a mesomorphic molecule.
- Mesogenic tendency of a substance depends upon suitable magnitudes of molecular rigidity and flexibility.
- Mesogenic properties of a substance is susceptible to suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of favorable molecular rigidity and flexibility.

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