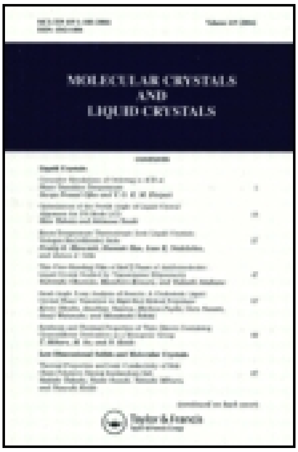

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A Novel Homologous Series of Thermotropic Mesogens of Ethylene Derivatives: α-4-[4′-n-Alkoxy Benzoyloxy] Phenyl β-4″ Methoxy Benzoyl Ethylenes

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A Novel Homologous Series of Thermotropic Mesogens of Ethylene Derivatives: α-4-[4′-n-Alkoxy Benzoyloxy] Phenyl β-4″Methoxy Benzoyl Ethylenes

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A novel homologous series consists of 12 compounds. The shorter chain homologues do not show liquid crystal phases, but from six carbons onwards, the nematic phase is exhibited enantiotropically, with some members also showing a smectic phase. The phase behavior of the transition curves of the series shows a usual trend. The texture of the nematic phase is the threaded or Schlieren type and that of smectic phase is a smectic A. An odd–even effect is observed for smectic–nematic and nematic–isotropic transition curves. Analytical data confirm the molecular structure. The transition temperatures were determined by an optical polarizing microscopy. The mesogenic properties of the novel series are compared with a structurally similar homologous series. The average smectic–nematic and nematic–isotropic thermal stabilities are 133.4°C and 159.8°C, respectively, with a mesogenic temperature range of 10°C to 62°C.

Keywords Liquid crystal; mesogen; mesogenic; nematic; smectic

Introduction

The molecular geometry, shape and size, of a molecular structure has a direct relation with molecular rigidity and flexibility, which in turn influences the mesomorphic properties [1–3]. The rigid core of a structure is made up of ring structures (aromatic or heterocyclic) bridged through two central groups, and the flexible portion is made up of lateral and/or terminal end groups or chains. The novel homologous series consists of three phenyl rings linked through two central bridges –COO– and –CH=CH–CO–, which act as a rigid core. The left and right terminal end groups of the molecule are n-alkoxy and $–OCH_3$ respectively, and these act as flexible units of the molecule without any lateral substitution. Thus, the induced mesomorphism can be assessed and discussed in terms of molecular rigidity and flexibility and their correlation with molecular structure and suitable magnitudes of anisotropic intermolecular forces of attraction.

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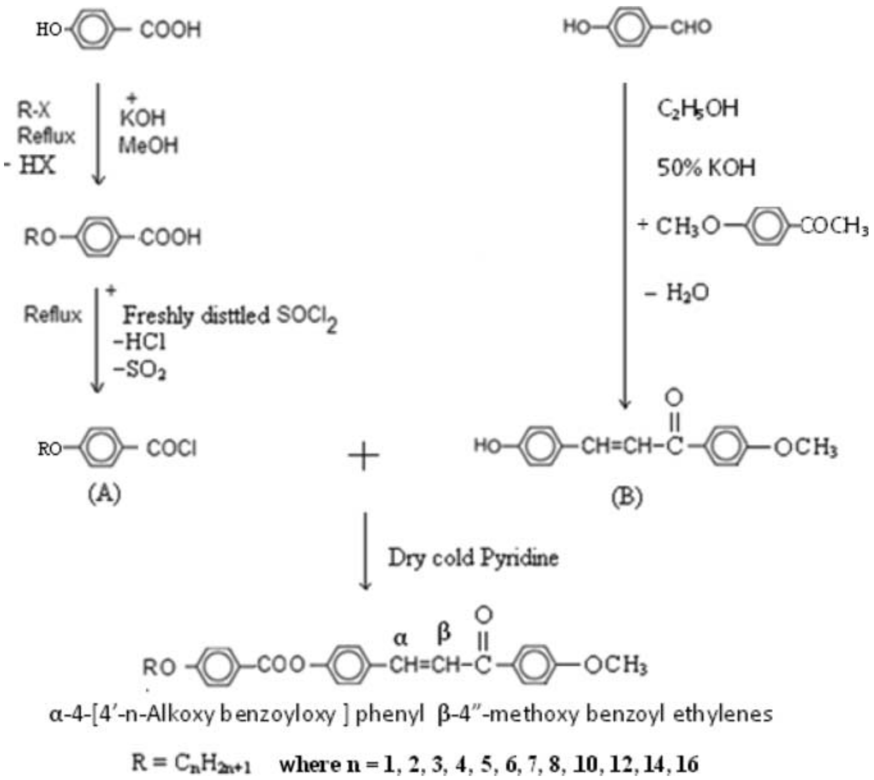
Experimental

Synthesis

4-Hydroxybenzoic acid is alkylated by suitable alkylating agents and the resulting n-alkoxy benzoic acids were converted to the corresponding n-alkoxybenzoyl chloride (A) using thionyl chloride by the method of Dave and Vora [4]. α-4-Hydroxy phenyl β-4′ methoxy benzoyl ethylene (B) was prepared by reacting 4-hydroxy benzaldehyde with p-methoxyacetophenone by the usual established method [5]. Components (A) and (B) were condensed in dry cold pyridine by a known method [6–8]. The final products were decomposed, filtered, washed, dried, and recrystallized until constant transition temperatures were obtained. The transition temperatures were determined by the hot stage polarizing microscopy. 4-Hydroxybenzoic acid, alkylating agents (R-X), thionyl chloride, pyridine, KOH, methanol, ethanol, 4-hydroxybenzaldehyde, and 4-methoxyacetophenone were used as received. The synthetic route to the series is outlined in Scheme 1.



Scheme 1. Synthetic route to the novel series.

Characterization

Selected members of the novel homologous series were characterized by elemental analysis (Table 1), infra red (IR) spectroscopy, and ^{1}HNMR spectroscopy techniques. Microanalysis was performed on a Perkin-Elmer PE2400 CHN analyzer. IR spectra were recorded

Table 1. Elemental analysis for the ethyloxy, butyloxy, heptyloxy, and tetradecyloxy derivatives

		Elements % found (% calculated)	
Sr. No.	Molecular formula	C	H
1.	$C_{25}H_{22}O_5$	74.63 (74.60)	5.47 (5.42)
2.	$C_{27}H_{26}O_5$	75.35 (75.32)	6.05 (6.01)
3.	$C_{30}H_{32}O_5$	76.27 (76.30)	6.78 (6.81)
4.	$C_{37}H_{46}O_5$	77.89 (77.86)	8.07 (8.03)

on Perkin-Elmer spectrum GX, and ^{1}HNMR spectra were recorded on a Bruker spectrometer using $CDCl_3$ as solvent. The mesogenic properties of the members of the series were recorded by polarizing microscopy. The textures of nematic and smectic mesophases were determined by the miscibility method. Thermodynamic properties enthalpy (ΔH) and entropy (ΔS) are discussed qualitatively.

Analytical Data

Spectral Data

NMR in ppm for octyloxy derivative

> 0.983 (–CH_3 of –OC_8H_{17}), 1.422 (–$(CH_2)n$– of –OC_8H_{17}), 3.675 (–OCH_2 of –OC_8H_{17}), 6.565 and 6.582 (–CH=CH–CO–), 7.404, 7.093, and 7.636 (phenyl ring).

NMR in ppm for dodecyloxy derivative

> 0.945 (−CH_3 of $OC_{12}H_{23}$), 1.465 (–$(CH_2)n$– of –$OC_{12}H_{23}$ group), 3.689 (–OCH_2 of –$OC_{12}H_{23}$), 6.575 and 6.669 (–CH=CH–CO–), 6.691, 7.610, and 7.632 (phenyl ring).

IR in cm^{-1} for hexyloxy derivative

> 720 (–$(CH_2)n$– of –OC_6H_{13}), 815 (phenyl ring), 1175 (C–O of –OC_6H_{13}), 1215, 1260, and 1640 (–COO–), 930 (–CH=CH–).

IR in cm^{-1} for decyloxy derivative

> 760 (–$(CH_2)n$– of –$OC_{10}H_{21}$), 830 (phenyl ring), 1150 (C–O of –$OC_{10}H_{21}$), 1250, 1610, and 1680 (–COO–), 945 (–CH=CH–).

Texture Determination

- Tetradecyl – Nematic – Threaded
- Decyl – Smectic – Smectic-A Type
- Hexyl – Smectic – Smectic-A Type
- Octyl – Nematic – Schlieren

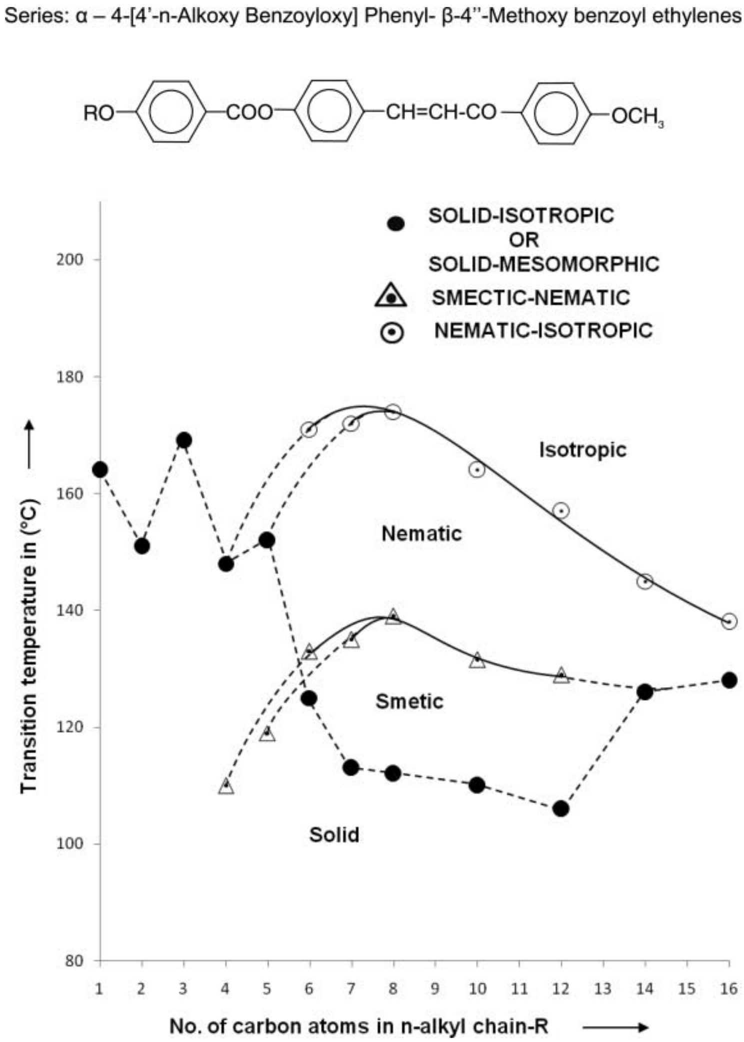


Figure 1. The phase behavior of the novel series.

Results and Discussion

4-n-Alkoxybenzoic acids are dimeric, where two molecules are joined through hydrogen bonding. Dimerisation disappears on breaking of hydrogen bonding by esterification. The methyl to pentyl derivatives of the novel series are non-mesogenic, but all others are mesogenic. The pentyl to dodecyl derivatives are enantiotropically smectogenic and nematogenic in character. The tetradecyl and hexadecyl derivatives of the series are only enantiotropically nematogenic without the exhibition of a smectic phase. The phase behavior of the novel series is shown in the phase diagram (Fig. 1) with the number of carbon atoms present in n-alkyl chain versus the transition temperatures (also shown in Table 2) of the members of the series as determined by the hot stage polarizing microscopy. The phase diagram indicates the following features:

Table 2. Transition temperatures of the novel series

Compound No.	n-alkyl group $-C_nH_{2n+1\ (n)}$	Transition temperatures (°C)		
		Smectic	Nematic	Isotropic
1.	1	—	—	164.0
2.	2	—	—	151.0
3.	3	—	—	169.0
4.	4	—	—	148.0
5.	5	—	—	152.0
6.	6	125.0	133.0	171.0
7.	7	113.0	135.0	172.0
8.	8	112.0	139.0	174.0
9.	10	110.0	131.5	164.0
10.	12	106.0	129.0	157.0
11.	14	—	126.0	145.0
12.	16	—	128.0	138.0

- The solid-isotopic or mesomorphic transition curve rises and falls as the series is ascended with an overall falling nature.
- The smectic–nematic transition curve initial rises, passes through maxima, and then falls in usual manner up to the decyloxy homologue, but it rises by 1° in dodecyl derivative. The curve is extrapolated [8] to the pentyl, butyl, and tetradecyl derivatives to predict their latent transition temperatures (LTT) for the smectic phase, which are exhibited monotropically as 111°C, 118°C, and 126°C. The curve shows very narrow range of odd–even effect.
- The nematic–isotropic transition curve initially rises and then adopts a descending tendency as the series is ascended and behaves in the usual manner with an odd–even effect. Both curves for the odd and even members are extrapolated [8] to predict the LTT for nematic–isotropic transition of the butyl and pentyl members of the series, which coincide with the melting points of the respective homologues.

The smectic and nematic mesophases commence from the fifth member of the series. The non-mesogenic behavior of the first five homologues is attributed to their high crystallizing tendency arising from their amount of energy released to stabilize in crystalline solid state at room temperature. These non-mesogenic molecules are unable to resist thermal vibration exposed upon them and are disaligned on the plane of the surface without any 2D order, i.e., molecules are oriented randomly in all possible directions with high order of disorder or entropy ($\Delta S = \Delta H/T$). Thus, the non-mesogenic members of the series sharply transform into the isotropic state at their melting point without passing through a mesogenic state. The exhibition of the nematogenic mesophase with or without smectic phase is attributed to the disalignment of molecules at an angle less than 90° under the influence of suitable magnitudes of anisotropic intermolecular forces of attraction. Under such situations, the sample molecules (thermodynamic system) are able to resist thermal vibrations exposed upon them to float on the surface with their molecular arrangement statistically parallel in two dimensions controlled by entropy (ΔS) at the transition temperature. The observed smectogenic property exhibited by the hexyloxy to dodecyloxy homologues are

Table 3. Average thermal stability of three homologous series in °C

Series	1	S_1	S_2
Smectic–Nematic or isotropic	133.4 (C_6–C_{12})		106.6 (C_{10}–C_{16})
Commencement of smectic phase	C_6	—	C_{10}
Nematic–isotropic	159.8 (C_6–C_{16})	166.6 (C_5–C_{14})	119.8 (C_8–C_{16})
Commencement of nematic phase	C_6	C_5	C_8

attributed to lamellar packing of molecules in their crystal lattices, causing a layered arrangement of molecules. Such layers of molecules tend to slide out of plane under the influence of applied heat, resisting thermal vibrations, maintaining a 2D array of molecules in a floating condition. The smectic–nematic mesophase range is from 8°C to 23°C for the hexyloxy and dodecyloxy homologues respectively. Similarly, the nematic–isotropic phase range varies from 10°C to 42°C. Overall, the mesogenic (smectic plus nematic) phase range varies from a minimum of 10°C at the hexadecyloxy homologue to a maximum of 62°C at the octyloxy homologue. Thus, the novel series is predominantly nematogenic and partly smectogenic. Variations in the degree of mesomorphism and an odd–even effect from homologue to homologue are due to sequential addition of methylene units in the n-alkyl chain. The odd–even effect diminishes for higher homologues because the longer n-alkyl chain may coil, bend or flex, or couple to lie in the major axis of the core that hinders the odd–even effect [9]. The mesogenic properties of the series, including the average thermal stability and the commencement of mesophases (Table 3) of the novel series, are compared with two structurally similar homologous series as shown in Fig. 2.

The homologous series 1 and S_1 [10] are identical in all respects except for the linking groups of –COO– and –CH=CH–COO– respectively. Therefore, the length to breadth ratio and the ratio of molecular polarity to polarizability, molecular rigidity and flexibility, the magnitude of anisotropic intermolecular forces of attraction differs appreciably [9]. Homologous series 1 and S_2 [5] are identically similar in all respects except for the terminal units of –OCH_3 and –H respectively. Therefore, the observed differences of mesogenic properties and the degree of mesomorphism are directly related to the structural differences among series 1, S_1, and S_2. The average thermal stabilities and the commencement of smectic and nematic phases are shown in Table 3.

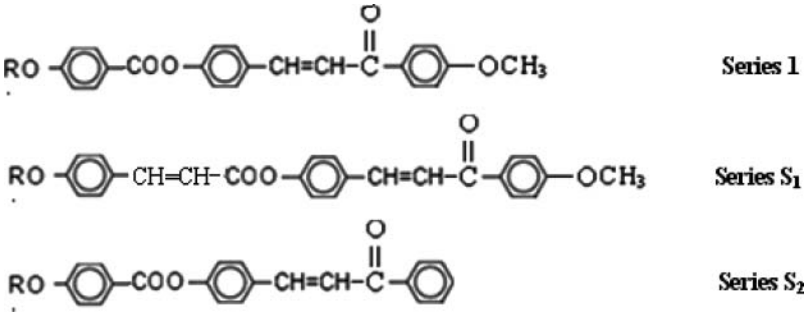


Figure 2. The molecular structure of the series under comparison.

Table 3 indicates that all the three structurally similar homologous series, 1, S_1 and S_2, under comparison are partly smectogenic and partly nematogenic. The smectic–nematic thermal stability of series 1 is 133.4°C, and that of S_2 is 106.6°C, but S_1 does not show the smectic phase. The nematic–isotropic thermal stability of series 1 is lower than that of series S_1 and higher than that of series S_2. The smectic and nematic mesophases commence from sixth and fifth members of series 1 and S_1 respectively; while the smectic and nematic phases commence relatively later from the decyloxy and octyloxy derivative of the series S_2. Homologous series 1 and S_1 differ in respect of their central bridges (–COO– and –CH=CH–COO–) linking the first and middle phenyl rings. Therefore, the length to breadth ratio and the ratio of molecular polarity to polarizability appreciably differs and the magnitudes of end-to-end anisotropic intermolecular forces of attractions differ as a consequence of differing molecular rigidity and flexibility [1–3]. Molecules of series 1 enable lamellar packing, while it is absent in the case of molecules of series S_1. Both the central bridges are comparable, although the vinyl carboxylate –CH=CH–COO– has a greater length, which causes more non-coplanarity due to a twist generated as the oxygen atoms of the vinyl carboxy group affect the adjacent hydrogen atoms of aromatic rings in case of –COO– central bridge; the similar effect causes considerable strain on the molecule. Consequently, a twist around C–O bond will occur forcing the phenyl ring out of the plane of the molecule. Thus, the coplanarity of the molecule is reduced to a lesser extent than the –CH=CH–COO– group, making phenyl ring broader. On account of these differences, the smectic–nematic thermal stability of series S_1 is lower than series 1. The enhanced length of the vinyl carboxy central group by the –CH=CH– unit increases conjugation, molecular rigidity, and lateral attractions [1,2,3,5]. Hence, the intermolecular attractions due to –CH=CH– unit increases, while in the case of –COO– group the multiple bond is absent. Consequently, the stereochemistry of the molecule containing –COO– does preserve the linearity of the molecule, but results in a less thermally stable nematogenic phase due to the relatively poor end-to-end attractions. Moreover, early or late commencement of mesophase depends upon the extent of non-coplanarity caused by the molecule as discussed above. On comparing the thermal stabilities of series 1 and S_2, they differ in respect of right terminal end group, which causes difference in end-to-end attractions due to the polarity difference of $-OCH_3$ and –H terminal units. Thus, the smectic phase commences from the hexyloxy homologue in series 1, while it commences from the decyloxy homologue in series S_2. Thus, variations in mesogenic properties from series to series for the same homologue varies with different polarity of a right terminal end group.

Conclusions

1. The present series is predominantly nematogenic and partly smectogenic.
2. The central group bearing a multiple bond induces conjugation and increases molecular rigidity to emerge more thermally stable mesophase or mesophases.
3. The group efficiency order derived on the basis of thermal stability for smectic and nematic mesophases are as follows.

Smectic: $-OCH_3$ with –COO– > –H with –COO– > $-OCH_3$ with –CH=CH–COO–
Nematic: $-OCH_3$ with –CH=CH–COO– > $-OCH_3$ with –COO– > –H with –COO–

4. The variation of molecular rigidity and flexibility are the basis of inducing mesogenic properties in a substance.

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References

[1] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.

[2] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.

[3] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.

[4] Dave, J. S., & Vora, R. A. (1970). *Liquid Crystals and Ordered Fluids*, Plenum Press: New York, 477 pp; (b) *Vogel's Text Book of Practical Organic Chemistry,* 4th ed., Longman: Singapore; (c) Doshi, A. V., & Ganatra, K. J. (1999). *Proc. Ind. Acad. Sci. (Chem. Sci.)*, *4*, 11, 562.

[5] Chauhan, M. L., & Doshi, A.V. (2007). *J. Indian Chem. Soc.*, *84*, 774.

[6] Patel, V. R., & Doshi, A. V. (2010). *Derpharma Chemica*, *2*, 429.

[7] Patel, R. B., & Doshi, A.V. (2011). *Derpharma Chemica*, *3*, 147.

[8] Chauhan, M. L., Pandya, R. N., & Doshi, A. V. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 228. (b) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 220; (c) Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 3; (d) Doshi, A. V., Odedara, D. A., & Patel, R. B. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 97; (e) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104.

[9] Gray, G. W. (1962) *Molecular Structure and the Properties of Liquid Crystal*, Academic Press: London; (b) Gray, G. W., & Windsor, P. A. (1974). *Liq. Cryst. Plastic Cryst.,* Vo l. 1., Ellis Horwood: Chichester, UK, Chap. 4.

[10] Chauhan, H. N., & Doshi, A.V. (2012). *Derpharma Chemica*, *4*, 731.