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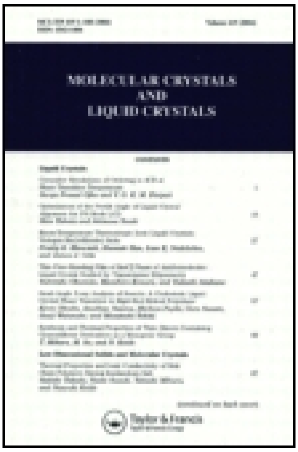

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Synthesis and Evaluation of Liquid Crystalline Properties of a Novel Homologous series: α-3-[4′-n-Alkoxy Benzoyloxy] Phenyl-β-4″-Nitro Benzoyl Ethylenes

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Synthesis and Evaluation of Liquid Crystalline Properties of a Novel Homologous series: α-3-[4′-*n*-Alkoxy Benzoyloxy] Phenyl-β-4″-Nitro Benzoyl Ethylenes

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The titled homologous series consists of 11 members. The methyl and ethyl homologues are nonmesomorphic because of very high melting points, however, the propyl to hexadecyl derivatives are enantiotropic nematic with absence of smectogenic. The texture of nematic mesophase is threaded or Schlieren. The nematic-isotropic transition curve of the phase diagram behaves in a normal manner with the exhibition of an odd–even effect. The transition temperatures of the series and liquid crystal properties are observed through optical polarizing microscopy and a hot stage. The novel materials were characterized by elemental analysis, infrared, and ^1H NMR spectroscopy. Analytical data support the molecular structures. The liquid crystal properties of the novel series are compared with structurally similar homologous series. The novel series is entirely nematogenic with absence of smectic character and of a middle-ordered melting type. The nematic-isotropic thermal stability varies between around 120°C and 180°C.

Keywords Anisotropic; liquid crystal; mesomorphic; nematic; smectic

Introduction

The basic prime requirement to induce liquid crystalline properties in a substance is a suitable compromise of molecular rigidity and flexibility [1–3]. Molecular rigidity and flexibility occurs as a consequence of the molecular shape, size, and aromaticity types of the central, terminal, and lateral groups, and their polarities, molecular polarity, and polarizability, etc. Thus keeping these issues in view to synthesize novel liquid crystals (LC) substances, the molecular structure of the novel series was designed with three phenyl rings bridged through −COO− and −CH=CH−CO− central groups, and −OR, $-NO_2$ as left and right terminal groups, respectively, without any lateral groups. The aim of the present work is to further establish the relationship between liquid crystal properties and molecular structure [4].

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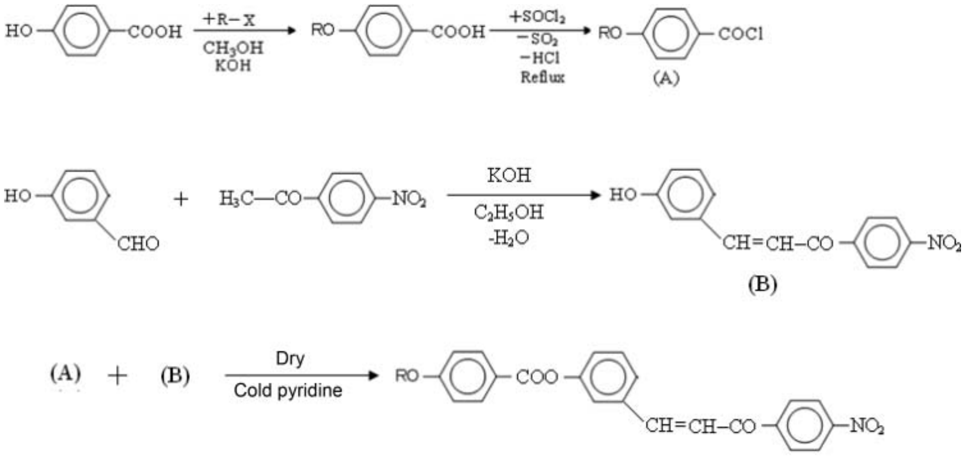
Experimental

Synthesis

4-Hydroxybenzoic acid was alkylated by a suitable alkylating agent and the corresponding 4-*n*-alkoxybenzoic acids were converted to the acid chlorides (A) using freshly distilled thionyl chloride by the modified method of Dave and Vora [5]. α-3-[4′-*n*-alkoxy benzoyloxy] phenyl-β-4″-nitro benzoyl ethylene (B) was prepared by reacting 3-hydroxybenzaldehyde and 4-nitroacetophenone by an established method [6]. Components (A) and (B) were condensed in dry cold pyridine with constant shaking of the reaction mixture [7]. The final products were individually filtered, washed, dried, and purified until constant transition temperatures were obtained. The synthetic route to the series is shown in Scheme 1. 4-Hydroxybenzoic acid, *n*-alkyl halide, methanol, KOH, HCl, thionyl chloride, 4-nitroacetophenone, 3-hydroxybenzaldehyde, ethanol, etc., required for synthesis were used as received, except for solvents that were used after purification, drying, and distillation.



where R= C_nH_{2n+1}, n = 1,2,3,4,5,6,8,10,12,14,16.

Scheme 1. Synthetic route to the series.

Characterization

Some of the homologues of the novel series were characterized by elemental analysis, infrared (IR), and ^{1}H NMR spectroscopy techniques. Microanalysis of the compounds was performed on a Perkin-Elmer PE 2400 CHN analyzer (Sophisticated Analytical Instrumentation facility (SAIF) Punjab University, Chandigarh) with results shown in Table 1. Nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ as solvent and IR spectra were recorded using a Perkin-Elmer GX spectrometer (Vaibhav Laboratory, Ahmedabad). The liquid crystal properties, transition temperatures, and melting temperatures were investigated by using optical polarizing microscopy. The texture of the nematic mesophase was determined by the miscibility method. Thermodynamic quantities enthalpy (ΔH) and entropy (ΔS) are discussed qualitatively instead of differential scanning calorimetry.

Table 1. Elemental analysis for propyloxy, pentyloxy, tetradecyloxy, and hexadecyloxy derivatives

Sr. no.	Molecular formula	Elements % found (% calculated)		
		C	H	N
1	$C_{27}H_{23}NO_6$	69.68 (69.60)	4.90 (4.87)	3.29 (3.25)
2	$C_{28}H_{25}NO_6$	70.55 (70.59)	5.42 (5.45)	3.01 (3.05)
3	$C_{36}H_{41}NO_6$	73.80 (73.85)	7.38 (7.35)	2.43 (2.39)
4	$C_{38}H_{45}NO_6$	74.42 (74.39)	7.72 (7.67)	2.30 (2.28)

Analytical Data

NMR in ppm for the Octyloxy Derivative. 0.876 ($-CH_3$ of OC_8H_{17} group), 1.279 ($-CH_2-$ of $-OC_8H_{17}$), 4.006 ($-OCH_2-CH_2-$ of $-OC_8H_{17}$), 3.223 ($-CH=CH-$ group), 6.990 ($-CH=CH-CO-$ group), 6.906 and 6.9278 (p-substituted phenyl ring), 7.885 and 7.907 (m-substituted phenyl ring). NMR supports the structure.

NMR in ppm for Decyloxy Derivative. 0.876 ($-CH_3$ of $-OC_{10}H_{21}$ group), 1.256 ($-CH_2-$ of $-OC_{10}H_{21}$), 4.013 ($-OCH_2-CH_2-$ of $-OC_{10}H_{21}$), 4.289 and 4.30 ($-CH=CH-CO-$ group), 7.764 and 7.925 (p-substituted phenyl ring), 6.903 (m-substituted phenyl ring). NMR supports the structure.

IR in cm^{-1} for Hexyloxy Derivative. 625 ($-CH_2$)$-$ group of $-OC_6H_{13}$), 770 (m-substituted phenyl ring), 1180 (C$-$O of $-OC_6H_{13}$ group), 1250, 1600, and 1685 ($>C=O$ of COO ester group), 1435 ($-NO_2$ group), 825 ($-CH=CH-$ group). IR supports the structure.

IR in cm^{-1} for Dodecyloxy Derivative. 645 ($-CH_2-$ group of $-OC_{12}H_{25}$), 820 (p-substituted phenyl ring), 770 (m-substituted phenyl ring), 1165 (C$-$O group), 1250, 1605, and 1685 ($>C=O$ of COO ester group), 1435 ($-NO_2$ group), 930 ($-CH=CH-$ group). IR supports the structure.

Texture by miscibility method:
Butyloxy homologue..........Threaded nematic
hexyloxy homologue..........Schlieren nematic

Results and Discussion

4-*n*-Alkoxy benzoic acids are dimeric. Their dimerization disappears by esterification due to the breaking of hydrogen bonding. The novel mesogenic series consists of 11 homologues. The methyl and ethyl homologues are not liquid crystalline, however, all the other homologues from propyl to hexadecyl are enantiotropically nematogenic without the exhibition of smectogenic character. The transition temperatures (Table 2) were plotted versus the number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy terminal chain. The phase diagram shows the phase behavior of the series (Fig. 1). The solid-isotropic or nematic transition curve rises and falls in a zigzag manner as the series is ascended with an overall descending tendency. The nematic-isotropic transition curve initially rises and then gradually falls as the series is ascended and overall behaves in a normal manner.

Table 2. Transition temperatures in °C of series 1

Compound no.	R=C_nH_{2n+1} (n)	Smectic	Nematic	Isotropic
1	1	—	—	202.00
2	2	—	—	203.0
3	3	—	168.0	184.0
4	4	—	160.0	186.0
5	5	—	140.0	188.0
6	6	—	123.0	183.5
7	8	—	108.0	165.0
8	10	—	110.0	145.0
9	12	—	106.0	132.0
10	14	—	96.0	123.0
11	16	—	100.0	118.0

The odd–even effect is observed with a very narrow temperature difference. The curves for odd and even homologues merge into each other between octyl and nonyl derivatives of the series and the odd–even effect disappears from the nonyl derivative of the series. The nematogenic phase temperature range varies between 18°C and 60.5°C. The isotropic temperatures of LC homologues vary between 118°C and 188°C.

α-3-Hydroxy phenyl β-4′-nitro benzoyl ethylene is not mesomorphic, but, on condensing it with dimerized 4-n-alkoxybenzoic acids, through their acid chlorides, the resultant esters exhibit liquid crystalline properties, which commence from the propyl homologue of the series. Hydrogen bonding of the carboxylic acids disappears on esterification [8]. The methyl and ethyl derivatives of the series are not mesomorphic because of their high crystallizing tendency, which arises from their strong intermolecular attractions due to presence of shorter methyl and ethyl n-alkyl chains, but the lack of anisotropic intermolecular forces of attraction precludes mesomorphism. As the n-alkyl chain length increases, the crystalline character gradually diminishes and the amorphous character of a resultant product increases. The molecules of methyl and ethyl homologues initially attempt to resist the exposed thermal vibrations strongly, but then suddenly lose their ability to withstand the heat. Therefore, finally they sharply and smoothly transform into the isotropic state. The exhibition of the nematogenic mesophase from the propyl to hexadecyl homologues is attributed to the disalignment of molecules at an angle of less than 90° with the plane of a surface due to the occurrence of suitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of favorable molecular rigidity and flexibility in floating condition [1–4]. Thus, the molecules arrange themselves in a statistically parallel orientational order at a particular temperature t_1 and continue to float in the same manner up to a higher temperature t_2 with two-dimensional order of the molecules. From and beyond t_2 temperature the molecules are randomly oriented in all possible direction, which is the isotropic liquid state. The nematic mesophase formation takes place in a reversible manner from t_1 and t_2 and on cooling the melt. The temperature difference t_2 and t_1 is called nematogenic phase temperature range, which varies from 18°C to 60.5°C in the novel series. The absence of smectogenic character is attributed to the absence of lamellar packing of molecules in their crystal lattices, and a sliding layered arrangement of molecule does not occur in floating condition. The occurrence of an odd–even effect and the variation of mesomorphic properties from homologue to homologue for the same series is attributed

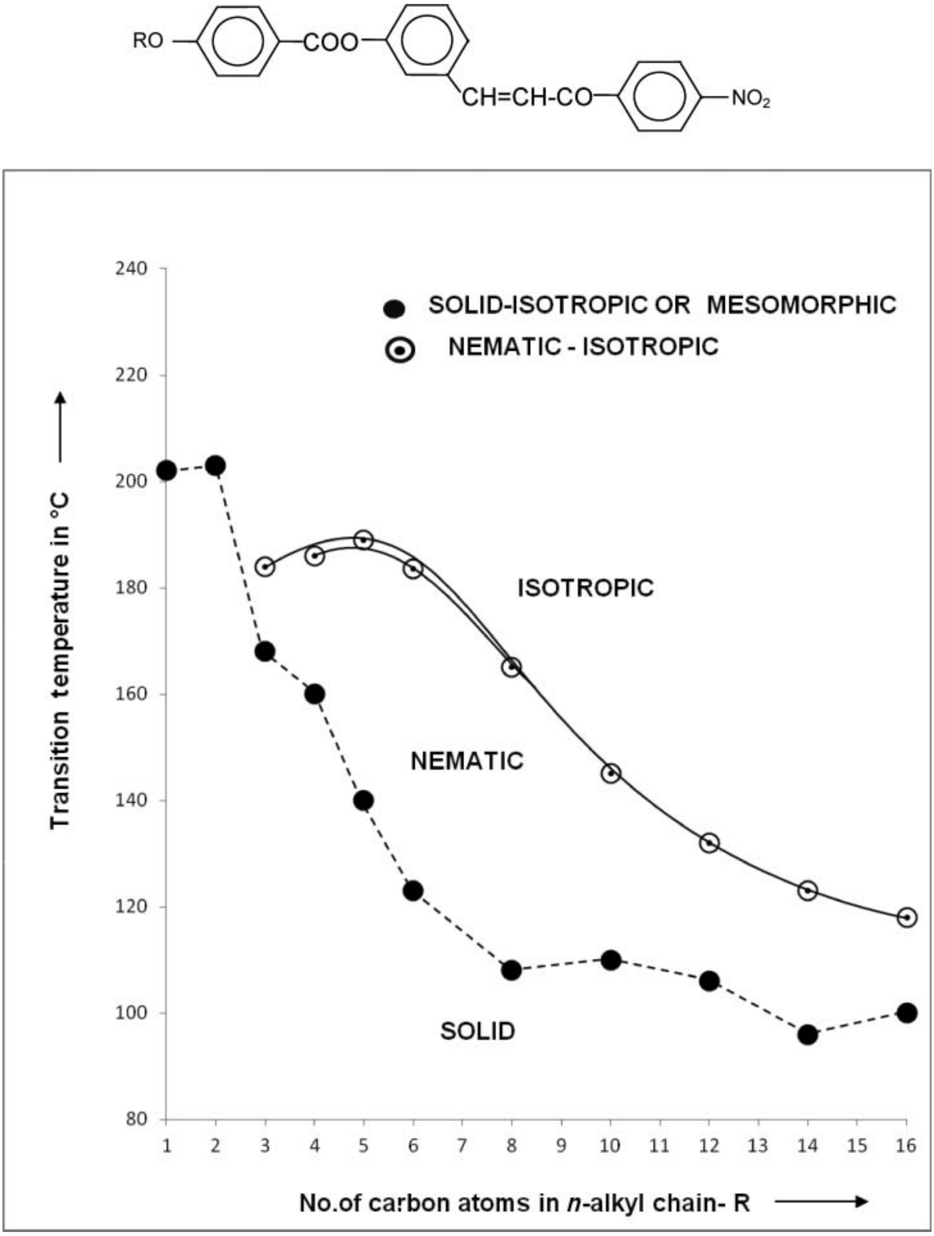


Figure 1. Phase behavior of series.

to the sequentially added methylene unit [4] at the *n*-alkyl chain of left *n*-alkoxy terminal chain. The maximum mesomorphic (nematic) phase temperature range is 60.5°C at the hexyl homologue and the minimum phase length is 18°C at the hexadecyl homologue. The smooth descending tendency of N-I transition curve is attributed to the gradual variation of molecular rigidity in combination with flexibility [1–3] caused by the progressively and sequentially added methylene unit. The odd–even effect disappears as series is ascended

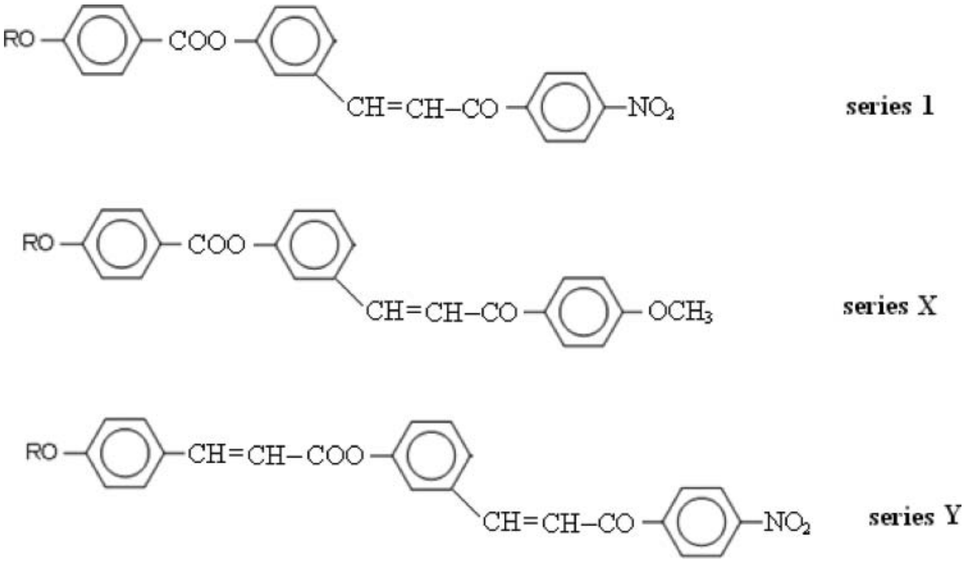


Figure 2. Structurally similar series.

from and beyond nonyl derivative because the longer *n*-alkyl chain may coil, bend, flex, or couple to lie with major axis of the core [4].

The present series is entirely nematogenic with middle-ordered melting type. The statement that "a homologous series with nitro group as substituent is nematogenic" is very well supported by the present investigation and it supports earlier research [4,8]. The liquid crystal properties of the novel homologous series 1 are compared with the structurally similar homologous series X [9] and Y [10] as shown below.

Figure 2 represents similar structures with minor changes of either at the terminal end group or a central bridge. Homologous series X and Y are selected for the comparative study of mesomorphic properties with the novel homologous series 1. Table 3 shows the relative thermal stability and commencement of the mesophase mentioned as below.

Homologous series 1, X, and Y consist of three phenyl rings and two central bridges −CH=CH−CO− as common and −COO− and −CH=CH−CO− as other central bridge that contribute to the overall molecular rigidity and *n*-alkoxy (−OR), $-NO_2$, and $-OCH_3$ end groups that contribute to the molecular flexibility without any laterally substituted

Table 3. Average relative thermal stability in °C

Series →	1	X	Y
Smectic-nematic or	—	129.25	—
Smectic-isotropic		(C_6–C_{12})	
Commencement of smectic phase		C_6	
Nematic-isotropic	158.25	163.5	175.7
Commencement of	(C_3–C_{16})	(C_5–C_{16})	(C_3–C_{14})
smectic phase	C_3	C_5	C_3

flexible group. All of the three series have their identical geometrical shape, but their molecular length and right-sided terminal end group and/or central group differs. The homologous series 1 and Y are identical in all respects, except with respect to their central bridge linking first and middle phenyl ring, that is, −COO− and −CH=CH−COO−, respectively. The homologous series 1 and X are identical in all respect except in respect of their right-sided terminal end groups $-NO_2$ and $-OCH_3$ bonded to the third phenyl ring. Thus, mesomorphic properties and degree of mesomorphism are differed due to their differing features as described above. The homologous series 1 and X differ with respect to the end groups $-NO_2$ and $-OCH_3$. The electronegativity of oxygen is greater than nitrogen, therefore the Ph-NO_2 and Ph-OCH_3 bond polarities are different. Moreover, the N−O bond polarity of $-NO_2$ and C−H bond polarity of $-OCH_3$ are also different. Thus, the vector sum of all bond polarities differs considerably for series 1 and X. Hence, molecular polarities of series 1 and X vary due to the variation in molecular flexibility [1–3], which causes variation in the N-I thermal stability 158.25°C and 163.5°C with the commencement of nematogenic mesophase formation from the third and fifth members of the series 1 and X, respectively. The difference of thermal stability by 5.25°C is attributed to the difference of molecular polarities and the molecular flexibility caused by $-NO_2$ and $-OCH_3$ terminal end groups of series 1 and X, respectively.

The difference in molecular polarities and molecular flexibility also reflects in the lamellar packing of molecules in crystal lattices of series X. Homologous series X is smectogenic with a thermal stability of 129.25°C and the smectic mesophase formation takes place from the C_6 to C_{12} derivatives. The absence of lamellar packing in crystal lattices of the molecules of series 1 precludes the formation of the smectic mesophase. The extent of noncoplanarity also contributes to the lamellar packing of molecules and hence to the smectogenic mesophase formation. In short, the molecular flexibility and the difference in arrangement in space of the $-NO_2$ and $-OCH_3$ causes a difference in noncoplanarity of the molecules of series 1 and X. On comparing the LC properties of series 1 and Y, the geometrical shape is identical, but they differ only through the central groups −COO− and −CH=CH−COO−. Thus, the molecules of series 1 and Y differ in molecular length, molecular rigidity, molecular length to breadth ratio, and hence these differences causes a difference in the magnitudes of anisotropic intermolecular forces of attractions. As discussed above, the molecular structure of the novel homologous series 1 and known series Y resemble each other except the central bridge, which is −COO− and −CH=CH−COO− in case of homologous series Y. Both these central bridges are comparable, though the vinyl carboxylate −CH=CH−COO− has a greater length and causes more noncoplanarity due to the twist obtained as the oxygen atoms of the vinyl carboxy group bump into the adjacent hydrogen atoms of the phenyl rings. On account of the enhanced length of the vinyl carboxy −CH=CH−COO− central bridge, increased conjugation by the −CH=CH− unit the rigidity of the molecule and lateral attractions increase, and hence the magnitudes of anisotropic intermolecular forces of attractions [4] increase. While in case of the −COO− central bridge, the relative length is shorter and it does not link the phenyl rings through at least one multiple bond or a hydrogen-bonded ring system. Consequently, although linearity is preserved, the mesophase thermal stability is lower. Hence, the molecules of series Y under comparison tend to pack efficiently with higher thermal stability of 175.7°C and that of series 1 tend to pack a little less efficiently with lower thermal stability 158.25°C. The commencement of the nematogenic mesophase takes place from third (C_3) member of series 1, which is very well matched to series Y under comparison. The variation in mesomorphic properties from homologue to homologue in the same series and for the same homologue from series to series is due to the sequentially added methylene ($-CH_2-$) unit in the *n*-alkyl chain of left *n*-alkoxy terminal chain, and due to right-sided terminal end group and the central group that remains the same throughout each series, respectively. Thus, the present investigation is consistent with previous research [4,8].

Conclusions

The conclusions drawn on the basis of present investigation are as follows.

1. The group efficiency order derived on the basis of thermal stability for nematic and smectic mesophase formation is as follows.
   (a) Nematic:
   $$\begin{array}{ccccc} -NO_2 & > & -OCH_3 & > & -NO_2 \\ \text{with} & & \text{with} & & \text{with} \\ -CH{=}CH-COO- & & -COO- & & -COO- \\ & & \text{central bridge} & & \text{central bridge} \end{array}$$
   (b) Smectic: $-OCH_3$ > $-NO_2$
2. Presence of $-NO_2$ group in a mesogenic compound preferably induces nematogenic character.
3. Molecular rigidity in combination with flexibility can induce mesophase formation irrespective of the anisotropic forces of attraction.
4. Resultant magnitudes of anisotropic intermolecular forces of attraction as a consequence of the overall molecular rigidity and flexibility is a direct result of favorable molecular shape, size, polarity of central, lateral, and terminal end group or groups as well as molecular polarizability.
5. The liquid crystalline properties and the degree of mesomorphism depend upon the molecular structure.
6. The novel series is entirely nematogenic with a middle-ordered melting type and considerable phase length.

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References

[1] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.
[2] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.
[3] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.
[4] (a) Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystal*, Academic Press: London and New York; (b) Gray, G. W., & Windsor, P. A. (1974). *Liquid Crystals and Plastic Crystal,* Vol. 1. Ellis, Horwood Ltd.: Chichester, Halsted Press, A Division of John Wiley and Sons. Inc.: New York, London. Chap. 4.
[5] (a) Dave, J. S., & Vora, R. A. (1970). *Liquid Crystals and Ordered Fluids*, Plenum Press: New York, p. 477; (b) Vogel, A. I. (1989), in *Text Book of Practical Organic Chemistry,* 4th & 5th edition; ELBS, and Longman group Ltd., Singapore.

[6] (a) Doshi, A. V., & Ganatra, K. J. (1999). *Proc. Ind. Acad. Sci. (Chem. Sci.)*, *4*(11), 562–568; (b) Suthar, D. M., & Doshi, A. V. (2012). *Der Pharma Chemica*, *4*(2), 777–782; (c) Suthar, D. M., & Doshi, A. V. (2012). *Der Pharma Chemica*, *4*(2), 813–818.

[7] (a) Chauhan, M. L., Pandya, R. N., & Doshi, A. V. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 228–234; (b) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 220–227; (c) Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 3–9; (d) Doshi, A. V., Odedara, D. A., & Patel, R. B. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 97–103; (e) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104–110.

[8] Prajapati, H. R., & Doshi, A. V. (2011). *Der Pharma Chemica*, *3*(2), 370–375.

[9] The manuscript of the paper submitted for publication Mole. Cryst. Liq. Cryst. Manuscript No. 183, entitled “Synthesis and Evaluation of mesogenic behavior based on Molecular Structure of a Novel series with $-CH{=}CH-CO-$ central bridge by Chaudhari R.P., Chauhan M.L. and Doshi A.V. paper accepted.

[10] Suthar, D. M., & Doshi, A. V. (2013). *Mol.Cryst. Liq. Cryst.*, *570*(1), 76–83.