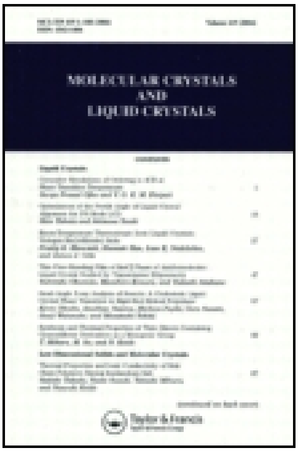

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Synthesis of Novel Mesomorphic Homologous Series: α-4-[-4′-n-Alkoxy cinnamoyloxy] Phenyl-β-3″ Nitrobenzoyl Ethylenes

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Synthesis of Novel Mesomorphic Homologous Series: α-4-[-4′-n-Alkoxy cinnamoyloxy] Phenyl-β-3″ Nitrobenzoyl Ethylenes

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Eleven novel mesomorphic homologues were synthesized and evaluated for their mesomorphic properties. The methoxy to n-butyloxy homologues are nonmesomorphic, while the other homologues are enantiotropic mesomorphic. The n-pentyloxy, n-hexyloxy, and n-octyloxy homologues are polymesomorphic, i.e., smectic and nematic mesophases are exhibited enantiotropically. Only the nematic mesophase is exhibited by the n-decyloxy to n-hexadecyloxy homologues. Analytical data confirm the structure and textures of molecules. The nematic mesophase shows a threaded-type texture, and that of smectic phase is of smectic A type. The mesomorphic properties are compared with a structurally similar homologous series. The average thermal stability for the smectic and nematic mesophases is 154.6°C and 163.8°C, respectively, as observed through optical polarizing microscope with heating stage.

Keywords Liquid crystal; mesogen; mesomorphic; nematic; smectic

Introduction

Various central groups linking two phenyl rings have been widely reported previously, except for the –CH=CH–CO– linking group [1–3]. Lohar and Doshi [1a] tried to exploit –CH=CH–CO– linking group between two phenyl rings, but did not succeed in generating liquid crystal mesophase formation, largely because of an unsuitable combination of molecular rigidity and flexibility [1–4].

However, Doshi continued attempts to exploit the –CH=CH–CO– linking group in combination with other groups linking three phenyl rings. Chauhan and Doshi [1b] and Patel and Doshi [1c] successfully observed mesophase formation in the molecules of a homologous series, which included the –CH=CH–CO– moiety as one of the central groups in combination with –COO– and –CH=CH–COO– central groups, respectively, bridging three phenyl rings. Thus, suitable magnitudes of molecular rigidity and flexibility have a direct relation with molecular structure to cause mesophase formation with appropriate selection of core, terminal, central linking groups, and/or lateral groups.

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Table 1. Elemental analysis for propyloxy, butyloxy, decyloxy, and dodecyloxy derivatives

	Element % found (% calculated)		
Molecular formula	C	H	N
$C_{27}H_{23}NO_6$	70.62 (70.89)	5.07 (5.03)	3.02 (3.06)
$C_{28}H_{25}NO_6$	73.35 (73.46)	5.33 (5.30)	2.92 (2.97)
$C_{34}H_{37}NO_6$	73.35 (73.51)	6.69 (6.66)	2.46 (2.52)
$C_{36}H_{41}NO_6$	73.98 (74.09)	7.11 (7.03)	2.36 (2.40)

The novel homologous series reported here consists of three phenyl rings bridged through –CH=CH–COO– and –CH=CH–CO– central groups with a left n-alkoxy terminal end group and a meta-substituted nitro group at the third phenyl ring to broaden the molecule. Hence, the effect of such molecular structure on mesophase formation can be correlated in terms of molecular polarity, polarizability, aromaticity, molecular width, or broadening, and the results are discussed and compared with a structurally similar homologous series.

Experimental

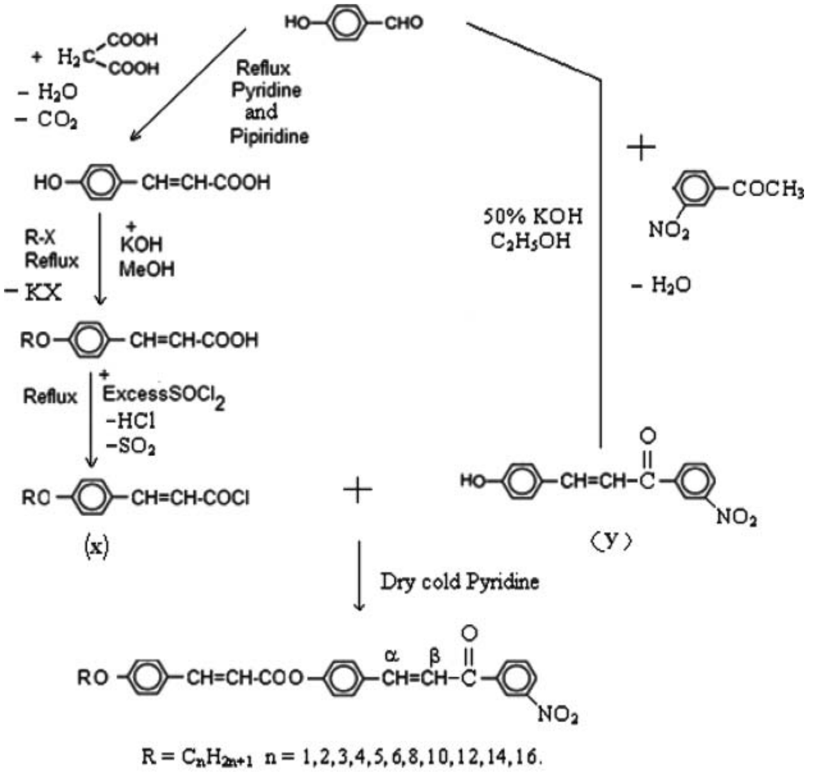
Characterization

Selected homologues of the novel series were characterized by infrared (IR) and ^{1}H NMR techniques. Nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ as solvent and IR spectra were recorded using the PerkinElmer GX spectrometer. Microanalysis was performed on the PerkinElmer PE 2400 CHN analyzer with results shown in Table 1. The mesogenic properties, transition, and melting temperatures were investigated by using optical polarizing microscopy. The textures of the smectic and nematic mesophases were determined by the miscibility method.

Synthesis

4-Hydroxycinnamic acid was synthesized by reacting 4-hydroxybenzaldehyde and malonic acid. The alkylation of the hydroxy group was performed using the suitable corresponding alkylating agent. 4-Hydroxybenzaldehyde, malonic acid, alkylating agents, MeOH, KOH, $SOCl_2$, EtOH, m-nitroacetophenone, etc., required for the synthesis were used as received (Scheme 1).

α-4-Hydroxy phenyl β-3′-nitrobenzoyl ethylene (y) was synthesized by the method of Patel and Doshi [1c]. 4-n-Alkoxycinnamic acids and corresponding acid chlorides were prepared by a modified method of Dave and Vora [5]. The 11 benzoylesters were synthesized by condensing equimolar proportions of 4-n-alkoxycinnamoyl chloride (x) and α-4-hydroxy phenyl β-3′-nitrobenzoyl ethylene [6,7] (y) in ice-cool dry pyridine. The products were crystallized from alcohol until constant transition temperatures were obtained.



α-4-[-4′-n-Alkoxy cinnamoyloxy] phenyl-β-3″-nitrobenzoyl ethylenes

Scheme 1. Synthetic route to the series.

Analytical Data

NMR in ppm for Octyloxy Derivative

0.886 (–CH_3 of alkoxy), 1.288 (–CH_2– of alkoxy), 1.806 (–OCH_2–CH_2), 4.019 (–OCH_2 of alkoxy), 6.943, and 8.035 (p-sub. phenyl ring) 7.259 (complex) (m-sub. phenyl ring). NMR supports the structure.

IR in cm^{-1} for Hexyloxy Derivative

650 and 760 (m-sub. phenyl ring), 840 (p-sub. phenyl ring), 950 trans (–CH=CH–), 1160 (C–O of alkoxy), 1350 and 1410 (–NO_2 group), and 1260, 1700 (–COO– group). IR supports the structure.

IR in cm^{-1} for Tetradecyloxy Derivative

650 and 770 (m-sub. phenyl ring), 850 (p-sub. phenyl ring), 1150 (C–O of alkoxy), 1250 and 1700 (–COO group), and 1420 and 1500 (–NO_2 group). IR supports the structure.

Table 2. Transition temperature of series in °C

	Transition temperatures in °C			
Compound No	R = $-C_nH_{2n+1}$ (n)	Sm	Nm	Isotropic
1	1	–	–	153.0
2	2	–	–	171.0
3	3	–	–	150.0
4	4	–	–	162.0
5	5	138.0	149.0	176.0
6	6	132.0	158.0	178.0
7	8	134.0	157.0	170.0
8	10	–	144.0	160.0
9	12	–	140.0	153.0
10	14	–	126.0	152.0
11	16	–	148.0	158.0

Note: Sm – smectic; Nm – nematic.

Texture

The pentyloxy homologue shows a threaded type texture and the hexyloxy homologue shows a smectic A type texture.

Results and Discussion

The reported novel homologous series consists of 11 members, which were evaluated for their mesomorphic characteristics. The transition temperatures of the series under discussion are recorded in Table 2. The pentyl to hexadecyl members of the series exhibit threaded or Schlieren textures on heating the solid crystalline or a smectic mesophase reversibly on heating and cooling to isotropic liquid, while the methyl to butyl homologues are nonmesomorphic. The pentyl, hexyl, and octyl members of the series show a smectic A texture on heating the crystalline solid reversibly.

Thus, the pentyl, hexyl, and octyl homologues are enantiotropically polymesomorphic with the exhibition of smectic and nematic mesophases, while the decyl, dodecyl, tetradecyl, and hexadecyl derivatives of the series are enatiotropically nematogenic only without exhibition of any smectogenic character even in the monotropic condition. Table 2 represents the dependence of transition temperatures on the number of carbon atoms in the terminal n-alkyl chain of molecules. The average thermal stability and other mesomorphic behavior of the titled homologous series 1 are compared with the structurally similar homologous series A as shown in Fig. 1.

The phase behavior of the homologues of the series under discussion is shown in Fig. 2. The solid mesomorphic or isotropic transition curve adopts a zigzag path of rising and falling tendency as the series is ascended. The plot of the phase diagram (Fig. 2) shows absence of odd–even effect in the nematic–isotropic and smectic–nematic transition curves. Smectic–nematic transition curve initially rises, passes through maxima, and then falls smoothly, and on extrapolation [8] it exactly merges and coincides into the solid–nematic transition temperature (144°C) of the decyl derivative indicating and proving disappearance

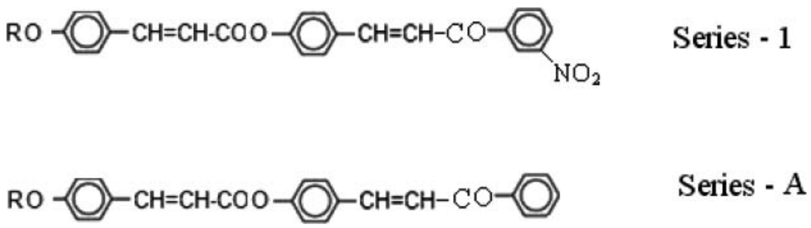


Figure 1. Structurally similar homologous series.

of smectogenic character of the present series from and beyond the decyl derivatives of the series.

The nematic–isotropic transition curve shows a descending tendency as the series is ascended except for the final derivative, which shows a negligible rise of 6°C. Thus, all three curves of the present series behave in a normal manner, i.e., the behavior of the

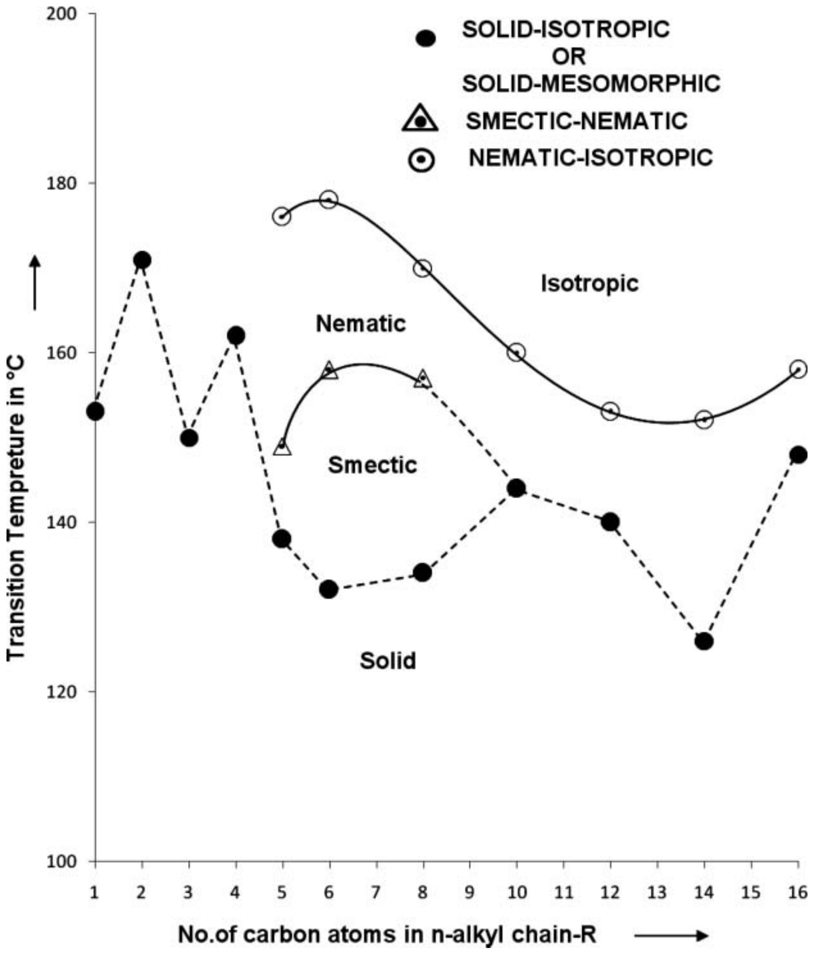


Figure 2. Phase behavior of series.

Table 3. Average thermal stability in (°C)

Series	(1)	(A)
Nematic–isotropic	163.8 (C_5–C_{16})	144.5 (C_6–C_{16})
Commencement of nematic phase	C_5	C_6
Smectic–isotropic	154.6 (C_5–C_8)	–
Commencement of smectic-phase	C_5	–

nematic–isotropic transition curve suggests that the enthalpy change value of the homologue gradually decreases from the pentyl to tetradecyl derivative and slightly increases in case of the hexadecyl derivative. Similarly, the behavior of the smectic–nematic transition curve suggests that the enthalpy change values corresponding to the pentyl, hexyl, and octyl homologues initially increase and then decrease to reach a minimum for emergence of the smectic mesophase. Hence, a low and high value of enthalpy corresponds to a low and a high amount of heat energy. On comparing the molecular geometry and other parameters affecting intermolecular attractions, series 1 and A differ in respect to the lateral substitution of the –NO_2 group (series 1). Therefore, series A is linear, while series 1 is nonlinear. The opposing effects [9,10] to the molecular geometry of the meta-substituted nitro group operates (1) in effect due to the widening of a molecule causing the reduction in the intermolecular adhesion by increasing the intermolecular distance, and on other hand (2) increased molecular width increases molecular polarizability causing an increase in the intermolecular adhesion. Thus, closeness of molecular packing depends upon the net resultant intermolecular forces of attractions, which depends upon the predominating effect out of two opposing effects (1) and (2). In the present study, the later effect is the predominating effect. Table 3 summarizes the average thermal stabilities and molecular structure of the present series and other structurally related series A [1c] chosen for the comparative study.

The molecular geometry of homologous series 1 and A under comparison consists of three phenyl rings linked through the –CH=CH–COO– and –CH=CH–CO– central linkages with the n-alkoxy left terminal group, and meta substituted –NO_2 and –H on the third phenyl ring for series 1 and A, respectively. The variation in mesomorphic characteristics can be attributed to the effect of the presence of the meta substituted –NO_2 and –H in the third phenyl ring, which causes a different magnitude of anisotropic forces of attractions as a consequence of their molecular rigidity and flexibility [2–4] related to molecular polarity and polarizability for the occurrence of mesophase formation [8,11]. On comparing the mesomorphic characteristics of series 1 with series A, it is observed that the homologues of both the series differing in respect of only a meta substituted nitro group of series 1.

The introduction of the –NO_2 group in place of –H causes a considerable and significant difference in the magnitude of the anisotropic forces [9,10] for the pentyloxy to hexadecyloxy homologues, which serve to stabilize a statistically parallel orientation, as the order of the molecules by end-to-end attractions is conducive to nematogenic mesophase formation. This effect persists even in the homologues with relatively longer n-alkoxy groups. Such nematogenic mesophase formation takes place in the case of a series A with a linear molecular geometry in which the –NO_2 group is replaced by a –H from the hexyloxy to hexadecyloxy homologues. The presence of the highly polar nitro group in the present series 1 promotes the formation of a smectic mesophase due to enhanced lateral attractions in addition to the end-to-end terminal attractions, which facilitates the lamellar packing required for occurrence of the smectic mesophase formation [5] for the pentyl, hexyl, and octyl homologues. Thus, series 1 exhibits smectogenic character in addition to nematogenic character, while smectogenic character is absent in case of series A.

The higher smectic and nematic thermal stabilities of series 1 when compared with series A are understandable because of the difference in the suitable magnitude of anisotropic forces of intermolecular attractions related to molecular polarity and polarizability from the –NO_2 and –H groups. The early commencement of smectic mesophase is attributed to suitable extent of noncoplanarity caused by the molecules of series 1, while it does not commence until the final hexadecyl derivative of series A. The variation observed in mesomorphic properties from homologue to homologue in the same series is due to sequential addition of a methylene unit. Likewise, the variation from series to series is attributed to the change from the –NO_2 group to the –H.

Conclusions

(1) The variation in molecular rigidity caused by the –CH=CH–CO– central group and/or the flexibility caused by the –NO_2 group confers variation in liquid crystal properties of a substance.
(2) The study suggests that the replacement of –H by highly polar –NO_2 group though favorable to induce the nematic mesophase can also induce smectogenic character in the presence of the –CH=CH–CO– central bridge of a molecule.
(3) The present novel series is predominantly nematogenic and partly smectogenic with a middle order melting behavior and a 10°C–46°C mesophase length.

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References

[1] (a) Doshi, A. V. (1987). Study of mesomorphism and explorationof characterstics. PhD Thesis, Saurashtra University, Rajkot; (b) Chauhan, M. L., & Doshi, A.V. J. (2007). *Indian Chem. Soc.*, *84*, 774; (c) Patel, R. B., & Doshi, A. V. (2011). *Der Pharma Chem.*, *3*, 147.
[2] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.
[3] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.
[4] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.
[5] (a) Dave, J. S., & Vora, R. A. (1970). *Liquid Crystals and Ordered Fluids*, Plenum Press: New York, p. 477; (b) A. I. Vogel (ed.). (1989). In: *Text Book of Practical Organic Chemistry,* 4th ed., Logman Group Ltd.: Singapore; (c) Doshi, A. V., & Ganatra, K. J. (1999). *Proc. Ind. Acad. Sci. (Chem. Sci.)*, *4*, 11, 562.
[6] Patel, V. R., & Doshi A. V. (2010). *Der Pharma Chem.*, *2*, 429.
[7] Chauhan, B. C., & Shah, R. R., & Doshi, A. V. (2011). *Der Pharma Chem.*, *3*, 110.
[8] 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, New York.

[10] Gray, G. W., & Windsor, P. A. (1974). *Liquid Crystal and Plastic Crystals*, vol. 1, Ellis Horwood Ltd.: Chichester, UK, Halsted Press: New York, London, Chap. 4.

[11] (a) 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.