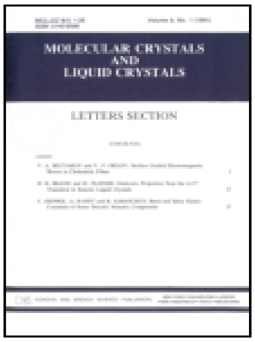

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The Mesomorphic Properties of Chalcone Dimer Derivatives

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A homologous series of symmetrical dimers viz bis (4-n-alkoxy benzoyloxy) α-phenyl β-benzoyl-ethylenes was synthesized and studied with a view to understanding the relation between molecular structure and the mesomorphic behavior. Twelve members of the dimeric series were synthesized, and the methoxy to butyloxy homologues are not liquid crystals, but the pentyloxy to hexadecyloxy are liquid crystals. The pentyl to heptyl dimers are only nematogenic, but the higher homologues show smectogenic mesomorphism prior to nematogenic mesophase formation. The phase diagram of phase transition curves behaves in a normal manner except for the smectic to nematic transition curve which behaves in an unexpected manner. The smectic and nematic thermal stabilities are 103°C and 131.7°C, respectively. The smectogenic and nematogenic phase lengths vary between 17.4°C to 28.3°C and 2.1°C to 29.9°C, respectively. The liquid crystal properties of presently investigated novel chalcone dimers are compared with known monomeric chalcones.

Keywords Liquid crystal; mesogen; mesophase; nematic; smectic

Introduction

Liquid crystalline materials of conventional and unconventional molecules have shown a great deal of scientific technological, pharmaceutical, and medicinal or biological potential in applications [1–5]. There are several potential applications of symmetrical and non-symmetrical LC dimers. Among the dimers, chalcone derivatives play a significant role in prevention of various degenerative diseases, and human ailments [6]. Chalcones and their derivatives contribute in their role as biogenetic precursors, anti-inflammatory [4], anticancer, and antioxidant agents [7], as well as for protective efficacy against radiation induced oxidative stress [8]. The simplest oligomer is known as a dimer in which two mesogenic units are bonded through a flexible spacer. The proposed present investigation is aimed to synthesize a symmetrical chalcones dimer derivatives with two 4-*n*-alkoxy benzoyloxy units bonded through α-4-hydroxy phenyl β-4′-hydroxy benzoyl ethylene. The flexible section of the dimers will consist of alkoxy terminal chains $C_nH_{2n+1}—O—$ (where, $n = 1–8, 10, 12, 14,$ and 16). Four phenyl rings bonded through two carboxy groups and one central chalconyl group act as the rigid core of a molecule without the attachment of any lateral groups. The present investigation will include the synthesis of chalconyl homologue

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dimer derivatives, characterization of some selected derivatives by elemental analysis, infra red [IR], ^{1}HNMR, mass spectroscopy, thermography by polarizing microscopy equipped with a heating stage, and the texture determination of mesophases by a miscibility method. Finally, the comparative study of the LC properties of the present series will be compared with other known series. Thus, present study is planned with a view to understanding and establishing the relation between molecular structure [9–11] and the mesogenic behavior of chalconic novel dimers on the basis of the molecular rigidity and flexibility [12–15]. Doshi et al. have reported number of conventional and unconventional chalconic (α, β ethylene derivatives) homologous series [16–20].

Experimental

Synthesis

4-*n*-Alkoxy benzoic acids were synthesized by alkylating, 4-hydroxy benzoic acid with a suitable alkylating agent by a modified method of Dave and Vora [21] and component-A, component-B, α-4-hydroxy phenyl β-4′- hydroxyl benzoyl ethylene (m.p. 202°C–203°C yield 80%) were prepared by the usual established method [22, 23] using 4-hydroxy benzaldehyde and 4-hydroxy acetophenon. Components A (2 moles) and B (one mole) were condensed in dry cold pyridine through the corresponding acid chlorides. [24, 25]. The final chalconic ester dimeric homologue derivatives were individually decomposed, filtered, washed, dried, and recrystallised until constant transition temperatures obtained.

4-Hydroxy benzoic acid, alkyl halides, MeOH, KOH, EtOH, 4-hydroxy benzaldehyde, 4-hydroxy aceetophenone, thionyl chloride, pyridine, etc. required for synthesis were used as received except solvents which were dried and purified prior to use. The synthetic route to the novel dimeric chalconic series is shown in Scheme 1.

Characterization

Some of members of a novel series were characterized by elemental analysis (Table 1), IR spectroscopy, ^{1}HNMR spectra, mass spectrometry, and textural identification. Elemental analysis was performed on EuroEA Elemental Analyzer. FTIR data were acquired with a Shimadzu FTIR-8400 spectrophotometer in the frequency range of 4000–400 cm^{-1} with samples embedded in KBr pellets. ^{1}HNMR spectra were recorded in DMSO-d_6 using a BRUKER Avance-III (400 MHz) spectrometer and mass spectra were recorded on Shimadzu GC-MS Model No.QP-2010 instrument. The phase transition temperatures and the type of textures were measured by a miscibility method on microscopic observations, the sample being prepared as a thin film sandwiched between a glass slide and a cover.

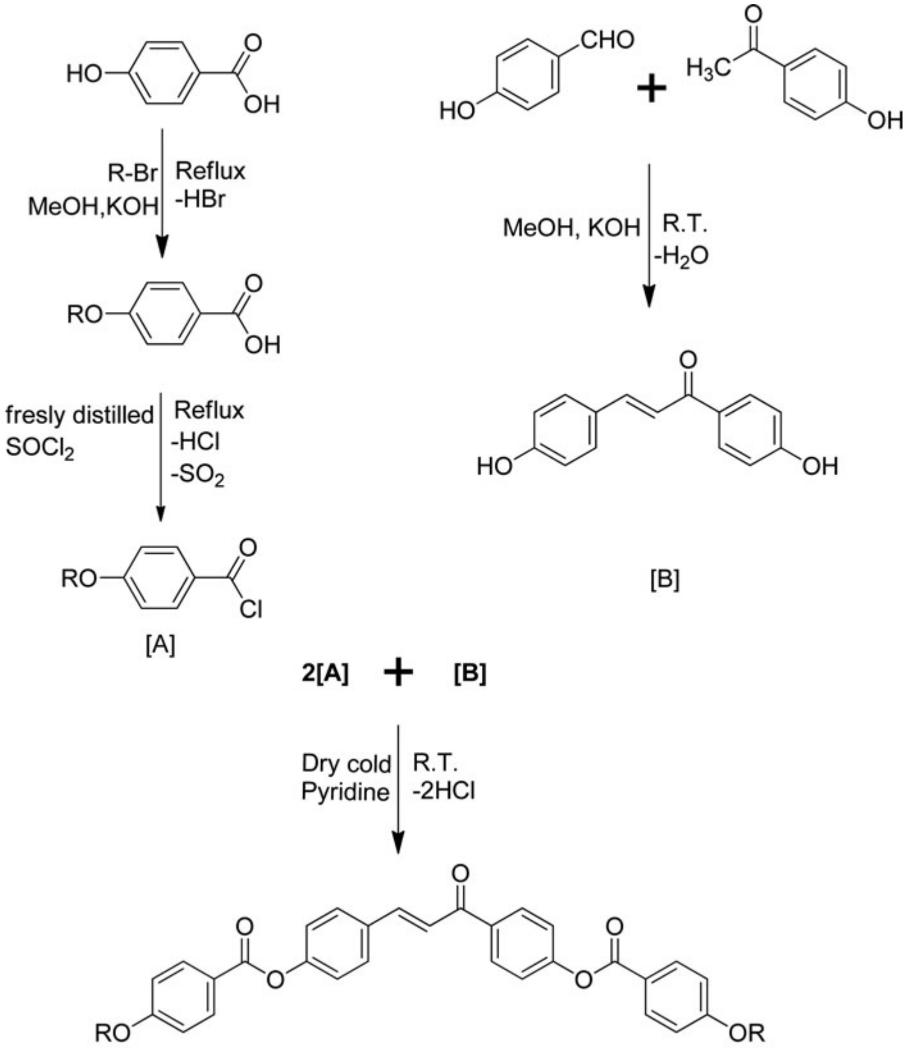
Analytical Data

Elemental Analysis

Spectral Data.

NMR in ppm for Hexyloxy Derivative

0.82–0.86 (t, 6H, CH_3, alkyl chain), 1.25–1.76 (m, 16H, $-(CH_2)_4-$, alkyl chain), 3.95–3.98 (t, 4H, $-CH_2-O$, alkoxy chain), 6.89–8.08 (m,16H, aromatic proton), 7.75, and 8.03



Bis(4-n-alkoxy benzoyloxy)α-phenyl β-benzoyl-ethylenes

Where, R= C_nH_{2n+1}, n=1 to 8, 10, 12, 14, 16

Scheme 1. Synthetic route of novel series.

(d, 2H, olelfinic proton(−CH=CH−)). The NMR data are consistent with the molecular structure.

NMR in ppm for Octyloxy Derivative

0.82–0.84 (t, 6H, CH_3, alkyl chain), 1.23–1.77 (m, 24H, $-(CH_2)_6-$, alkyl chain), 3.96–4.00 (t, 4H, $-CH_2-O$, alkoxy chain), 6.90–8.10 (m,16H, aromatic proton), 7.47, and 8.04 (d, 2H, olelfinic proton(−CH=CH−)). The NMR data are consistent with the molecular structure.

Table 1. Elemental analysis for (1) ethyloxy, (2) pentyloxy, and (3) tetradecyloxy derivatives

		Elements % found			Elements % calculated		
Sr. no.	Molecular formula	C	H	O	C	H	O
1	$C_{33}H_{28}O_7$	73.82	5.29	20.90	73.87	5.26	20.87
2	$C_{39}H_{40}O_7$	75.51	6.45	18.03	75.46	6.50	18.04
3	$C_{57}H_{76}O_7$	78.55	8.67	12.78	78.40	8.77	12.83

IR in cm^{-1} for Decyloxy Derivative

2929, 2843 (C—H Str. of polyethylene group), 1726 (C=O Str. of ester group), 1510, 1604 (C=C Str. of aromatic ring), 1417 (aliphatic C—H bond), 1068, 1261 (C—O Str. of ester group), and 42 (para substituted phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Dodecyloxy Derivative

2926 (C—H Str. of aromatic ring), 2856 (C—H Str. of polyethylene group), 1728 (C=O Str. of ester group), 1506, 1618 (C=C Str. of aromatic ring), 1464 (aliphatic C—H bond), 1022, 1166, 1288 (C—O Str. of ester group), and 848 (para-substituted phenyl ring). The IR data are consistent with the molecular structure.

Mass Spectra of Butyloxy Derivative

m/z (rel.int%): 592$(M)^+$

Mass Spectra of Heptyloxy Derivative

m/z (rel.int%): 676$(M)^+$

Texture Determination by Miscibility Method

- Pentyloxy homologue: Nematic Threaded type
- Heptyloxy homologue: Nematic Schlieren type
- Octyloxy homologue: Smectic-A
- Tetradecyloxy homologue: Smectic-C

Result and Discussion

The resently synthesized novel series Bis (4-*n*-alkoxy benzoyloxy) α-phenyl β-benzoylethylenes consists of 12 homologue dimer derivatives of chalcones in which variable *n*-alkyl chains bonded to first and last phenyl rings in para position through ether linkages as a flexible unit. Mesomorphism commences from the fifth dimer of a series. The pentyl, hexyl, and heptyl dimers are only nematogenic, whereas the octyl, decyl, dodecyl, tetradecyl, and hexadecyl homologue dimers possess smectogenic character prior to nematogenic character. The remaining homologues are nonmesogenic. The transition and melting temperatures were determined by an optical polarizing microscope equipped with a heating stage (Table 2). Transition temperatures of liquid crystal (LC) and nonliquid crystal (NLC) dimers were plotted against the number of carbon atoms present in *n*-alkyl chain bonded to phenyl rings through oxygen atom as terminal end groups. Transition curves, viz., Solid-isotropic/mesomorphic, smectic-nematic, and nematic-isotropic are drawn by linking like or related points to depict a phase diagram showing phase behavior of a novel

Table 2. Transition temperatures in °C of series-1

		Transition temperature in °C		
Compound no.	R=*n*-alkyl group C_nH_{2n+1}	Sm	*N*	Isotropic
1	1	—	—	170.5
2	2	—	—	161.2
3	3	—	—	145.2
4	4	—	—	149.9
5	5	—	136.4	162.5
6	6	—	113.8	143.7
7	7	—	160.6	185.6
8	8	80.5	102.1	121.8
9	10	71.3	96.6	108.5
10	12	74.5	91.9	102.4
11	14	86.0	108.3	111.5
12	16	73.4	116.1	118.2

Sm, Smectic; N, Nematic.

series (Fig. 1). Solid-isotropic/mesomorphic transition curve follows a zigzag path of rising and falling values with overall descending tendency as the series is ascended except for the tetradecyloxy and hexadecyloxy derivatives. The nematic-isotropic transition curve adopts a descending tendency as the series is ascended with the exhibition of an odd-even effect and behaves predominantly in normal established manner except for the tetradecyl

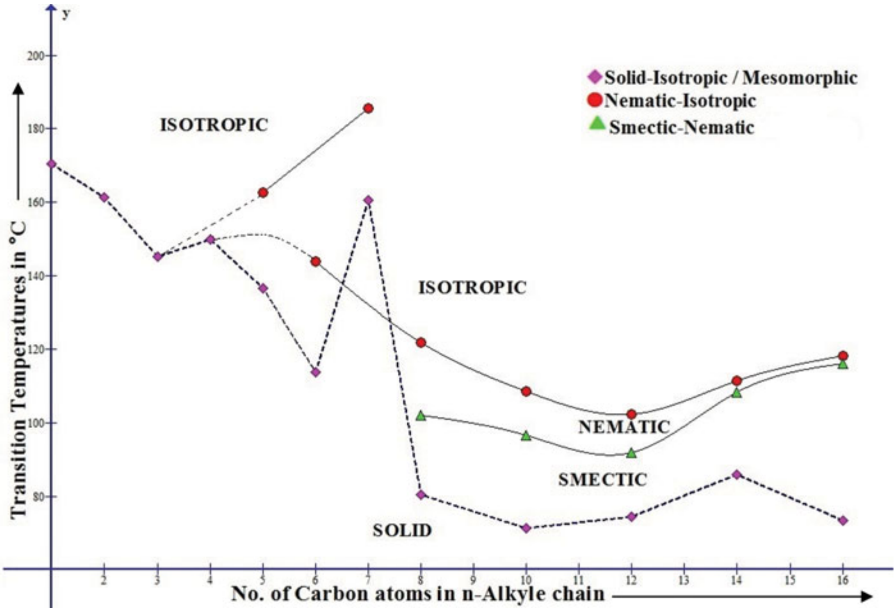


Figure 1. Phase behavior of series.

and hexadecyl derivatives. The smectic-nematic transition curve is descended from the octyloxy dimer to the lowest dodecyl derivative, passes through minima and ascends until the last hexadecyloxy homologue without exhibition of an odd-even effect. Analytical and spectral data confirmed the molecular structures of the novel dimers. The nematic-isotropic transition curve is extrapolated [26–28] for nonnematogenic behavior of the propyloxy and butyloxy homologues to predict their nematic-isotropic transition temperatures keeping in view of the trend of the concerned curves. The curves for odd and even members of the dimers merge into each other at the third homologue of the series after extrapolation. The total mesophase length (Sm + N or only N) vary between 25.3°C at the hexadecyloxy dimer. The average thermal stability for smectic and nematic phases are 103°C and 131.7°C, respectively. Thus the novel dimer series is predominantly nematogenic and partly smectogenic of a middle ordered melting type and relatively short degree of mesomorphism. The transition and melting temperatures generally alternate in a decreasing order. The variations in mesomorphic behavior from homologue to homologue are observed with the number of carbon atoms present in *n*-alkyl chains of left and right flexible terminal end groups. The two mesogenic units bonded to two phenyl rings connected by two carboxy group strengthens the molecular rigidity. The first to fourth members of the series do not have the suitable combination of anisotropic forces of intermolecular attractions as a consequence of combined effect of equivalent molecular rigidity required to induce mesomorphisam, not even in the monotropic condition. Thus, they have a strong crystal tendency and sharply melt to the isotropic liquid without passing through a liquid crystal phase. The rest of the novel dimers do have molecules with suitable magnitudes of intermolecular anisotropic forces of attractions which resist exposed thermal vibrations for some temperature difference during which they disalign at an angle less than 90° with the floating surface. The molecules of pentyl, hexyl, and heptyl dimers are floated with only statistically parallel orientational order. Whereas the octyl, decyl, dodecyl, tetradecyl, and hexadecyl dimers have a sliding layered ordered arrangement initially and then show a statistically parallel orientational ordered arrangement. The appearance of the nematogenic mesophase formation is attributed to the suitable magnitudes of end-to-end intermolecular attractions for definite temperature range; whereas appearance of smectogenic mesophase formation is attributed to the presence of lamellar packing of molecules in their crystal lattices causing sliding layered network arrangement with maintenance of some degree of temperature range against thermal treatment through polarizing microscopy. The mesophase disappears above the isotropic temperature of LC homologues. The molecules under the microscopic examination are randomly oriented in all possible direction with high order of disorder or high magnitudes of entropy ($\Delta S{=}\Delta H/T$), but on cooling the same (enantiotropic homologue) mesophase reappears at the same temperature at which the mesophase was formerly appeared, i.e., reversal of transition temperature reappears in case of enantiotropic dimer homologue. Changing trend of mesomorphic properties from homologue to homologue in the same dimer series is attributed to the sequential addition of methylene unit or units at the *n*-alkyl chain bonded to phenyl ring through ethereal linkage. The extrapolated nematic-isotropic transition curve [29, 30] for odd and even homologues merge into propyl and butyl dimers which matches to solid-isotropic point of propyl and butyl dimers, thus the nonmesomorphicity of propyl and butyl derivatives are very well supported by appropriate extrapolation method. The mismatching or deviating trend from normal behavior of smactic-nematic and nematic-isotropic transition curve is attributed to the presence of two mesogenic units with two identical flexible end group units which may contribute equitable or identical rigidity and flexibility from both ends of a single dimer molecule. The mesomorphic behavior of presently investigated novel homologous dimer series-1 is

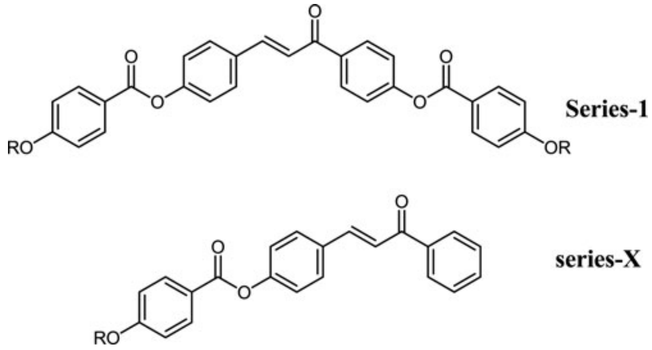


Figure 2. Structurally similar homologous series.

compared with other monomeric known identical series of chalcones-X [31] as shown in Fig. 2.

The presently investigated chalcone dimer series and a monomeric chalcones series chosen for comparative study are identical with respect to three phenyl rings bonded through one of the $-COO-$ and only one $-CH{=}CH-CO-$ central bridges linking first and second as well as second and third phenyl rings, respectively, including one of the left *n*-alkoxy terminal end group. However, they differ with respect to the presence and absence of a $-OOC-C_6H_4-OR$ mesogenic unit in series-1 and a series-X, respectively. Therefore, observed difference in mesogenic behavior between dimer series-1 and monomeric series-X are attributed to their differing features as presence and absence of one mesogenic unit as shown above. Differing mesogenic unit $-OOC-C_6H_4-OR$ contain $-COO-$ central group, one phenyl ring, and flexible unit $-OR$, i.e., $-C_nH_{2n+1}$. Thus, absence of mesogenic unit of series-X reduces molecular length, aromaticity, and ratio of the molecular polarity to polarizability, length to breath ratio, and many other factors conducive to these effects. One of these effects is suitable magnitudes of anisotropic forces of intermolecular end-to-end and lateral attractions as a consequence of resultant molecular rigidity and flexibility, which are main causes of inducing mesomorphism and extend or contract degree of mesomorphism, etc. Thus, following Table 3 indicates some difference of mesomorphic behaviors between series-1 and X depending upon their structural variations.

Table 3 indicates that both series [1andX] under comparative study,

- Do exhibit smectogenic and nematogenic characters.

Table 3. Average thermal stabilities in °C

Series ——→	[1]	[*X*]
Smectic-isotropic or	103.6	106.6
Smectic-nematic	[C_8-C_{16}]	[C_{10}-C_{16}]
	C_8	C_{10}
Commencement of smectic phase		
Nematic-isotropic	131.7	119.8
Commencement of nematic phase	[C_5-C_{16}]	[C_8-C_{16}]
	C_5	C_8

- Smectic thermal stability of dimer series-1 is lower than the series-X, chosen for comparison.
- Nematic thermal stability of dimer series-1 is higher than the series-X.
- Smectic and nematic mesophases of series-1 commences (C_8 and C_5) earlier than a series-X (C_{10} and C_8) under comparison.
- In general, mesomorphism commences from fifth member of dimer series-1, whereas it commences late from octyloxy chalcone derivative of series-X.

Early or late commencement of mesophase depends upon the suitable magnitudes of anisotropic force of intermolecular attractions as a consequence of a favorable molecular rigidity and flexibility as well as the extent of noncoplanarity caused by a molecule. The presences of one more mesogenic unit in a series of dimer derivatives facilitate lamellar packing of molecules in their crystal lattices favorably earlier. Moreover, presence of one more mesogenic unit, increases molecular length, polarity, polarizability, rigidity, flexibility, dispersion forces, end-to-end and lateral attractions depending upon molecular closeness which resist or withstand exposed thermal vibrations relatively of greater magnitudes than a molecule of series-X. Thus, nematic mesophase formation facilitated to stabilize more strongly, than in the molecule of series-X and hence, the nematic thermal stability of series-1 is greater than a series-X. The early commencement of smectic mesophase is attributed to the favorable intermolecular forces arising from additional mesogenic unit which build up lamellar packing of molecules in the crystal lattices of dimer series molecules earlier than the molecules of series-X.

Conclusions

- A dimer homologous series of chalcones is predominantly nematogenic and partly smectogenic with middle ordered melting type.
- As numbers of methylene units are increasing in *n*-alkyl chain of flexible units, the nematic character of a substance is gradually reduced by smectogenic character. i.e., lamellar packing of molecules in the crystal lattices depends upon the length of *n*-alkyl chain, of a terminal unit.
- The behavior of smectic-nematic or smectic-isotropic transition curve depdnded upon number of msogenic units of a dimer.
- As molecular rigidity or number of aromatic rings are increased in a molecule, the thermal stability for smectic decreases and the thermal stability for nematic increases.
- As aromaticity of a molecule increased, the commencements of smectic and nematic mesophase formation tend to pass from higher number of a homologue, i.e., early or late commencement of smectic and nematic mesophase is related to aromaticity of a molecule or with the length of n-alkyl chain of terminal end group or end groups of chalconic dimer molecule.
- The mesomorphic behaviors of chalconic dimer derivatives are susceptible and sensitive to number of mesogenic unit or units present in a molecule.
- Mesophase formation efficiency order derived for chalcones on the basis of (a) thermal stabilities (b) early commencement of mesophase, are as under (a) smectic: Two mesogenic units < one mesogenic unit.
- Nematic: One mesogenic unit < Two mesogenic units.
- (b) smectic: Two mesogenic units > one mesogenic unit.
- Nematic: Two mesogenic units > one mesogenic unit.

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