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Synthesis, Characterization and Mesophase Behavior of New Liquid Crystalline Compounds Having Chalcone as a Central Linkage

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Mesogens with a chalcone central linkage are rare. It is believed that the chalcone linkage is not conducive to mesomorphism. But when chalcone linkage is present with other central linkages like azomethine, ester or azo it becomes condusive to mesomorphism. In the present study two new homologous series viz. 1-(4'-butyloxybiphenyl-4-yl)-3-(4-alkoxyphenyl) prop-2-en-1-one (Series-I) and 4-[3-(4'-butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl] phenyl 4-alkoxybenzoate (Series-II) were synthesized having the chalcone as a central linkage. Series-I having only chalcone central linkage through it exhibit mesomrphism due to the presence of alkoxybiphenyl group at one end which is rich source to provide to increase linearity and rigidity of the molecule. Series-II which contains chalcone as well as ester as a central linkage and it also exhibit mesomorphism.

The compounds of the both series have been characterized by standard methods. Their liquid crystalline properties have been investigated by optical polarizing microscopy and DSC studies.

Keywords Biphenyl; chalcone; ester; mesomorphism; mesophase; nematic phase; smectic phase

Introduction

Mesogens with different central linkages are known [1]. However most of these central linkages have an even number of linking groups. The chalcone linkage has an odd number of atoms. Chalcones represent one of the most abundant and ubiquitous groups of natural products [2]. In the past few years, they have been shown to possess interesting biological properties including anti-invasive [3], anticancer [4], inhibitory activation [5], antimalarial [6], antimicrobial [7], antimutagenic [8], radioprotective [9], and anti-inflammatory effects [10] and synthetic intermediates in the presence of other compounds [11]. Recently, it has been noted that, among many organic compounds reported for their second harmonic generation, chalcone derivatives are known for their excellent blue light transmittance and good crystallizability [12–15]. It has also been documented that the chalcone possesses a remarkable

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nonlinear optical (NLO) property, which is an essential element for optical communications devices. The other importance of this compound is its high photosensitivity and thermal stability, which are used in developing various crystalline electro-optical devices [16–18] and also having fluorescent properties [19].

The chalconyl group is also known to be a good photosensitive group [20,21]. The photoreaction of chalconyl groups takes place by irradiation with relatively longer wavelength UV light than that of the cinnamoyl group. Photosensitive polymers containing chalcone derivatives have been studied for photoalignment film [22–25].

In view of the outstanding behavior of chalcone, a systematic study focusing on the synthesis and characterization of these compounds has been carried out in our present laboratory over the past few years [26–28]. A very recent investigation of the molecular structures and characteristics of a series of chalcone derivatives, with Schiff base and α -methyl Schiff base bridging group has been reported [29].

Biphenyl provides rich source of liquid crystals which are thermally more stable than those of benzene substituted analogues, which increase linearity and rigidity of the molecules. It plays an important role in the formation of liquid crystal having ferroelectric and anti- ferroelectric properties [30–37], which are widely used in display device and/or electro-optical devices nowadays. It is believed that the chalcone linkage is not conducive to mesomorphism, but when chalcone linkage is present with other central linkages like azomethine, ester or azo it becomes condusive to mesomorphism. In this article, we report another series of some newly analogues derived from 4-butoxy biphenyl as a terminal group and synthesized two homologues series viz., 1-(4'-butyloxybiphenyl-4-yl)-3-(4-alkoxyphenyl)prop-2-en-1-one (Series-I) and 4-[3-(4'-butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl]phenyl 4-alkoxybenzoate (Series-II) to study the effect of different structural modifications on mesomorphism. The synthetic procedure and thermal properties of these two series are described in detail.

Experimental

Reagents and Technique

For the synthesis of compounds of the homologous series, following materials were used. 4-Hydroxy benzoic acid, 4-hydroxybenzaldehyde Merck (Germany), alkyl bromide (Lancaster, England). 4-hydroxy biphenyl (National Chemical, India), Acetyl Chloride, Anhydrous AlCl₃ (Rankem, India). The solvents were used after purification using the standard methods described in the literature [38].

Elemental analyses (C, H, N) were performed at G.N.F.C.(Gujarat Narmda Valley Fertilizer Company Ltd., Bharuch). Infrared spectra were recorded with a THERMO SCIENTIFIC NICOLET ISO-10 spectrophotometer in the frequency range 4000–400 cm⁻¹ with samples embedded in KBr discs. ¹H-NMR spectra of the compound were recorded with JEOL-GSX-400 using CDCl₃ as a solvent and TMS as an internal reference, ¹³C NMR spectra of the compound were recorded with BRUKER AVANCE II 400 NMR Spectrometer and Mass spectra (EI) of the compounds at SAIF (Sofisticated Analytical Instrument Facilities), Chandigarh. Thin-layer chromatography analyses were performed by using aluminium-backed silica-gel plates (Merck 60 F524) and examined under short-wave UV light.

The phase-transition temperatures were measured using a METTLER TOLEDO DSC-1 at heating and cooling rates of 5°C min⁻¹, respectively. The optical microscopy studies were carried out with a "Leitz Loborlux 12" POL (Wetzler, Germany) polarizing microscope equipped with a Mettler FP52 hot stage. The textures of the compounds were observed using polarized light with crossed polarizers with sample in thin film sandwiched between a glass slide and coverslip.

Synthesis

Synthesis of 4-Alkoxy Benzaldehyde. 4-Alkoxy benzaldehydes were prepared by a reported method [39–42]. The m.p. of these compounds were compared with the reported one and they are almost similar to reported values.

Synthesis of 4-n-Alkoxy Benzoic Acid. 4-n-Alkoxy benzoic acid were prepared as reported by Dave and Vora method [43]. The m.p. of these compounds were compared with the reported one and they are almost similar to reported values.

Synthesis of 4-Butoxy Biphenyl. In a round-bottom flask, 4-hydroxy biphenyl (1 mmol) was dissolved in a dry acetone solution containing K_2CO_3 (1.5 mmol). The solution was heated to $40^{\circ}C$. 1-Bromobutane (1.02 mmol) was then added dropwise (1–2 hr) and the mixture thus obtained was heated for 10–12 hr before being cooled down to room temperature. The resulting solution was then poured into cruised ice and the precipitate thus formed was filtered off and dried. The precipitate was purified and recrystallized with acetone.

Synthesis of 1-(4'-Butoxybiphenyl-4-yl) Ethanone. Crystallised 4-butoxy-biphenyl (1 mmol.) was dissolved in dry, redistilled carbon disulphide, contained in a three-necked flask, equipped with stirrer, dropping-funnel, and condenser. The solution was cooled to 0-2°C and sieved, anhydrous aluminium chloride (1.12 mmol.) was added quickly, with stirring. Acetyl chloride (1 mmol.) was then added during 5-10 min, and the temperature raised gradually to 35°C. The mixture was kept at 35°C until the reaction seemed to be over, whereupon the whole was refluxed for 45 min. Ice-cold, concentrated hydrochloric acid was then added to the cooled mixture to decompose the yellow-green complex. The condenser was removed, and steam passed under the surface of the solution to remove the solvent and complete the decomposition of the complex. Stirring was continued as the mixture was cooled quickly, in order to obtain the brownish-pink solid in a finely divided state. The solid was separated, dried, and triturated twice by stirring for 15 min. with ether. The insoluble 4'-acetyl derivative was thus separated from the isomeric 3-ketone, which is soluble in ether. However, when the aluminium chloride was dried for several hours at 100-120°C and the amounts of acetyl chloride and aluminium chloride were increased to 1.1 and 1.17 mmol, respectively, the yields were 60–77% in three consecutive preparations [44].

Synthesis of 1-(4'-Butoxybiphenyl-4-yl)-3-(4-alkoxyphenyl)prop-2-en-1-one (Series-I). A mix of 1-(4'-butoxybiphenyl-4-yl) ethanone (1 mmol) and n-alkoxy benzaldehyde (1 mmol) were dissolved in the alcoholic sodium hydroxide solution (80 ml ethanol and 10% NaOH solution). The reaction mixture was heated at 80 °C for 7 hr. The mixture was left at room temperature overnight. An HCl aqueous solution was added to the mixture, and then yellow precipitate was obtained. The

precipitate was washed with water until a neutral aqueous solution was obtained. Then, the solid was washed with methanol and dried under vacuum at 60°C. The obtained yellow solid recrystallized from acetone. The product was purified by flash column chromatography using a mixture of hexane/ethyl acetate (7/1) as eluent [45,46].

Data

Compound I-12. Yield 75%. m.p.115°C. Found: C,82.05; H, 8.62; Calc. for $C_{37}H_{48}O_3$; C, 82.22; H, 8.88; %. EI-MS m/z (rel.int %): 540 (M)⁺ IR (KBr): $v_{\rm max}/{\rm cm}^{-1}$ 2855–2956 cm⁻¹ (C-H aliphatic), 1691 cm⁻¹ (C=O of chalcone), 1603 cm⁻¹ (C=C of vinyl gr. of chalcone), 1577 cm⁻¹ (C=C of aromatic), 1254 cm⁻¹ (C-O-C), 1070 cm⁻¹ (C-O), ¹H NMR (CDCl₃): δ 0.86–0.90 ppm (t, CH₃), 1.27–1.82 ppm (m, CH₂), 3.98–4.04 ppm (t, OCH₂), 6.94–7.55 ppm (m, Ar-H), 6.88 & 7.80 ppm (2H, d, olefinic proton). ¹³C NMR (CDCl₃): 14.15 ppm (CH₃), 22.71–31.92 ppm (CH₂), 67.78 ppm (OCH₂), 114.78–141.91 ppm (-CH=CH-, Chalcone), 126.61–133.55 ppm (Ar-C), 190.87 (-C=O, Chalcone).

Synthesis of 3-(4-Hydroxyphenyl)-1-(4'-butoxybiphenyl-4-yl)prop-2-en-1-one. A mix of 1-(4'-butoxybiphenyl-4-yl) ethanone (1 mmol) and 4-hydroxy benzaldehyde (1 mmol) were dissolved in the alcoholic sodium hydroxide solution (80 ml ethanol and 10% NaOH solution). The reaction mixture was heated at 80°C for 7 hr. The mixture was left at room temperature overnight. An HCl aqueous solution was added to the mixture, and then yellow precipitate was obtained. The precipitate was washed with water until a neutral aqueous solution was obtained. Then, the solid was washed with methanol and dried under vacuum at 60°C. The obtained yellow solid was purified by recrystallization from acetone [45,46].

Synthesis of 4-[3-(4'-Butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl] Phenyl 4-alkoxybenzoate (Series-II). To a mixture of 3-(4-hydroxyphenyl)-1-(4'-butoxybiphenyl-4-yl)prop-2-en-1-one (1 mmol) and 4-n-alkoxy benzoic acid (1 mmol) in 150 ml of distilled dichloromethane, 0.1 mmol of dimethyl aminopyridine (DMAP) was added under an argon atmosphere. The mixture was cooled in an ice-water bath, and after 10 min, 1 mmol of dicyclohexylcarbodiimide (DCC) was added under an argon atmosphere. The mixture was stirred overnight at room temperature, the salts were filtered off, and the solvent was evaporated. The crude product was purified by flash column chromatography using a mixture of hexanes/ethyl acetate (7/1) as eluent [47,48].

Data

Compound II-12. Yield 82%. m.p.70°C. Found: C,79.86; H, 7.80; Calc.for $C_{44}H_{52}O_5$; C, 80.00; H, 7.88; %. EI-MS m/z (rel.int %): 660 (M + 2)⁺ IR (KBr): v_{max}/cm^{-1} 2850–2956 cm⁻¹ (C-H aliphatic), 1726 cm⁻¹ (C=O of ester), 1690 cm⁻¹ (C=O of chalcone), 1606 cm⁻¹ (C=C of vinyl gr. of chalcone), 1585 cm⁻¹ (C=C of aromatic), 1256 cm⁻¹(C-O-C), 1070 cm⁻¹ (C-O), ¹H NMR (CDCl₃): δ 0.86–0.90 ppm (t, CH₃), 1.27–1.82 ppm (m, CH₂), 3.98–4.04 ppm (t, OCH₂), 6.94–7.55 ppm (m, Ar-H), 8.02 & 8.14 ppm (2H, d, olefinic proton). ¹³C NMR (CDCl₃): 14.15 ppm (CH₃), 22.71–33.75 ppm (CH₂), 68.28 ppm (OCH₂), 114.77–141.91 ppm (-CH=CH-,

Chalcone), 114.61–133.54 ppm (Ar-C), 163.53 ppm (C=O ester), 170 (-C=O, Chalcone).

Synthesis (Reaction Scheme)

Series-I

Synthesis of 4-n-Alkoxy Benzaldehyde.

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

Synthesis of 4-Butoxy Biphenyl.

HO
$$\leftarrow$$

$$\begin{array}{c} C_4 H_9 Br \\ \hline K_2 CO_3 \ Dry \ Acetone \\ \hline Reflux \ 10-12 \ hrs \end{array} \qquad H_9 C_4 O \longrightarrow \begin{array}{c} \\ \hline 4-butoxybiphenyl \end{array}$$

Synthesis of 1-(4'-Butoxybiphenyl-4-yl) Ethanone.

Synthesis of 1-(4'-Butoxybiphenyl-4-yl)-3-(4-alkoxyphenyl)prop-2-en-1-one.

Where $R=C_nH_{2n+1}$, n=1 to 8,10,12,14,16 1-(4'-butoxybiphenyl-4-yl)-3-(4-alkoxyphenyl)prop-2-en-1-one

Series-II

Synthesis of 4-n-Alkoxy Benzoicacid.

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

Synthesis of 4-Butoxy Biphenyl.

$$\begin{array}{c|c} & & & \\ \hline & &$$

Synthesis of 1-(4'-Butoxybiphenyl-4-yl) Ethanone.

Synthesis of 3-(4-Hydroxyphenyl)-1-(4'-Butoxybiphenyl-4-yl)prop-2-en-1-one.

3-(4-hydroxyphenyl)-1-(4'-butoxybiphenyl-4-yl)prop-2-en-1-one

Synthesis of 4-[3-(4'-butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl] phenyl 4-alkoxybenzoate.

DCC, DMAP Dry
$$CH_2CI_2$$
 Stirrer R.T. 24hrs
$$H_9C_4O \longrightarrow CH \longrightarrow CH \longrightarrow CH \longrightarrow CH \longrightarrow CH$$

4-[3-(4'-butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl]phenyl 4-alkoxybenzoate

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

Results and Discussion

In order to investigate the influence of the terminal group and central linkages on mesomorphic and thermal stability, 12 homologous from each of the two series 1-(4'-butoxybiphenyl-4-yl)-3-(4-alkoxyphenyl)prop-2-en-1-one (Series-I) and 4-[3-(4'-butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl]phenyl-4-alkoxybenzoate (Series-II) have been synthesized. The mesomorphic properties of all the synthesized compounds have been characterized by differential scanning calorimetry (DSC) and polarizing optical microscope (PMO) attached with Mettler hot stage.

The transition temperatures of both series are given in Tables 1 and 2. In Series-I compounds I_1 – I_6 gives sharp melting point and directly convert to isotropic liquid i.e., the compounds are non-mesogenic, while I_7 & I_8 exhibit enantiotropic nematic mesophase. Compounds I_{10} & I_{12} exhibit smectic as well as nematic mesophase, while compounds I_{14} & I_{16} exhibit only smectic mesophase (SmC). In second homologous Series-II all the compounds are mesogenic in nature. Compounds II_1 - II_7 exhibit enantiotropic nematic mesophase, compounds II_8 , II_{10} & II_{12} exhibit enantiotropic smectic as well as nematic mesophase, while compounds II_{14} and II_{16} exhibit only SmC mesophase. It is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus [49], Gray and Goodby [50].

DSC is a valuable method for the detection of phase transition. It yields quantitative results; therefore we may draw conclusions concerning the nature of the phases that occur during the transition. In the present study, enthalpies of two derivatives of Series-I and Series-II were measured by DSC. DSC data of Series-I and Series-II are recorded in Table 3 which helps the further confirms the mesophase type. Table 3 shows the phase transition temperatures, associated enthalpy (Δ H) and molar entropy (Δ S) for compounds of Series-I ($I_{12} \& I_{16}$) and Series-II ($I_{13} \& I_{16}$) and Series-II ($I_{14} \&$

Table 1. Transition temperature of Series-I

Compounds	R=n alkoxy	Transition temperature°C						
		Cr		SmC		N		I
$\overline{I_1}$	Methyl	•	160	_	_	_	_	•
I_2	Ethyl	•	148	_	_	_	_	•
$\overline{I_3}$	Propyl	•	153	_	_	_	_	•
I_4	Butyl	•	140	_	_	_	_	•
I_5	Pentyl	•	132	_	_	_	_	•
I_6	Hexyl	•	137	_	_	_	_	•
I_7	Heptyl	•	112	_	_	•	134	•
I_8	Octyl	•	106	_	_	•	130	•
I_{10}	Decyl	•	51	•	89	•	123	•
I ₁₂	Dodecyl	•	48	•	66	•	115	•
I_{14}	Tetradecyl	•	62	•	96	_	_	•
I ₁₆	Hexadecyl	•	57	•	73	_	_	•

II₁₆). Enthalpy values of the various transitions agree well with the existing related literature values [51]. The DSC curves of representative compounds are shown in Figures 1–4. Microscopic transition temperature values are almost similar to DSC data.

Table 3 shows the comparison of S-N and N-I transition temperature of the compound I-12 of Series-I and structurally related compound II-12 of the Series-II. The SmC mesophase range of the compound I-12 is lower by 7°C when compared with compound II-12 of the Series-II. The N-I transition temperature of the compound I-12 of Series-I is higher by 45°C when compared with compound II-12 of the Series-II.

Table 2. Transition temperature of Series-II

Compounds	R=n alkoxy	Transition temperature°C						
		Cr		SmC		N		I
$\overline{II_1}$	Methyl	•	102	_	_	•	120	•
II_2	Ethyl	•	95	_	_	•	114	•
II_3	Propyl	•	98	_	_	•	111	•
II_4	Butyl	•	89	_	_	•	104	•
II_5	Pentyl	•	82	_	_	•	98	•
II_6	Hexyl	•	79	_	_	•	93	•
II_7	Heptyl	•	77	_	_	•	89	•
II_8	Octyl	•	61	•	73	•	85	•
II_{10}	Decyl	•	46	•	70	•	78	•
II_{12}	Dodecyl	•	41	•	66	•	70	•
II_{14}	Tetradecyl	•	50	•	67	_	_	•
II ₁₆	Hexadecyl	•	58	•	64	_	_	•

			•		
Series	Compound	Transition	Peak Temp. (Microscopic temp.)°C	ΔH Jg^{-1}	$\frac{\Delta S}{Jg^{-1}K^{-1}}$
I	I ₁₂	Cr-Sm	47.24 (48)	19.33	0.4027
		Sm-N	65.73 (66)	13.29	0.2013
		N-I	114.29 (115)	19.57	0.1701
	I_{16}	Cr-Sm	56.72 (57)	52.78	0.9259
		Sm-I	72.47 (73)	6.44	0.0882
II	II_{12}	Cr-Sm	40.80 (41)	1.19	0.0290
		Sm-N	66.04 (66)	52.99	0.8028
		N-I	69.36 (70)	13.98	0.1997
	II_{16}	Cr-Sm	57.56 (58)	21.39	0.3688
		Sm-I	63.70 (64)	38.51	0.6017

Table 3. DSC data for Series-I and II compounds

In Series-I first six compounds do not exhibit mesomorphism. They give sharp melting points. This is because of lower alkoxy chain which does not increase polarity and polarizability of the molecules. As the carbon chain increase, the linearity and polarizability of the molecules increase which increase end to end cohesive force and molecule becomes lamellar showing nematic mesophase. In Series-I smectic mesophase (SmC) appears from higher homologues I₁₀, I₁₂, I₁₄ & I₁₆ while in Series-II smectic (SmC) mesophase appears from II₈, II₁₀, II₁₂, II₁₄ & II₁₆. This is because the long chains become attracted and interwined, which facilitates the lamellar packing required for smectic phase generation. As a result, the smectic tendency increase and eventually eliminates the nematic phase.

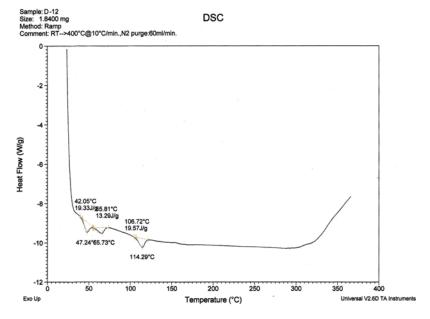


Figure 1. DSC Curve of the compound I₁₂ of Series-I. (Figure appears in color online.)

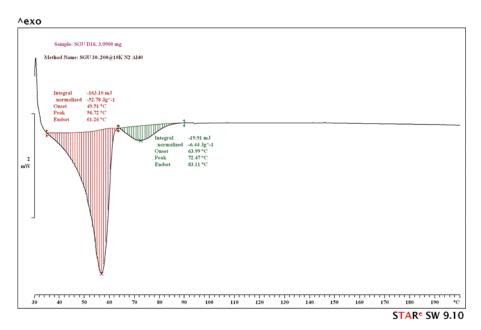


Figure 2. DSC Curve of the compound I₁₆ of Series-I. (Figure appears in color online.)

In these both series S-I transition usually begins at about the tetradecyloxy and hexadecyloxy derivatives together with the N-I transition temperatures for the lower homologous constitute one smoothly falling mesorphic – isotropic transition temperatures. From the plot of transition temperatures against the number of carbon

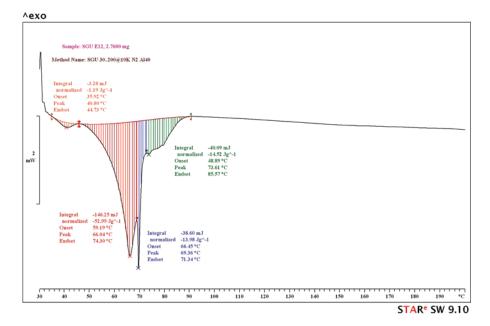


Figure 3. DSC Curve of the compound II₁₂ of Series-II. (Figure appears in color online.)

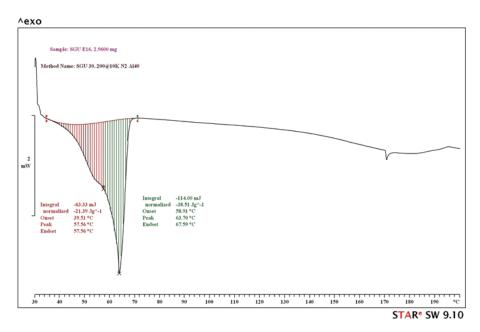


Figure 4. DSC Curve of the compound II₁₆ of Series-II. (Figure appears in color online.)

atoms (Figs. 5 and 6), it can be noticed that a smooth falling tendency for mesophase to isotropic has been observed throughout both the series. Both the series also exhibit falling tendency of SmC-N transition temperature for higher homologues. This is in agreement with the observation reported for such homologous series [1].

Series-I consist chalcone as a cetral linkage. Mesogens with different central linkages are known. However most of these central linkages have an even number of linking groups. The chalcone linkage has an odd number of atoms. Moreover, very few low molecular mesogens with the chalcone linkage are known. Chalcone-(-CH=CH-CO-) linkage is less conducive to mesomorphism compared to -CH=N-,-COO- linkages due to the non-linearity and angle strain arising from the keto group[19]. Nguyen *et al.* [52] have reported that a ketonic group linking two phenyl rings (benzophonene derivatives) is non-conducive to mesomorphism due to the angular shape of such molecules resulting from the angle of keto group.

Series-I having biphenyl as a central core which is highly polar than benzene analogues. In general, the molecules of a liquid crystalline compounds possessing middle and terminal polar groups. Molecules which form liquid crystal have dipole in their structure often a strong dipole towards the centre and weak dipole towards

Table 4. Different transition temperatures and range of mesophases observed in Series I and II

Series	Compound	SmC	N	I	SmC mesophase range (°C)	Nematic mesophase range (°C)
I	$\begin{matrix} I_{12} \\ II_{12} \end{matrix}$	48	66	115	18	49
II		41	66	70	25	04

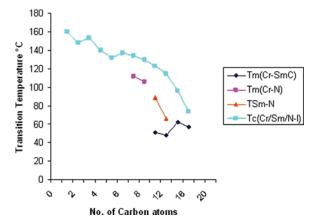


Figure 5. Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for Series-I. (Figure appears in color online.)

the end of the molecules. When more than two benzene rings are linked through more than one central group, the liquid crystalline properties enhance the most. However, linearity and rigidity are increased by linking up the benzene rings directly and thus biphenyl provides a rich source of liquid crystals which are thermally more stable than those benzene substituted analogues. It is observed that the biphenyl ring plays an important role in the formation of liquid crystals which increase the stability and phase length of the mesophase. This is the fact that through Series-I having only chalcone as a central linkage it is conducive to mesomophism due to terminal butoxy biphenyl ring.

In both the series there is a common features are both having biphenyl core and one of the chalcone linkage. In Series-I only higher homologues from heptyloxy derivatives shows liquid crystalline properties while in Series-II all the compounds are mesogenic in nature. This is because in Series-II there are additional ester group and benzene ring, which increase over all polarisability of the molecule, enhance

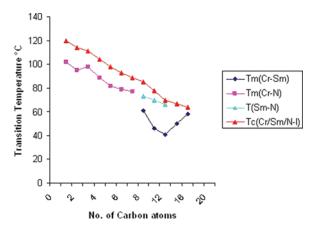


Figure 6. Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for Series-II. (Figure appears in color online.)

the liquid crystalline properties are most. There is decreases in thermal stabilities of liquid crystal phases in Series—II compounds, may be attributed to have it having additional ester linkage and alkoxy benzene ring as terminal substitution. An increase in the breadth forces the long axes of the molecules apart, as a result of which the interactions are decreased and consequently the liquid crystal temperatures are lowered. A change in the degree of conjugation due to chalcone linkage will alter both polarisability than ester group. The effect of the change in resultant moments is subtle, however, consequentially; the decrease in the polarisability will cause a decrease in the thermal stability of liquid crystal phase in Series -II. Variation of central ester linkage and benzene ring in Series-II made it possible to observe the effects of structural changes on mesomorphic system which had not studied previously.

Conclusion

In this article we have presented the synthesis and characterization of mesogenic two homologous series viz. 1-(4'-butoxybiphenyl-4-yl)-3-(4-alkoxyphenyl)prop-2-en-1-one (Series-I) which containing only chalcone as a central linkage and 4-[3-(4'-butoxybiphenyl-4-yl)-3-oxoprop-1-en-1-yl]phenyl-4-alkoxybenzoate (Series-II) which containing chalcone as well as ester linkage and additional benzene ring. In Series-I the lower member up to hexyloxy derivatives do not exhibit mesomorphism because their polarity and polarizability of the molecules do not increase. Series-I consist chalcone as a central linkage which is less conducive to mesomorphism though the higher member of this series exhibit mesomorphism. This is because of the butoxy biphenyl ring which is increase linearity and polarizability of the molecule which make it possible to conducive to mesomorphism. In Series-II it consist chalcone as well as ester linkage and another benzene ring which make it more conducive to mesomorphism. Hence, in Series-II all the compounds show mesomrphism. The study of these both two homologues series have brought out the fact that -CH=CH-CO- linkage is less conducive to mesomorphism compared to -CH=N-, -COO- linkages due to the non-linearity and angle strain arising from the keto group through it exhibit mesomorphism when it attached with polar group like butoxy biphenyl. The study has provided for the first time, mesogenic compounds with only chalcone linkage. The present study completes our objective of analyzing and establishing the effect of different structural modifications on mesomorphism.

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References

- [1] Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystals*, Academic press: London and New York.
- [2] Tomazela, D. M., Pupo, M. T., Passador, E. A. P., da Silva, M. F. D. G. F., Vieira, P. C., Fernandes, J. B., Rodrigues, F. E., Oliva, G., & Pirani, J. R. (2000). *Photochemistry*, 55, 643.

- [3] Mukherjee, S., Kumar, V., Prasad, A. K., Raj, H. G., Bracke, M. E., Olsen, C. E., Jain, S. C., & Parmar, V. S. (2001). *Bioorg. Med. Chem*, 9, 337.
- [4] Lawrence, N. J., McGown, A. T., Ducki, S., & Hadfield, J. A. (2000). Anti-Cancer Drug Des., 15, 135.
- [5] Bois, F., Boumendjel, A., Mariotte, A. M., Conseil, G., & Di Petro, A. (1999). Bioorg. Med. Chem, 7, 2691.
- [6] Ran, V. J., Saxena, A. S., Srivastava, S., & Chandra, S. (2000). Bioorg. Med. Chem. Lett., 10, 2159.
- [7] Kidwai, M., Sapra, P., Misra, P., Saxena, R. K., & Sing, M. (2001). Bioorg. Med. Chem., 9, 217.
- [8] Edenharder, R., Ranscher, R., & Platt, K. L. (1997). Mutat. Res., 379, 21.
- [9] Blickenstaff, R. T., Hanson, W. R., Reddy, S., & Witt, R. (1995). Bioorg. Med. Chem., 3, 917
- [10] Hsieh, H. K., Tsao, L. T., Wang, J. P., & Lin, C. N. (2000). J. Pharm. Pharmacol, 52, 163.
- [11] Choudary, B. M., Lakshmi, K. M., Venkat, R. C. R., Koteswara, R. K., & Figueras, F. (1999). J. Mol. Catal. A, 146, 279.
- [12] Fichou, D., Watanabe, T., Takeda, T., Miyata, S., Goto, Y., & Nakayama, M. (1988). Jpn. J. App. Phy., 27, L429.
- [13] Uchida, T., Kozawa, K., Sakai, T., Aoki, M., Yoguchi, H., Abdureyim, A., & Watanabe, Y. (1998). Mol. Cryst. Lig. Cryst., 315, 135.
- [14] Goto, Y., Hayashi, A., Kimura, Y., & Nakayama, M. (1991). J. Crystal Growth, 108, 688.
- [15] Zhao, B., Lu, W.-Q., Zhou, Z.-H., & Wu, Y. (2000). J. Mater. Chem., 10, 1513.
- [16] Williams, D. (Ed.) (1983). Nonlinear Optical Properties of Organic and Polymeric Materials, American Chemical Society: Washington, DC.
- [17] Chemla, D. S., & Zyss, J. (1987). Nonlinear Optical Properties of Organic molecular Crystals, Academic Press: London, Vols. 1 and 2.
- [18] Fichou, D., Watanabe, T., Tanaka, T., Miyata, S., Goto, G., & Nakayama, M. (1988). Japan J. Appl. Phys., 27, L 429.
- [19] Chudgar, N. K., & Shah, S. N. (1989). Liq. Cryst., 4(6), 661-668.
- [20] Panda, S. P. (1974). J. Appl. Polym. Sci., 18, 2317-2326.
- [21] Zair, S. A. (1979). J. Appl. Polym. Sci., 23, 1355-1372.
- [22] Makita, Y., Ogawa, T., Kimura, S., Ankara, M., Kimura, S., Matsuki, Y., & Takeuchi, Y. (1997). IDW '97, FMC3-3, 363-366.
- [23] Makita, Y., Natsui, T., Kimura, S., Nakata, S., Kimura, M., Matsuki, Y., & Takeuchi, Y. (1998). J. Photopolym. Sci. Technol., 11(2), 187–192.
- [24] Makita, Y., Natsui, T., Kimura, S., Nakata, M., Kimura, S., Matsuki, Y., & Takeuchi, Y. (1998). SID 98 Digest, LP-H, 750-753.
- [25] Nakata, S., Kuriyama, K., Kimura, M., Natsui, T., Makita, Y., Matsuki, Y., Bessho, N., & Takeuchi, Y. (1999). SID 98 Digest, LP-3, 512-515.
- [26] Thaker, B. T., Patel, D. M., Tandel, P. K., Jesani, M. S., Vyas, C. J., & Vansadia, A. D. (2005). Phase Transitions, 78(6), 521–527.
- [27] Thaker, B. T., Patel, P. H., & Vansadiya, A. D. (2007). Mol. Cryst. Liq. Cryst., 479, 95/[1133]–110/[1148].
- [28] Thaker, B. T., Patel, D. M., & Kanojiya, J. B. (2009). Mol. Cryst. Liq. Cryst., 509, 145/[887]–164/[906].
- [29] Thaker, B. T., Patel, P. H., Vansadiya, A. D., & Kanojiya, J. B. (2009). Mol. Cryst. Liq. Cryst., 515, 135–147.
- [30] Jeon, Y. J., Lee, J. C., & Shivkumar, B. (1999). Liq. Cryst., 26(8), 1129-1133.
- [31] Gallot, B., & Main, C. G. (2002). Lig. Cryst., 29(1), 141-153.
- [32] Kumar, P. A., & Pisipati, V. G. K. M. (2001). Mol. Cryst. Liq. Cryst., 365, 147.
- [33] Kaspar, M., Sierenyak, H., Glogarova, M., Pakhomov, S. A., Vanek, P., & Trunda, B. (1995). Liq. Cryst., 29, 775.

- [34] Barmatov, E. B., Borbovesky, A. Y., Barmatova, M. V., & Shibaev, V. P. (1999). Liq. Cryst., 26(4), 581–587.
- [35] Almeria, N., & XN Zu-Sheng, (1999). Liq. Cryst., 26(3) 309-318.
- [36] Cooray, N. F., Suzuki, Y., & Kawakmura, I. (1999). Liq. Cryst., 26(8), 1197–1203.
- [37] Chen, Y., & Wu, W. J. (1998). Liq. Cryst., 25(3), 309–318.
- [38] Saleh, A. A., Pleune, B., Fettinger, J. C., & Poli, R. (1997). Polyhedron, 16, 1391.
- [39] Gray, G. W., & Jones, B. (1954). J. Chem. Soc., 1467.
- [40] Hildesheimer, A. (1901). Manatsh. Chem., 22, 487.
- [41] Stoermer, R., & Wodarg, F. (1928). Chem. Berg., 61B, 2323.
- [42] Weygard, C., & Gabler, R. (1940). J. Prakt Chem., 155, 332; (1938). J. Prakt. Chem., 151, 215.
- [43] Dave, J. S., & Vora, R. A. (1970). In: Liquid crystal and Org. Flu, Johnson, J. F. & Poater, R. S. (Eds.), Plenum press: New York, 477.
- [44] Gray, G. W., Hartley, J. B., & Jones, B. (1955). J. Chem. Soc., 1412.
- [45] Mihara, T., Nomura, K., Funaki, K., & Koide, N. (1997). Polymer J., 29(4), 303.
- [46] Mihara, T., Tsutsumi, M., & Koide, N. (2002). Mol. Cryst. Liq. Cryst., 382, 53-64.
- [47] Pinol, R., Ros, M. B., Serrano, J. L., & Sierra, T. (2004). Liq. Cryst., 31(9), 1293-1303.
- [48] Yeop, G. Y., Ha, S. T., Lim, P. L., & Boeg, P. L. (2006). Mol. Cryst. Liq. Cryst., 452, 63.
- [49] Sackmann, H., & Demus, D. (1996). Mol. Cryst. Liq. Cryst., 2, 81.
- [50] Gray, G. W., & Goodby, J. W. (1984). Smectic Liquid Crystal: Texture and Structures. Leonard Itill.
- [51] Marzotko, D., & Demus, D. (1975). Dramana, 1, 189.
- [52] Nguyen, H. T., Zanna, J. J., & Dubois, J. C. (1979). Mol. Cryst. Liq. Cryst., 53, 43.