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Vinay S. Sharma, Anuj S. Sharma, Upendra H. Jadeja & Deepak Suthar

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New chalcone based liquid crystals with allylidene amino linking unit: Synthesis and characterization

Vinay S. Sharma^a, Anuj S. Sharma^b, Upendra H. Jadeja^c, and Deepak Suthar^d

^aDepartment of Chemistry, Faculty of Basic and Applied Science, Madhav University, Sirohi, Rajasthan, India; ^bDepartment of Chemistry, School of Science, Gujarat University, Ahmedabad, Gujarat, India; ^cPresident Science College, Gujarat University, Ahmedabad, Gujarat, India; ^dDepartment of Physics, Faculty of Basic and Applied Science, Madhav University, Sirohi, India

ABSTRACT

In this study, the synthesis, structural characterization and mesomorphic properties of newly thirteen calamitic shaped compounds derived from allylidene amino chalcone and 4-n-alkoxy benzoyloxy benzoic acid. Comp.H₁ to H₃ exhibited nonliquid crystalline nature, while comp.H₄ to comp.H₁₈ displayed enantiotropical smectic C phase. Phase transition temperatures of present synthesised compounds were determined by optical polarising microscopy (POM), differential scanning calorimetric (DSC) and powder X-ray diffraction (PXRD) techniques. Thermal stabilities of smectic to isotropic phase are 150.0 °C and temperature range of mesophase is in decreasing order from comp.H₃ to comp.H₁₈ respectively. The presences of SmC phase are the type of broken fan and needle type in present synthesized series. It is also shown that presence of chalcone amino allylidene central linking group favors a calamitic liquid crystalline behaviour in molecules with lower member to higher member aliphatic side chain in alkoxy group (-OR).

KEY WORDS

Allylidene amino; chalcone; mesophase; smectic C



GRAPHICAL ABSTRACT



1. Introduction

The arrangement of molecules in liquid crystals (LCs) takes place in a number of ways leading to various phases of different order and symmetry between crystalline solid and

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CONTACT Vinay S. Sharma 🖾 vinaysharma3836@gmail.com 🗈 Department of Chemistry, Faculty of Basic and Applied Science, Madhav University, Sirohi, Rajasthan, India.

isotropic liquid [1-4]. Calamitic molecules of conventional and unconventional liquid crystalline materials have been intensively investigated for scientific and technological potent applications such as sensing materials, optoelectronic display materials and biologically active molecules [5-6]. Study on LC state is planned with a view to understand and establish the effect of molecular structure on LC properties [7] as a consequence of molecular rigidity and flexibility by using different linking group [8]. Molecules incorporated with two or more than two linking group have attracted a great attention from the researchers in designing a new calamitic rod shaped liquid crystalline materials [9]. Literature studies revealed that the chalcone has been widely employed as a linking group for the synthesis of calamitic liquid crystals [10-11]. Chalcones with presence of electron-pulling and electron-pushing functional groups on the benzene rings leads calamitic shaped of molecules [12-14]. Several kinds of chalcone monomer, dimer and polymeric compounds of different shapes have been evaluated for their materials properties. Tandel et al. synthesized polymer chalcone exhibited nematic phase [15]. Doshi et al. reported chalconyl ester and chalconyl vinyl ester linkage group inbuilt between three phenyl rings and studied the effect on mesomorphism by substituted groups at terminal and lateral side [16-19]. Yeap et al. have also synthesized mesomorphic compounds containing on ester-chalcone linkage [20]. Recently, Gallardo and his coworkers reported polycatenar liquid crystals series based on bent shaped chalcone and cyanopyridine molecules [21]. Patel et al. reported rod type homologous series having chalconyl ester central linkage group and hexyloxy tail group [22]. Furthermore, S.Kumar et al. reported chalcone based LCs compounds possessing short alkyl chain at one end and other end with variable chain lengths. These derivatives were reported to exhibit SmC, SmA and nematic phase [23]. Previously, Yellamaggad and co-worker have reported the bent-core unsymmetrical dimers in which cholesteryl ester and chalconyl moiety are present, which enhances the biaxiality and chirality of the system [24]. Furthermore, Bhoya et al. reported chalconyl-ester linking group based homologous series [25].

Figure 1 indicates the reported liquid crystal materials based on allylidene amino and chalcone group in literature [26–27]. Our research group also reported some linear and nonlinear homologous series which consisted three phenyl rings bonded through vinyl



Figure 1. Different type of LCs material based on allylidene amino-chalcone group.

ester (-CH=CH-COO-) and ester (-COO-) linkage group connected with chalconyl central group having alkoxy terminal group at left end and different terminal group or lateral substitution on right side [28–30]. We have also reported the single chalconyl linkage group between two phenyl rings exhibited monotropy or enantiotropy mesophase with low thermal stability [31–33]. In continuation of our efforts to synthesized newly liquid crystalline materials, we have introduce some new calamatic liquid crystal based on two ester group (-COO-) with chalcone (-CH=CH-CO-) and allylidene amino (-N=CH-CH=CH-) group. We have compared the thermal stability and temperature range of mesophase of series-1 with series- A_1 and series- A_2 which was previously reported by our research group. Here in, we present five phenyl ring based calamitic LCs having four linking units. The aim of this work is to better understand how the chemical nature of different linking group affect liquid crystalline property, and to achieve this, we have introduce one more phenyl ring connected through ester group in present newly synthesized series.

2. Experimental

2.1. General

For the synthesis of target compounds in present newly homologous series, the following materials were used: 4-hydroxy benzoic acid, 4-hydroxy benzaldehyde, 4-amino acetophenone were purchased from SRL, (Mumbai), Alkyl halides (R-Br) were purchased from Lancaster, (England), cinnamaldehyde was purchased from (Sigma Aldrich), DCC (Dicyclohexyl carbodimide) was purchased from Fluka Chemie (Switzerland), Dimethyl amino pyridine DMAP (4,4'-dimethylamino pyridine) was purchased from Finar chemicals (India), Dichloro methane, Ethanol, MeOH, required for synthesis were used as received except solvents which was dried and distilled prior to use. The molecular structures of the target products and the intermediates were confirmed by spectroscopic techniques. Representative homologous series were characterised by elemental analysis, Infrared spectroscopy, ¹H NMR spectra. IR (cm⁻¹, KBr) spectra were recorded by Perkin-Elmer spectrum GX in the frequency range of 4000-400 cm⁻¹, ¹H NMR spectra were recorded on Bruker (300 MHz, CDCl₃) using tetramethylsilane as an internal standard. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyser. The textural observation was carried out by using a polarising optical microscope equipped with hot stage along with the temperature controller and camera. Decomposition temperatures were determined using of Shimadzu (DSC) differential Scanning Calorimeter with a heating rate of 5°C to 10.0 °C min⁻¹.

2.2. Synthesis of compounds in present series

2.2.1. Synthesis of 4-n-alkoxy benzoic acid (C)

4-n-alkoxy derivatives of 4-hydroxy benzoic acid were prepared by reported method by Dave and Vora [34].

2.2.2. Synthesis of Methyl-4-hydroxy benzoate (A)

Equimolar proportion of p-hydroxy benzoic acid and absolute methanol shacked well in presence of two drops of concentrated H_2SO_4 and reaction mixture was refluxed for two to three hours. Then reaction mixture was dumped into ice, and allowed it to settle down. Solid white precipitate of methyl-4-hydroxy benzoate is obtained. Product was filtered, washed, dried and then purified by alcohol. Fine crystals are obtained (M.P.126°C, yield 79%) [35].

2.2.3. Synthesis of 4-(Methoxy carbonyl) phenyl 4'-n-alkoxy benzoate (D)

4-(methoxy carbonyl) phenyl 4'-n-alkoxy benzoate has been prepared by esterification of the appropriate 4-n-alkoxy benzoic acid (C) (2.02 mmol) and methyl-4-hydroxy benzoate (A) (2.02 mmol), dicyclohexyl carbodiimide (DCC) (2.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.2 mmol) in dry CH_2Cl_2 (DCM) (60 ml) was stirred at room temperature for 48 h. The white precipitate of DCU is obtained which was isolated by filtration and remove, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (2:4) [36].

Comp. D₄: IR (KBr): v_{max}/cm^{-1} 3033 (C-H str.), 679 polymethylene group of $-OC_4H_9$ chain group, 1740 (-COO- group), 1240 (C-O str.). ¹HNMR: 0.88 (t, 3H, $-OC_4H_9$), 1.45 (sex, 3H, $-OC_4H_9$), 1.76 (q, 2H, $-OC_4H_9$), 4.06 (t, 2H, $-OC_4H_9$), 3.82 (s, 3H, $-OCH_3$), 7.12 & 8.01 (d, 4H, first phenyl ring), 7.38 & 8.11 (d, 4H, second phenyl ring). Elemental analysis: calculated for $C_{19}H_{20}O_5$: C, 69.51; H, 6.09; found: C, 69.41; H, 5.91; O, 5.89%.

2.2.4. Synthesis of 4-((4'-n-alkoxy benzoyl) oxy) benzoic acid (E)

4-((4'-n-alkoxy benzoyl) oxy) benzoic acid (E) were prepared by dissolving comp.D in ethanol (40 ml) and 10% aq. KOH (2 ml) was added. The resultant mixture was heated at reflux for 6 to 7 hours then cooled to room temperature, poured into ice cold water (80 ml) and then acidified with dil.HCl. The crude product obtained by filtration was recrystallized by using MeOH/DCM [37].

Comp. E₄: IR (KBr): v_{max}/cm^{-1} , 3071 (C-H str.), 3301 (-OH of carboxylic group), 1680 (C=O str. of carboxylic group), 1750 (-COO- group), 648 polymethylene group of $-OC_4H_9$ group. ¹HNMR: 0.88 (t, 3H, $-OC_4H_9$), 1.44 (sex, 2H, $-OC_4H_9$), 1.72 (q, 2H, $-OC_4H_9$), 4.07 (t, 2H, $-OC_4H_9$), 10.8 (s, 1H, -COOH group), 7.11 & 8.01 (d, 4H, first phenyl ring), 7.58 & 8.23 (d, 4H, second phenyl ring). Elemental analysis: calculated for $C_{18}H_{18}O_5$: C, 68.78; H, 5.73%; found: C, 68.69; H, 5.68%.

2.2.5. Synthesis of 1-(4-(((E)-3-phenyl allylidene) amino) phenyl) ethan-1-one (F)

1-(4-(((E)-3-phenyl allylidene) amino) phenyl) ethan-1-one (F) was synthesized by refluxing the mixture of cinnamaldehyde (2 mmol.) and 4-amino acetophenone (2 mmol.) in EtOH for 3 hr. in presence of few drops acetic acid as catalyst. The yellow precipitate is obtained which was further wash with ethanol several times. The obtain

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residue was further purified by using column chromatography on silica gel eluting with chloroform: methanol as eluent (4:1) [38]. IR (KBr): v_{max}/cm^{-1} 3079 (-C-H str.), 1661 (-C=O group of -COCH₃), 1580 (-C=C-) aromatic, 962 (*trans*, alkene), 1590 (-CH=N). ¹HNMR: 2.03 (s, 3H, -CH₃), 8.41 (s, 1H, -CH=N), 7.22 (d, *J*=15.1 Hz, 1H, -CH=CH-CH=N), 6.83 (d, *J*=15.1 Hz, 1H, -CH=CH-CH=N), 7.38, 7.54 (d, 5H, first phenyl ring), 7.33, 8.02 (d, 4H, second phenyl ring). Elemental analysis: calculated for C₁₇H₁₅ON: C, 81.92; H, 6.02; N, 5.62; found: C, 80.69; H, 5.95; N, 5.54.

2.2.6. Synthesis of (2E)-3-(4-hydroxy phenyl)-1-(4-(((E)-3-phenyl allylidene) amino) phenyl) prop-2-en-1-one (chalcone) (G)

Chalcone (G) was prepared by usual established method reported in literature [38]. (brownish yellow, Yield: 67%), IR (KBr): v_{max}/cm^{-1} 3460 (-OH str.-bonded), 3079-3020 (-C-H str. aliphatic alkyl group), 2932, 1598 (CH=N), 1667 (-C=O, group), 1584-1610 (-C=C-) aromatic, 1280 (-O-CH₂- ether linkage), 962 (Trans alkene). Elemental analysis: calculated for C₂₄H₁₉O₂N: C, 81.58; H, 5.38; O, 9.06; N, 3.96%; found: C, 81.48; H, 5.28; O, 8.77; N, 3.89%.

2.2.7. General procedure for the synthesis of final target compounds (H)

The final target compounds (H) has been prepared by esterification of the appropriate compound (E) (2 mmol) and compound (G) (2 mmol), dicyclohexyl carbodiimide (DCC) (2.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.2 mmol) in dry CH_2Cl_2 (DCM) (40 ml) was stirred at room temperature for 48 h. The slightly yellowish precipitate of DCU is obtained which was isolated by filtration and remove, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4) [39]. The characterization data of target compounds mention in supporting information. The synthesis route of target compounds was mention in below Scheme 1.

Compound H₁: IR (KBr): v_{max}/cm^{-1} 2960 (C-H str. of alkane), 1640 (C=O str. of carbonyl carbon of chalconyl group), 1601 (C=C str. of alkene in chalcone), 1760 (-COO- group), 770 (C-H bending of alkene), 1120 (C-O str. of ether linkage), 1240 (C-O str. of carbonyl (>C=O) group), 960 (*trans*, -CH=CH- group). ¹H-NMR: 3.81 (t, 3H, -OCH₃), 7.81 & 7.52 (d, 2H, -CH=CH-CO-), 7.44 (d, 1H, -N=CH-CH=C-), 6.83 & 7.20 (d, 2H, -N=CH-CH=CH-), 8.07 & 7.10 (d, 4H, Ar), 7.32 & 7.72 (d, 6H, Ar), 7.87 & 7.38 (d, 6H, Ar), 7.61, 7.40, 7.31 (d, 5H, Ar). Elemental analysis: calculated for $C_{39}H_{25}O_6N$: C, 77.61%; H, 4.14%; O, 15.92%; N, 2.32%; found: C, 77.25%; H, 4.03%; O, 15.97%; N, 2.23%.

Compound H₂: IR (KBr): v_{max}/cm^{-1} 2960 (C-H str. of alkane), 1650 (C=O str. of carbonyl carbon of chalconyl group), 1610 (C=C str. of alkene in chalcone), 1730 (-COO- group), 992 (C-H bending of alkene), 1120 (C-O str. of ether linkage), 1240 (C-O str. of carbonyl (>C=O) group, 960 (*trans*, -CH=CH- group). ¹H-NMR: 1.32 (t, 3H, $-OC_2H_5$), 4.06 (t, 2H, $-OC_2H_5$), 7.82 & 7.52 (d, 2H, -CH=CH-CO-), 7.46 (d, 1H, -N=CH-CH=CH-), 6.83 & 7.21 (d, 2H, -N=CH-CH=CH-), 8.07 & 7.10 (d, 4H,Ar), 7.32 & 7.71 (d, 6H, Ar), 7.87 & 7.38 (d, 6H, Ar), 7.61, 7.40, 7.32 (d,5H, Ar). Elemental

Step-1



($R = C_n H_{2n+1}$, n = 1 to 8, 10, 12, 14, 16, 18)

Scheme 1. (i) MeOH, conc.H₂SO₄, Reflux, 30 min; (ii) R-Br, KOH, MeOH, Reflux; (iii) KOH, EtOH, Reflux; (iv) DCC, DMAP, DCM, 24 hr. rt stirring; (v) EtOH, few drops of acetic acid, Reflux; (vi) KOH, EtOH, rt stirring; (vii) DCC, DMAP, DCM, 48 hr. rt stirring.

analysis: calculated for $C_{40}H_{27}O_6N$: C, 77.79%; H, 4.37%; O, 15.55%; N, 2.26%; found: C, 77.48%; H, 4.29%; O, 15.48%; N, 2.23%.

Compound H₃: IR (KBr): v_{max}/cm^{-1} 2950 (C-H str. of alkane), 810 (-(CH₂-)n group of -OC₃H₇ chain), 1650 (C=O str. of carbonyl carbon of chalconyl group), 1610 (C=C str. of alkene in chalcone), 1750 (-COO- group), 1420 (-C=C str. of aromatic ring), 984 (C-H bending of alkene), 1188 (C-O str. of ether linkage), 1240 (C-O str. of carbonyl (>C=O) group, 962 (*trans*, -CH=CH- group). ¹H-NMR: 0.92 (t, 3H, -OC₃H₇), 1.76 (p, 2H, -OC₃H₇), 4.06 (t, 2H, -OC₃H₇), 7.87 & 7.51 (d, 2H, -CH=CH-CO-), 7.48 (d, 1H, -N=CH-CH=C-), 6.84 & 7.22 (d, 2H, -N=CH-CH=CH-), 8.06 & 7.12 (d, 4H, Ar), 7.30 & 7.72 (d, 6H, Ar), 7.86 & 7.38 (d, 6H, Ar), 7.61, 7.40, 7.31 (d, 5H, Ar). Elemental analysis: calculated for C₄₁H₂₉O₆N: C, 77.97%; H, 4.59%; O, 15.21%; N, 2.21%; found: C, 77.91%; H, 4.48%; O, 15.17%; N, 2.15%.

Compound H₄: IR (KBr): v_{max}/cm^{-1} 2940 (C-H str. of alkane), 1640 (C=O str. of carbonyl carbon of chalconyl group), 1601 (C=C str. of alkene in chalcone), 1760 (-COO- group), 1440 (-C=C str. of aromatic ring), 994 (C-H bending of alkene), 1188 (C-O str. of ether linkage), 1246 (C-O str. of carbonyl (>C=O group), 960 (*trans*, -CH=CH- group), 740 polymethylene (-CH₂-) of $-OC_4H_9$. ¹H-NMR: 0.90 (t, 3H, $-OC_4H_9$), 1.76 (p, 2H, $-OC_4H_9$), 4.06 (t, 2H, $-OC_4H_9$), 7.88 & 7.52 (d, 2H, -CH=CH-CO-), 7.48 (d, 1H, -N=CH-CH=C-), 6.84 & 7.22 (d, 2H, -N=CH-CH=CH-), 8.08 & 7.10 (d, 4H, Ar), 7.31 & 7.74 (d, 6H, Ar), 7.87 & 7.38 (d, 6H, Ar), 7.61, 7.40, 7.32 (d, 5H, Ar). Elemental analysis: calculated for $C_{42}H_{31}O_6N$: C, 78.13%; H, 4.80%; O, 14.88%; N, 2.17%; found: C, 78.09%; H, 4.73%; O, 14.83%; N, 2.09%.

Compound H₈: IR (KBr): v_{max}/cm^{-1} 2950 (C-H str. of alkane), 1610 (C=O str. of carbonyl carbon of chalconyl group), 1610 (C=C str. of alkene in chalcone), 1740 (-COO- group), 1440 (-C=C str. of aromatic ring), 991 (C-H bending of alkene), 1180 (C-O str. of ether linkage), 1240 (C-O str. of carbonyl (>C=O group), 960 (*trans*, -CH=CH- group), 632 polymethylene (-CH₂-) of $-OC_8H_{17}$. ¹H-NMR: 0.90 (t, 3H, $-OC_8H_{17}$), 1.76 (p, 2H, $-OC_8H_{17}$), 1.46 (sext, 2H, $-OC_8H_{17}$), 1.28-1.32 (m, 8H, $-OC_8H_{17}$), 4.06 (t, 2H, $-OC_8H_{17}$), 7.88 & 7.52 (d, 2H, -CH=CH-CO-), 7.48 (d, 1H, -N=CH-CH=C-), 6.84 & 7.22 (d, 2H, -N=CH-CH=CH-), 8.08 & 7.10 (d, 4H, Ar), 7.31 & 7.74 (d, 6H, Ar), 7.87 & 7.38 (d, 6H, Ar), 7.61, 7.40, 7.32 (d, 5H, Ar). Elemental analysis: calculated for $C_{46}H_{39}O_6N$: C, 78.74%; H, 5.56%; O, 13.69%; N, 1.99%; found: C, 78.71%; H, 5.48%; O, 13.63%; N, 1.93%.

Compound H₁₀: IR (KBr): v_{max}/cm^{-1} 2950 (C-H str. of alkane), 1640 (C=O str. of carbonyl carbon of chalconyl group), 1760 (-COO- group), 1440 (-C=C str. of aromatic ring), 991 (C-H bending of alkene), 1188 (C-O str. of ether linkage), 1246 (C-O str. of carbonyl (>C=O group), 960 (*trans*, -CH=CH- group), 681 polymethylene (-CH₂-) of $-OC_{10}H_{21}$ group. ¹H-NMR: 0.90 (t, 3H, -CH₃ of polymethylene $-OC_{10}H_{21}$), 1.28-1.32 (m, 12H, $-OC_{10}H_{21}$), 1.76 (p, 2H, $-OC_{8}H_{17}$), 1.46 (sext, 2H, $-OC_{8}H_{17}$), 4.06 (t, 2H, $-OC_{10}H_{21}$), 7.88 & 7.52 (d, 2H, -CH=CH-CO-), 7.48 (d, 1H, -N=CH-CH=C-), 6.84 & 7.22 (d, 2H, -N=CH-CH=CH-), 8.08 & 7.10 (d, 4H, Ar), 7.31 & 7.74 (d, 6H, Ar), 7.87 & 7.38 (d, 6H, Ar), 7.61, 7.40, 7.32 (d, 5H, Ar). Elemental analysis: calculated for $C_{48}H_{43}O_6N$: C, 79.01%; H, 5.89%; O, 13.16%; N, 1.92%; found: C, 78.94%; H, 5.84%; O, 13.12%; N, 1.89%.

3. Result and discussions

3.1. Mesomorphic behaviour study

Here in present investigation, we have synthesized novel liquid crystalline compounds having four linking group joint via five phenyl ring in present series-1 from small alkyl chain (H_1) to higher alkyl chain (H_{18}) at left end side group. In present work, we have study the effect of variation in tail group on mesomorphic property of presently synthesized homologous series. A newly ester-chalcone-allylidene amino linking group based homologous series (H) synthesised from condensation of 4-((4'-n-alkoxy benzoyl) oxy) benzoic acid (E) and (2E)-3-(4-hydroxy phenyl)-1-(4-((E)-3-phenyl allylidene) amino) phenyl) prop-2-en-1-one (G) (chalcone) is synthesized and evaluated their LC behaviour with some thermometric data to compare mesomorphic behaviours and the molecular structure through molecular rigidity and flexibility with structurally similar previously reported series by our group. The thermotropic mesophase behaviour of all newly synthesised compounds was primarily investigated by polarising optical microscope (POM). The exact temperature of phase transition and associated enthalpy values were determined by differential scanning calorimetry (DSC) analysis. The presence of SmC phase is confirmed by XRD technique at transition temperature. We have totally prepared thirteen compounds in present series from lower member to higher member, out of thirteen compounds, ten compounds (H_4 to H_{18}) shows enantiotropic SmC phase with wide temperature range.

3.1.1. POM study

We have studied the effect of changing aliphatic alkyl chain length in alkoxy (-OR) group to form calamatic rod type shaped chalcone mesogens. Here, in present article, we have synthesized five phenyl ring based calamatic rod-shaped homologous series having two ester (-COO-), chalcone (-CH=CH-CO-) in presence of allylidene amino (-N=CH-CH=CH-) linking group with no any terminal substituent on right terminal end. The transition temperature of present series-1 is listed in Table 1. As seen in Table 1, compounds H_1 to H_3 shows non LCs property, however comp. H_4 to H_{18} display

		Transition temperatures in °C						
Sr.no	R = n-alkyl group	Cr-I	Cr-SmC		SmC-N		SmC-I	
1	H ₁	218.0	-	-	-	-	-	
2	H ₂	201.0	-	-	-	-	-	
3	H ₃	198.0	-	-	-	-	-	
4	H ₄		157.0		-	-	191.0	
5	H ₅		146.0		-	-	180.0	
6	H ₆		141.0		-	-	161.0	
7	H ₇		128.0		-	-	142.0	
8	H ₈		139.0		-	-	152.0	
9	H ₁₀		125.0		-	-	140.0	
10	H ₁₂		123.0		-	-	138.0	
11	H ₁₄		118.0		-	-	136.0	
12	H ₁₆		112.0		-	-	132.0	
13	H ₁₈		104.0		-	-	128.0	

Table 1. Transition Temperature in °C by POM (Series-1).

(Cr-I = Crystal to isotropic phase; Cr-SmC = crystal to smectic C phase; SmC-I = Smectic C to isotropic phase).



Figure 2. Phase diagram of series-1.

smectic C phase on heating and cooling condition which was further confirmed by DSC analysis. Mesophase formation was found to be dependent on the number, position and the molecular length of the side alkyl chain which increases the flexibility of molecules attached to the alkoxy side group (-OR). As shown in Table 1, compound H_4 has higher melting type temperature (191°C) and high temperature range of solid crystal to SmC phase (138.0°C) as compared to higher members of compounds in present series-1.

The phase diagram of present series-1 is shown in Fig. 2 which indicates the phase behaviour of Cr-SmC/I and SmC-I transition curve present in prepared series-1. It can be seen that, as series increases from lower homologue H_4 to higher homologue H_{18} , the transition temperature is decreases from upper to lower members of prepared series-1. Cr-SmC/I phase transition curve exhibit a smooth falling tendency from H_1 homologue to H₇ homologue and formerly increases at H₈ homologue then continued to descend upto last homologue H₁₈. Odd-even effect is present at (H₇-H₈) homologue in Cr-SmC/I and SmC-I phase transition curve. In addition of decreasing tendency from H_4 to H_{18} homologous in SmC-I transition curve except H_8 homologue, this is due to the presence of odd-even parity of carbon present in methylene group in side alkoxy (-OR) group. The decreasing tendency in melting and clearing temperature could be due to the lowering the vander waals interactions between aromatic phenyl cores and higher degree of flexibility due to presence of long alkyl chain in alkoxy group at left terminal part [40]. Comp.H₁ to H₃ shows non liquid crystalline property due to presence of short alkyl spacer chain group and high crystallising tendency to directly transform isotropic liquid without showing any LCs phase.

3.1.2. Textural study

The crystalline compounds placed on clear glass slide sheltered by coverslip were heated to the isotropic state and heating and cooling rate (2 °C/min) respectively and observing mesophase texture image. Microphotographs of the textures observed for compounds H_{14} and H_{12} are depicted in Fig. 3. Comp.H₈ shows fan like texture image of SmC



Figure 3. Microphotograph texture image (a) comp.H8 at 139.0°C on heating.



Figure 4. Structurally similar analogous series.

phase at 139.0°C on heating condition and again reappear on cooling condition. Comp. H_{14} shows needle type texture image of SmC phase at 118.0°C on cooling condition. It can be noted that, presence of mesophase in present series is enantiotropical type, condition; (b) comp. H_{14} at 118.0°C on cooling condition.

3.1.3. Comparative study

Some LC properties evaluated from thermotropic data of presently investigated newly series-1 compared with series- A_1 [41] and series- A_2 [41] mention in Fig. 4. All three series are similar with respect to presence of chalcone and allylidene amino linkage group with varying alkyl side chain in left terminal end. The linearity and polarizability of series-1 is higher as compare to other series- A_1 and series- A_2 due to the presence one more phenyl ring joint through ester linkage group. Series- A_1 and series- A_2 shows only nematic phase however present synthesized series display only SmC phase, this is due to the presence of second ester (-COO-) linking group which more favors to smectic phase as compare to nematic phase and also the effect of polarizability, polarity and



Figure 5. Space filling diagram of structurally similar series.

Series	Series-1	Series-A ₁	Series-A ₂			
SmC-I	150.0 (H ₄ -H ₁₈)	_	_			
SmC-N	_	_	_			
Cr-N	-	133.09 (C ₃ -C ₁₈)	138.5 (C ₄ -C ₁₈)			
Cr-SmC	129.3 (H ₄ -H ₁₈)	_	_			
N-I	_	163.27 (C ₃ -C ₁₈)	186.9 (C ₄ -C ₁₈)			

Table 2	Average	thermal	stability	in	٥(
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(SmC-I = smectic C to isotropic; SmC-N = smectic C to nematic; Cr-N = solid to nematic; Cr-SmC = solid to smectic C; N-I = nematic to isotropic).

dipole moment of molecules. Thus, changing in liquid crystalline properties like thermal stability and temperature range, commencement of mesophase will be influenced by the magnitudes of changing structures of homologous series-1 as compare to series- A_1 and series- A_2 .

Figure 5 shows the space filling diagram of series-1, series- A_1 and series- A_2 . It can be seen that, the geometrical shape of all series are calamatic rod type. In series- A_2 and series- A_3 , molecules incorporated with four phenyl ring connected through three linking unit while in series-1 one more phenyl rings and mesogenic unit is present. It is also shown that present synthesised series-1 shows good thermal stability of mesophase as compare to other two series- A_1 , - A_2 . Series-1 shows only smectic phase, this is due to the formation of lamellar packing order in molecules to form smectic mesophase and then passing through isotropic liquid without showing any nematic phase. However, due to shorter molecular length of series- A_1 and series- A_2 as compare to series-1 to exhibits no any lamellar packing arrangement of molecules and passing nematic phase without showing smectogenic mesomorphism.

Thermal stability of present newly synthesised series-1, series- A_1 and series- A_2 are listed in Table 2. From the Table 2, series-1 display only smectic mesophase with good thermal stability while other two structurally similar series exhibited only nematic phase.



Figure 6. Temperature range of phase transition in series-1, -A1, -A2.

Nematic thermal stability of series- A_2 is higher as compare to series- A_1 due to the presence of vinyl ester linking group which increase the molecular length as well as thermal stability of mesophase. The temperature range of phase transition in present series-1 comparative with series- A_1 and series- A_2 is shown in Fig. 6. It can be seen that, total temperature range of mesophase of series- A_2 is higher as compare to series- A_1 and series-1.Temperature range of smectic to isotropic phase in comp. H_4 and H_5 is higher as compare to higher member of compounds in series-1. Temperature range of series- A_1 is in between series-1 and series- A_2 respectively. From, Fig. 6, it is also shown that the commencement of mesophase in series- A_1 is early (H_3) as compare to series- $1(H_4)$ and series- A_2 (H_4).These observations of series-1 are further established by using DSC analysis where phase transition associated with Cr-SmC, SmC-I phase transition.

3.1.4. Chemical reactivity

The nature of the electronic transition and frontier molecular orbital (FMO) distributions are investigated by using density functional theory (DFT) at the B3LYP/6-311 level in Dichloromethane solution using the CPCM solvation model with default convergence criteria. The calculated FMO distributions of comp. H_1 and comp. H_{12} are presented in Fig. 7 and Fig. 8. From Fig. 7, it is noted that the HOMO is localized on the phenylallylidene amino unit while the LUMO is localized on chalconyl-phenyl unit. A close examination of these orbitals reveals that the HOMO of $comp.H_1$ from both series is predominantly localized on the fourth phenyl unit with amino allylidene group while the LUMO is mostly concentrated on chalconyl-phenyl group. Presence of allylidene amino linking group shows significant influence on the HOMO orbitals however the chalconyl group appearances impact on the LUMO orbitals. It can be noted that the electronic properties of comp.H₁, H₁₂ (series-1) could have originated from the chalconyl and amino allylidene group inbuilt with phenyl ring. The HOMO-LUMO gap of comp.H₁ (series-1) is 2.294 eV which is higher as compare to comp.H₁₂ (series-1). Thus, the substitution of higher alkyl spacer chain in alkoxy group (-OR) may affect the reactivity and stability of the compounds.



Figure 7. The molecular orbitals and energies for the HOMO and LUMO of the comp.H1.



Figure 8. The molecular orbitals and energies for the HOMO and LUMO of the comp.H12.

3.2. DSC study

The thermal behaviour of mesogenic compounds was also investigated with DSC measurements at heating and cooling scan rate of 10° C min⁻¹ under nitrogen atmosphere. The phase transition temperatures obtained in DSC agree very well with POM observation. DSC thermographs of compounds H₅, H₆, H₁₆, H₁₈ are presented in Fig. 9.



Figure 9. DSC thermograms of compound (a) H5; (b) H6; (c) H16; (d) H18 on heating.

All compounds are thermally stable as confirmed by the reproducibility of thermograms on several heating and cooling cycles. In Fig. 9, compound H₅ exhibits three endothermic peaks at 114.62°C, 144.12°C and 178.61°C in heating cycle, which correspondence to the presence of crystal to crystal (Cr-Cr'), crystal to SmC (Cr'-SmC) and SmC-I phase. That was further confirmed by POM analysis. While on cooling condition, again these exothermic peaks were traced at 173.24°C, 143.68°C and 115.61°C. Compound H₆ exhibits three endothermic peaks at 103.91°C, 142.52°C and 163.64°C on heating cycle correspondence to crystal to crystal, crystal to SmC and SmC to isotropic phase while on cooling cycle; it appears at 161.58°C, 138.32°C and 106.78°C. Compound H₁₆ shows three endothermic peaks at 88.67°C, 111.24°C and 132.12°C on heating cycle which reveals with POM results. On cooling cycle, again this exothermic peak exhibits at 134.68°C, 112.94°C and 82.34°C. Compound H₁₈ shows three endothermic peaks at 79.92°C, 105.74°C and 124.72°C in heating condition while on cooling condition it appears at 125.01°C, 101.69°C and 80.64°C. The phase transition temperatures, enthalpy and entropy values for the present synthesized series are summarized in Table 3.

3.3. XRD study

The mesophase structures of novel chalconyl amino allylidene ester LCs were further confirmed by X-ray diffraction (XRD) studies of comp.H₅ and H₈ filled in Lindemann capillaries. The XRD pattern obtained for comp.H₅ and H₈ at 146.0°C and 139.0°C for

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Comp.	Transition	Heating scan(°C)	Cooling scan(°C)	ΔH	ΔH	ΔS	ΔS
H5	Cr-Cr'	114.62	115.61	4.82	3.42	0.0124	0.0088
	Cr'-SmC	144.12	143.68	12.92	11.34	0.0309	0.0272
	SmC-I	178.61	173.24	7.21	3.82	0.0159	0.0085
	Cr-Cr'	103.61	106.78	5.32	9.56	0.0141	0.0251
H ₆	Cr'-SmC	142.52	138.32	21.24	7.43	0.0511	0.0180
	SmC-I	163.64	161.58	7.32	8.82	0.0167	0.0194
	Cr-Cr'	88.67	82.34	3.16	7.23	0.0087	0.0088
H_{16}	Cr'-SmC	111.24	112.94	19.65	10.42	0.0511	0.0269
	SmC-I	132.12	134.68	7.87	9.02	0.0194	0.0221
	Cr-Cr'	79.92	80.64	8.56	6.45	0.0242	0.0182
H ₁₈	Cr'-SmC	105.74	101.69	14.67	12.43	0.0387	0.0331
	SmC-I	124.72	125.01	7.41	5.32	0.0186	0.0133

Table 3: Transition temperature (°C) and enthalpy (kJ/mol) and entropy change (J mol⁻¹k⁻¹) by DSC measurement.

(Cr-Cr' = solid to solid crystal; Cr-SmC = solid to SmC; Cr-N = solid to nematic; N-I = nematic to isotropic).



Figure 10. XRD patterns of compound H5 at 146°C.

the smectic C phase are shown in Fig. 10 and Fig. 11. The sharp reflection in the small angle region with d-spacing 34.21 Å of comp.H₈ and 33.04 Å of comp.H₅. No any diffuse peak at wide angle region in both compound. In comp.H₈, the layer spacing of 34.21Å in the smectic C phase is slightly smaller than the molecular length of 37.05 Å while in comp.H₅; the layer spacing of 33.04 Å in the smectic phase is smaller than its molecular length 35.31Å, indicating the tilted organization of the molecules in the layers. Figure 12 represents the proposed mechanism to indicate the arrangement of lamellar packing in molecules to exhibit SmC phase in present series-1. Higher member compounds display smectic C property at lower temperature as compare to lower member of present series because of the long aliphatic methylene group increasing the flexibility, polarizability of molecules to induce mesophase at lower transition temperature.



Figure 11. XRD patterns of compound H8 at 139°C.



Figure 12. Propose mechanism of present series-1.

4. Conclusion

In summary, we have reported the synthesis and phase behaviour of presently new homologous series containing five aromatic rings connected to four mesogenic unit as central part. A new calamatic rod type homologous series of chalcone derived LCs compounds possessing allylidene amino and ester linking unit at central part and other end 80 😉 V. S. SHARMA ET AL.

with variable chain lengths. The nature of the mesophases has been established by using POM, DSC and XRD studies. The lower member H_1 to H_3 shows non mesogenic behaviour due to presence of short alkyl spacer in n-alkyl chain. Comp.H₄ to H_{18} shows enantiotropic smectic C phase with good temperature range.

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