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New Liquid Crystalline Compounds Involving Ester-Chalcone Linkages Having 1,3,5-Trisubstituted Pyrazole as a Terminal Group

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Mesogens with chalcone central linkage are rare. It has been observed that –CO–CH=CH– linkage is less conducive to mesomorphism compared to –CH=N– (azomethine), –COO– (ester), –N=N–(azo) linkages due to the non linearity and angle strain arising from the keto group. But when –CO–CH=CH– linkage is present with other central linkages it becomes condusive to mesomorphism. In the present investigation two homologous series were synthesized having chalcone as a one of the central linkage. The homologous series have been derived from 1,3,5-trisubstituted pyrazole, p-hydroxy acetophenone, and alkoxy acid. Viz. 4(4′-n-alkoxybenzoloxy) phenyl-propane-3-one(1-phenyl-3-methyl-2-pyrazoline-5-one) [series-I] and 4(4′-n-alkoxybenzoloxy) phenyl-propane-3-one(1-phenyl(4″-methyl)-3-methyl-2-pyrazoline-5-one) [series-II]. The compounds of the both series have been characterized by elemental analyses, FT-IR, ^{1}H-NMR, and Mass spectrometry methods. Their liquid crystalline properties have been investigated by optical polarizing microscopy and DSC studies. All the derivatives are mesomorphic in nature. C_1 to C_5 of both the series exhibit only nematic phase. C_6 to C_8 in series-I and C_7 & C_8 in series-II exhibit smectic as well as nematic phase. Whereas C_{10}–C_{16} in series-I and C_8–C_{16} in series-II showing only smectic phase.

Keywords: chalcone; ester; mesomorphic; nematic phase; smectic phase; trisubstitude pyrazole

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INTRODUCTION

The mesomorphic behaviour of an organic compound is basically dependent on its molecular architecture in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. A number of mesogenic homologous series have been reported that have –COO–, –CH=N–, –N=N–, –CH=CH–, –CH=CHCOO–, –C=C–, –C≡C– etc., groups as their central linkages. Many mesogenic homologous series contain two central linkages, both of which may either be ester [1–3] or azomethine groups [4,5] or one of which may be ester and the other azomethine [6,7]. In the literature there are few reports of mesogenic compounds having chalcone linkages. However, many years ago Vora *et al.* [8] have reported homologous series of polymer containing chalcone linkage. Soon after that Chudghar *et al*. [9] reported homologous series containing ester-chalcone linkages. Recently Yeap *et al*. [10] have also synthesized mesomorphic compound containing ester-chalcone linkage. In our previous work we have reported the homologous series containing Schiff base-chalcone linkage [11].

Chalcone is one of the important chemical compounds and is being studied extensively because of its significant application in various sectors. In the fields of biology and biochemistry, chalcone has been claimed to be one of the compounds that plays a vital role in antitumor [12,13], antiinflammatory [14,15] and antimalaria [16] activities. It has also been documented that the chalcone possesses a remarkable 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 [17–19] and also having fluorescent properties [9].

However, heterocyclic compounds provide a great synthetic and structural versatility due to presence of number of potential substitution positions. Furthermore heteroatoms offer the possibility of several modes of co-ordination. In particular, pyrazoles derivatives allow structural design to tune the molecular shape for the appearance of mesomorphic properties. The mesogenic series with hetero atoms have created wide interest in liquid crystal field. The introduction of heteroatom causes considerable changes in chemical and physical properties and influences the type of liquid crystal phase, also phase transition temperatures and other properties of the mesogens [20]. Mesogenic heterocyclic homologous series containing nitrogen, oxygen etc. as heteroatom are reported. Schubert *et al*. [21] have reported

mesogenic pyron derivatives. Demus *et al*. [22,23] have reported number of dioxygen derivatives exhibiting mesomorphic behaviour. Pavluchenko *et al.* [24] have reported mesomorphic homologous series containing benzoxazole and benzthiazoles hetero atoms. Nash and Gray [25] have also reported some heterocyclic mesogens and have tried to explain the mesogenic behaviors of these heterocyclic moieties. Indeed, some 3, 5-disubstituted pyrazoles and 4-substituted pyrazoles have demonstrated their ability to show liquid crystalline behavior [26–31].

In our previous work [32] we have synthesized two homologous series containing ester-chalcone linkages having substituted benzene ring as a terminal group. An attempt have been made to synthesized two new homologous series containing same central linkages but different terminal heterocyclic moiety to study the influence of the terminal group on mesomorphic and thermal stability of these compounds.

In this article, we report series of some newly analogues derived from 1,3,5-trisubstituted pyrazole as terminal groups and synthesized two homologues series, Viz. 4(4′-n-alkoxybenzoloxy) phenyl-propane-3-one (1-phenyl-3-methyl-2-pyrazoline-5-one) [series-I] and 4(4′-n-alkoxybenzoloxy) phenyl-propane-3-one(1-phenyl(4″-methyl)-3-methyl-2-pyrazoline-5-one) [series-II] in which the ester and chalcone are essential central linkages.

All the compound of both the series has been characterized by elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The liquid crystalline behaviors of these compounds were observed by DSC study and polarizing microscope.

EXPERIMENTAL

Reagents and Technique

For the synthesis of compounds of the homologous series, following materials were used. 4-Hydroxy benzoic acid, 4-hydroxy acetophenone, alkyl bromide (Lancaster, England). The solvents were used after purification using the standard methods described in the literature [33].

Elemental analyses (C, H, N) were performed at CDRI(Central Drugs Research Institute), Lucknow. Infrared spectra were recorded with a Perkin-Elmer2000 FT-IR spectrophotometer in the frequency range 4000-400 cm^{-1} with samples embedded in KBr discs. ^{1}H-NMR spectra of the compound were recorded with JEOL-GSX-400 using $CDCl_3$ as a solvent and TMS as an internal reference and Mass spectra (EI) of the compounds at SAIF(Sofisticated Analytical Instrument Facilities), IIT Madras, Chennai. ^{13}C NMR spectra of the compound

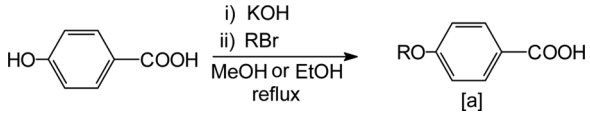
were recorded with BRUKER AVANCE II 400 NMR Spectrometer, SAIF, Chandigarh. Thin-layer chromatography analyses were performed by using aluminium-backed silica-gel plates (Merck 60 F524) and examined under short-wave UV light.

The phase-transition temperatures were measured using a shimadzu DSC-50 at heating and cooling rates of 5°C min^{-1}, respectively. The DSC data are shown in Table 3. The optical microscopy studies were carried out with a "Leitz Loborlux 12" POL(Wetzler,Gerrmany) 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-n-alkoxy benzoic acid

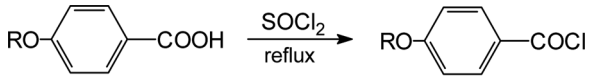
4-n-Alkoxy benzoic acid were prepared as reported by Dave and Vora method [34]. The m.p. of these compounds were compared with the reported one and they are almost similar to reported values.



[a]

Synthesis of 4-n-alkoxy benzoyl chlorides

4-n-alkoxy benzoyl chlorides were prepared by reported method [34]. The m.p. of these compounds were compared with the reported one and they are almost similar to reported values.

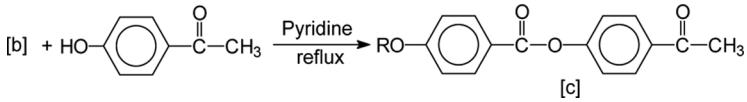


[b]

Synthesis of 4-(4′-n-alkoxybenzoloxy)-acetophenone

4-hydroxy aetophenone (0.01 mole, 1.22 gm) was dissolved in dry pyridine (10.0 ml) and was added drop wise with occasionally stirring into ice-cold 4-n-alkoxy benzoyl chloride (0.01mole, 2.41 gm) in a round bottom flask. Then mixture was refluxed on hot water bath for two hours and was allowed standing overnight. The mixture was acidified

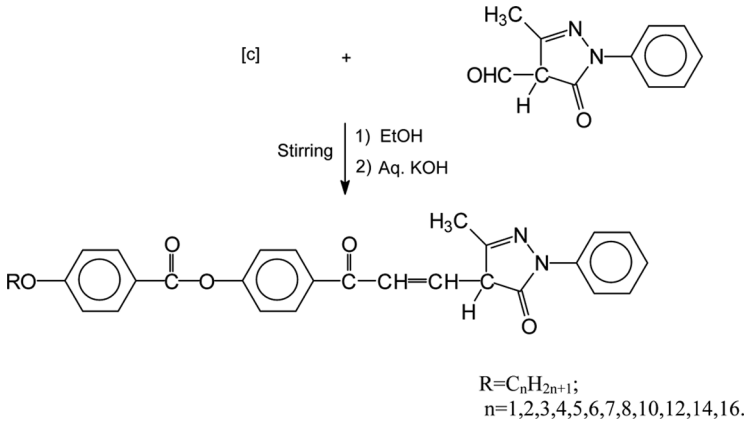
with cold 1:1 dilute hydrochloric acid to precipitate the product. The solid obtained was filtered, washed successive with saturated $NaHCO_3$ solution, dilute NaOH solution and two to three times with water thus crude solid was obtained which has number of times purified by hot water until the constant transition temperature were obtained. The transition temperatures are in good accordance with the literature [35].



Synthesis of Compound Series-I and Series-II [36–39]

Series-I Synthesis of 4(4′-n-alkoxybenzoloxy) phenyl-propen-3-one(1-phenyl-3-methyl-2-pyrazolin-5-one)

Take 4-(4′-n-alkoxybenzoloxy) acetophenone (0.005 mole 1.6 gm) and 1-phenyl-3-methyl-4-formyl-2-pyrazolin-5-one in flat bottom flask containing 25 ml absolute alcohol and stirred it on a stirrer, till both the reactants were dissolved completely. Then cold 10% aq. KOH solution added dropwise and continue the stirring further for four hours. The reaction mixture was allowed to stand for overnight. The mixture was neutralized by cold dilute HCl up to pH (6.5–7.0). Then solid obtained was filtered, washed with water and dried. The crude products were purified by using column chromatography and crystallized from methanol. The melting points and transition temperatures for this homologous series are given in Table 1.



$R=C_nH_{2n+1}$;
n=1,2,3,4,5,6,7,8,10,12,14,16.

TABLE 1 Transition Temperature of Series-I

Compounds	R = n alkoxy	Transition temperature °C		
		Sm	N	I
C_1	Methyl	–	126	223
C_2	Ethyl	–	116	220
C_3	Propyl	–	131	231
C_4	Butyl	–	110	212
C_5	Pentyl	–	146	197
C_6	Hexyl	63	104	192
C_7	Heptyl	87	101	174
C_8	Octyl	78	93	140
C_{10}	Decyl	89	–	125
C_{12}	Dodecyl	55	–	113
C_{14}	Tetradecyl	64	–	107
C_{16}	Hexadecyl	51	–	121

Note: Sm: Smectic; N: Nematic; I: Isotropic.

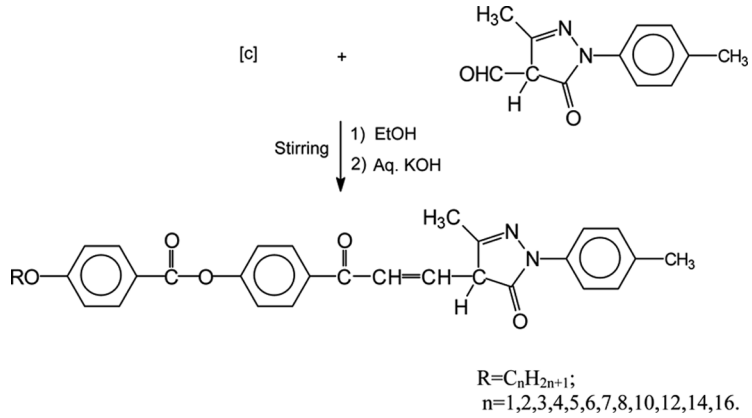
Data

Series-I Compound-C_{12}

Yield 70%. M.P.113°C. Found: C, 75.05; H, 7.21; N, 4.63 Calc. for $C_{38}H_{44}O_5N_2$; C, 75.01; H, 7.24; N, 4.61%. EI-MS m/z (rel.int %): 607 $(M\text{-}1)^+$ IR (KBr): Vmax/cm^{-1} 2850–2935 cm^{-1} (C–H aliphatic), 1776 cm^{-1} (C=O of ester), 1677 cm^{-1} (C=O of chalcone), 1606 cm^{-1} (C=C of vinyl gr. of chalcone), 1582 cm^{-1} (C=C of aromatic), 1255 cm^{-1} (C–O–C), 1056 cm^{-1} (C–O), ^{1}H NMR ($CDCl_3$): δ 0.89–0.93 ppm (CH_3), 1.28–1.82 ppm (CH_2), 2.38 ppm (–CH_3 of the pyrazolone ring) 4.01–4.05 ppm (OCH_2), 6.91–7.26 ppm (Ar–H), $\alpha = 8.06$ ppm, $\beta = 6.94$ ppm (R–CO–$C^{\alpha}H$=$C^{\beta}H$–R).

Series-II Synthesis of 4(4′-n-alkoxybenzoloxy) phenyl-propen-3-one(1-phenyl(4″-methyl)-3-methyl-2-pyrazolin-5-one)

Take 4-(4′-n-alkoxybenzoloxy) acetophenone (0.005 mole 1.6 gm) and 1-phenyl(4″-methyl)-3-methyl-4-formyl-2-pyrazolin-5-one in flat bottom flask containing 25 ml absolute alcohol and stirred it on a stirrer, till both the reactants were dissolved completely. Then cold 10% aq. KOH solution added dropwise and continues the stirring further for four hours. The reaction mixture was allowed to stand for overnight. The mixture was neutralized by cold dilute HCl up to pH (6.5–7.0). Then solid obtained was filtered, washed with water and dried. The crude products were purified by using column chromatography and crystallized from methanol. The melting points and transition temperatures for this homologous series are given in Table 2.



Data

Series-II Compound-C_{12}

Yield 86%. M.P.107°C. Found: C, 75.21; H, 7.35; N, 4.47 Calc. for $C_{39}H_{46}O_5N_2$; C, 75.24; H, 7.39; N, 4.50%. EI-MS m/z (rel.int %): 621 $(M\text{-}1)^+$ IR (KBr): Vmax/cm^{-1} 2850–2953 cm^{-1}(C-H aliphatic), 1708 cm^{-1} (C=O of ester), 1642 cm^{-1} (C=O of chalcone), 1607 cm^{-1} (C=C of vinyl gr. of chalcone), 1580 cm^{-1} (C=C of aromatic), 1260 cm^{-1} (C–O–C), 1063 cm^{-1} (C–O), ^1H NMR ($CDCl_3$): δ 1.01–1.06 ppm (CH_3), 1.41–1.87 ppm (CH_2), 2.45 ppm (CH_3 of the pyrazolone

TABLE 2 Transition Temperature of Series-II

		Transition temperature °C		
Compounds	R = n alkoxy	Sm	N	I
C_1	Methyl	–	124	224
C_2	Ethyl	–	119	218
C_3	Propyl	–	128	216
C_4	Butyl	–	115	204
C_5	Pentyl	–	136	207
C_6	Hexyl	73	143	195
C_7	Heptyl	81	105	168
C_8	Octyl	69	–	147
C_{10}	Decyl	86	–	113
C_{12}	Dodecyl	69	–	107
C_{14}	Tetradecyl	57	–	105
C_{16}	Hexadecyl	59	–	115

Note: Sm: Smectic; N: Nematic; I: Isotropic.

ring) 4.01–4.16 ppm (OCH_2), 7.01–7.39 ppm (Ar–H), $\alpha = 7.04$ ppm, $\beta = 8.19$ ppm (R–CO–$C^{\alpha}H$=$C^{\beta}H$–R).

Results and Discussion

In our recent work, 12 homologous from each of the two series, 4(4′-n-alkoxybenzoloxy) phenyl-propane-3-one(1-phenyl-3-methyl-2-pyrazoline-5-one) [series-I] and 4(4′-n-alkoxybenzoloxy) phenyl-propane-3-one(1-phenyl(4″-methyl)-3-methyl-2-pyrazoline-5-one) [series-II] have been synthesized having ester-chalcone central linkages containing terminal heterocyclic ring and their mesomorphic properties have studied. 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 temperature of both series are given in Tables 1 and 2. In series-I the compounds (C_1–C_5) exhibit enatiotropic nematic mesophase and (C_6–C_8) exhibit enantiotropic smectic and nematic mesophases. While compound $C_{10,}$ C_{12}, C_{14}, and C_{16} exhibit only

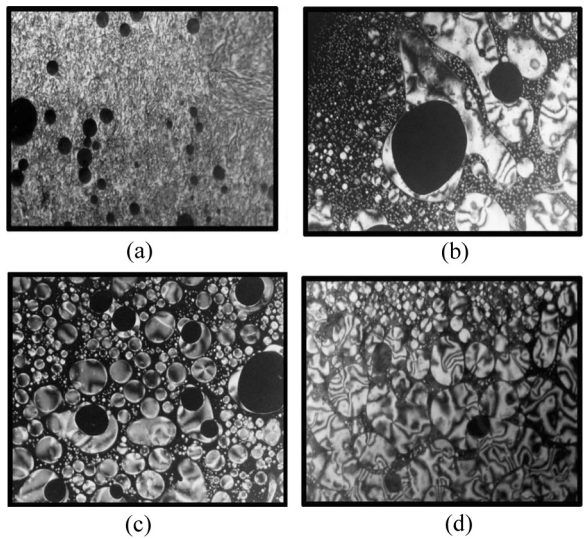


FIGURE 1 (a) Texture of SmC phase of C_7 of series-I at 87°C, (b) Schlieren texture of the Nematic phase of C_3 of series-I at 130°C on cooling, (c) Schlieren texture of the Nematic phase of C_5 of series-II at 136°C on cooling, and (d) Schlieren texture of the Nematic phase of C_6 of series-II at 143°C.

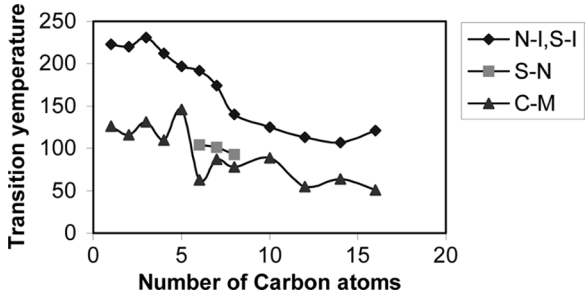


FIGURE 2 Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for series-I.

enantiotropic smectic mesophase. In second homologous series-II, the compound (C_1 to C_5) exhibit enatiotropic nematic mesophase C_6 and C_7 exhibit enantiotropic smectic and nematic phases. While compound C_8, C_{10}, C_{12}, C_{14}, and C_{16} exhibit only enantiotropic smectic mesophase. The texture of the series I & II are given in Figure 1. On cooling the isotropic liquid, small droplets appear, which coalesce to a classical schlieren (threaded) texture characteristic of the nematic phase. It is consistent with the assignment of each mesophase type using the classification systems reported by Gray and Goodby [40]. The plot of transition temperature against the number of carbon atom in the alkoxy chain are shown in Figures 2 and 3. In which Cr-M transition temperature, a regular alternation of the temperature occurring between homologous containing odd and even number carbon atoms in alkyl chain. In the present work N-I transition temperature for the series I and II of compounds do not behave in this way. This is because of the terminal 1,3,5-trisubstituted pyrazole ring plays some role either in

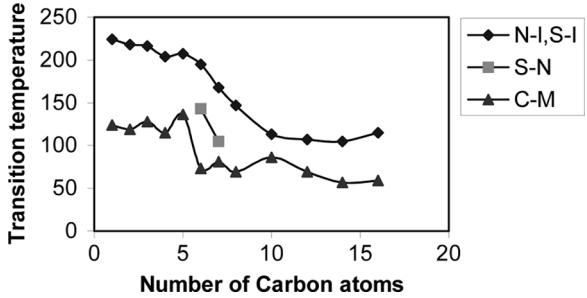


FIGURE 3 Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain for series-II.

packing of the molecule in crystal lattice or due to the stereochemistry of the molecule is not symmetrically linear.

The series also exhibits smectic properties, the Sm-N transition temperature fond to fall a number of carbon increase in alkyl chain. In series-I and II only two or three compound exhibit smectic and nematic both mesophases. Therefore, we could not give the trend for Sm-N curve.

In these both series Sm-I transition usually begins at about the decyl, dodecyl, hexadecyl and octadecyl ethers together with the N-I transition temperatures for the lower homologous contains an even number of carbon atoms in alkyl chain, constitute one smoothly falling mesorphic – isotropic transition temperatures. From the plot of transition temperatures against the number of carbon atoms (Figures 2 and 3), it can be noticed that Cr-M transition temperatures decreased with increase in the length of terminal alkoxy chain. This is in agreement with the observation reported for such homologous series [41].

Cr-M transition shows some what large transition temperature changes for $n = 5$ to $n = 6$. This could be explained as, a common pattern of behavior is that the lower homologues are nematic, the middle members exhibit a smectic mesophase followed by nematic mesophase and the long chain members, i.e., C_{10}, C_{12}, C_{14}, C_{16} are purely smectic as observed in Tables 2 and 3.

The Cr-M for $n = 5$ in series-I is observed at 146°C. The increment of each methylene unit brings about regular changes in the transition temperature of the series as reported by Gray [41]. For shorter chain compounds C_5, the separation of the aromatic nuclei is at a minimum and terminal cohesive forces are strongest and predominant. As nematic phase is highly disordered which required high energy to overcome such forces, therefore, C_5 compound exhibit nematic phase at high temperature.

TABLE 3 DSC Data for Series-I and II Compounds

Series	Compound	Transition	Peak temp. (Microscopic temp.) °C	ΔH Jg^{-1}	ΔS $Jg^{-1}K^{-1}$
I	C_6	Cr-Sm	61.66 (63)	11.31	0.033
		Sm-N	101.91 (104)	29.87	0.079
		N-I	190.28 (192)	35.31	0.076
	C_{12}	Cr-Sm	53.72 (55)	148.70	0.455
		Sm-I	111.60 (113)	0.833	0.002
II	C_6	Cr-Sm	72.80 (73)	48.51	0.140
		Sm-N	146.73 (143)	2.767	0.006
		N-I	197.01 (195)	2.368	0.005
	C_{10}	Cr-Sm	87.47 (86)	80.34	0.222
		Sm-I	112.35 (113)	7.618	0.019

However, in the middle members e.g., n = 6 (C_6), the smectic properties appear, because the alkyl chain is increasing the lateral cohesive forces and the molecules may maintain themselves in the layer arrangement. The smectic phase is highly ordered–one compared to nematic mesophase, which requires lower energy to observe smectic behavior. Therefore, smectic mesophase observed in compound n = 6 (C_6), at 63°C. Therefore, such large differences in Cr-N and Cr-Sm temperature have been observed in present two series.

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. Data are recorded in Table 3. Which helps the further confirm the mesophase type. Table 3 shows the phase transition temperatures, associated enthalpy (ΔH) and molar entropy (ΔS) for compound of series-I (C_6, C_{12}) and series-II (C_6, C_{10}). Enthalpy values of the various transitions agree well with the existing related literature values [42]. The DSC curves of representative compounds are shown in Figures 4 to 7. Microscopic transition temperature values are almost similar to DSC data.

Table 4 shows the comparison of Sm-N and N-I transition temperature of compound n = 6, series I, and structurally related compounds n = 6, series II. The Sm-N mesophase range of compound n = 6 (series-I) is lower by 29°C, respectively, when compared with

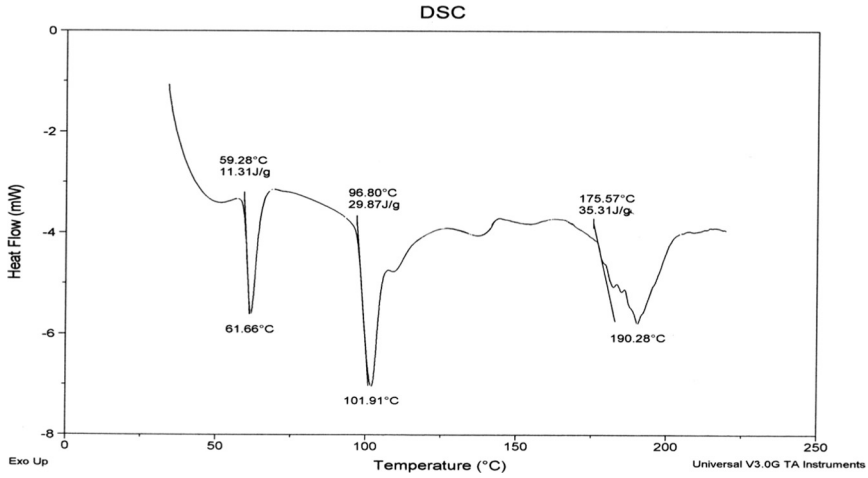


FIGURE 4 DSC Curves of the compound C_6 of series-I.

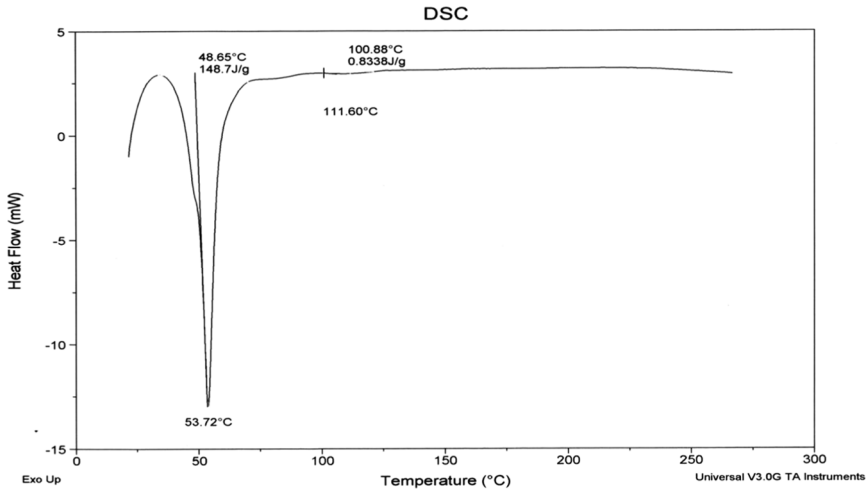


FIGURE 5 DSC Curves of the compound C_{12} of series-II.

compound n = 6 (series-II). The N-I transition temperature of compound, series-I, is higher by 36°C, respectively, when compared with compound 6 (series-II).

Although the mesomorphic phase stability is greater in series-II compounds than that of series I, this is because of presence of $-CH_3$

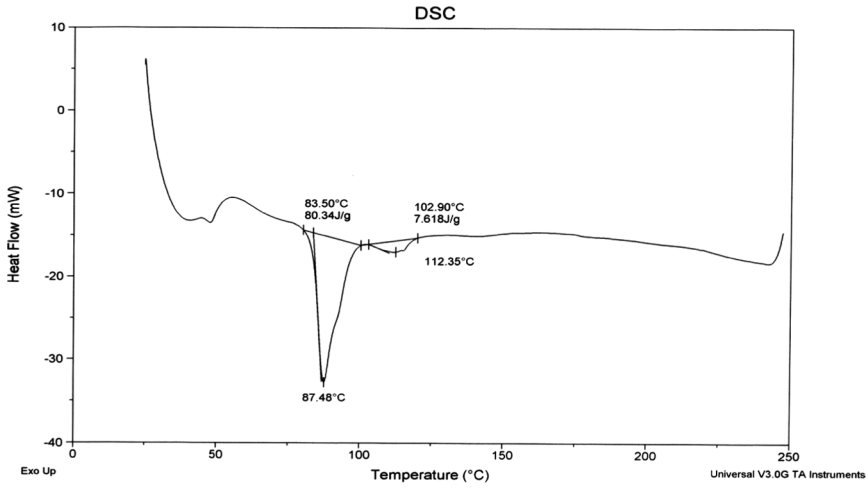


FIGURE 6 DSC Curves of the compound C_6 of series-II.

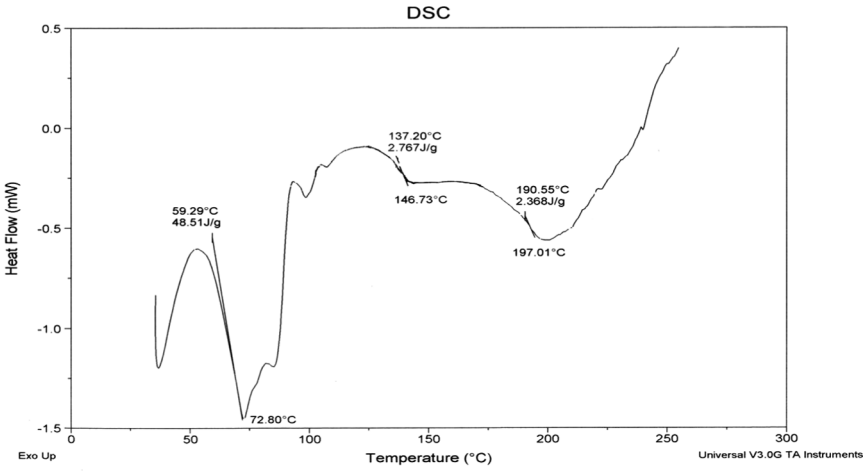


FIGURE 7 DSC Curves of the compound C_{10} of series-II.

group at pera- position on 1-phyenyl ring (which is attached to pyrazoline ring) produce a steric hindrance. The order of group efficiency derived by Dave and Dewar [43,44] based on the magnitude of the groups slope value. The decreasing order of the group efficiency is in the decreasing order of group polarizability. The increase in N-I transition temperature with increasing alkoxy chain in compounds of series-I can be explained by increasing overall polarizability of the molecule.

The FT-IR spectra of the mesomorphic ester-chalcone central linkage exhibit different vibration modes corresponding to the stretching and bending mode of different functional groups present in the molecule. The FT-IR spectra of representative compound of homologous series-I and Series-II are shown in Figures 8 and 9. IR spectra of ester-chalcone central linkage show strong or medium bands around 1706 $cm^{-1}$and 1620 cm^{-1}, 1686 cm^{-1} attributed to υ(C=O) of ester

TABLE 4 Different Transition Temperatures and Range of Mesophases Observed in Series I and II

Series	Compound	SmC	N	I	Sm-N mesophase range (°C)	N-I mesophase range (°C)
I	n = 6	63	104	192	41	88
II	n = 6	73	143	195	70	52

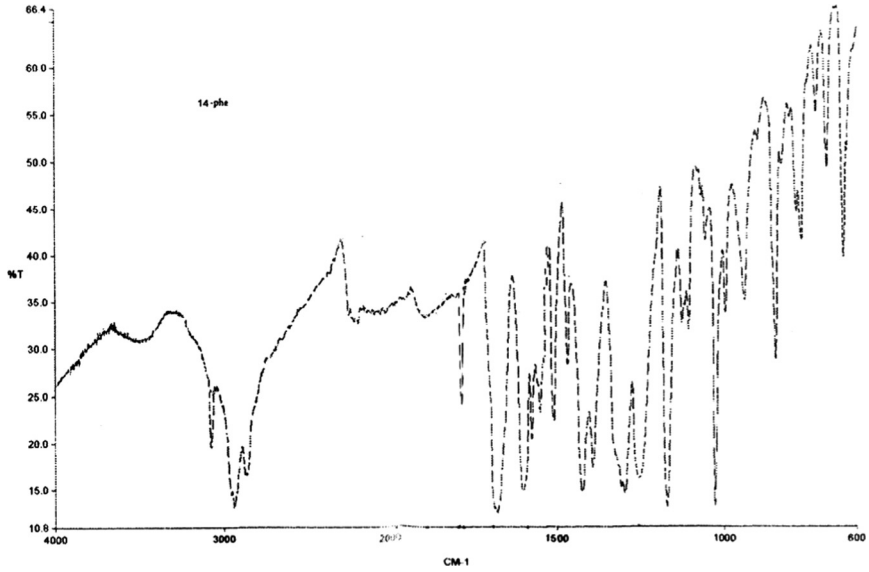


FIGURE 8 IR Spectra of C_{12} of series-I.

group chalcone and pyrazoline ring respecting strong band appeared at around 1606 cm^{-1} is attributed to υ(C=C) vinyl group of chalcone.

In the present case all the spectra of mesomorphic compound show two sharp bands at around 2919 cm^{-1} and 2849 cm^{-1} are due to

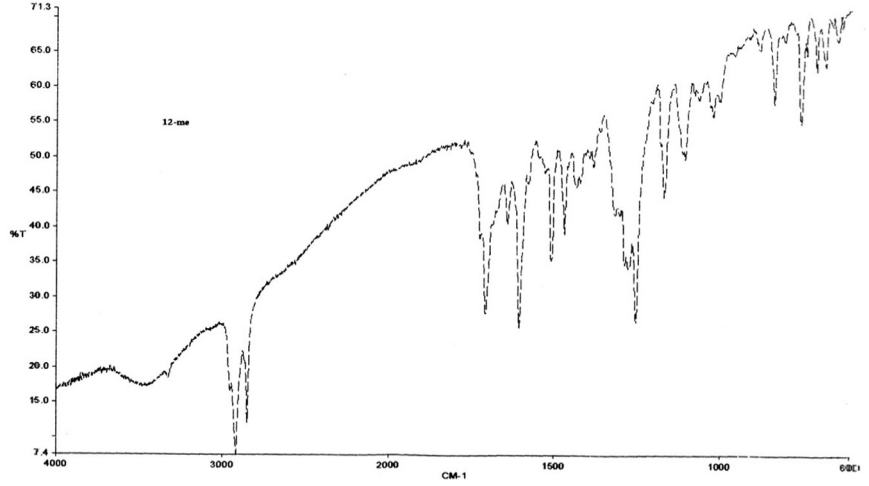


FIGURE 9 IR Spectra of C_{12} of series-II.

aliphatic υ(C–H) symmetrical and asymmetrical stretching vibration of $-CH_3$ and $-CH_2$ groups of n-alkyl chain. Another two bands are also observed 1465 cm^{-1} and 1391 cm^{-1} are due to aliphatic $-CH_3$ and $-CH_2$ deformation vibrations. The sharp and medium band observed at around 1578–1513 cm^{-1} region due to aromatic ν(C=C) stretching. The weak band observed at around 631–763 cm^{-1} is due to rocking vibration of $-CH_2$ groups of alkyl chain. Out of plane deformation of ring hydrogen band is establishing the position of substituent on aromatic nuclei is well known. Although correlation can often be useful in analysis of spectra of the mesomorphic compounds but their performance is variable. Infrared spectra of the present class of the compounds often show long wavelength regions crowded with a large number of bands of similar intensities, and it is difficult to know which bands belongs to this class. Further more compounds often contain more than one aromatic nucleus and are often substituted with strongly electronegative groups, such as alkoxy, which tend to upsets the correlations.

^{1}H-NMR spectra of representative compounds are shown in Figures 10 and 11 and the chemical shifts (δ, ppm) are noted. The ^{1}H NMR spectra of ester-chalcone central linkage type of compounds exhibited six signals present in spectra, indicating six type of different enviroment proton present in these type of compound. The first signal

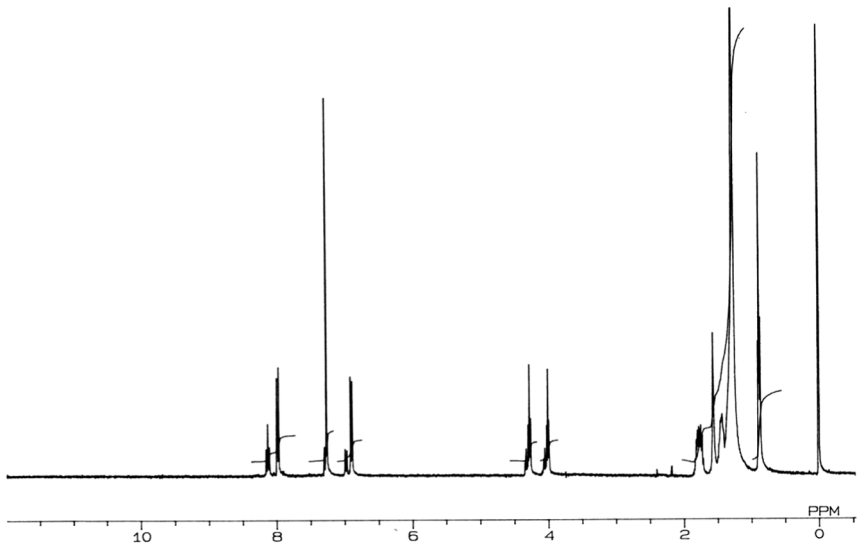


FIGURE 10 ^{1}H NMR spectra of C_6 of series-I.

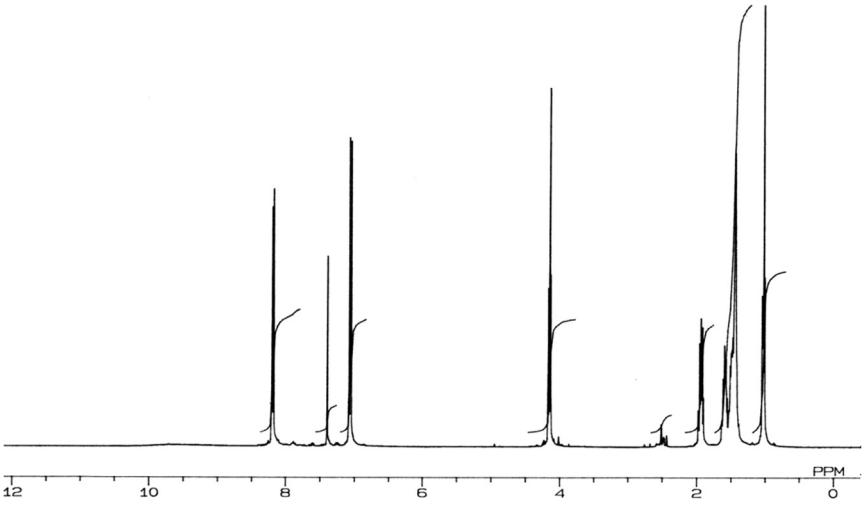


FIGURE 11 ^{1}H NMR spectra of C_7 of series-II.

observed between δ 0.91–0.95 ppm, which is sharp and triplet corresponding terminal methyl proton of straight chain of n- alkoxy group. The multiplate signals observed between δ 1.28–1.82 ppm are due to methylene ($-CH_2$) proton of straight alkyl chain of n-alkoxy group and δ 2.38 ppm $-CH_3$ proton of the pyrazolone ring. The triplet signal observed between δ 4.09–4.15 ppm is attributed to $-OCH_2$ proton of n-alkoxy group like to phenyl ring. The multiplate signal observed between δ 6.88–8.13 ppm are corresponding to substituted phenyl rings. The 'α' and 'β' types of proton in the central linkage [$COC^{\alpha}H = C^{\beta}H$] sharp singlet at δ 8.14 ppm and δ 6.91 ppm respectively.

The mass spectra of series-I and series-II are shown in Figures 12 and 13. The m/z ratios obtained from the spectra of each samples are matched with route for mass fragmentation and abundances in the mass spectrum. The molecular wt. obtained from the mass spectra are almost equivalent to the calculated value of the compounds.

In series-I and II there are two linkages, one is ester and other is chalcone. Mesogens with different central linkages are known [41]. 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. –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 [9]. Nguyen *et al.* [45] have reported that a

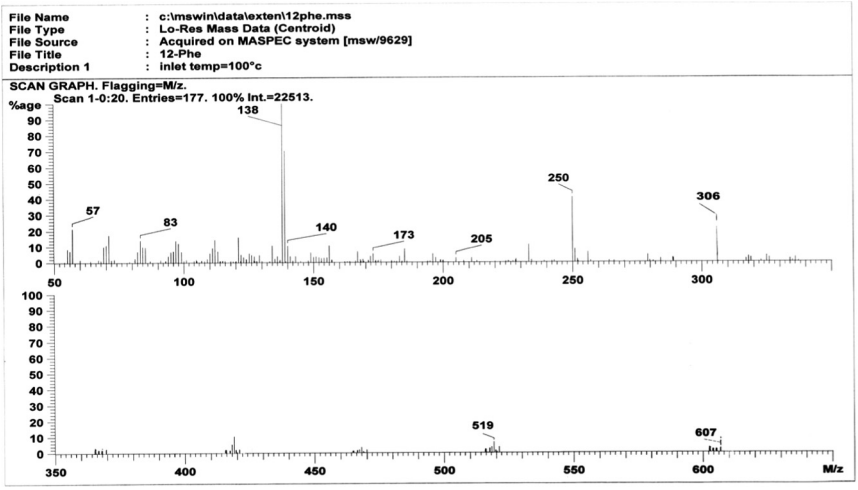


FIGURE 12 Mass Spectra of C_{12} of Series-I.

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. But when molecule having two linkage in which one is chalcone and other is –CH=N or –COO– it becomes conducive to the mesomorphism [9,11,32].

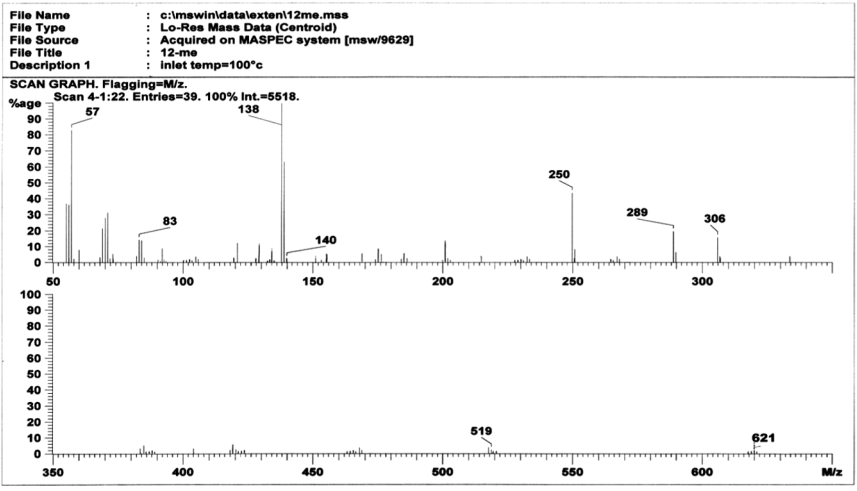
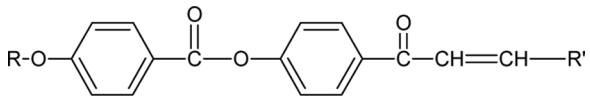


FIGURE 13 Mass Spectra of C_{12} of Series-II.

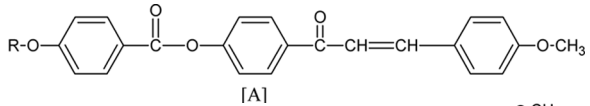
INFLUENCE OF THE TERMINAL GROUP

In this paper we have just presented compounds with the general structure

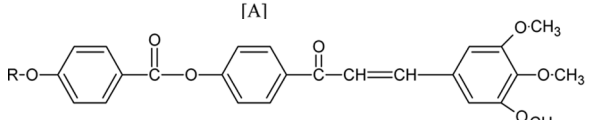


Where R′ = 1,3,5-trisubstituted pyrazole ring.

In our previous paper [32] we presented two homologous series A & B as following structure,



[A]



[B]

In order to have better understanding we have synthesized the present two new homologous series containing substituted pyrazolone ring as a terminal group.

On comparision of the present pyrazole ring with previous benzene ring we have observed that the transition temperature range of the present homologous series containing pyrazole as a terminal group becomes higher than the previous one and also mesophase stability of these series becomes higher than simple benzene analogous due to the introduction of pyrazole ring as a terminal group. Because pyrazole ring having highly delocalized system as a result of it shows very high thermal stability compare to benzene analogous.

CONCLUSION

In this article we have presented the synthesis and characterization of mesogenic two homologous series of 1,3,5-trisustituted pyrazole having ester-chalcone linkage. All the compounds of the series exhibit enantiotropic mesomorphism. The mesophase range of present series-I is higher than those of structurally related compounds of series-II that has been attributed to the high polarizability of the molecule because the bulky group reduced the polarity of molecule and decreases the mesophase stability of compound. Both series show nematic mesophase

and higher homologues show smectic mesophase. The above studies on a limited number of heterocyclic mesogens strongly suggests that dominant effect of the hetero atom is to produce change in conjugative interactions within the molecule which effect factors such as polarizability and dipolarity. Intermolecular effects produced by the lone pair of electrons are apparently, in certain case.

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