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B. T. Thaker^a, D. B. Solanki^a, B. S. Patel^a, A. D. Vansadia^a & Y. T. Dhimmar^a

^a Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat, India

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Synthesis and Characterization of Novel Liquid Crystalline Compounds Containing a Pyrazole Ring

B. T. THAKER,* D. B. SOLANKI, B. S. PATEL,
A. D. VANSADIA, AND Y. T. DHIMMAR

Department of Chemistry, Veer Narmad South Gujarat University, Surat,
Gujarat, India

We report the synthesis and liquid crystalline properties of two new homologous series of calamitic liquid crystals containing a substituted pyrazole ring within the central core of 4-(4-n-alkoxybenzoyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazole-3-one and 4-(4-n-alkoxybenzoyl)-5-methyl-2-(4-methylphenyl)-2,4-dihydro-3H-pyrazole-3-one and characterization of the compounds done by elemental analysis, FT-IR, ¹H-NMR, and mass spectrometry. Phase transition behavior of these compounds was assessed with the help of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Both series show liquid crystalline properties from the heptyl homologue. Middle members of Series-A and Series-B exhibit nematogenic behavior and higher homologues exhibit only smectogenic behavior.

Keywords Calamitic; mesomorphic; nematic; pyrazole; smectic phase

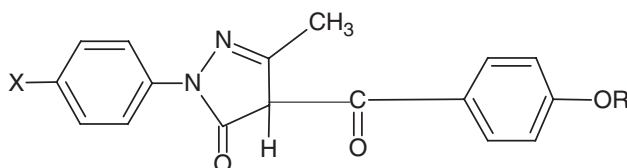
1. Introduction

The detailed study of many mesogenic homologous series has helped to establish some general rules for the effect of chemical constitution in the nematogenic and smectogenic compounds [1]. There have been a variety of compounds reported with liquid crystalline properties, but heterocyclic moieties are less explored compared to homocyclic moieties [2]. Furthermore, heteroatoms offer the possibility of several modes of co-ordination. Thermotropic liquid crystals are of great technological importance [3–10]. Many series of liquid crystalline compounds contain heterocyclic groups have been synthesized because of their interesting properties [11]. Various mesomorphic heterocyclic compounds have been reported [12–16]. Heterocyclic compounds provide a great synthetic and structural versatility due to the number of potential substitution positions.

Terminal substituents and potentially mesogenic systems play an important role. Pyrazole has proven to be very efficient as a starting material for various kinds of mesogenic compounds. Some of these groups are highly polar and others are mildly polar [17]. The five-membered pyrazole ring has aromatic character [18], planar conformation and a high dipole moment perpendicular to the principle molecular axis. Indeed, some 3,5-disubstituted pyrazoles and 4-substituted pyrazoles have demonstrated their ability to show liquid crystalline behavior both as themselves [19–23] and with metal co-ordination [24–27]. Calamitic

*Address correspondence to B. T. Thaker, Department of Chemistry, Veer Narmad South Gujarat University, Surat-395007, Gujarat, India. E-mail: btthaker1@yahoo.co.in

mesomorphism has also been described in a number of pyrazoles derived from 4-alkoxy substituted aromatic β -diketones [28, 29]. These compounds exhibit classical nematic and smectic-A and C mesophases despite the fact that the type of mesophase depends on the nature and length of the terminal chain. It has been shown that the short chains give rise to rather narrow mesophase ranges or no mesophases at all; therefore, the intermediate and long chains are of great interest. In an earlier study, we described the preparation and mesomorphic study of pyrazolone derivatives as a terminal moiety [30]. Here, we present the synthesis of new liquid crystalline compounds derived from a 4-*n*-alkoxy substituted aromatic β -diketone with pyrazolone derivatives of different chain length and the study of their thermal behavior. The general structure of the compounds is given in Scheme 1.



Where, X= H or CH₃; R= C_nH_{2n+1}, *n* = 2 to 8, 10, 12, 14, 16, 18

Scheme 1.

2. Experimental

2.1 Reagents

For the synthesis of compounds of the homologous series, raw materials were purchased from standard chemical suppliers. 4-Hydroxy benzoic acid and alkyl bromides were purchased from Venus Chemicals. 5-Methyl-2-phenyl-2,4-dihydro-3H-pyrazole-3-one and 5-methyl-2-(4-methylphenyl)-2,4-dihydro-3H-pyrazole were obtained from Nutan Dye Chem, Pandesara, Surat, and used without further purification. Acetone, ethanol, methanol, 1,4-dioxane, HCl, KOH, Ca(OH)₂, NaOH, and thionyl chloride were used after distillation and purified using the standard method described in literature [31].

2.2 Synthesis

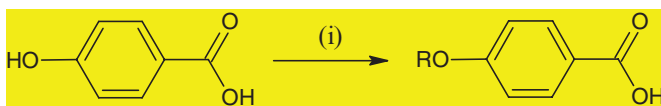
2.2.1. Synthesis of 4-*n*-alkoxy Benzoic Acids. 4-*n*-Alkoxy benzoic acids were prepared as reported by Dave and Vora method [32, 33]. The melting point (m.p.) of each compound was consistent with the reported value.

2.2.2. Synthesis of 4-*n*-alkoxy Benzoyl Chlorides. 4-*n*-Alkoxy benzoyl chlorides were prepared by a reported method [34]. The m.p. of each compound was consistent with the reported value.

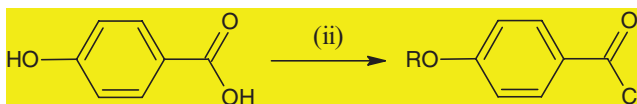
2.2.3. Synthesis of 4-(4-alkoxybenzoyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (Series-A). 5-Methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (0.098 mol) was taken in dioxane (100 ml). A solution was obtained by gentle heating and stirring. Calcium hydroxide (10.0 g, 0.14 mol) was then added. The reaction mixture became paste. The 4-*n*-alkoxy benzoyl chloride (0.1 mol) was mixed or dissolved in 50 ml of dioxane, and was added drop wise. The reaction mixture was then refluxed with stirring for 2 hr; during this period,

the bright yellow complex formed initially turned yellowish brown. The complex was then decomposed by pouring the reaction mixture into chilled dil. HCl solution (500 ml, 3 N). A yellowish brown paste separated first, solidified after 2–3 min, was collected over a sintered glass funnel, and was washed with distilled water until the washings were colorless and dried in air. The desired compounds obtained were crystallized from ethanol.

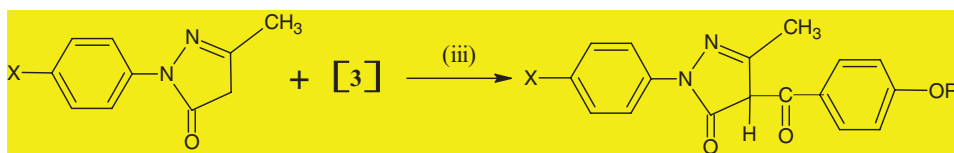
Reaction Scheme:



[1] [2]



[2] [3]



R = C_nH_{2n+1}, n = 2 to 8, 10, 12, 14, 16, 18

X = H [Series-A];

X = CH₃ [Series-B]

Reaction reagents and conditions:

- (i) KOH, RBr, MeOH or EtOH, reflux, 8–10 hr,
- (ii) SOCl₂, reflux, 3 hr,
- (iii) Ca(OH)₂, 1,4-dioxane, reflux, 3–4 hr.

The purity of the compounds has been checked by TLC. It shows one spot, indicating a single compound. All the compounds were purified by column chromatography using silica gel (100–200 mesh) and ethyl acetate: petroleum ether (7:3) solvent system.

Series-B was similarly prepared by the above method. Here, we used 5-methyl-2-(4-methylphenyl)-2,4-dihydro-3H-pyrazole-3-one instead of 5-methyl-2-phenyl-2,4-dihydro-3H-pyrazole-3-one.

2.3 Characterization

Micro analysis was performed with a Carlo Erba 1108 C, H, N microanalyzer from RSIC (Regional Sophisticated Instrumentation Centre), CDRI (Central Drugs Research Institute), Lucknow. Infrared (IR) spectra for all the compounds were obtained using a Perkin–Elmer

model Specrum BX, FT-IR Spectrophotometer in KBr disc in the region 4000–400 cm^{-1} . $^1\text{H-NMR}$ spectra were recorded on a BRUKER AVANCE II 400 NMR Spectrometer in CDCl_3 solutions at SAIF (Sophisticated Analytical Instrumentation Facility), Punjab University, Chandigarh. Mass fragmentation was determined by using GC-MS Mass Spectrometer at SAIF (Sophisticated Analytical Instrumentation Facility), IIT Madras, Chennai. The textures of the mesophase were studied with a Leitz Laboulux polarizing microscope provided with a Kofter heating stage at Applied Chemistry Department, M S University of Baroda, Vadodra. Thermal properties of the compounds were investigated by Differential Scanning Calorimetry (DSC) using a Mettler M-3 thermobalance (Switzerland) with a microprocessor TA-3000 at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere at SICART, V.V. Nagar.

2.3.1 Series-A, Compound A_{10} , Molecular Formula: $\text{C}_{27}\text{H}_{34}\text{O}_3\text{N}_2$. Elemental analysis: calculated C 74.65%; H 7.83%; N 6.45%, found C 74.62%; H 7.80%; N 6.41%.

FT-IR (KBr pellet): 2852, 2919 cm^{-1} ($-\text{CH}_3$ stretching), 1606 cm^{-1} ($\text{C}=\text{N}$ stretching of pyrazolone), 1700 cm^{-1} ($\text{C}=\text{O}$ stretching of acyl group), 1672 cm^{-1} ($\text{C}=\text{O}$ stretching of pyrazolone in keto form), 1579, 1469, 1431 cm^{-1} ($\text{C}=\text{C}$ ring stretching of pyrazolone), 1306 cm^{-1} ($\text{C}-\text{N}$ stretching of pyrazolone), 1037 and 1254 cm^{-1} ($\text{C}-\text{O}-\text{C}$ symmetric and assymmetric stretching respectively).

$^1\text{H-NMR}$ (CDCl_3): 0.86–0.89 ppm (t, 3H, CH_3 of aliphatic chain), 1.24–1.84 ppm [m, ($-\text{CH}_2$) n - of alkoxy chain], 4.00–4.03 ppm (t, 2H, CH_2O of alkoxy chain), 3.90 ppm (s, 1H, CH proton of pyrazolone at 4-position), 2.20 ppm (s, 3H, CH_3 attached to pyrazolone ring at 5-position), 6.91–8.05 ppm (m, Ar-H), **Mass (GC-MS):** Molecular ion peak: m/z –436 ($\text{M} + 2$) $^+$.

2.3.2 Series-B, Compound B_{14} , Molecular Formula: $\text{C}_{32}\text{H}_{44}\text{O}_3\text{N}_2$. Elemental analysis: calculated C 76.19%; H 8.73%; N 5.55%, found C 76.15%; H 8.70%; N 5.52%.

FT-IR (KBr pellet): 2851, 2918 cm^{-1} ($-\text{CH}_3$ stretching), 1606 cm^{-1} ($\text{C}=\text{N}$ stretching of pyrazolone), 1700 cm^{-1} ($\text{C}=\text{O}$ stretching of acyl group), 1671 cm^{-1} ($\text{C}=\text{O}$ stretching of pyrazolone in keto form), 1580, 1469, 1437 cm^{-1} ($\text{C}=\text{C}$ ring stretching of pyrazolone), 1308 cm^{-1} ($\text{C}-\text{N}$ stretching of pyrazolone), 1020 and 1258 cm^{-1} ($\text{C}-\text{O}-\text{C}$ symmetric and assymmetric stretching respectively).

$^1\text{H-NMR}$ (CDCl_3): 0.86–0.89 ppm (t, 3H, CH_3 of aliphatic chain), 1.26–1.84 ppm [m, ($-\text{CH}_2$) n - of alkoxy chain], 4.00–4.03 ppm (t, 2H, CH_2O of alkoxy chain), 3.88 ppm (s, 1H, CH proton of pyrazolone at 4-position), 2.19 ppm (s, 3H, CH_3 attached pyrazolone ring at 5-position), 2.35 ppm (s, 3H, CH_3 of substituted phenyl ring at 2-position on pyrazolone), 6.88–8.05 ppm (m, Ar-H), **Mass (GC-MS):** Molecular ion peak: m/z –504 (M) $^+$.

3. Results and Discussion

In the present study, 12 homologues from the series, 4-(4- n -alkoxybenzoyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-ones (**Series-A**), 4-(4- n -alkoxybenzoyl)-5-methyl-2-(4-methylphenyl)-2,4-dihydro-3H-pyrazol-3-ones (**Series-B**) were synthesized as per synthetic routes given in the scheme and their mesomorphic properties are studied. These compounds have been subjected to elemental analysis. The elemental analysis data agree with theoretical values as per expected structure. The FT-IR spectra of the representative compounds (A_{10} , B_{14}) are shown in Fig. 1. $^1\text{H-NMR}$ spectra of representative compounds are shown in Fig. 2. The mass spectra of these compounds are shown in Fig. 3. The m/z

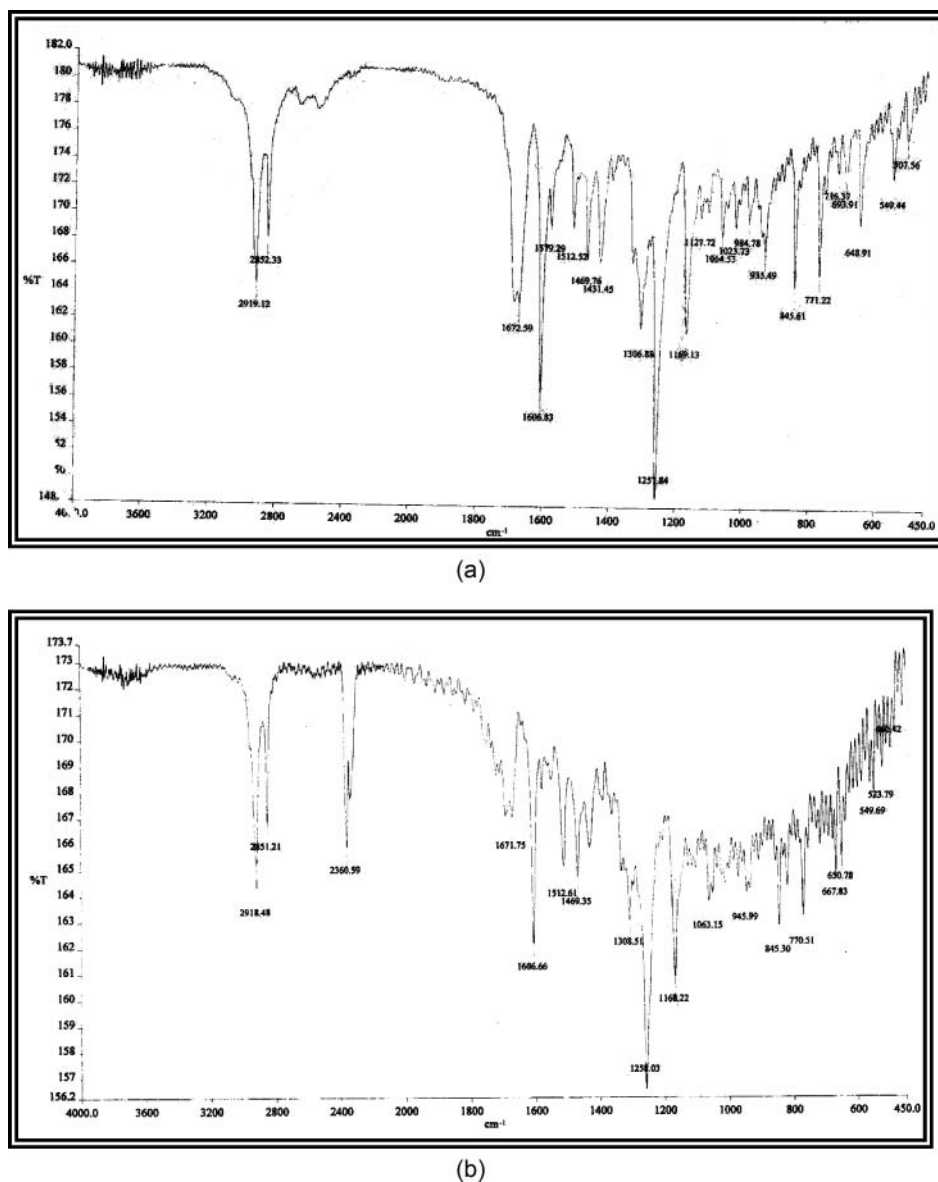


Figure 1. (a) FT-IR for compound A_{10} (Series-A). (b) FT-IR for compound B_{14} (Series-B).

ratios obtained from the spectra of a representative sample is matched with the molecular ion peak.

3.1 Thermal and Phase Behavior

Mesomorphic properties and thermal stability for the new homologous series-A and B were determined by hot stage polarizing microscopy and DSC and are given in Tables 1 and 2. The plot of the temperature versus number of carbon atoms is given in Fig. 4. Phase

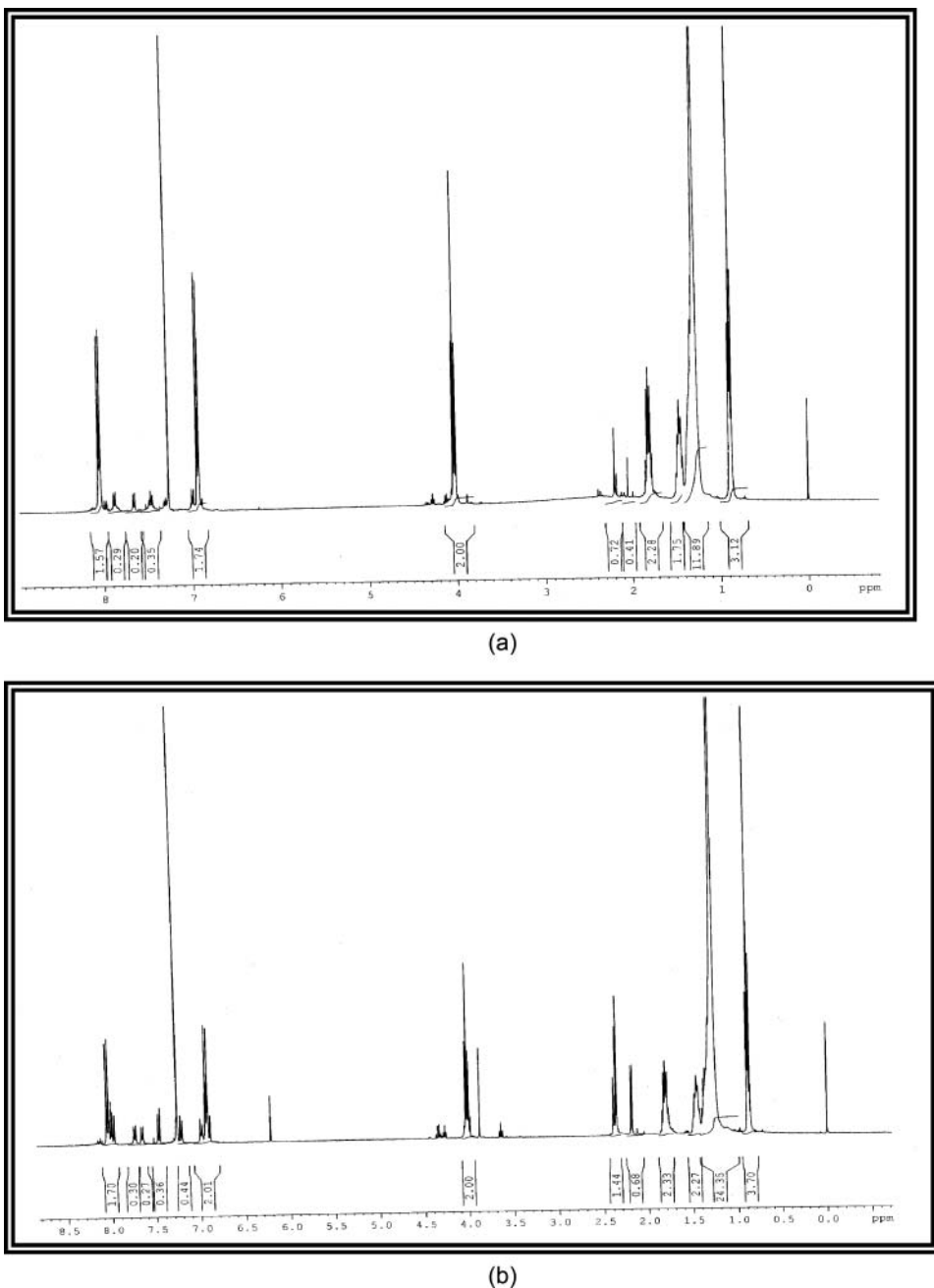
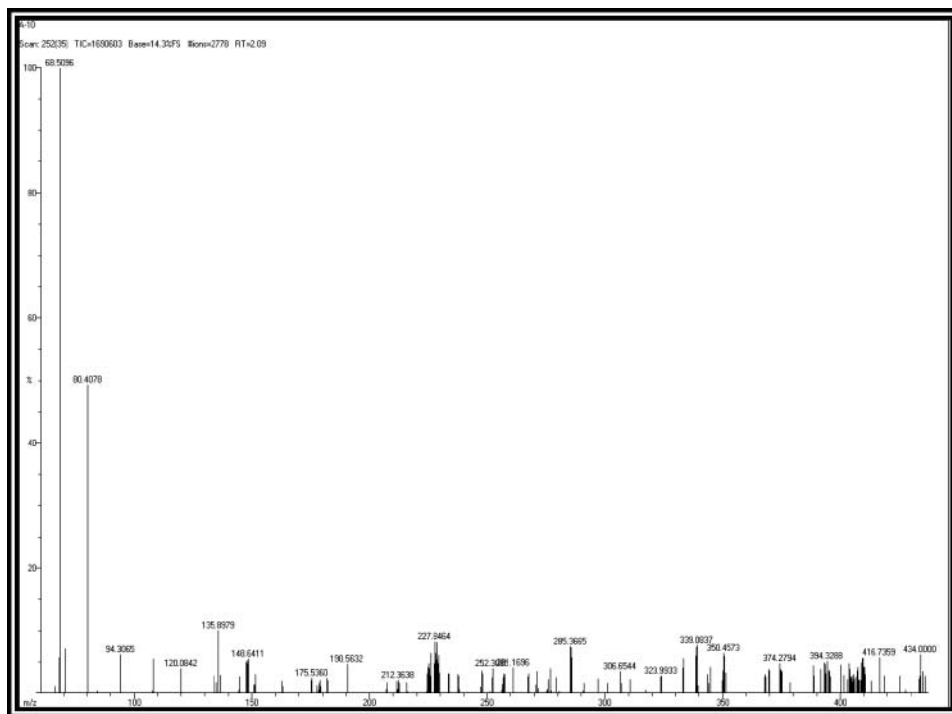
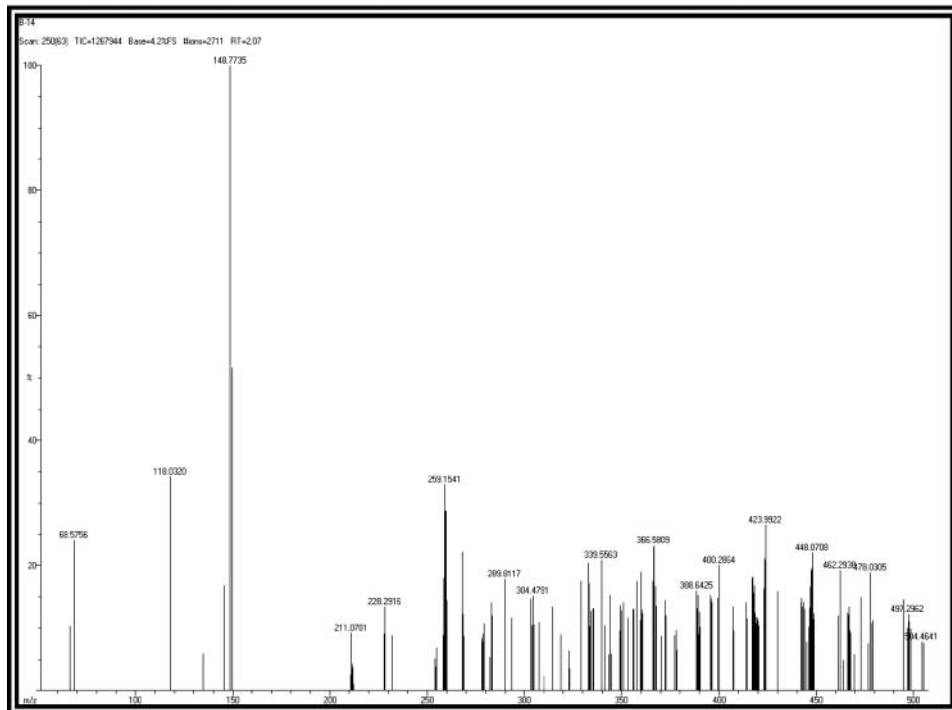


Figure 2. (a) ^1H NMR for compound A_{10} (Series-A). (b) ^1H NMR for compound B_{14} (Series-B).

identification was based on the optical textures, and the magnitude of the isotropization on enthalpies is consistent with the assignment of each mesophase type, using the classification system reported by Sackmann and Demus [35], Gray and Goodby [36]. The transition temperatures obtained from polarizing microscopy were compared with those from DSC. The DSC curves of the different compounds are shown in Fig. 5 and their comparative

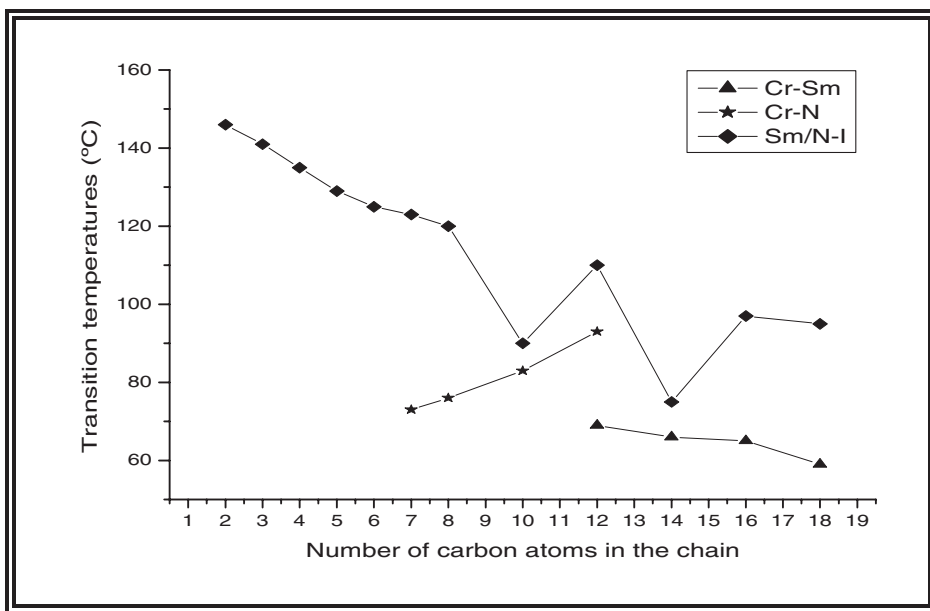


(a)

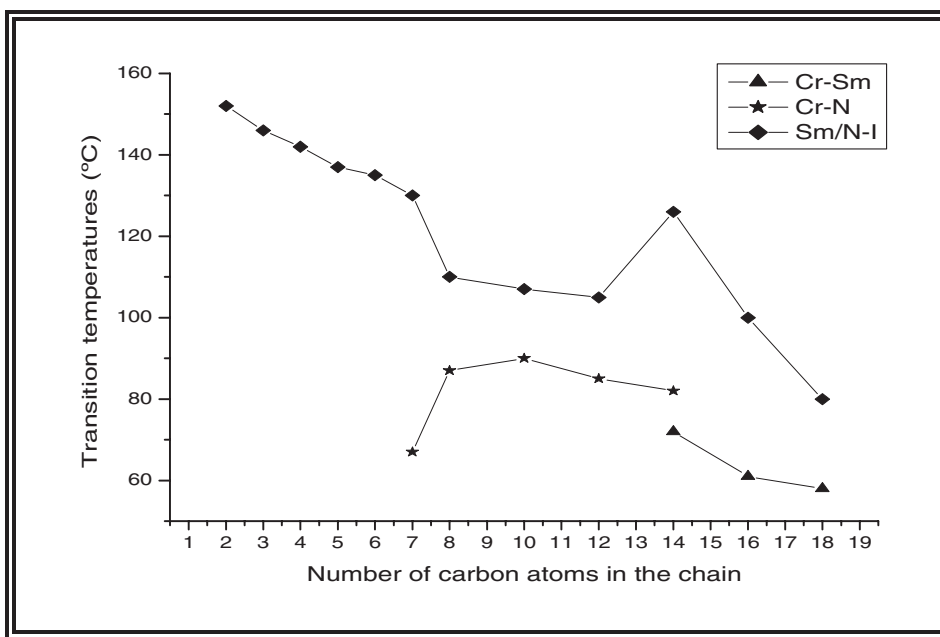


(b)

Figure 3. (a) Mass for compound A₁₀ (Series-A). (b) Mass for compound B₁₄ (Series-B).



(a)



(b)

Figure 4. (a) Transition temperature graph for Series-A. (b) Transition temperature graph for Series-B.

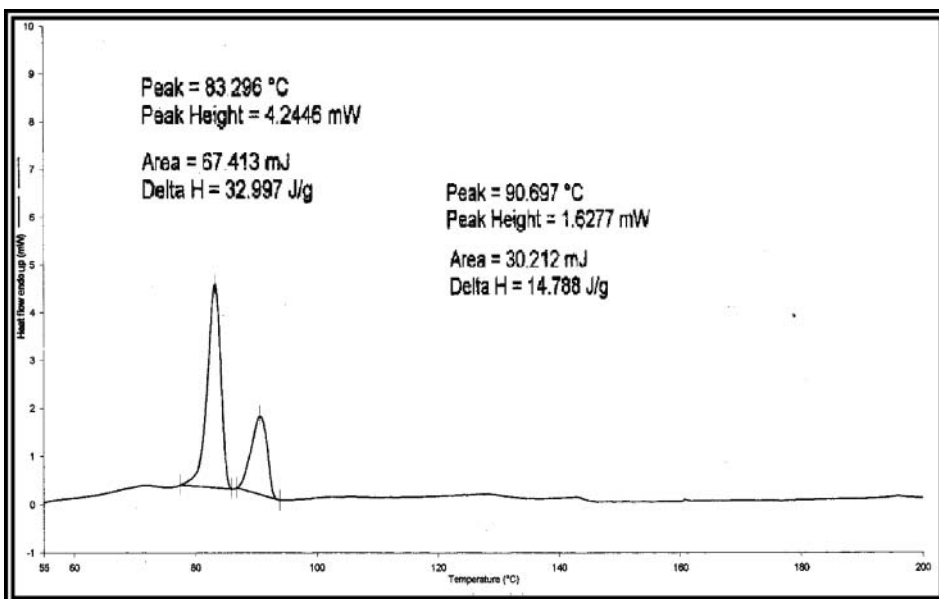
Table 1. Transition temperature data of series-A

Code no.	Transition temperature in °C		
	Sm	N	I
A ₂	—	—	146
A ₃	—	—	141
A ₄	—	—	135
A ₅	—	—	129
A ₆	—	—	125
A ₇	—	73	123
A ₈	—	76	120
A ₁₀	—	83	90
A ₁₂	69	93	110
A ₁₄	66	—	75
A ₁₆	65	—	97
A ₁₈	59	—	95

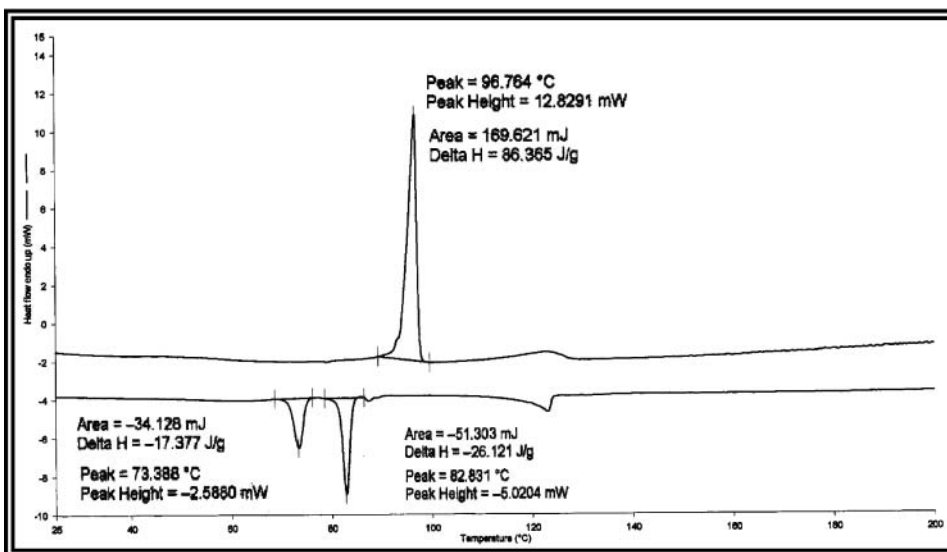
parameters are given in Table 3. The phase transitions obtained from DSC almost match those from optical polarizing microscope. In order to understand better why the pyrazolone derivatives are mesogenic with alkoxy terminal phenyl ring, we must remember that the most favorable geometry for a molecule showing calamitic mesophases is linear. All of the molecules described here have a nonlinear core, the deviation from linearity being variable depending on the type of compound [37]. In the present work compound 1 to 6 of both the series are not mesomorphic. This can be accounted for by considering the short terminal chain, which does not provide the linearity and flexibility to the molecular core [38]. In series-A, compounds A₇, A₈, A₁₀ show an enantiotropic nematic phase. The smectic mesophase starts from compound A₁₂; this compound shows both smectic and

Table 2. Transition temperature data of series-B

Code no.	Transition temperature in °C		
	Sm	N	I
B ₂	—	—	152
B ₃	—	—	146
B ₄	—	—	142
B ₅	—	—	137
B ₆	—	—	135
B ₇	—	67	130
B ₈	—	87	110
B ₁₀	—	90	107
B ₁₂	—	85	105
B ₁₄	72	82	126
B ₁₆	61	—	100
B ₁₈	58	—	80



(a)



(b)

Figure 5. (a) DSC curve of compound A₁₀ (Series-A). (b) DSC curve of compound B₁₄ (Series-B).

nematic mesophases. It shows a smectic A phase and thread like nematic mesophase. After, the A₁₂ compound, compounds A₁₄ to A₁₈ only show a smectic C mesophase, which is due to increasing the length of terminal alkoxy chain. The increase in the length of alkoxy terminal chain disrupts the nematic mesomorphic stability [39]. Compounds A₁₄ to A₁₈ only show a smectic mesophase, which indicates that pyrazolone compounds tend toward higher levels of structural order, perhaps due to the higher molecular symmetry and

Table 3. Transition temperature and DSC data of Series-A and B

Code no.	Transition	Peak temp. (Microscopic temp.) °C	$\Delta H \text{ Jg}^{-1}$	$\Delta S \text{ Jg}^{-1} \text{ K}^{-1}$
A ₁₀	Cr–N	83.29 (83)	32.997	0.0926
	N–I	90.69 (90)	14.788	0.0406
A ₁₄	Cr–Sm	65.00 (66)	—	—
	Sm–I	74.80 (75)	72.006	0.2070
B ₁₄	Cr–Sm	73.38 (72)	–17.377	–0.2367
	Sm–N	82.83 (82)	–26.121	–0.3153
	N–I	126 (126)	—	—
B ₁₆	Cr–Sm	61.23 (61)	26.084	0.0780
	Sm–I	100.10 (100)	48.992	0.1313

increased molecular rigidity. In series-B, compounds B₇ to B₁₂ show a nematic phase while B₁₄ shows a smectic as well as a nematic phase. B₁₆ and B₁₈ show only a smectic phase.

The mesomorphic phase stability is greater in series-A than in series-B, in which CH₃ group at para-position on the 1-phenyl ring (which is attached to pyrazoline ring). This is because alkyl substitution gives more stability than –H and also the alkyl group is more conducive to mesomorphism. This stability order may be related to a difference in linearity and subsequent packing of the molecules in the crystal lattice. The group efficiency derived by Dave and Dewar [40, 41] is in the decreasing order of group polarizability.

The two homologous series made it possible to observe the effects of structural changes on mesomorphic behavior in a novel structural system.

4. Conclusion

Pyrazolone heterocyclic rings with a terminal alkoxy phenyl ring unit appear to increase molecular rigidity. In the entire series compounds having alkoxy chain C₁ to C₇ do not exhibit liquid crystallinity; this is because the short carbon chain is not conducive to mesomorphism, which is exhibited only in long carbon chain C₈ to C₁₈ compounds. The presence of lone pairs of electrons on the two nitrogen atoms of the pyrazolone ring enhances the polarization of the molecules giving more conjugation, which increase the dipole moment of the compound. This fact would explain the high fusion and transition temperatures, but as the length of the alkoxy terminal chain is increased, the transition temperatures are decreased.

Acknowledgment

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