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New Liquid Crystalline Compound with 1, 3, 5- Trisubstituted Pyrazole in the Mesogenic Core: Synthesis, Characterization and Mesomorphic Behavior

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Two new homologous series of 1,3,5-tri substituted pyrazole derivatives derived from 1-X 3-methyl 5-pyrazolone (X = phenyl or tollyl), p- amino acetophenone and alkoxy aldehyde have been synthesized, viz. 4-(4′-n-alkoxy propenoyl) imine-4″-(1-phenyl-3-methyl 5-one) pyrazole and 4-(4′-n-alkoxy propenoyl) imine-4″-(1-tollyl-3-methyl 5-one)pyrazole. The compounds of both the series have been characterized by elemental analyses, FT-IR, ^{1}H-NMR, Mass spectrometry methods. Their liquid crystalline properties have been investigated by optical polarizing microscopy and DSC studies. All the derivatives are mesomorphic in nature showing nematic phase. The use of phenyl and tollyl substituted pyrazole core has a very dramatic effect on the melting clearing points. The mesomorphic behavior has been analyzed in terms of structure property relationship.

Keywords: mesophase; nematic phase; schiff base – chalcone; thermal behavior; tri substituted pyrazole

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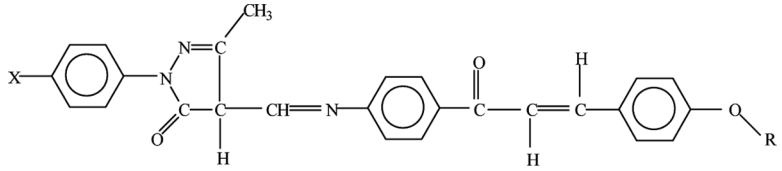
INTRODUCTION

The detailed study of many mesogenic homologous series has helped to evolve 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 less explored, compared to homocyclic moieties [2]. 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. Indeed, some 3, 5-disubstituted pyrazoles and 4-substituted pyrazoles have demonstrated their ability to show liquid crystalline behavior [3–8]. Pyrazole has proven to be very efficient as starting materials for various kind of mesogenic compounds. Terminal substitution's play a vital role in imparting liquid crystallinity to potentially mesogenic group like H, OH, I, Br, Cl , Me, OMe, OR and NO_2 occupy the *p p′* position of the central core. Some of these group are highly polar and others mildly polar [9]. We considered it of interest to investigate some structural modification that would allow a grater understanding of the relationship between the structure and appearance of mesomorphic behavior in imine-chalcone compound. Here we present the synthesis of new compounds derived from pyrazolone with a rode shape by substitution of the 1, 3, 5-position of the pyrazole with several moieties of different chain length with chalcone as a bridging group having the general structure (I).



(I)

Where, X=H or CH_3; R=C_nH_{2n+1}, n=1 to 8, 10, 12, 14, 16.

EXPERIMENTAL

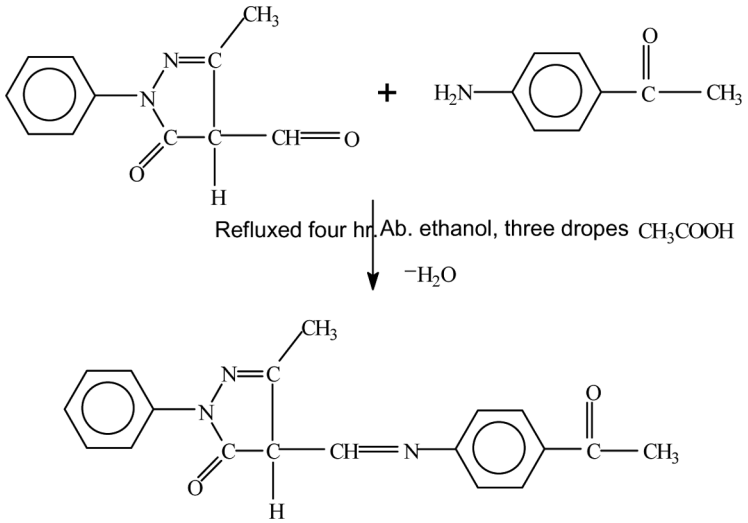
Materials and Methods

All chemicals were reagent grade and used as purchased without further purification.

Synthesis of alkoxy benzaldehyde. Alkoxy benzaldehyde has been synthesized by the reported method [10].

Synthesis of 4(1-phenyl-3-methyl-5-one) pyrazolone amino)-acetophenone

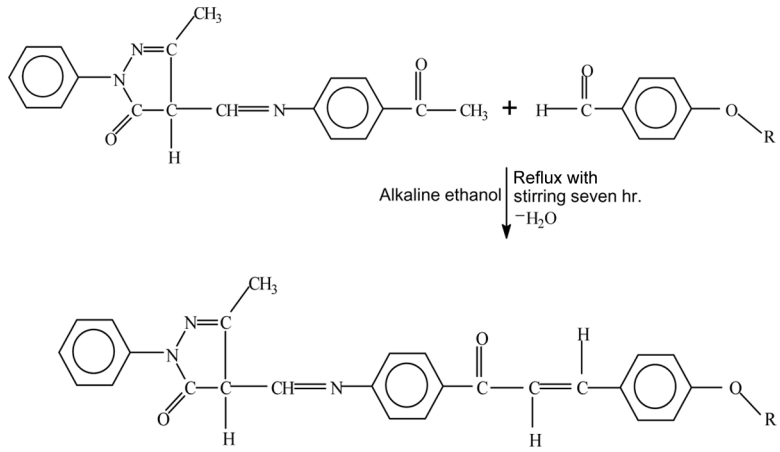
A mixture of 1 mmol (1-phenyl-3-methyl 5-one) pyrazole and 1 mmol of 4-amino acetophenone and three drops of acetic acid in 10 ml of absolute ethanol was heated at reflux for 4 h. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The solid was collected and recrystallized from ethanol.



Synthesis of 4-(4′-n-alkoxy propenoyl)imine-4″-(1- phenyl-3-methyl 5-one) pyrazole

1 mmol of 4-(1-phenyl-3-methyl 5-one) pyrazolone amino) – acetophenone and 1 mmol of n- alkoxy benzaldehyde were dissolved in mixed solvents such as ethanol (80 ml) with 10% of aq. NaOH (180 ml). This reaction mixture was heated at 80°C for 7hr. and the mixture was kept at room temperature overnight. An aqueous solution of HCl was added to the mixture, and then yellow precipitate was obtained. The precipitate was washed with water until a neutral aqueous solution was obtained. The solid was washed with ethanol, filtered and dried under vacuum at 60°C. The yellow solid was

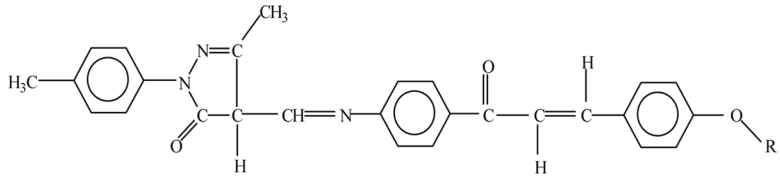
purified by recrystallisation from acetone. The product was obtained in 52% yield.



Series-SA

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

Series SB have been similarly prepared by above method. Here, we used 4-(1-tollyl-3-methyl 5-one) pyrazole instead of 4-(1-phenyl-3-methyl 5-one) pyrazole.



Series-SB

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

Micro analysis was performed with a Carlo Erba 1108 C, H, N microanalyser from R.S.I.C. (Regional Sophisticated Instrumentation Centre), C.D.R.I. (Central Drugs Research Institute), Lucknow. Infrared spectra for all the compounds were obtained using a Perkin-Elmer RX1 FT-IR spectrophotometer in the 400–4000 cm^{-1} range. ^{1}H-NMR spectra were recorded on a Jeol FX-300 MHz spectrometer in $CDCl_3$ solutions from I.I.T., Madras. Mass spectra were obtained using FIRMEGAN Mat-8230 mass spectrometer from S.A.I.F. (Sophisticated Analytical Instrumentation Facility), Chandigarh. The textures of the mesophase were studied with Letiz Labourlux

polarizing microscope provides 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 Calorimeter (DSC) Mettler TA-4000 system with a heating rate of 10°C/min. at Garda Chemicals, Panoli.

RESULTS AND DISCUSSION

In present study, 12 homologues from each of the two series, 4-(4′-n-alkoxy propenoyl) imine-4″-(1-phenyl-3-methyl 5-one) pyrazole and 4-(4′-n-alkoxy propenoyl) imine-4″-(1-tollyl-3-methyl 5-one) pyrazole, are synthesized and characterized.

The characterization of the compounds of both the series have been done by elemental analyses. The physical data of both the series compounds are listed in Table 1 and 2. The elemental analyses are good agreements with proposed structure of the compounds.

The characteristic IR- frequencies of the mesogenic compounds are given in Table-3 and the IR spectra of representative compounds are shown in Figure 1 to 3. ^{1}H-NMR spectral data of the representative compounds are given in Table 4 and their spectra shown in Figure 4 and 5. The mass spectrum of compound (SA-12) is shown in Figure 6, which shows the molecular mass peak $[M\text{-}1]^+$ at 596 m/e, whereas molecular mass of the compound is 597. Which indicates the compound is pure and single compound. From the above data the mesogenic compound has structure (I) as shown earlier.

TABLE 1 Analytical Data of Series SA Compounds

Code No.	Molecular Formula	M.Wt. (g/m)	M.P.°C	Yield %	Analysis % Found (Calculated) C	H	N
SA_1	$C_{27}H_{23}N_3O_3$	437	185	74	71.38 (71.3)	4.81 (4.85)	6.13 (6.16)
SA_2	$C_{28}H_{25}N_3O_3$	451	183	78	71.76 (71.7)	5.15 (5.13)	5.95 (5.98)
SA_3	$C_{29}H_{27}N_3O_3$	465	180	76	72.15 (72.18)	5.33 (5.38)	5.85 (5.81)
SA_4	$C_{30}H_{29}N_3O_3$	479	175	72	72.54 (72.57)	5.67 (5.63)	5.66 (5.64)
SA_5	$C_{31}H_{31}N_3O_3$	493	163	78	72.98 (72.93)	5.84 (5.87)	5.44 (5.49)
SA_6	$C_{32}H_{33}N_3O_3$	507	159	75	73.24 (73.27)	6.15 (6.10)	5.30 (5.33)
SA_7	$C_{33}H_{35}N_3O_3$	521	142	80	73.65 (73.61)	6.35 (6.32)	5.23 (5.20)
SA_8	$C_{34}H_{37}N_3O_3$	535	139	72	73.94 (73.90)	6.56 (6.52)	5.04 (5.07)
SA_{10}	$C_{36}H_{41}N_3O_3$	563	137	78	74.44 (74.47)	6.84 (6.89)	4.81 (4.83)
SA_{12}	$C_{38}H_{45}N_3O_3$	597	132	70	75.05 (75.01)	7.21 (7.24)	4.63 (4.61)
SA_{14}	$C_{40}H_{49}N_3O_3$	619	125	72	75.49 (75.47)	7.52 (7.55)	4.42 (4.40)
SA_{16}	$C_{42}H_{53}N_3O_3$	647	120	74	75.94 (75.91)	7.85 (7.83)	4.24 (4.22)

TABLE 2 Analytical Data of Series SB Compounds

Code No.	Molecular Formula	M.Wt. (g/m)	M.P.°C	Yield %	Analysis % Found (Calculated) C	H	N
SB_1	$C_{28}H_{25}N_3O_3$	551	175	80	71.75 (71.78)	5.10 (5.13)	5.95 (5.98)
SB_2	$C_{29}H_{27}N_3O_3$	465	169	76	72.14 (72.19)	5.53 (5.59)	5.84 (5.81)
SB_3	$C_{30}H_{29}N_3O_3$	479	165	78	72.54 (72.57)	5.67 (5.69)	5.61 (5.65)
SB_4	$C_{31}H_{31}N_3O_3$	493	158	82	72.91 (72.93)	5.85 (5.88)	5.45 (5.48)
SB_5	$C_{32}H_{33}N_3O_3$	507	151	74	73.29 (73.28)	6.14 (6.11)	5.33 (5.38)
SB_6	$C_{33}H_{35}N_3O_3$	521	145	78	73.61 (73.61)	6.35 (6.33)	5.21 (5.20)
SB_7	$C_{34}H_{37}N_3O_3$	535	137	84	73.94 (73.90)	6.54 (6.52)	5.07 (5.01)
SB_8	$C_{35}H_{39}N_3O_3$	549	132	82	74.18 (74.20)	6.75 (6.71)	4.93 (4.95)
SB_{10}	$C_{37}H_{43}N_3O_3$	577	124	88	74.71 (74.74)	7.03 (7.01)	4.73 (4.72)
SB_{12}	$C_{39}H_{47}N_3O_3$	605	119	86	75.21 (75.24)	7.35 (7.39)	4.47 (4.50)
SB_{14}	$C_{41}H_{51}N_3O_3$	633	116	83	75.66 (75.69)	7.66 (7.69)	4.33 (4.31)
SB_{16}	$C_{43}H_{55}N_3O_3$	661	108	82	76.15 (76.11)	7.94 (7.96)	4.10 (4.13)

Thermal Study and Phase Behavior

Mesomorphic properties and thermal stability for the two new homologous series-A and B were measured by hot stage polarizing

TABLE 3 Characteristic IR Frequencies for the Series-SA and SB Compounds

Functional group	Bond and it's mode of vibration	Intensity		Position of absorption band (cm^{-1}) SA_{10}	SB_{14}
$-CH_3-$ CH_2(Aliphatic)– CH Aldihydic	C–H (str.)	S	s	2870–2937	2870–2935
–CH=N (Schiff base)	CH=N (str.)	S	s	1608	1610
–C=O Chalcone	C=O (str.)	M	m	1675	1677
–C=C	–C=C– (str.)	W	w	1577	1582
–C=C Vinyl group of Chalcone	–C=C– (str.)	S	s	1604	1606
C–H in CH_3	C–H– (ben.)	M	m	1392	1392
C–H in CH_3	C–H– (ben.)	S	s	1425	1422
$-CH_2$	C–H– (ben.)	S	s	1468	1470
–C–O–C	–C–O–C (str.)	S	s	1257	1255
–C–O–C	–C–O (str.)	M	m	1056	1056
$-(CH_2)_n-$	C–H (roc.)	M	m	727	716
	(C–H) out of plane bending	S	s	846,771	846,771

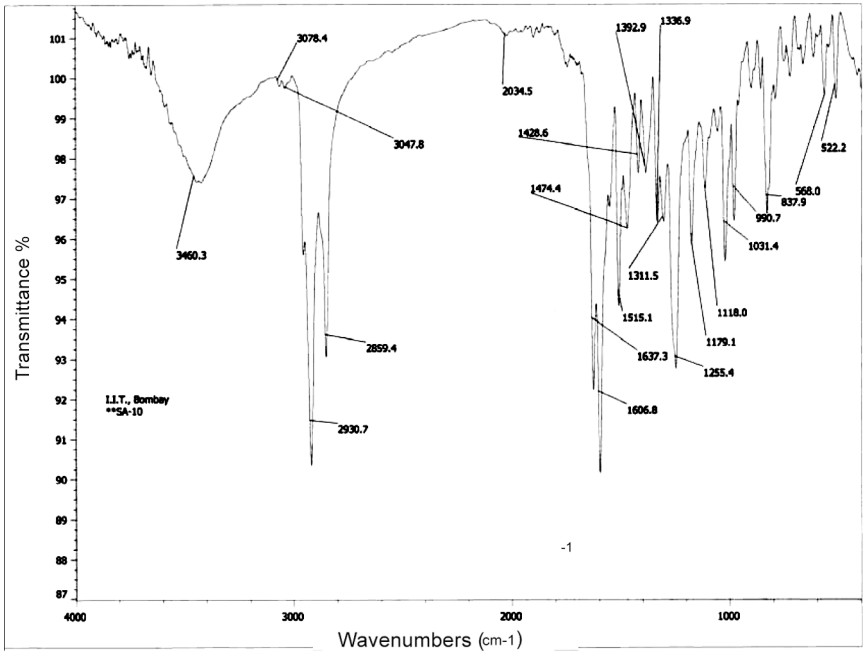


FIGURE 1 IR spectra of compound SA-10.

microscopy. The transition temperature of the compounds of series A and B are given in Table 5 and 6. Data for both the analogous compounds of both series are included for comparison. The entire compound prepared show mesomorphic behavior with nematic phase. This gives that both the series are nematogenic. It indicates in such compounds the lateral cohesion forces are very weak as a result of smectic phase will not appear even at higher number of homologous compound. Nash and Gray [11] have assessed same effects of nematic properties arising from such changes in terminal group of the type 4-MeO·C_6H_4·C_6H_4·N: CH·R-4′ (where R is the phenyl, pyridyl or certain five membered heterocyclic rings).

It has been observed that compounds of series SA show a wide mesomorphic temperature range then that of series SB compounds. The plots of transition temperature *Vs*. number of carbon atom for homologues series SA and SB are shown in Figure 7 and 8 respectively. Both the plots exhibit odd – even effect for the N-I transition temperature range [12]. Although the mesomorphic phase stability is greater in series SA compounds than that of series SB, this is

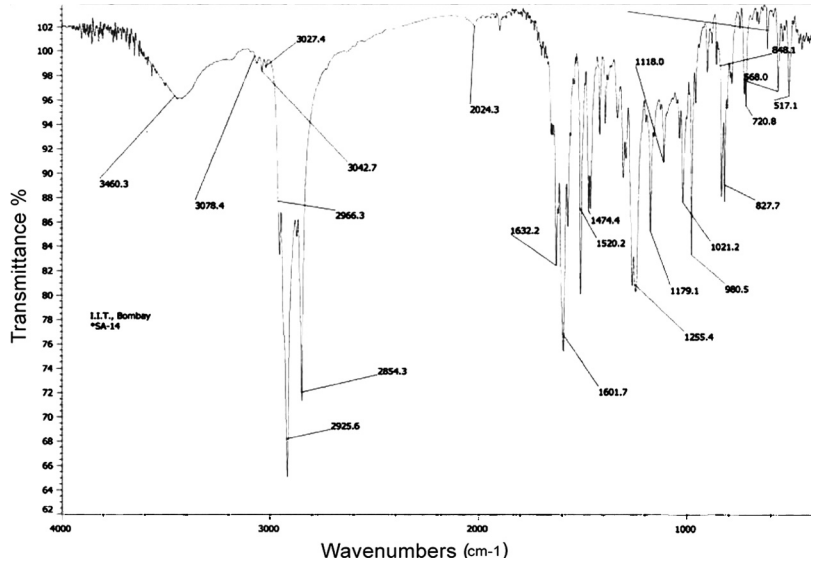


FIGURE 2 IR spectra of compound SA-14.

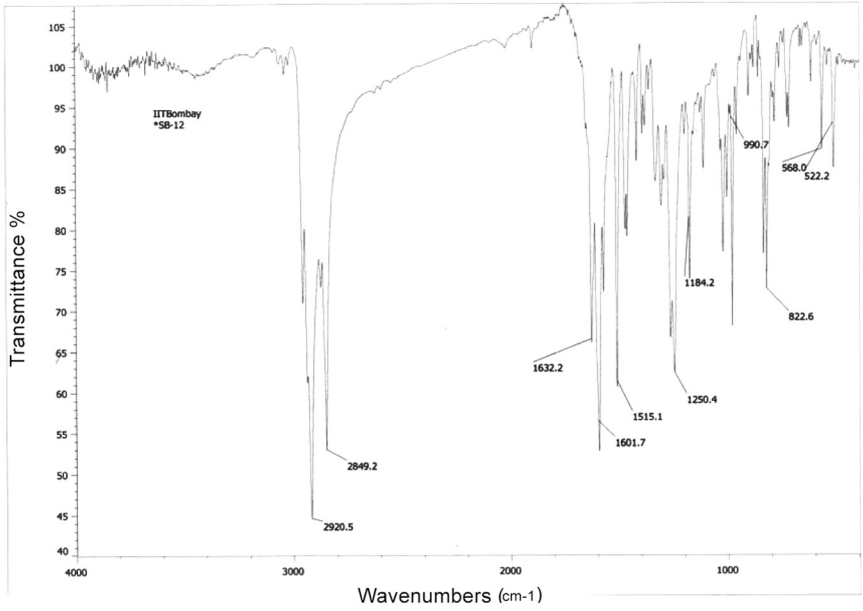


FIGURE 3 IR spectra of compound SB-16.

TABLE 4 ^{1}H-NMR Spectral Data for the Representative Compounds of Series-SA and SB

Code No.	$-CH_3$ Proton of aliphatic chain	$-CH_2$ Proton of aliphatic chain	$-CH_2O$ Proton of alkoxy	Phenyl multiple	R–CO–CH=CH–R α β	$-CH_3$ Proton of pyrazoline	$-CH_3$ Proton of phenyl substituted pyrazoline ring	–CH=N Proton of schiff base
SA14	0.89–0.93 (t)	1.28–1.82 (m)	4.01–4.05 (t)	6.91–7.26 (m)	$\alpha = 8.06$ $\beta = 6.94$	2.38	–	8.56
SB16	1.01–1.06 (t)	1.41–1.97 (m)	4.01–4.16 (t)	7.01–7.39 (m)	$\beta = 7.07$ $\alpha = 8.19$	2.35	2.45	8.45

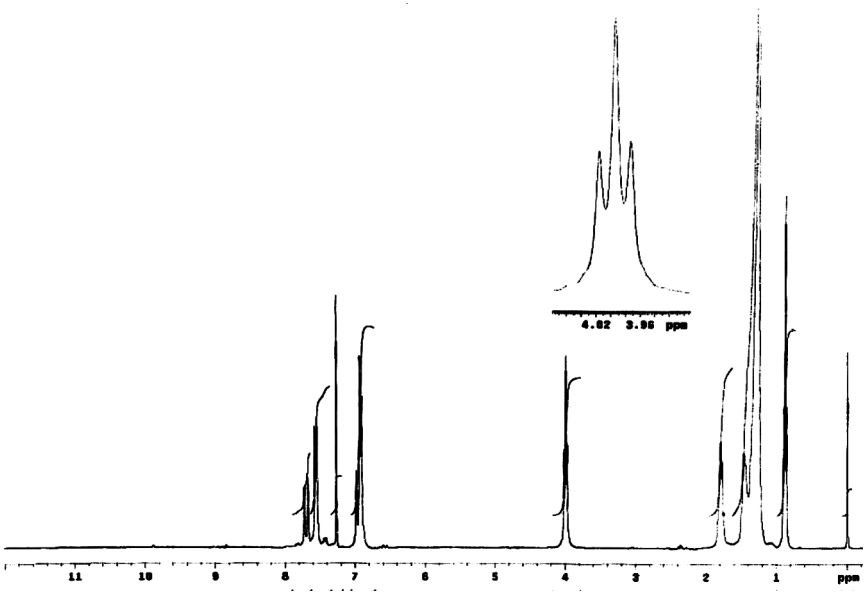


FIGURE 4 ^{1}H-NMR spectra of compound SA-14.

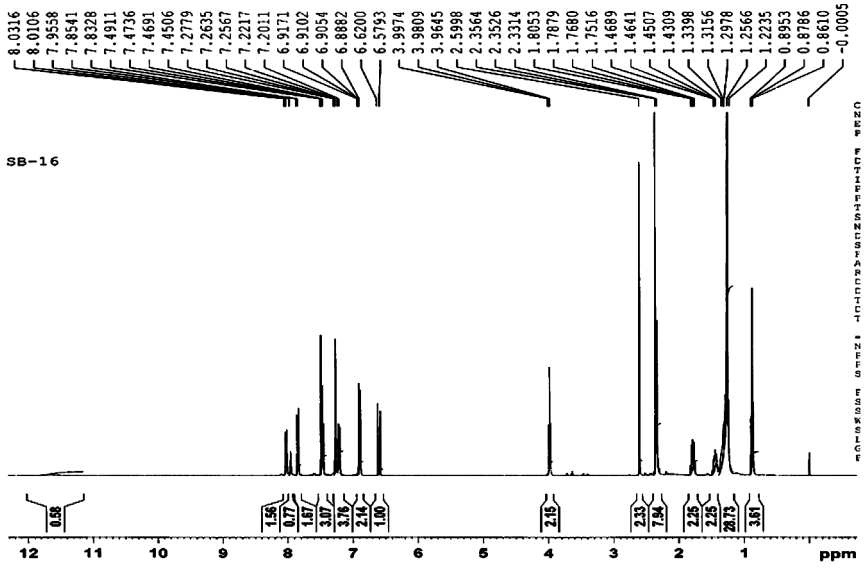


FIGURE 5 ^{1}H-NMR spectra of compound SB-16.

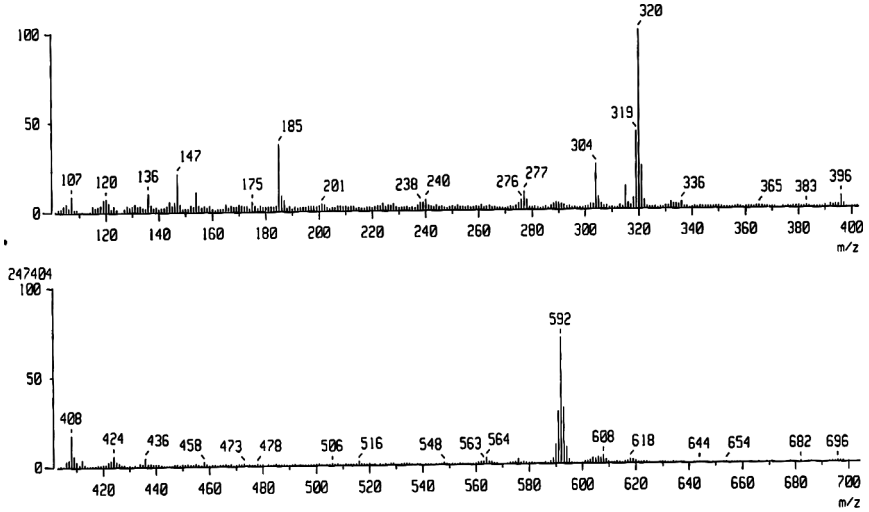


FIGURE 6 Mass spectra of SA-12.

because of presence of $-CH_3$ 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 [13,14] based on the magnitude of the groups slope value. The decreasing order of the

TABLE 5 Transition Temperature Data of Series-SA

		Transition temperature °C		
Code no.	R = n Alkoxy	Sm	N	I
SA-1	Methyl	–	–	185
SA-2	Ethyl	–	140	170
SA-3	Propyl	–	122	167
SA-4	Butyl	–	128	154
SA-5	Pentyl	–	117	142
SA-6	Hexyl	–	101	130
SA-7	Heptyl	–	105	123
SA-8	Octyl	–	110	118
SA-10	Decyl	–	99	106
SA-12	Dodecyl	–	79	101
SA-14	Tetradecyl	–	85	98
SA-16	Hexadecyl	–	73	93
SA-18	Octadecyl	–	81	90

TABLE 6 Transition Temperature Data of Series-SB

Code no.	R = n Alkoxy	Transition temperature °C		
		Sm	N	I
SB-1	Methyl	–	–	175
SB-2	Ethyl	–	157	169
SB-3	Propyl	–	150	165
SB-4	Butyl	–	153	158
SB-5	Pentyl	–	141	151
SB-6	Hexyl	–	142	145
SB-7	Heptyl	–	124	137
SB-8	Octyl	–	128	132
SB-10	Decyl	–	113	124
SB-12	Dodecyl	–	115	119
SB-14	Tetradecyl	–	100	116
SB-16	Hexadecyl	–	103	108
SB-18	Octadecyl	–	94	101

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 SA can be explained by increasing overall polarizability of the molecule.

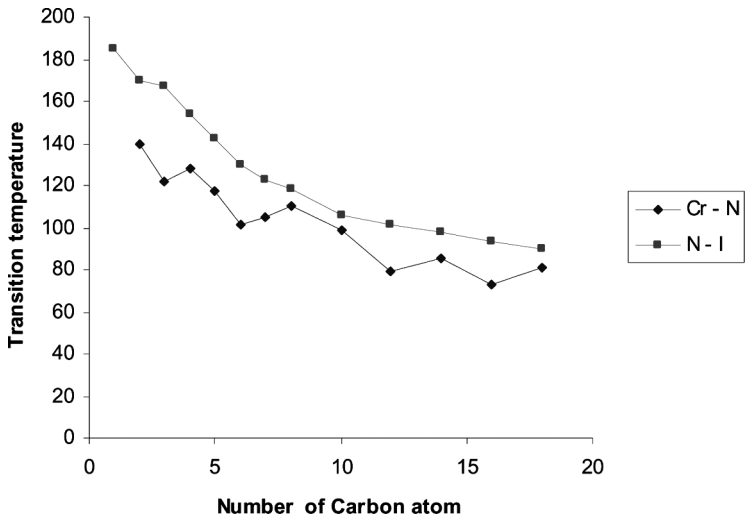


FIGURE 7 Transition temperature Vs No. of carbon atom of series SA compounds.

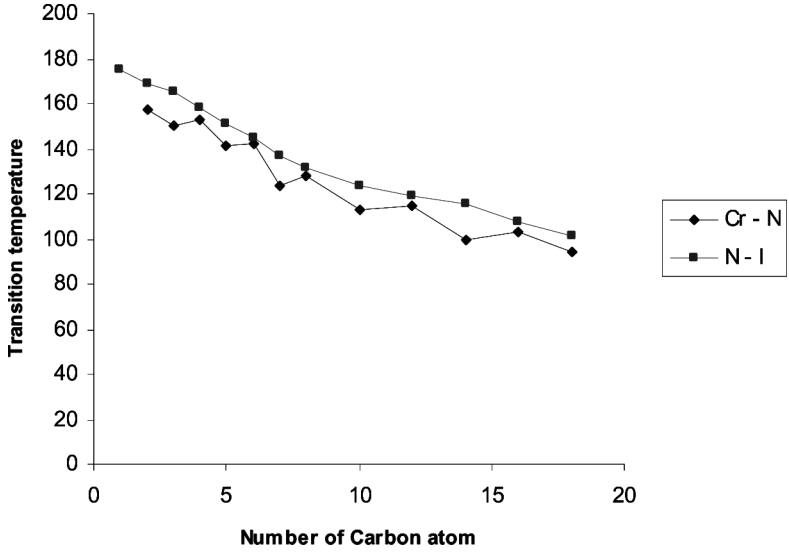


FIGURE 8 Transition temperature Vs No. of carbon atom of series SB compounds.

The microscopic temperature and DSC data of the few compounds are listed in Table 7. The DSC curves of representative compounds are shown in Figure 9 to 11. Microscopic transition temperature values are almost similar to DSC data.

The texture of mesomorphic compound SA-10 and SB-5 have been shown in Figure 12. The SA-10 is exhibiting Schlieren texture of nematic phase at 99°C. Whereas SB-5 exhibits mosaic texture of nematic phase at 143°C.

TABLE 7 DSC Data of the Representative Compounds of Series-SA and SB

Code No.	Transition	Peak Temp. (Microscopic temp.) °C	ΔH (Jg^{-1})	ΔS ($Jg^{-1}K^{-1}$)
SA_{10}	Cr→N	98.73 (99)	22.17	0.0596
	N→I	104.82 (106)	48.26	0.1277
SA_{14}	Cr→N	84.21 (85)	18.56	0.0519
	N→I	98.27 (98)	35.01	0.3562
SB_{10}	Cr→N	112.29 (113)	30.34	0.0787
	N→I	122.89 (124)	19.65	0.0494
SB_{16}	Cr→N	103.01 (103)	27.18	0.0722
	N→I	107.52 (108)	12.67	0.0329

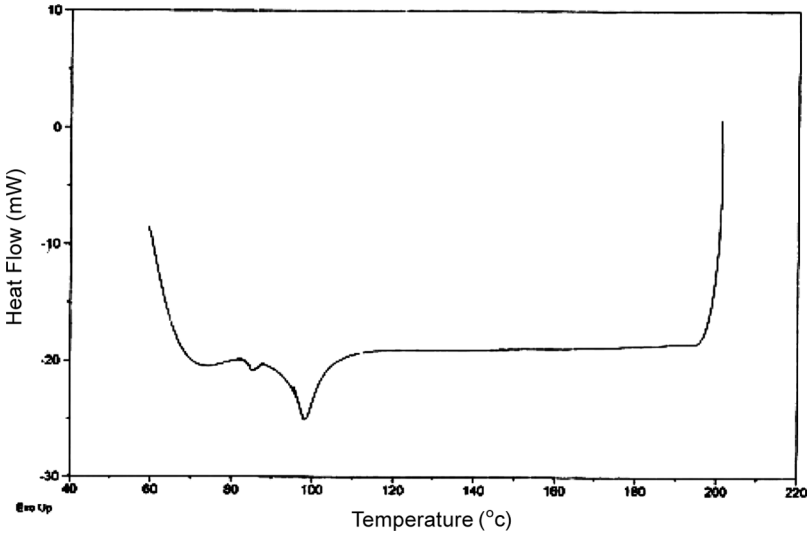


FIGURE 9 DSC curve of SA-14.

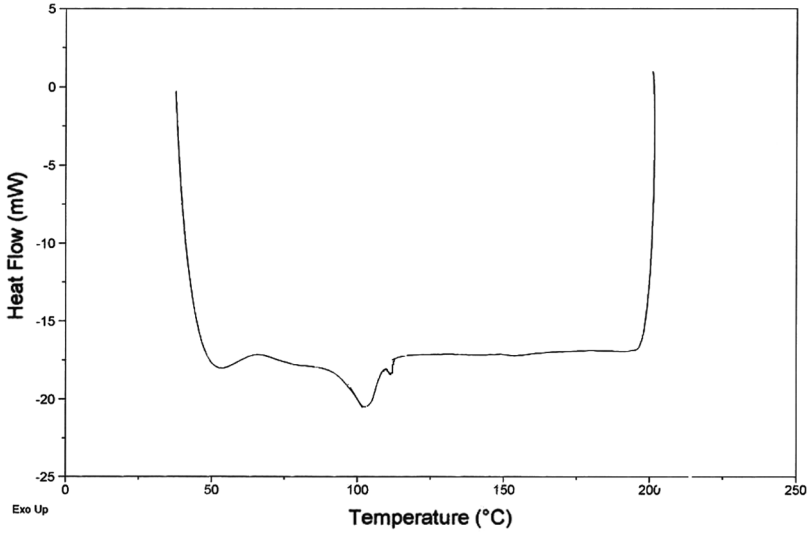


FIGURE 10 DSC curve of SB-16.

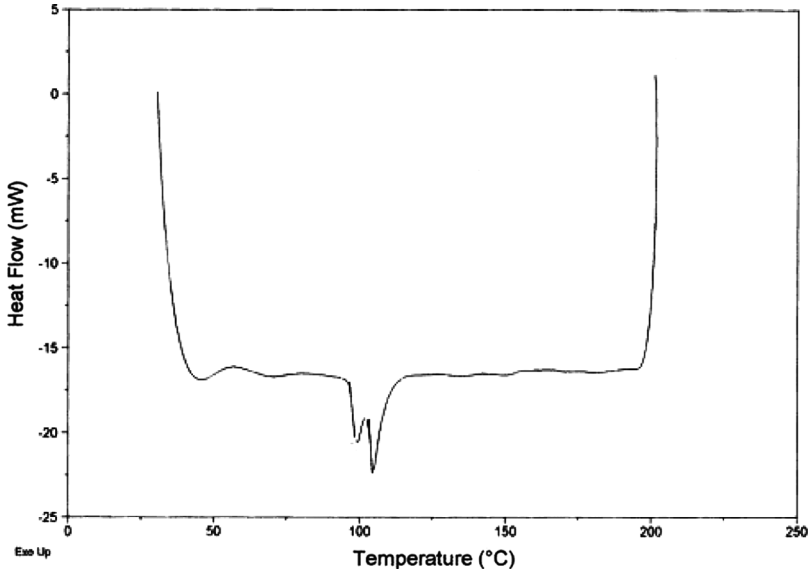
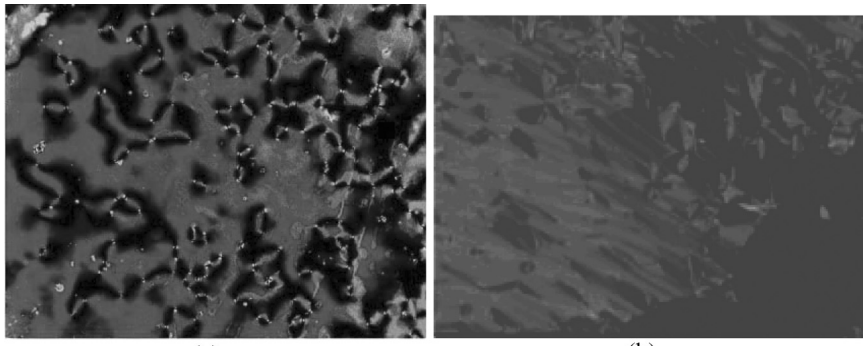


FIGURE 11 DSC curve of SA-10.

CONCLUSIONS

A series of tri substituted pyrozole containg liquid crystals have been synthesized and characterized. The introduction of pyrazolone with trisubstituted unit in the rigid core induced enantiotropic behavior. The bulky group reduced the polarity of molecule and decreases the



(a) (b)

FIGURE 12 (a) The Schlieren texture of the nematic phase of SA-10 at 99°C (b) The Mosaic texture of nematic phase of SB-5 143°C.

mesophase stability of compound, both series show nematic 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. However, further studies will have to be made if a clear understanding of the influence of heterocyclic rings on crystal and mesophase thermal stabilities is to be gained.

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