Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Phase Transitions and Thermodynamic Parameters of N-(*p*-*n*-octyloxybenzylidene)-*p*-*n*-alkoxyanilines—A Dilatometric Study

K. Fakruddin[a]; R. Jeevan Kumar[a]; V. G. K. M. Pisipati[b]; D. Madhavi Latha[b]; B. T. P. Madhav[b]; P. V. Datta Prasad[c]
[a] Department of Physics, S. K. University, Anantapur, India [b] Liquid Crystal Research Centre, ECE Department, Koneru Lakshmaiah University, Vaddeswaram, India [c] Department of Physics, The Hindu College, Machilipatnam, India

First published on: 08 July 2010

To cite this Article Fakruddin, K. , Kumar, R. Jeevan , Pisipati, V. G. K. M. , Latha, D. Madhavi , Madhav, B. T. P. and Prasad, P. V. Datta(2010) 'Phase Transitions and Thermodynamic Parameters of N-(*p*-*n*-octyloxybenzylidene)-*p*-*n*-alkoxyanilines—A Dilatometric Study', Molecular Crystals and Liquid Crystals, 524: 1, 102 — 118
To link to this Article: DOI: 10.1080/15421406.2010.484614
URL: http://dx.doi.org/10.1080/15421406.2010.484614

Mol. Cryst. Liq. Cryst., Vol. 524: pp. 102–118, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.484614

Taylor & Francis
Taylor & Francis Group

Phase Transitions and Thermodynamic Parameters of N-(*p-n*-octyloxybenzylidene)-*p-n*-alkoxyanilines—A Dilatometric Study

K. FAKRUDDIN,[1] R. JEEVAN KUMAR,[1]
V. G. K. M. PISIPATI,[2] D. MADHAVI LATHA,[2]
B. T. P. MADHAV,[2] AND P. V. DATTA PRASAD[3]

[1]Department of Physics, S. K. University, Anantapur, India
[2]Liquid Crystal Research Centre, ECE Department,
Koneru Lakshmaiah University, Vaddeswaram, India
[3]Department of Physics, The Hindu College, Machilipatnam, India

The variation of density with temperature in four compounds, N-(p-n-octyloxybenzylidene)-p-n-alkylanilines, 8O.Om's, viz. N-(p-n-octyloxybenzylidene)-p-n-propoxyaniline, 8O.O3, N-(p-n-octyloxybenzylidene)-p-n-butylaniline, 8O.O4, N-(p-n-octyloxybenzylidene)-p-n-hexylaniline, 8O.O6, and N-(p-n-octyloxybenzylidene)-p-n-heptylaniline, 8O.O7, is presented. The density and thermal expansion coefficient results reveal that the phase transitions present in these compounds are of first order. Using the thermal expansion coefficient, the temperature dependence of a number of thermodynamical (thermoacoustic and anharmonic) parameters of these compounds are estimated. These results reveal that all the parameters show characteristic change in the vicinity of the phase transformation. The results are discussed in light of the body of data available.

Keywords nO.Om compounds; phase transitions; thermodynamic parameters

Introduction

In the area of soft condensed matter physics, dilatometric studies (the density) of liquid crystal (LC) phase transitions involving different structural organizations are an intriguing topic. The density studies involving temperature variation and across different phase transformations in LC materials are well known [1–7] to provide information regarding the nature of the phase transition and the growth of the pretransitional effects. Further, such studies provide complementary and confirmatory experimental evidence for the results obtained by using other techniques, like polarizing thermal microscopy (TM) and differential scanning calorimetry (DSC), regarding the determination of phase transition temperatures, the nature of the transition, and the thermal stability of the phase of interest.

Address correspondence to V. G. K. M. Pisipati, Liquid Crystal Research Centre, ECE Department, Koneru Lakshmaiah University, Vaddeswaram 522 502, India. E-mail: venkata_pisipati@hotmail.com

The compounds, viz. N-(p-n-octyloxybenzylidene)-p-n-propoxyaniline, 8O.O3, N-(p-n-octyloxybenzylidene)-p-n-butylaniline, 8O.O4, N-(p-n-octyloxybenzylidene)-p-n-hexylaniline, 8O.O6, and N-(p-n-octyloxybenzylidene)-p-n-heptylaniline, 8O.O7, differ from their counterparts (nO.m) without electronegative oxygen atom on the aniline side, regarding the clearing temperatures, the polymorphism, and the manifestation of nematic phase. It has been reported [1,2] that the position of the electronegative oxygen in the molecular moiety plays an important role regarding the clearing temperature, the phase variants, and the manifestation of nematic phase. The compounds 8O.O3, 8O.O4, 8O.O6, and 8O.O7 exhibit N, NC, NCG, and NC phases with clearing temperatures 105.9°C, 116.3°C, 111.0°C, and 105.6°C, respectively, and their counterparts 8O.3, 8O.4, 8O.6, and 8O.7 exhibit [3] (with no oxygen atom on the right side of the molecular moiety) NABG, ABG, ACBG and ACBG with clearing temperatures well below 100°C. If there is no oxygen atom in the molecular moiety (n.m) the clearing temperatures fall below 50°C and in some cases the liquid-crystalline nature is observed in and around room temperature. If the oxygen atom is on the right side only (n.Om), there is not much difference regarding the observed clearing temperatures, but the phase variants differ.

As a part of our systematic studies on nO.m, n.Om, n.m, and nO.Om homologues, the density measurements as a function of temperature are carried out for the above four (nO.Om) compounds and the nature of the phase transitions across isotropic-nematic (IN) and nematic-smectic-C (NC) are reported in the present manuscript. A number of thermodynamical (acoustic and anharmonic) parameters are estimated from the thermal expansion coefficient derived from density [8]. The results are discussed with the literature data on similar compounds.

Experimental

The liquid-crystal compounds are synthesized following the standard procedure described elsewhere [2]. The corresponding ingredients are imported from Frinton Laboratories (Hainesport, NJ). The synthesized compound is subjected to repeated crystallization from absolute ethanol until the transition temperatures show consistency. The transition temperatures agree with the literature data and they are given in Table 1. A U-shaped bi-capillary pycnometer in conjunction with the cathetometer was used for the density measurements. The absolute error in the measurement of density is $\pm 10^{-4}$ g cm^{-3}. The cooling rate during the measurement was 0.5 K h^{-1}.

Theory

The procedure for the estimation of various thermoacoustic and anharmonic parameters using the coefficient of thermal expansion (α) is described below [8].

The coefficient of volume expansion $(\alpha) = 1/V_m\,(dV_m/dT)$, where $dT = T_2 - T_1$, $dV_m = V_{m2} - V_{m1}$.

The Moelwyns-Hughes parameter (C_1) and reduced molar volume ($V^{\sim}$) may be expressed as

$$C_1 = \left(\frac{13}{3}\right) + \left(\frac{1}{\alpha \mathrm{T}}\right) + \left(\frac{4\alpha T}{3}\right) \tag{1}$$

$$V^{\sim} = \left\{\frac{\left(\frac{\alpha \mathrm{T}}{3}\right)}{(1+\alpha T)} + 1\right\}^3 \tag{2}$$

Table 1. The transition temperatures in °C along with the enthalpy values of the compounds studied

Compound name	Phase variant	Method		I-N	N-C	C-G	N/C/ G-K	Ref.
8O.O3	N	DSC	Heating	106.39			99.23	+[2]
			ΔH/J/gm	1.47			62.58	
			Cooling	103.96			84.33	
			ΔH/J/gm	1.80			51.41	
		TM	Cooling	105.20			85.30	
		PW	Cooling	105.00			85.30	
8O.O4	NC	DSC	Heating	112.05	—		105.92	+[2]
			ΔH/J/gm	2.35	—		74.43	
			Cooling	109.45	93.70		82.97	
			ΔH/J/gm	2.25	1.55		57.36	
		TM	Cooling	116.3	100.00		90.00	
		PW	Cooling	116.00	100.00		90.00	
8O.O6	NCG	DSC	Heating	111.80	104.23	—	93.85	+[2]
			ΔH/J/gm	4.93	4.09	—	73.12	
			Cooling	108.75	100.77	84.35	79.53	
			ΔH/J/gm	5.43	3.73	2.83	56.58	
		TM	Cooling	110.75	103.20	85.60	76.40	
		PW	Cooling	111.00	100.80	85.6	76.50	
8O.O7	NC	DSC	Heating	108.62	104.09		95.49	+[2]
			ΔH/J/gm	3.43	2.86		83.84	
			Cooling	105.54	100.63		87.13	
			ΔH/J/gm	2.56	2.45		60.68	
		TM	Cooling	105.6	100.80		87.60	
		PW	Cooling	106.00	100.80		87.60	

1. Ajeetha, N. Ramakrishna, M. Datta Prasad, P.V., & Pisipati, V.G.K.M., (2006). *Mol. Cryst. Liq. Cryst.*, *452*, 3.

The isochoric temperature coefficient of internal pressure (X) is given by

$$X = -\frac{2(1+2\alpha T)}{V^{\sim c_1}} \tag{3}$$

The Sharma parameter [8] S_0 is given by the expression

$$S_0 = \left(-\frac{\mathrm{X}}{2}\right)(3+4\alpha T) \tag{4}$$

Then, the Huggins parameter [8] F of a liquid crystal is related to S_0 by the equation

$$F = 2\left[1+\left(\frac{\mathrm{S}_0}{(3+4\alpha T)}\right)\right] - \left(3+\frac{4\alpha T}{3}\right) \tag{5}$$

The isothermal microscopic Grunessian parameter (Γ) is a measure of volume dependence of the harmonicity of the normal mode frequency (ν) of molecular vibrations of a material and is related to F and S_0 as

$$\tau = \left(\frac{2}{3}\right)\alpha T + \left(\frac{2 - F + 4\alpha T}{2\alpha T}\right) \tag{6}$$

The fraction free volume (f) is a measure of disorder due to increase of mobility of molecules in a liquid crystal and can be expressed in terms of isothermal Grunessian parameter (Γ) as

$$f = \frac{1}{(\tau + 1)} = \frac{V_a}{V} \tag{7}$$

where V_a is the available volume.

Thermal parameter A^* is a dimensionless parameter that shows that at low temperatures, a liquid crystal tends to be ordered, and thereby makes A^* equal to unity

$$A^* = 1 + \left(\frac{f}{\tau}\right) \tag{8}$$

The Grunessian parameter (Γ_p) for liquid crystals can be found from

$$\tau_p = \left(\frac{2}{3}\right)\alpha T + \left(\frac{1}{2\alpha T}\right) + 2 \tag{9}$$

Results and Discussion

Dilatometric Studies

The phase transition temperatures observed in density measurements along with the literature values are given in Table 1. The data reveal that the values are in good agreement with the literature data. Further, it is found from the literature [1,2] that the presence of an oxygen atom makes the clearing temperatures rise compared to those compounds of Schiff bases, which have oxygen on any one side of the central core. The phase variants exhibited by these compounds are shown in Table 1. The compounds 8O.O3 exhibit a single phase variant nematic phase (N) in between the isotropic liquid and the crystal, and, the compounds 8O.O4 and 8O.O7 exhibit a divariant nematic and smectic-C phase (NC). The compound 8O.O6 exhibits a tri variant, viz. nematic, smectic-C, and smectic-G, phase (NCG).

The density is found to decrease with the increase of temperature in the liquid-crystalline phases except in the vicinity of phase transitions, where it shows a steep increase before it attains equilibrium value of the next (lower temperature) phase. The temperature variation of density $\rho(T)$ and thermal expansion coefficient $\alpha(T)$ with temperature for all the compounds are presented in Figs. 1 to 4. The density jump ($\Delta\rho/\rho$) is calculated as the vertical distance between the density values (ρ_1 and ρ_2) obtained by the linear extrapolation from either sides of the transitions (which are in fact the average value of the above two extrapolated density values; *i.e.*,, [[$(\rho_1 - \rho_2)$]/ [$(\rho_1 + \rho_2)/2$]]). The observed density jump ($\Delta\rho/\rho$) and the thermal expansion coefficient maxima ($\alpha_{max.}$) across IN, NC of the above compounds are presented in Table 2.

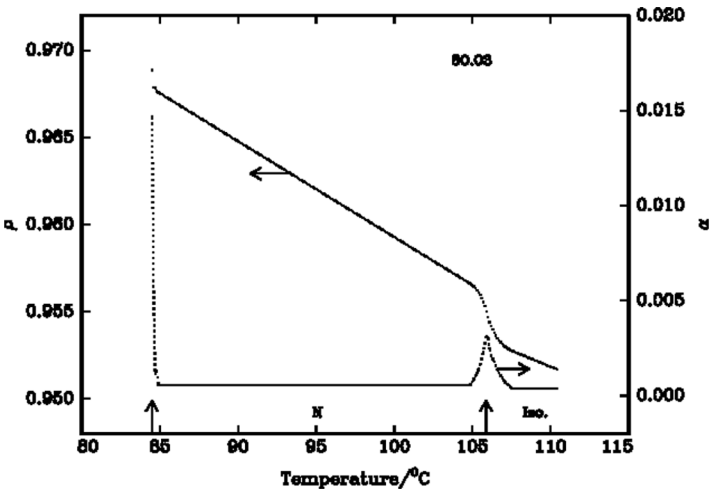

Figure 1. Variation of density and thermal expansion coefficient with temperature in 8O.O3.

The molar volume (M_v), molecular weight/density, in the isotropic phase of at $(T_{NI}+5)$°C is $374.1\times10^{-6}\,m^3\,mol^{-1}$, $390.3\times10^{-6}\,m^3\,mol^{-1}$, $423.4\times10^{-6}\,m^3\,mol^{-1}$, and $439.0\times10^{-6}\,m^3\,mol^{-1}$ for compounds 8O.O3, 8O.O4, 8O.O6, and 8O.O7 respectively. Figure 5 exhibits the variation of molar volume at $(T_{NI}+5)$°C with the chain number for the 8O.Om series. The slope of the graph shows that the increment of molar volume per the methylene unit is $16.5\times10^{-6}\,m^3\,mol^{-1}$ for this series. If the additive of molar volume is assumed in the isotropic liquid, the increment for the methylene group for these compounds is of the same order for those reported $(16.4-17.2\times10^{-6}\,m^3\,mol^{-1})$ for CH_2 unit contribution in normal isotropic liquids [9] and other nO.m compounds [10,11].

Isotropic–Nematic Transition (IN). The density jumps across IN transition in the case of 8O.O3, 8O.O4, 8O.O6, and 8O.O7 are 0.42, 0.40, 0.37, and 0.39%,

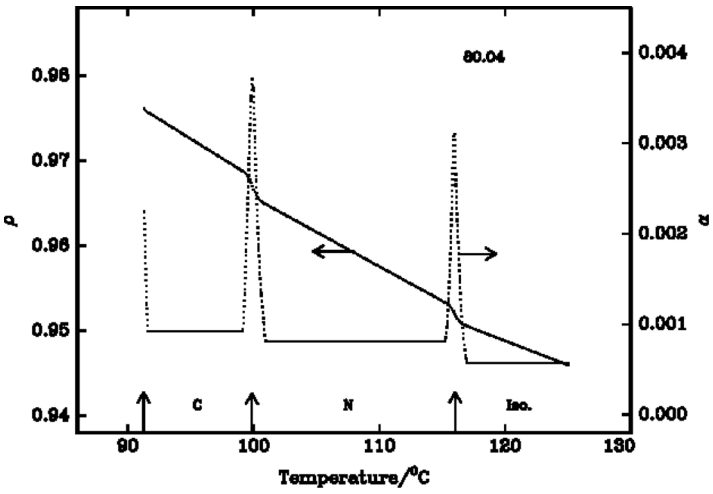

Figure 2. Variation of density and thermal expansion coefficient with temperature in 8O.O4.

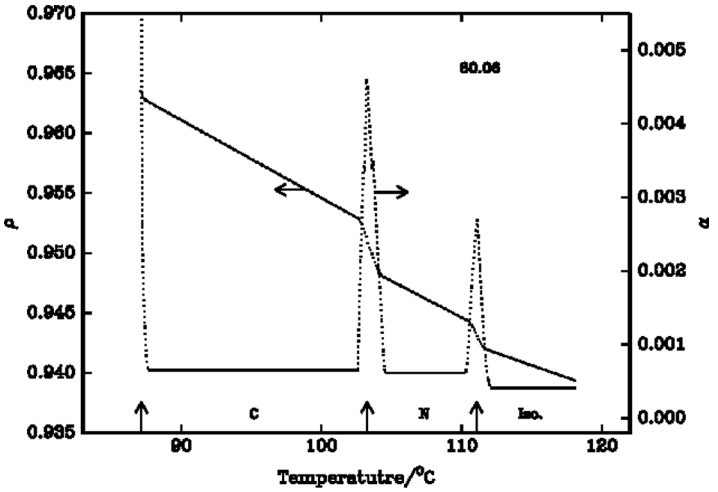

Figure 3. Variation of density and thermal expansion coefficient with temperature in 8O.O6.

respectively. The compounds of 8O.Om series exhibit a thermal expansion coefficient maxima of $31.5 \times 10^{-4\circ}C^{-1}$, $31 \times 10^{-4\circ}C^{-1}$, $26.6 \times 10^{-4\circ}C^{-1}$, and $26.0 \times 10^{-4\circ}C^{-1}$ for 8O.O3, 8O.O4, 8O.O6, and 8O.O7, respectively. These values suggest the first-order nature of the transition as expected at an IN interface. The percentage of density values is within the range (0.2 to 0.4) of the values reported [1,2] in the literature across the isotropic and nematic interface.

Nematic–Smectic-C Transition. The nematic to smectic-C (SC) transition is observed in three compounds, viz. 8O.O4, 8O.O6, and 8O.O7. A transition from an orientational ordered nematic phase to smectic-C phase possessing a layered structure with a tilted order in addition to the orientational and short-range positional orders should be first order. The density jump ($\Delta\rho/\rho = 0.25$, 0.39, and

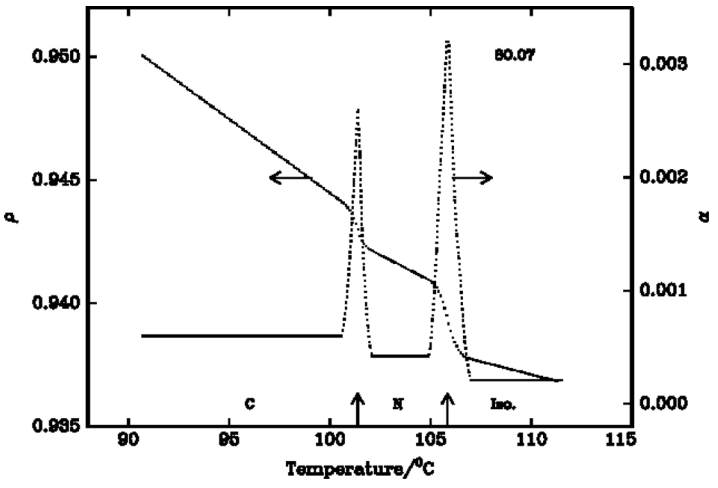

Figure 4. Variation of density and thermal expansion coefficient with temperature in 8O.O7.

Table 2. The density jump, thermal expansion coefficient maxima, and density slope in different phases of the compounds

Compound	Phase variant	% of $(\Delta\rho/\rho)_{I\text{-}N}$	$\alpha_{I\text{-}N} \times 10^{-4} {}^{\circ}C^{-1}$	% of $(\Delta\rho/\rho)_{N\text{-}C}$	$\alpha_{N\text{-}C} \times 10^{-4} {}^{\circ}C^{-1}$	$(d\rho/dT)_{iso} \times 10^{-4} {}^{\circ}C^{-1}$	$(d\rho/dT)_{N} \times 10^{-4} {}^{\circ}C^{-1}$	$(d\rho/dT)_{C} \times 10^{-4} {}^{\circ}C^{-1}$
8O.O3	N	0.29	31.50			3.70	5.70	
8O.O4	NC	0.18	31.00	0.25	37.13	5.70	8.10	9.20
8O.O6	NCG	0.19	26.58	0.39	44.73	4.10	6.10	6.50
8O.O7	NC	0.28	32.00	0.14	26.04	2.10	4.20	6.00

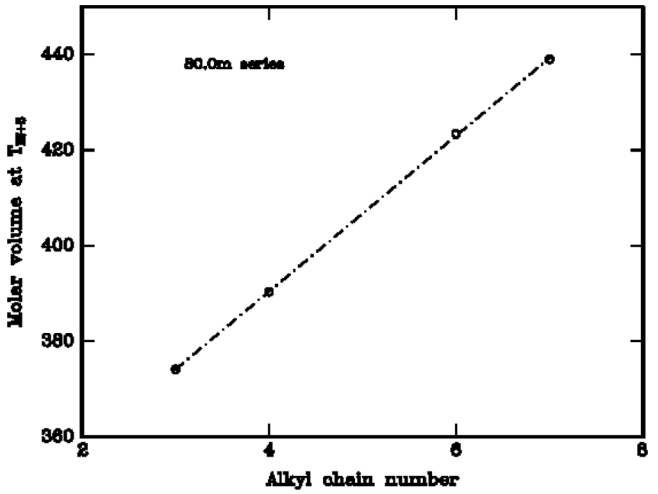

Figure 5. Change of molar volume with the chain length.

0.14%) and the thermal expansion coefficient maxima ($\alpha = 37.1 \times 10^{-4\circ}C^{-1}$, $44.7 \times 10^{-4\circ}C^{-1}$, and $26.1 \times 10^{-4\circ}C^{-1}$) for the above three compounds confirm the NC transition as first order. The values obtained for these compounds are slightly lower to those obtained for 7O.O5 (0.45). Very few compounds exhibit NC transition in nO.m compounds [12].

As expected, the magnitude of slopes in different phases is increasing from the isotropic to higher ordered liquid-crystalline phases. However, the values are lower when compared to nO.m compounds [9]. The slope values obtained for the compounds in different phases are given in Table 2.

The salient features observed from the dilatometric studies are

- The nature of the isotropic–nematic transition is found to be first order as expected [1,2].
- The percentage of jump observed across IN transition is between 0.18 to 0.44 and is found to be within the reported data on a number of compounds [3]. The large value found in the case of 5O.O5 by Ajeetha *et al.* [1,2] is not the true value representing the IN transition as it has a very small thermal range of nematic phase, and the nematic phase has not attained thermal equilibrium before transforming to crystalline phase. Hence, the large jump observed is the sum of the contributions due to IN and N-crystal phase transformations.
- Unlike the case of nematic–smectic-A transition, which exhibits either first-order or second-order depending on the McMillan parameter, the thermal range of the nematic phase and the alkyl chain length in the case of nO.m compounds, the nematic–smectic-C transition is of first order and the results obtained in the compounds studied agree with the literature data [13].
- The percentage jump observed in the case of 8O.O7 is small compared to other compounds and the body of the data reveals small jumps across this transition in other compounds [14].
- The observations on benzylidene aniline liquid crystals reveal that the compounds with the oxygen atom on both the sides of the rigid core (a) will have higher clearing temperatures compared to the compounds that possess an

Table 3. Thermal expansion coefficient and thermoacoustic and anharmonic parameters of 8O.O3

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim cl}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
110.0	11.578	1.129	4.087	−0.628	−1.283	1.120	1.439	4.073	0.197	1.048	120.27	5.623
109.0	11.591	1.129	4.084	−0.628	−1.283	1.120	1.440	4.075	0.197	1.048	119.99	5.629
108.0	11.614	1.129	4.079	−0.629	−1.282	1.120	1.441	4.078	0.197	1.048	119.74	5.641
107.0	7.989	1.254	6.112	−0.529	−1.616	1.118	1.118	3.635	0.216	1.059	100.45	3.828
106.5	6.811	1.419	10.841	−0.402	−2.180	1.078	0.615	3.563	0.219	1.062	76.32	3.237
106.4	6.715	1.458	12.573	−0.373	−2.343	1.060	0.477	3.577	0.218	1.061	70.70	3.188
106.3	6.673	1.484	13.941	−0.353	−2.460	1.045	0.379	3.592	0.218	1.061	66.94	3.167
106.2	6.646	1.514	15.770	−0.330	−2.604	1.025	0.261	3.614	0.217	1.060	62.61	3.153
106.1	6.649	1.570	20.051	−0.289	−2.896	0.981	0.025	3.667	0.214	1.058	54.75	3.153
106.0	6.742	1.641	28.146	−0.237	−3.331	0.907	−0.317	3.763	0.210	1.056	44.85	3.198
105.9 (I-N)	6.759	1.649	29.363	−0.231	−3.387	0.897	−0.361	3.777	0.209	1.055	43.71	3.207
105.8	6.674	1.598	22.788	−0.268	−3.057	0.954	−0.103	3.701	0.213	1.057	50.81	3.165
105.7	6.640	1.544	17.861	−0.308	−2.753	1.003	0.139	3.640	0.216	1.059	58.38	3.149
105.6	6.674	1.484	13.909	−0.353	−2.458	1.045	0.382	3.591	0.218	1.061	66.90	3.167
105.5	6.764	1.436	11.551	−0.389	−2.249	1.071	0.557	3.568	0.219	1.061	73.70	3.213
105.0	8.344	1.231	5.661	−0.547	−1.548	1.120	1.182	3.674	0.214	1.058	103.38	4.005
104.0	9.428	1.182	4.830	−0.586	−1.415	1.122	1.309	3.802	0.208	1.055	110.43	4.548
103.0	9.442	1.181	4.822	−0.586	−1.413	1.122	1.311	3.804	0.208	1.055	110.21	4.555
102.0	9.452	1.181	4.817	−0.587	−1.413	1.122	1.311	3.805	0.208	1.055	109.97	4.560
101.0	9.467	1.180	4.809	−0.587	−1.411	1.122	1.313	3.807	0.208	1.055	109.75	4.567
100.0	9.477	1.180	4.804	−0.587	−1.410	1.122	1.314	3.808	0.208	1.055	109.51	4.572
99.0	9.489	1.180	4.798	−0.588	−1.409	1.122	1.315	3.809	0.208	1.055	109.28	4.578
98.0	9.504	1.179	4.790	−0.588	−1.408	1.122	1.316	3.811	0.208	1.055	109.06	4.586
97.0	9.514	1.179	4.785	−0.588	−1.407	1.122	1.317	3.813	0.208	1.055	108.82	4.591
96.0	9.529	1.178	4.777	−0.589	−1.406	1.122	1.318	3.814	0.208	1.054	108.60	4.598
95.0	9.539	1.178	4.772	−0.589	−1.405	1.122	1.319	3.816	0.208	1.054	108.35	4.603

Table 4. Thermal expansion coefficient and thermoacoustic and anharmonic parameters of 8O.O4

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim cl}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
122.0	9.071	1.195	5.044	−0.575	−1.450	1.122	1.275	3.759	0.210	1.056	113.58	4.369
121.0	9.081	1.195	5.037	−0.575	−1.449	1.122	1.276	3.760	0.210	1.056	113.36	4.374
120.0	9.092	1.194	5.030	−0.576	−1.448	1.122	1.277	3.761	0.210	1.056	113.14	4.379
119.0	9.102	1.194	5.023	−0.576	−1.447	1.122	1.278	3.762	0.210	1.056	112.92	4.385
118.0	9.113	1.194	5.016	−0.576	−1.446	1.122	1.279	3.764	0.210	1.056	112.70	4.390
117.0	9.124	1.193	5.009	−0.577	−1.445	1.122	1.280	3.765	0.210	1.056	112.48	4.395
116.9	8.788	1.208	5.249	−0.565	−1.484	1.121	1.243	3.725	0.212	1.057	110.21	4.227
116.8	8.246	1.237	5.771	−0.542	−1.565	1.120	1.166	3.663	0.214	1.059	105.70	3.956
116.7	7.822	1.267	6.382	−0.518	−1.655	1.117	1.082	3.618	0.217	1.060	101.03	3.744
116.6	7.416	1.307	7.300	−0.487	−1.779	1.111	0.968	3.581	0.218	1.061	94.96	3.540
116.5	7.092	1.354	8.561	−0.452	−1.935	1.101	0.829	3.561	0.219	1.062	88.03	3.378
116.4	6.821	1.416	10.719	−0.405	−2.168	1.079	0.626	3.562	0.219	1.062	78.76	3.242
116.3	6.681	1.478	13.609	−0.358	−2.433	1.048	0.402	3.588	0.218	1.061	69.59	3.171
116.2	6.641	1.527	16.611	−0.321	−2.666	1.016	0.210	3.624	0.216	1.060	62.46	3.150
116.1	6.661	1.585	21.522	−0.277	−2.984	0.966	−0.046	3.686	0.213	1.058	53.95	3.159
116.0 (I-N)	6.767	1.652	29.912	−0.228	−3.412	0.892	−0.380	3.783	0.209	1.055	44.37	3.210
115.9	6.761	1.649	29.469	−0.230	−3.392	0.896	−0.364	3.778	0.209	1.055	44.76	3.207
115.8	6.652	1.575	20.522	−0.285	−2.925	0.976	0.002	3.673	0.214	1.058	55.41	3.155
115.7	6.660	1.496	14.628	−0.344	−2.516	1.037	0.333	3.600	0.217	1.060	66.85	3.160
115.6	6.793	1.425	11.089	−0.398	−2.205	1.076	0.595	3.564	0.219	1.061	77.26	3.228
115.5	7.036	1.364	8.877	−0.444	−1.971	1.098	0.797	3.559	0.219	1.062	86.28	3.350
115.4	7.422	1.307	7.282	−0.488	−1.777	1.111	0.970	3.582	0.218	1.061	94.78	3.543
115.3	7.785	1.271	6.449	−0.516	−1.664	1.117	1.073	3.615	0.217	1.060	100.19	3.725
115.2	7.930	1.259	6.202	−0.525	−1.629	1.118	1.106	3.629	0.216	1.060	101.95	3.798
115.1	7.931	1.259	6.201	−0.525	−1.629	1.118	1.106	3.629	0.216	1.060	101.93	3.798

(*Continued*)

Table 4. Continued

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim cl}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
115.0	7.931	1.259	6.201	−0.525	−1.629	1.118	1.106	3.629	0.216	1.060	101.90	3.798
101.0	8.035	1.251	6.046	−0.531	−1.606	1.119	1.127	3.640	0.216	1.059	99.35	3.850
100.5	6.829	1.413	10.617	−0.407	−2.158	1.080	0.635	3.561	0.219	1.062	75.91	3.246
100.4	6.699	1.467	13.013	−0.366	−2.382	1.055	0.445	3.581	0.218	1.061	68.34	3.180
100.3	6.643	1.522	16.289	−0.324	−2.642	1.020	0.229	3.620	0.216	1.060	60.56	3.151
100.2	6.654	1.578	20.786	−0.283	−2.941	0.973	−0.011	3.677	0.214	1.058	52.80	3.156
100.1	6.726	1.632	26.994	−0.243	−3.276	0.916	−0.275	3.750	0.211	1.056	45.28	3.190
100.0	6.868	1.691	36.829	−0.201	−3.693	0.841	−0.595	3.852	0.206	1.053	37.40	3.260
99.9 (N-C)	6.897	1.700	38.862	−0.194	−3.767	0.827	−0.651	3.871	0.205	1.053	36.15	3.275
99.8	6.836	1.680	34.645	−0.208	−3.610	0.856	−0.531	3.831	0.207	1.054	38.84	3.244
99.7	6.747	1.643	28.513	−0.235	−3.348	0.904	−0.331	3.767	0.210	1.056	43.76	3.201
99.6	6.654	1.577	20.735	−0.283	−2.938	0.974	−0.008	3.676	0.214	1.058	52.79	3.156
99.5	6.643	1.521	16.242	−0.325	−2.639	1.020	0.232	3.619	0.216	1.060	60.52	3.151
99.4	6.716	1.457	12.547	−0.373	−2.341	1.060	0.479	3.577	0.218	1.061	69.47	3.188
99.3	6.990	1.373	9.176	−0.437	−2.005	1.095	0.767	3.558	0.219	1.062	81.36	3.327
99.2	7.491	1.299	7.091	−0.494	−1.752	1.113	0.993	3.588	0.218	1.061	91.95	3.578
99.1	7.708	1.277	6.597	−0.511	−1.685	1.116	1.054	3.607	0.217	1.060	95.03	3.686
98.0	7.715	1.277	6.582	−0.511	−1.683	1.116	1.056	3.608	0.217	1.060	94.84	3.690

Table 5. Thermal expansion coefficient and thermoacoustic and anharmonic parameters of 8O.O6

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim c1}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
116.0	10.811	1.144	4.281	−0.616	−1.319	1.121	1.403	3.975	0.201	1.051	119.84	5.240
115.0	10.827	1.144	4.277	−0.616	−1.318	1.121	1.404	3.977	0.201	1.051	119.59	5.247
114.0	10.843	1.143	4.272	−0.617	−1.317	1.121	1.405	3.979	0.201	1.050	119.33	5.255
113.0	10.858	1.143	4.268	−0.617	−1.317	1.121	1.406	3.981	0.201	1.050	119.08	5.263
112.0	10.396	1.153	4.413	−0.608	−1.343	1.121	1.380	3.922	0.203	1.052	117.14	5.032
111.9	9.639	1.175	4.722	−0.591	−1.396	1.122	1.327	3.828	0.207	1.054	113.83	4.653
111.8	8.748	1.210	5.281	−0.564	−1.489	1.121	1.238	3.720	0.212	1.057	108.48	4.207
111.7	7.871	1.263	6.298	−0.522	−1.642	1.118	1.093	3.623	0.216	1.060	100.33	3.768
111.6	7.300	1.322	7.671	−0.476	−1.827	1.108	0.925	3.573	0.219	1.061	91.59	3.482
111.5	6.927	1.387	9.650	−0.426	−2.057	1.090	0.722	3.558	0.219	1.062	81.97	3.295
111.4	6.722	1.454	12.385	−0.376	−2.326	1.062	0.492	3.575	0.219	1.061	72.20	3.192
111.3	6.650	1.509	15.396	−0.335	−2.576	1.029	0.284	3.609	0.217	1.060	64.29	3.155
111.2	6.650	1.571	20.151	−0.288	−2.902	0.980	0.020	3.669	0.214	1.058	55.33	3.153
111.1 (I-N)	6.677	1.600	23.101	−0.266	−3.074	0.951	−0.117	3.705	0.213	1.057	51.11	3.167
111.0	6.657	1.581	21.082	−0.281	−2.958	0.971	−0.025	3.680	0.214	1.058	53.88	3.157
110.9	6.639	1.542	17.762	−0.309	−2.747	1.004	0.145	3.639	0.216	1.059	59.36	3.149
110.8	6.653	1.504	15.119	−0.338	−2.554	1.032	0.302	3.606	0.217	1.060	64.84	3.156
110.7	6.706	1.462	12.788	−0.369	−2.362	1.057	0.461	3.579	0.218	1.061	70.87	3.184
110.6	6.896	1.395	9.916	−0.421	−2.086	1.088	0.697	3.559	0.219	1.062	80.68	3.279
110.5	7.369	1.313	7.443	−0.483	−1.798	1.110	0.951	3.578	0.218	1.061	92.63	3.517
110.4	8.192	1.240	5.837	−0.540	−1.575	1.120	1.156	3.657	0.215	1.059	103.44	3.929
110.3	8.793	1.207	5.245	−0.566	−1.483	1.121	1.244	3.726	0.212	1.057	108.38	4.230
110.2	8.919	1.202	5.149	−0.570	−1.468	1.122	1.258	3.741	0.211	1.056	109.22	4.293
110.1	8.920	1.202	5.148	−0.570	−1.467	1.122	1.258	3.741	0.211	1.056	109.20	4.294
110.0	8.921	1.202	5.148	−0.570	−1.467	1.122	1.259	3.741	0.211	1.056	109.17	4.294

(*Continued*)

Table 5. Continued

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim c1}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
109.0	8.932	1.201	5.140	−0.570	−1.466	1.122	1.260	3.742	0.211	1.056	108.96	4.299
104.0	6.639	1.540	17.580	−0.311	−2.734	1.006	0.155	3.636	0.216	1.059	58.63	3.149
103.9	6.669	1.593	22.340	−0.271	−3.032	0.958	−0.083	3.696	0.213	1.058	51.15	3.163
103.8	6.756	1.647	29.158	−0.232	−3.378	0.898	−0.353	3.774	0.209	1.055	43.65	3.205
103.7	6.841	1.681	34.959	−0.207	−3.622	0.854	−0.541	3.834	0.207	1.054	39.03	3.247
103.6	6.817	1.673	33.330	−0.213	−3.557	0.866	−0.491	3.818	0.208	1.054	40.19	3.235
103.5	7.170	1.768	59.468	−0.147	−4.369	0.716	−1.099	4.032	0.199	1.049	27.66	3.409
103.4 (N-C)	7.216	1.777	63.417	−0.141	−4.463	0.698	−1.168	4.058	0.198	1.049	26.49	3.431
103.3	6.811	1.670	32.918	−0.215	−3.540	0.869	−0.478	3.814	0.208	1.054	40.47	3.232
103.2	6.821	1.674	33.640	−0.212	−3.570	0.864	−0.501	3.821	0.207	1.054	39.92	3.237
103.1	6.695	1.613	24.600	−0.257	−3.155	0.938	−0.180	3.723	0.212	1.057	48.24	3.175
103.0	6.645	1.517	15.940	−0.328	−2.617	1.023	0.251	3.616	0.217	1.060	61.72	3.152
102.0	8.758	1.209	5.273	−0.564	−1.487	1.121	1.239	3.721	0.212	1.057	105.79	4.212
101.0	8.768	1.209	5.265	−0.565	−1.486	1.121	1.240	3.723	0.212	1.057	105.58	4.217
100.0	8.778	1.208	5.256	−0.565	−1.485	1.121	1.242	3.724	0.212	1.057	105.37	4.222
99.0	8.788	1.208	5.248	−0.565	−1.484	1.121	1.243	3.725	0.212	1.057	105.15	4.227
98.0	8.798	1.207	5.240	−0.566	−1.482	1.121	1.244	3.726	0.212	1.057	104.94	4.233
97.0	8.809	1.207	5.232	−0.566	−1.481	1.121	1.245	3.727	0.212	1.057	104.73	4.238

Table 6. Thermal expansion coefficient and thermoacoustic and anharmonic parameters of 8O.O7

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim c1}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
110.0	16.864	1.076	3.458	−0.671	−1.161	1.115	1.564	4.761	0.174	1.036	128.59	8.267
109.0	16.897	1.076	3.456	−0.672	−1.161	1.115	1.565	4.765	0.173	1.036	128.28	8.283
108.0	16.929	1.076	3.454	−0.672	−1.160	1.115	1.565	4.770	0.173	1.036	127.98	8.299
107.0	16.979	1.076	3.451	−0.672	−1.159	1.115	1.566	4.776	0.173	1.036	127.69	8.324
106.5	9.398	1.183	4.846	−0.585	−1.418	1.122	1.307	3.798	0.208	1.055	111.00	4.533
106.4	8.123	1.245	5.924	−0.536	−1.588	1.119	1.144	3.650	0.215	1.059	101.70	3.895
106.3	7.372	1.313	7.433	−0.483	−1.796	1.110	0.952	3.578	0.218	1.061	91.68	3.518
106.2	7.016	1.368	9.006	−0.441	−1.986	1.097	0.784	3.559	0.219	1.062	83.62	3.339
106.1	6.847	1.408	10.413	−0.410	−2.137	1.083	0.652	3.560	0.219	1.062	77.81	3.255
106.0	6.706	1.463	12.812	−0.369	−2.364	1.057	0.460	3.579	0.218	1.061	69.94	3.183
105.9	6.640	1.534	17.163	−0.315	−2.705	1.010	0.178	3.631	0.216	1.059	59.72	3.149
105.8	6.679	1.602	23.270	−0.265	−3.084	0.950	−0.124	3.707	0.212	1.057	50.20	3.168
105.7 (I-N)	6.771	1.654	30.182	−0.227	−3.424	0.890	−0.389	3.785	0.209	1.055	42.96	3.212
105.6	6.771	1.654	30.166	−0.227	−3.423	0.890	−0.388	3.785	0.209	1.055	42.96	3.212
105.5	6.687	1.608	23.931	−0.261	−3.119	0.944	−0.152	3.715	0.212	1.057	49.34	3.171
105.4	6.645	1.562	19.392	−0.294	−2.854	0.987	0.058	3.659	0.215	1.059	55.69	3.151
105.3	6.644	1.519	16.077	−0.327	−2.627	1.022	0.242	3.617	0.217	1.060	61.81	3.152
105.2	6.707	1.462	12.782	−0.370	−2.362	1.057	0.462	3.579	0.218	1.061	69.87	3.184
105.1	6.970	1.377	9.315	−0.434	−2.021	1.094	0.753	3.558	0.219	1.062	82.02	3.317
105.0	7.480	1.300	7.122	−0.493	−1.756	1.112	0.989	3.587	0.218	1.061	93.20	3.572
104.5	10.846	1.143	4.272	−0.617	−1.317	1.121	1.405	3.979	0.201	1.050	116.41	5.257
104.0	10.854	1.143	4.269	−0.617	−1.317	1.121	1.406	3.980	0.201	1.050	116.28	5.261
103.5	10.866	1.143	4.266	−0.617	−1.316	1.121	1.406	3.982	0.201	1.050	116.17	5.267
103.0	10.874	1.143	4.263	−0.617	−1.316	1.121	1.407	3.983	0.201	1.050	116.04	5.271
102.5	10.882	1.142	4.261	−0.617	−1.315	1.121	1.407	3.984	0.201	1.050	115.91	5.275

(*Continued*)

Table 6. Continued

Temp. (°C)	C_1	$V^{\sim}$	$V^{\sim c1}$	X	X'	S_0	F	Γ	f	A^*	Δ	Γ_p
102.0	10.886	1.142	4.260	−0.617	−1.315	1.121	1.407	3.985	0.201	1.050	115.77	5.277
101.9	10.892	1.142	4.258	−0.618	−1.315	1.121	1.408	3.985	0.201	1.050	115.76	5.280
101.8	9.817	1.169	4.639	−0.596	−1.382	1.122	1.341	3.850	0.206	1.054	111.67	4.742
101.7	8.621	1.216	5.389	−0.559	−1.506	1.121	1.222	3.706	0.213	1.057	104.71	4.144
101.6	7.818	1.268	6.389	−0.518	−1.656	1.117	1.081	3.618	0.217	1.060	97.06	3.742
101.5	7.154	1.343	8.257	−0.460	−1.899	1.103	0.861	3.564	0.219	1.061	86.12	3.409
101.4	6.827	1.414	10.644	−0.406	−2.161	1.080	0.632	3.561	0.219	1.062	76.00	3.245
101.3	6.642	1.523	16.350	−0.324	−2.647	1.019	0.226	3.621	0.216	1.060	60.59	3.151
101.2 (N-C)	6.655	1.579	20.873	−0.282	−2.946	0.973	−0.015	3.678	0.214	1.058	52.81	3.156
101.1	6.639	1.537	17.386	−0.313	−2.721	1.008	0.166	3.634	0.216	1.059	58.54	3.149
101.0	6.674	1.484	13.920	−0.353	−2.459	1.045	0.381	3.591	0.218	1.061	66.05	3.167
100.9	6.799	1.423	11.006	−0.399	−2.197	1.076	0.601	3.564	0.219	1.061	74.62	3.231
100.8	7.036	1.364	8.881	−0.444	−1.972	1.098	0.796	3.559	0.219	1.062	83.00	3.350
100.7	7.412	1.308	7.313	−0.487	−1.781	1.111	0.966	3.581	0.218	1.061	91.01	3.538
100.6	7.918	1.260	6.221	−0.524	−1.632	1.118	1.103	3.628	0.216	1.060	97.97	3.792
100.5	8.503	1.222	5.497	−0.554	−1.523	1.121	1.205	3.692	0.213	1.058	103.47	4.085
100.0	9.097	1.194	5.026	−0.576	−1.448	1.122	1.278	3.762	0.210	1.056	107.42	4.382
99.0	9.106	1.194	5.021	−0.576	−1.447	1.122	1.279	3.763	0.210	1.056	107.18	4.387
98.0	9.120	1.193	5.012	−0.577	−1.445	1.122	1.280	3.765	0.210	1.056	106.97	4.393
97.0	9.131	1.193	5.005	−0.577	−1.444	1.122	1.281	3.766	0.210	1.056	106.75	4.399
96.0	9.140	1.192	4.999	−0.577	−1.443	1.122	1.282	3.767	0.210	1.056	106.52	4.404
95.0	9.154	1.192	4.990	−0.578	−1.442	1.122	1.283	3.769	0.210	1.056	106.31	4.411

oxygen atom on any one side of the rigid core. Further, it is reported that with the removal of the oxygen atom from the molecular moiety, the liquid-crystalline property can be brought to ambient temperature and in some cases below room temperature and the clearing temperatures are lowered compared to the above compounds. (b) The manifestation of nematic is observed in more compounds in the case of nO.Om compounds compared to nO.m or n.Om compounds [1,2]. The following table illustrates this.

	Alkyl chain number					
	3	4	5	6	7	16
	Phase variant					
8O.Om	N	NC	ABG	NCG	NC	—
8O.m	NABG	ABG	ABG	ACBG	ACBG	AB

Thermodynamic (Thermoacoustic and Anharmonic) Parameters

Using the volume expansion, α, and the relations described in the Theory section, the Sharma parameter, S_0, and other various thermodynamic parameters of the above compounds are evaluated at different temperatures. The different parameters are given Tables 3 to 6. The variation of Sharma parameter, S_0, with temperature in 8O.O3 and 8O.O7 compounds in different LC phases is shown in Fig. 6.

Figure 6 and the Tables 3 to 6 reveal

1. The Sharma parameter S_0 value is constant and is around 1.17 for all the compounds in all the phases except in the vicinity of phase transition, where it shows a minimum at the transition temperature in all the compounds. Figure 6 depicts the variation of S_0 in 8O.O3 and 8O.O7 compounds.

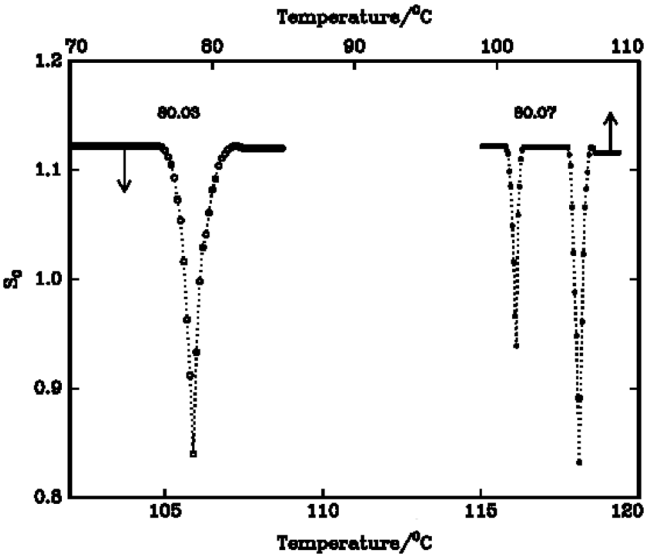

Figure 6. Variation of S_0 with temperature in 8O.O3 and 8O.O7.

2. The parameters $V^{\sim}$, $V^{\sim c1}$, isochoric temperature coefficient of internal pressure (X), and their variation with temperature are similar to that of thermal expansion coefficient α as expected, because they are proportional to α in all the compounds.
3. The parameters C_1, $X^{'}$, F, Γ, Δ, Γ_p, and their variation with temperature show a decrease with the decrease of temperature, *i.e.,*, exhibiting lower values in liquid-crystalline phases compared to the isotropic phase, which shows that molecular ordering increases as the temperature decreases in liquid-crystal phases.
4. The parameters A^* and f show almost constant values throughout the temperature range except in the vicinity of transition, either isotropic to nematic or liquid-crystalline phase to liquid-crystalline phase. The values show a consistency of around 0.2 and 1.04 + 0.01, respectively. Further, as in the case of polymers the approximate relations between S_0, A^*, f are $S = 5.55f$ and $A^* = 5.25f$ hold [15] true in these compounds also.

Acknowledgments

K. Fakruddin and R. Jeevan Kumar are grateful to the head of the Department of Physics, S. K. University, for providing facilities to carry out this work. Dr. V. G. K. M. Pisipati, D. Madhavi Latha, and B. T. P. Madhav express their thanks to the head of the ECE Department and the management of K. L. University, Vaddeswaram, India, for providing financial assistance and Dr. P. V. Datta Prasad expresses his deep appreciation to the management of the the Hindu College, Machilipatnam, India, for providing computational facilities.

References

[1] Ajeetha, N., Ramakrishna Nanchara Rao, M., Datta Prasad, P. V., & Pisipati, V. G. K. M. (2005). *Z. Naturforsch.*, *60a*, 746.
[2] Ajeetha, N., Ramakrishna Nanchara Rao, M., Datta Prasad, P. V., & Pisipati, V. G. K. M. (2006). *Mol. Cryst. Liq. Cryst.*, *457*, 3.
[3] Srnivasu, Ch., Pisipati, V. G. K. M., Prabhu, C. R., Murty, P. N., & Lakshiminarayana, S. (2007). *Z. Naturforsch.*, *62a*, 75.
[4] Burmistrov, V. A., Zavyaloy, A. V., Novikoy, I. V., Kuvshinova, S. A., & Aleksandriskii, V. V. (2005). *Russ. J. Phys. Chem.*, *79*, 130.
[5] Gogoi, B., Ghosh, T. K., & Alapati, P. R. (2005). *Cryst. Res. Tech.*, *40*, 709.
[6] Gogoi, B., Alapati, P. R., & Verma, A. L. (2002). *Cryst. Res. Tech.*, *37*, 1331.
[7] Datta Prasad, P. V., Ramakrishna Nanchara Rao, M., Lalitha Kumari, J., & Pisipati, V. G. K. M. (2009). *Phys. Chem. Liq.*, *47*, 123.
[8] Ranga Reddy, R. N. V., Suryanarayana, A., & Rama Murthy, V. (1999). *Cryst. Res. Tech.*, *34*, 10.
[9] Haller, I., Huggins, H. A., Lilienthal, H. R., & McGuire, T. R. (1973). *J. Phys. Chem.*, *73*, 950.
[10] Padmaja, S., Ramakrishna Nanchara Rao, M., Datta Prasad, P. V., & Pisipati, V. G. K. M. (2005). *Z. Naturforsch.*, *60a*, 296.
[11] Rao, N. V. S., Potukuchi, D. M., & Pisipati, V. G. K. M. (1991). *Mol. Cryst. Liq. Cryst.*, *196*, 71.
[12] Pisipati, V. G. K. M. (2003). *Z. Naturforsch.*, *58a*, 661.
[13] Pisipati, V. G. K. M., Rao, N. V. S., Potukuchi, D. M., Alapati, P. R., & Bhaskara Rao, P. (1989). *Mol. Cryst. Liq. Cryst.*, *167*, 167.
[14] Rao, N. V. S., & Pisipati, V. G. K. M. (1985). *Z. Naturforsch.*, *40a*, 466.
[15] Sharma, B. K. (1980). *Pramana Journal of Physics*, *14*, 477.