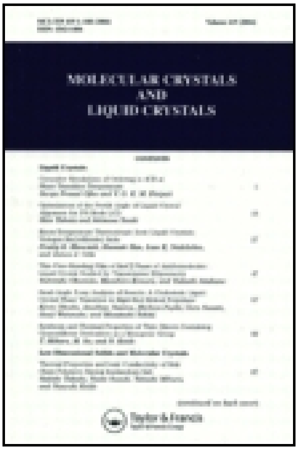

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Phase Transition Studies in 4(4′-n-Alkyloxy Benzoyloxy Benzylidene)-2″-Methylaniline Homologous Series

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Phase Transition Studies in 4(4′-n-Alkyloxy Benzoyloxy Benzylidene)-2″-Methylaniline Homologous Series

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As a part of our program of study of phase transitions in groups of liquid crystals, we report here the phase transition studies on 4(4′-*n*-Alkyloxy benzoyloxy benzylidene)-2″-methylaniline homologous series (alkyl = C_7, C_8, C_9, C_{10}, C_{11} and C_{12}) using a variety of experimental techniques. These are Differential Scanning Calorimetry, Thermal Microscopy, Electron Spin Resonance Spectroscopy and Density determination. The Isotropic-Nematic transition is found to be first order in all the compounds. The Nematic-Smectic A transition is exhibited by C_{10}, C_{11} and C_{12} homologues of the series only and is found to be weakly first order in all these three compounds. The experimental results are compared with those of the previous results and with those of the theoretical predictions of molecular field theory of Smectic A liquid crystals.

INTRODUCTION

The orientational and translational ordering of the molecules in liquid crystals define a rich variety of mesophases. The most common and possibly the most interesting mesophases between the crystal and isotropic liquid are nematic and smectic A phases. The study of phase transitions in liquid crystals is of fundamental research interest. The isotropic-nematic (IN) and nematic-smetic A (NA) phase transitions have been studied in many homologous series over the last two decades. In particular, the NA transition has been studied vigorously in an attempt to determine the order of the transition, pretransitional effects and universality class for the critical behavior. Various theoretical approaches (1–15) have predicted that the NA transition may be first order or second order with the possible existence of a tricritical point. Experimental investigations have revealed that the NA transition is first order for some compounds with a range of transition entropies and second order for others (16). Moreover, these observations are in good accord with the theoretical prediction that the transition entropy of the NA transition decreases with the increasing length of the nematic phase. Recent experimental studies (17–23) have shown the existence of a tricritical point which separates the first order and second order NA transition for different systems. In contrast, the IN phase transition is always found to be first order.

As a part of our program of study of phase transitions in groups of liquid crystal molecules, we report here the characterization of the phases and phase transitions for the compounds of homologous series, 4(4′-*n*-Alkyloxy benzoyloxy benzylidene) -2″-methylaniline (here after referred to as nBBMAs where $n = 7, 8, 9, 10, 11$ and 12) using a variety of experimental techniques. These are Differential Scanning Calorimetry (DSC), Thermal Microscopy, Electron Spin Resonance Spectroscopy (ESR) and density determination. Apart from the synthesis (22), no other studies have been reported on the nBBMA homologous series. However, we have reported the phase transition studies at IN and NA transitions in $n = 10$ and $n = 12$ homologues (23) of the series.

EXPERIMENTAL

The compounds were synthesized following the procedure given in Ref. 22. DSC data were recorded using a Du Pont 1090 thermal analyser. The thermal microscopy was performed using a polarizing microscope with an FP-82 Mettler hot stage and FP-80 central processor.

The ESR measurements of the orientational order parameter ($\eta = (3\,\mathrm{Cos}^2\theta - 1)/2$ where θ is the angle made by the molecular long axis with the director) were carried out using 3(Spiro-2N-oxyl-3′,3′-di-methyl oxazolidene)-5-α-cholestane as the spin probe. Since the elongated structure of the probe is similar to that of the liquid crystal host, we expect the order parameter for the probe to be comparable to that of the liquid crystal. The nitroxide probe dissolved easily in the isotropic phase of nBBMA which was contained in glass tubes with a diameter of 3 mm. ESR spectra were recorded with a Varian E-4-*x* band spectrometer. The temperature of the sample was controlled with a Varian variable temperature accessory and measured with a copper-constantan thermocouple placed inside the sample tube. The accuracy in temperature measurement is 0.5 °C. In a uniaxial liquid crystal phase the second rank order parameter, η, of the probe is related to the nitrogen hyperfine coupling constant, $\bar{a}$, by

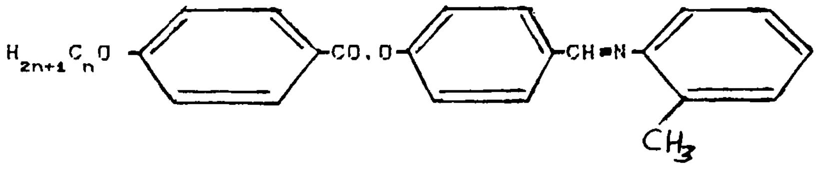
$$\eta = \frac{2(\bar{a} - a)}{(A_{\parallel} - a)}$$

where 'a' is the isotropic nitrogen hyperfine splitting measured in the isotropic phase and $A_{\parallel}$ the component of the nitrogen tensor perpendicular to the plane of oxazolidene ring and is taken to be 3.08×10^{-3}T (24).

The spectra obtained from the spin probe in nematic and smectic A phases, in all the compounds, consisted of just three symmetric lines, as expected for a mono domain sample. This form of the sample shows that the spin probe molecules are reorienting rapidly within the smectic layers on the time scale of the ESR experiment. So, the use of the above expression for calculating the orientational order parameter, η, in nematic and smectic A phase is justified. The density measurements were carried out using the bicapillary pycnometer technique. The temperature accuracy is 0.1°C and the density measurements have an absolute accuracy of 0.1 kg. m^{-3}.

RESULTS AND DISCUSSION

The molecular structure of the compounds is



The transition temperatures and transition enthalpy values of the compounds are presented in Table I. An interesting strucutral feature of these compounds is the presence of a lateral group in the ortho position of the aniline ring which reduces the transition temperatures in comparison with the compounds of 4(4′-*n*-alkoxy benzoyloxy)4″-benzylidene anilines and 4(4′-*n*-alkyloxy benzoloxy benzylidene)-4″-methylanilines. On comparison of the transition temperatures of the series nBBMA (2″) with those of nBBA and nBBMA(4″) (25,26) it is observed that the transition temperatures of nBBMA (2″) homologues are smaller than their counter parts in nBBA and nBBMA (4″) homologous series.

A DSC scan of the compund 8BBMA is presented in Figure 1. A sharp melting transition is indicative of the purity of the samples. DSC and thermal microscopy studies indicated the presence of a nematic phase in heptyl, octyl and nonyl homologues of the nBBMA series and nematic and smetic A phases in the decyl, undecyl and dodecyl homologues of the series.

The variation of the orientational order parameter, η, with temperature, measured for the nitroxide probe on the shifted temperature ($T_{NI} - T$) is shown in Figure 2 for all the compounds. η is found to vary smoothly across the NA transition in decyl and discontinuously in undecyl and dodecyl homologues of the series which indicates that the transition is second order in decyl homologue and first order in undecyl and dodecyl homologues. In contrast, there is a clear discontinuity in η at the IN transition in all of the compounds in keeping with its first order character.

TABLE I

The transition temperatures and transition enthalpy values of the compounds of nBBMA homologous series

Compound	I	N	S_A	K	Reference
7BBMA	*	110.2			Present work
	#	(109.7)			
	@	603.5			
8BBMA	*	111.2	–	78.9	Present work
	#	(111.9)	–		
	@	553.6	–	34999	
9BBMA	*	111.55	–	70.6	Present work
	#	(106.3)	–		
	@	628.2	–	29259	
10BBMA	*	113.5	86.2	69.9	23
	#	(113.5)	(86.2)		
	@	642.6	358.1	26836	
11BBMA	*	106.8	86.6	75.2	Present work
	#	(107.6)	(86.6)		
	@	900.9	627.8	33414	
12BBMA	*	106.1	89.7	77.2	Present Work
	#	(106.1)	89.7		
	@	787.9	784.0	34479	

*Transition temperature in ° C from DSC studies
#Transition temperature in ° C from density studies
@Transition enthalpy values in Joules/mole

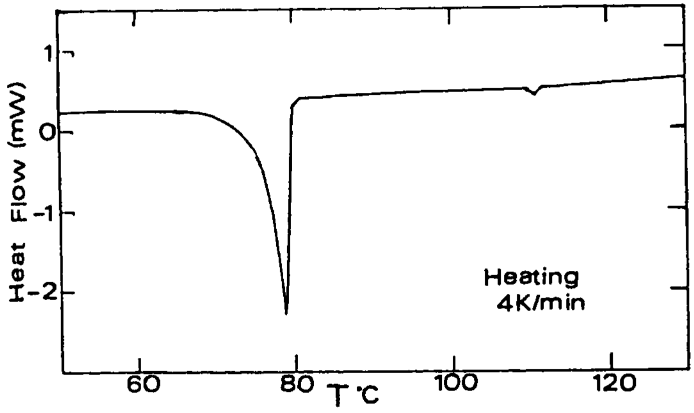


FIGURE 1 A DSC scan of the Compound 8BBMA.

The variation of density (gm/cm^3) with temperature on either side of the IN phase transition ($\pm 5\,^\circ$C) in C_7, C_8, C_9, C_{10}, C_{11} and C_{12} homologues of the nBBMA series is shown in Figure 3.

The transition entropies ($\Delta S/R$) at IN and NA transitions and the density jump ($\Delta\rho/\rho \times 100$) at IN transition; the Mc Millan parameter (T_{NA}/T_{IN} where T_{NA} and

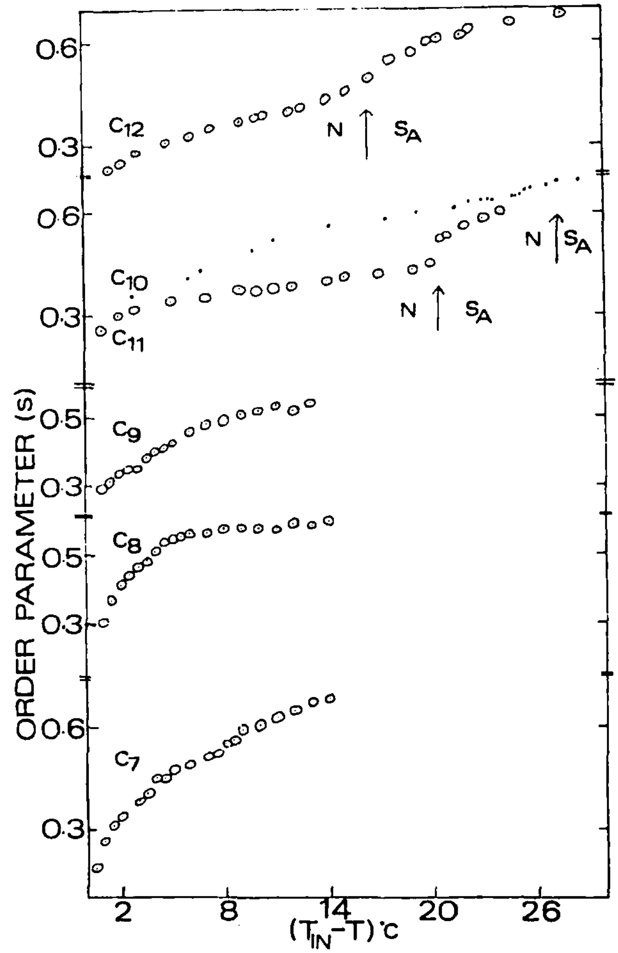


FIGURE 2 The variation of the orientational order parameter, η, with temperature in nBBMA compound.

T_{IN} are NA and IN transition temperatures respectively) for all the compounds are presented in Table II. The data for some other mesogens are also included for comparison.

The density in all the phases, excluding the vicinity of the transition region increases with decreasing temperature. The continuous rotational symmetry of the isotropic phase is broken at the IN transition. The IN transition, which involves a change of disordered phase into a long range orientationally ordered phase is universally accepted as a first order transition. The IN transition is inferred by a discontinuous change in density in all the compounds studied. Further, the coexistence of isotropic and nematic phases was observed for 0.6 °C to 0.8 °C. However, the significant jump in density at the transition is completed within 0.2 °C. The observed transition entropies ($\Delta S/R = 0.19$ in 7BBMA, $\Delta S/R = 0.17$ in 8BBMA, $\Delta S/R = 0.21$

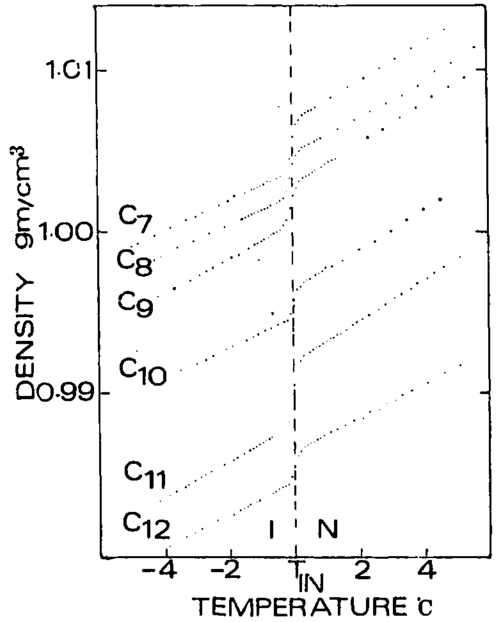


FIGURE 3 The variation of density with temperature on either side of the IN phase transition for the compounds of nBBMA series.

TABLE II

Transition entropy ($\Delta S/R$) at IN and NA transitions; density jump($\Delta\rho/\rho \times 100$) for IN transition and the Mc Millan parameter (T_{NA}/T_{IN}) for the compounds of nBBMA homologous series

		Transition entropy at		*Density Jump at*	
Compound	T_{NA}/T_{IN}	*IN*	*NA*	*IN*	Reference
7BBMA		0.19	–	0.31	Present work
8BBMA		0.17	–	0.26	Present work
9BBMA		0.21	–	0.25	Present work
10BBMA	0.930	0.20	0.12	0.25	23
11BBMA	0.947	0.2a	0.21	0.38	Present work
12BBMA	0.957	0.25	0.26	0.24	23
TB4A	0.928	0.32	0.15	–	28
TB5A	0.958	0.37	0.30	–	28
50.5	0.933	0.39	0.05	0.34	28,14
50.7	0.966	0.53	0.20	0.33	28,14
50.8	0.977	0.47	0.28	0.25	28,29
50.10	0.974	0.38	0.22	0.46	30,31

TB4A/TB5A	Terephthalylidene-bis-4′-n-alkylaniline
50.5/50.7/ 50.8/50.10	N(*p*- *n*- pentyloxy benzylidene) -4′-*n*-alkylaniline

in 9BBMA, $\Delta S/R = 0.20$ in 10BBMA, $\Delta S/R = 0.29$ in 11BBMA and $\Delta S/R = 0.25$ in 12BBMA) and a jump in density ($\Delta\rho/\rho \times 100$ is 0.31 in 7BBMA, 0.26 in 8BBMA, 0.25 in 9BBMA, 0.25 in 10BBMA, 0.38 in 11BBMA and 0.24 in 12BBMA) infer a first order transition in all compounds. However, the observed transition entropies as well as density jumps are slightly smaller at the IN transition in nBBMA compounds, except for 11BBMA, compared to other mesogens with similar molecular structure (see Tab. II). These results suggest that the IN transition in nBBMA compounds is a weaker transition than expected and the origin of this behavior may be associated with the molecular broadening caused by the lateral methyl group which increases the molecular biaxiality.

The NA transition is of particular interest because its order is determined by the molecular structure, unlike the IN transition which to a reasonable approximation is relatively insensitive to the molecular structure. The variation of density with temperature on either side of the NA phase transition (± 5 °C) in C_{10}, C_{11}, and C_{12} homologues of the nBBMA series is shown in Figure 4. The DSC studies indicate a small but noticeable transition entropy at the NA transition in the compounds 10BBMA, 11BBMA and 12BBMA. Also, a small density jump ($\Delta\rho/\rho \times 100$ is 0.091 in 10BBMA, 0.077 in 11BBMA and 0.064 in 12BBMA) at the NA transition is

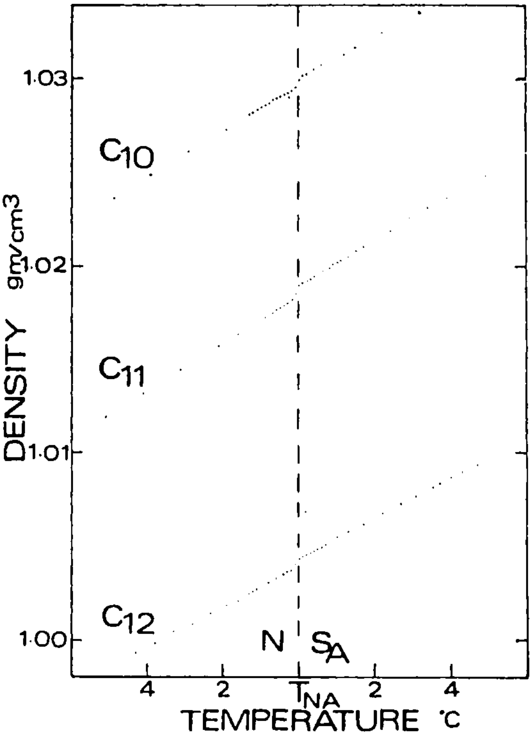


FIGURE 4 The variation of density with temperature on either side of NA phase transition in 10BBMA, 11BBMA and 12BBMA.

observed which compliment the results of DSC studies. However, the ESR studies show a continuous variation of the orientational order parameter, η, at the NA transition, of 12BBMA which indicate a second order transition. A small but noticeable jump is observed in order parameter at NA transition of 10BBMA and 11BBMA. The ratios $N = h_2/h_1$ where h_1 and h_2 are the heights of the DSC transition peaks obtained at the NA transition with two different temperature scanning rates: one (h_2) being twice the other (h_1) keeping the weight of the compound constant are $1 \leqslant N \leqslant 2$ for an isothermal first order transition and equals 2 for a second order transition (27). Our results are in good agreement with the reported values of $N(1.753 \pm 0.005$ for 10BBMA, 1.777 ± 0.005 for 11BBMA and 1.875 ± 0.005 for 12BBMA) suggesting it to be a weak first order transition in all the three compounds (23).

Mc Millan theory of the smectic A phase (2) predicts the relationship between the order of the NA transition and the length of the nematic phase which is in qualitative agreement with experiment. The NA transition is predicted to become strongly first order as the Mc Millan parameter (T_{NA}/T_{IN} where T_{NA} and T_{IN} are the NA and IN transition temperatures respectively) approaches unity. In additiion, there is a tricritical point separating second and first order transitions predicted to occur at $T_{NA}/T_{IN} = 0.87$. Recent experimental studies have reported the tricritical point to occur at different temperatures in different systems (17, 20, 21). For example, the tricritical point is reported to occur when $T_{NA}/T_{IN} = 0.978$ in binary mixtures of 40.8 + 60.8 (20), at $T_{NA}/T_{IN} = 0.955$ in mixtures of 40.6 + 60.6 (21). These values are smaller than that reported for nCBs for which $T_{NA}/T_{IN} = 0.944$ (17). All these results suggest that the NA transition is not universal and varies with molecular structure of the mesogen. The values of Mc Millan parameter and NA transition entropies are compared in Table II. The T_{NA}/T_{IN} values of 0.930 for 10BBMA; 0.947 for 11BBMA and 0.957 for 12BBMA suggest a smaller value than 0.930 for the tricritical point in the nBBMA homologous series. The ESR measurements of orientational order parameter for the probe do not indicate any discontinuity at the NA transition in 10BBMA and indicate small jumps in both 11BBMA and 12BBMA. So, the DSC and density results show that NA transition is weakly first order in all the three compounds. ESR measurements show a continuous change of orientational order parameter at the transition in 10BBMA. To see whether the results are consistent or not, we have compared them with the theoretical predictions of the decoupled model of the smectic A phase proposed by Kventsel *et al* (11) for the compounds 10BBMA and 12BBMA (23). In conclusion, the comparisons suggest that the NA transition entropy and the variation of orientational order parameter lead to the same conclusions, with a finite translational order parameter at the NA transition in all the three compounds, that the transition is very weakly first order in 10BBMA and weakly first order in 11BBMA and 12BBMA.

References

1. K. Kobayashi, *Physics Letters A*, **31**, 125 (1970) K. Kobayashi, *Mol. Cryst. Liquid Cryst.*, **13**, 137 (1971).
2. W. L. Mc Millan, *Phys. Rev. A*, **4**, 1238 (1971) W. L. Mc Millan, *Phys. Rev. A*, **6**, 936 (1972).

3. P. G. de Gennes, *Solid State Commun.*, **10**, 753 (1972).
4. R. Alben, *Solid State Commun.*, **13**, 1783 (1972).
5. B. I. Halperin, T. C. Lubensky and S. K. Ma, *Phys. Rev. Letters*, **32**, 293 (1974).
6. E. B. Priestly, P. Wojtowics and P. Sheng (Ed), *"Introduction to Liquid Crystals"*, Plenum Press, New York (1975).
7. R. B. Meyer and T. C. Lubensky, *Phys. Rev. A*, **14**, 2307 (1976).
8. A. Kloczkowski and J. Stecki, *Reprint of Inst. of Physical Chem.*, Warsaw, (1980).
9. M. Hosiono, H. Nakano and H. Kimura, *J. Phys. Soc. Jpn.*, **51**, 741 (1982).
10. J. Katriel and G. F. Kventsel, *Phys. Rev. A*, **28**, 3037 (1983).
11. G. F. Kventsel, G. R. Luckhurst and H. B. Zewdie, *Mol. Phys.*, **56**, 589 (1985).
12. L. Longa, *J. Chem. Phys.*, **85**, 2974 (1986).
13. L. Longa, *Z. Phys. B*, **64**, 357 (1986).
14. P. R. Alapati, D. M. Potukuchi, N. V. S. Rao, V. G. K. M. Pisipati, A. S. Paranjpe and V. R. K. Rao, *Liq. Cryst.*, **3**, 1461 (1988).
15. D. L. Johnson, C. Maze, E. Openheim and R. Reynolds, *Phys. Rev. Letters*, **34**, 1143 (1975).
16. B. Brisbin, R. J. de Hoff, T. E. Lockhart and D. L. Johnson, *Phys. Rev. Letters*, **43**, 1171 (1979).
17. J. Thoen, H. Marynissen and Van Dael, *Phys. Rev. Letters*, **24**, 204 (1984).
18. J. Thoen, *Mol. Cryst. Liq. Cryst.*, **124**, 195 (1985).
19. B. M. Ocko, R. J. Birgeneau and J. D. Litster, *Z. Phys. B*, **62**, 487 (1986).
20. K. Stine and C. W. Garland, Proc. 11th Internatl. L iq. Cryst. Conf., Berkely (USA), June 30 to July 4, 1986.
21. V. G. K. M. Pisipati, S. B. Rananavare and J. H. Freed, *Mol. Cryst. Liq. Cryst. Letters*, **4**, 1981 (1987).
22. N. Dixit, Ph. D. Thesis M.S. University, Baroda, India (1982).
23. P. R. Alapati and D. Saran, *Phys. Stat. Solidi (b)*, **168**, 39 (1991).
24. W. L. Hubbel and H. M. Mc Connel *J. Amer. Chem. Soc.*, **93**, 314 (1971).
25. J. S. Dave, G. Kurian and N. R. Patel, *Indian J. Chem.*, **19A**, 1161 (1980).
26. J. S. Dave and G. Kurian, *Mol. Cryst. Liq. Cryst.*, **42**, 175 (1977).
27. P. Navard and J. M. Hauding, *J. Thermal Analysis*, **29**, 405 (1984); *Mol. Cryst. Liq. Cryst. Letters*, **102**, 261 (1984); ibid **102**, 256 (1984).
28. A. Weigeleben, L. Ritcher, J. Deresch and D. Demus, *Mol. Cryst. Liq. Cryst.*, **59**, 329 (1980).
29. V. G. K. M. Pisipati, N. V. S. Rao, P. V. Datta Prasad and P. R. Alapati, *Z. Naturf.*, **40**, 472 (1984).
30. R. Caucifo, S. Melone, V. G. K. M. Pisipati, N. V. S. Rao and G. Torquati, *Nuovo Ciminto*, **7D**, 421 (1986).
31. N. V. S. Rao, V. G. K. M. Pisipati, P. V. Datta Prasad and P. R. Alapati, *Phase Transitions*, **5**, 187 (1985).