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High Pressure Studies on Mesomorphic and Polymesomorphic Transitions

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The paper presents the following results: (1) pressure induced mesomorphism in *p-p′-n*-butylazobenzene and biphenyl *p*-ethyl benzoate, (2) the monotropic nematic–isotropic transition in trans-*p-n*-propoxy-α-methyl cyanophenyl cinnamate becoming enantiotropic under pressure, (3) suppression of the cholesteric mesophase in cholesteryl nonanoate and the location of a solid–cholesteric–isotropic triple point at ~2.85 kbar, confirming an earlier observation of Keyes, Weston and Daniels on the same compound, (4) a measurement of dT/dp for the solid–smectic A, smectic A–cholesteric and cholesteric–isotropic transitions in cholesteryl myristate and a comparison with the values evaluated from the Clausius–Clapeyron equation using the known latent heat and volumetric data.

INTRODUCTION

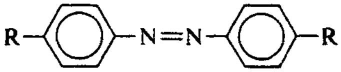
Robberecht[1] discovered that the monotropic cholesteric–isotropic transition in cholesteryl methyl carbonate becomes enantiotropic under pressure. More recently, we predicted the phenomenon of pressure induced mesomorphism in materials that are non-mesomorphic at atmospheric pressure and verified this experimentally for two compounds, viz., *p*-methoxy- and *p*-ethoxybenzoic acids.[2,3] In the present paper we report experimental phase diagrams for five more substances and discuss the results.

EXPERIMENTAL

A 100 ton single acting hydraulic press with a 4 in. diameter movable ram was used for the experiments. Line pressures were read by a calibrated Heise Gauge reading to an accuracy of 50 psi. The true pressure as seen by the sample was computed from the calibration curve obtained by measuring the resistance of a manganin gauge (see Ref. 2). Differential thermal analysis (DTA) was used as the probe to detect the phase transitions. A detailed description of the cell is given elsewhere.[4] The main features of this cell are (i) the sample is completely encapsulated in teflon so that there is no contamination from the pressure transmitting medium, and (ii) the sample thermocouple junction is surrounded by the substance under investigation, thus facilitating the detection of even very weak first order transitions. A Keithley nanovoltmeter (Model 148) was used to amplify the differential (ΔT) and the amplified signal fed to the y-axis of a Riken-Denshi X-Y recorder (model F-43). An amplification of ~2000 was sufficient to record the solid-nematic transition, but to record the nematic-isotropic and smectic-nematic transitions, a gain of 5000 to 10000 was necessary. Heating rates of 1-6°C/min were used to record the transitions. The following points need to be emphasized: firstly each point marked in the phase diagram is the average of at least 2 runs taken at different heating/cooling rates. (The solid-liquid crystal transition temperature was always taken from the heating cycle only, as during the cooling cycle the liquid crystalline phase invariably supercooled to different extents depending on the rate of cooling.) Secondly after the completion of a set of measurements, it was ascertained that the transition temperatures at atmopsheric pressure were reproducible, thus confirming that the sample did not undergo any decomposition during the experiment.

RESULTS AND DISCUSSION

1 (a) *p,p'-di-n-butylazobenzene* Van der Veen *et al.*[5] have synthesized low melting *p,p'*-di-*n*-alkylazobenzenes which have the following structural formula:



where R denotes the alkyl group. They found that up to R = butyl, the compounds are non-mesomorphic whereas the pentyl and hexylazobenzenes show a monotropic nematic phase. All the higher homologues show enantiotropic mesophases. We undertook experiments on butylazobenzene which has a low melting point of 26°C to see if we can induce mesomorphism by application of pressure, as we had done earlier for *p*-methoxy- and *p*-ethoxybenzoic acids.[2,3] The sample used in our experiments was synthesized by V. Surendranath in our chemistry laboratory. It was found that till a pressure of ~1 kbar there is only a single transition, viz., solid-isotropic (Figure 1a),

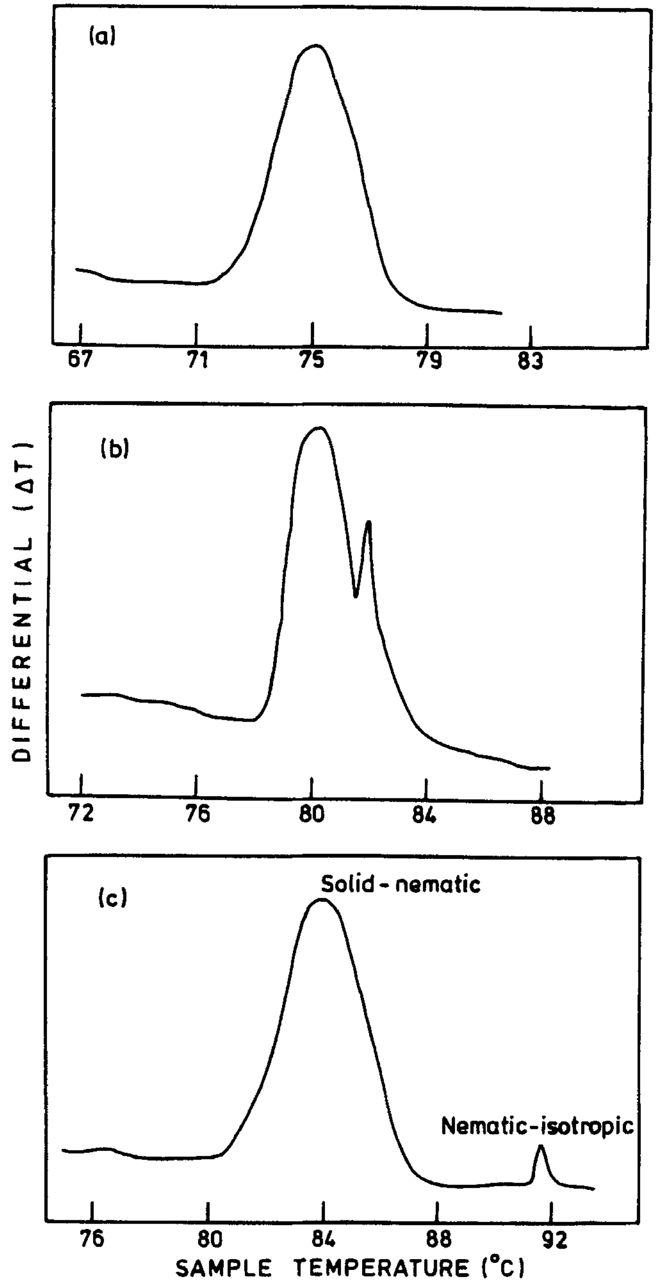


FIGURE 1 Raw DTA traces taken for *p,p'*-di-*n*-butylazobenzene at pressures of (a) 1 kbar, (b) 1.15 kbar, and (c) 1.5 kbar; heating rate 4°C/min.

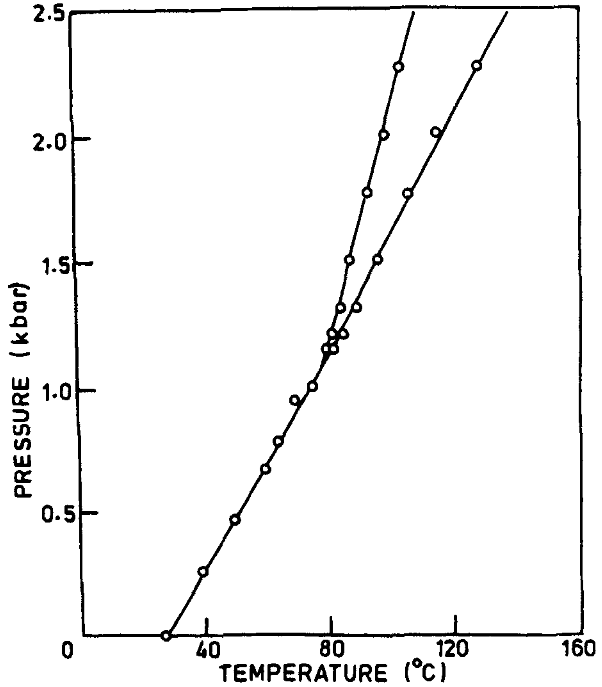
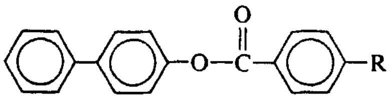


FIGURE 2 Phase diagram for *p,p′*-di-*n*-butylazobenzene.

while for pressures greater than 1.15 kbar there is a second transition much weaker than the first one (Figure 1b), the separation between the two transitions increasing with increase of pressure (Figure 1c). We therefore have another case of pressure induced mesomorphism. The phase diagram is shown in Figure 2. It is seen that there is a solid-liquid crystal-liquid "triple point" at about 1.1 kbar and 78°C. It is of course not possible to say what type of mesophase it is from DTA. The optical cell used by us to identify the phases in previous studies[6] could not be used here as this cell was not suitable for pressures beyond a few hundred bars. But considering the fact that all the higher homologues show only a nematic phase, it is most likely that the pressure induced phase in butylazobenzene is nematic.

(b) *Biphenyl-p-ethylbenzoate* A new homologous series, viz., biphenyl-*p*-alkyl benzoate having the following structural formula have been synthesized by Sadashiva in our chemistry laboratory.[7]



The first two members of this series are non-mesomorphic whereas the third member onwards they exhibit a nematic phase which is monotropic up to the fifth member and enantiotropic for higher derivatives. We have carried out experiments on the second member, i.e., biphenyl-*p*-ethyl benzoate and the phase diagram is given in Figure 3. We see that this compound also shows pressure induced mesomorphism with a triple point at about 1.2 kbar and ~215°C. All the runs were usually taken in the heating cycle only, but we happen to record a few runs in the cooling cycle also in this case. As a consequence, we noticed that a monotropic mesophase shows up at pressures of 1, 1.1 and 1.14 kbar, the mesophase-liquid transition becoming enantiotropic beyond 1.25 kbar. These three points are also marked in the phase diagram (Figure 3), the dashed line signifying that the transition is monotropic. (It is quite possible that such a pressure induced monotropic behaviour occurring initially before obtaining the enantiotropic mesophase could

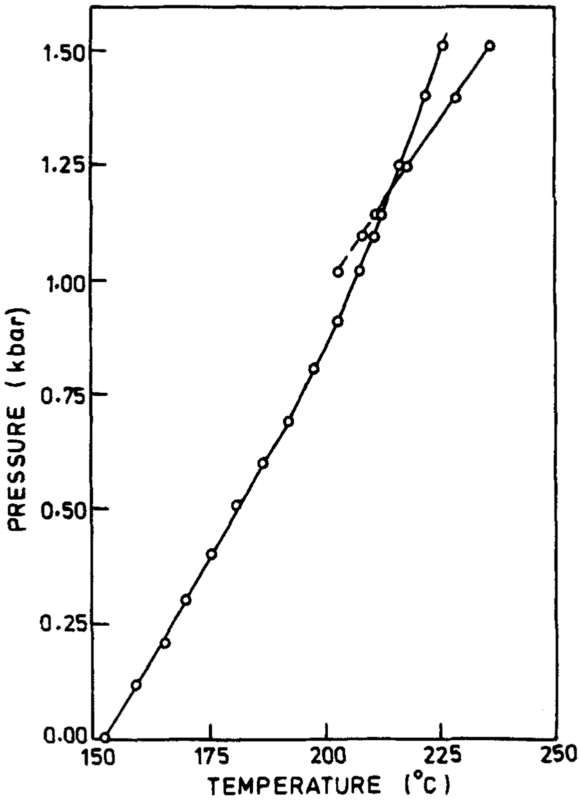
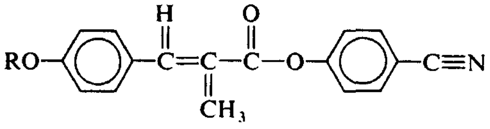


FIGURE 3 Phase diagram for biphenyl *p*-ethyl benzoate; the dashed line signifies that the transition is monotropic (see text).

conceivably have been missed in butyl azobenzene or even in *p*-methoxy- and *p*-ethoxy-benzoic acids wherein we did not take any runs in the cooling cycle.)

2 *Trans-p-n-propoxy-α-methyl-p′-cyanophenyl cinnamate* Recently Sadashiva[8] has synthesized another new series of compounds, viz., trans-*p*-*n*-alkoxy-α-methyl-*p*′-cyanophenyl cinnamates which have a high positive dielectric anisotropy. These have the structural formula:



$$\mathrm{RO{-}C_6H_4{-}\overset{H}{C}{=}\underset{CH_3}{C}{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_6H_4{-}C{\equiv}N}$$

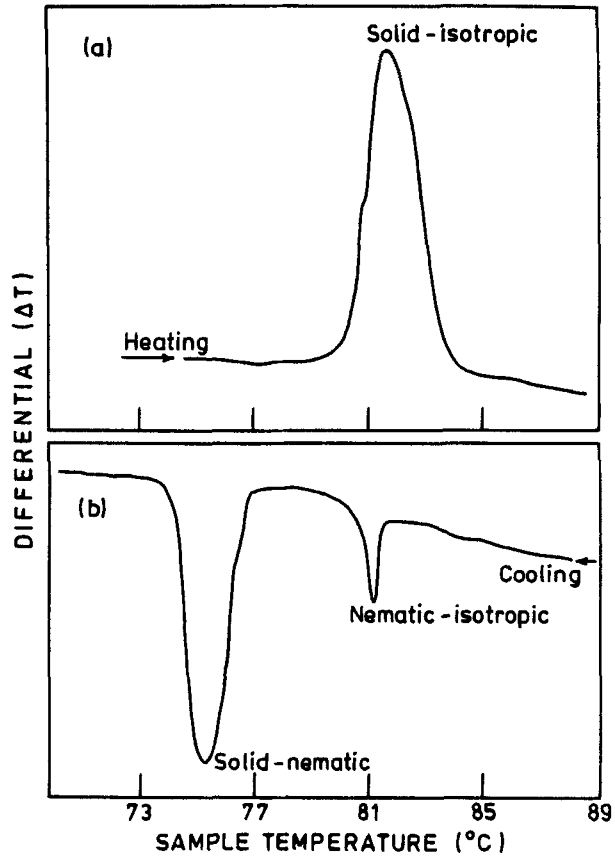


FIGURE 4 Raw DTA records taken for trans-*p*-*n*-propoxy-α-methyl-*p*′-cyanophenyl cinnamate at 470 bars; (a) heating, 3 C/min, (b) cooling, 4°C/min.

We have carried out experiments on the third member, i.e., the propoxy derivative, of this series, which shows a monotropic nematic phase with the solid–isotropic and isotropic–nematic transition temperatures of 71°C and 66.5°C respectively. Up to a pressure of ~470 bars, the nematic appeared only in the cooling cycle, i.e., was monotropic, as seen in Figures 4a and 4b. But at a pressure of ~580 bars the nematic phase appears in both heating and cooling cycles (Figures 5a and 5b) showing therefore that nematic–isotropic transition changes its nature from monotropic to enantiotropic between these

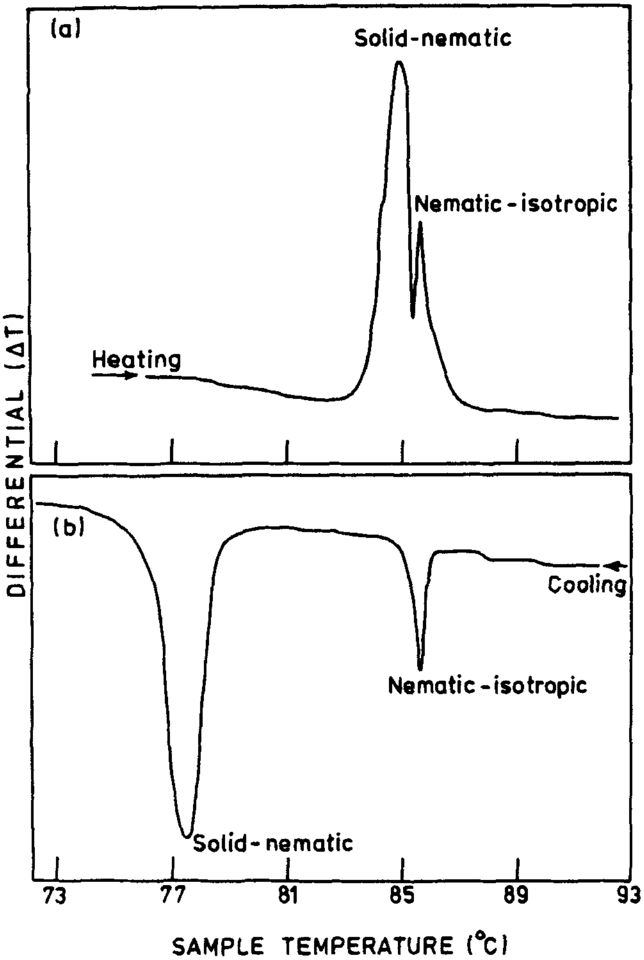


FIGURE 5 Raw DTA records taken for trans-p-n-propoxy-α-methyl-p'-cyanophenyl cinnamate at 580 bars; (a) heating, 3 C/min., (b) cooling, 4 C/min.

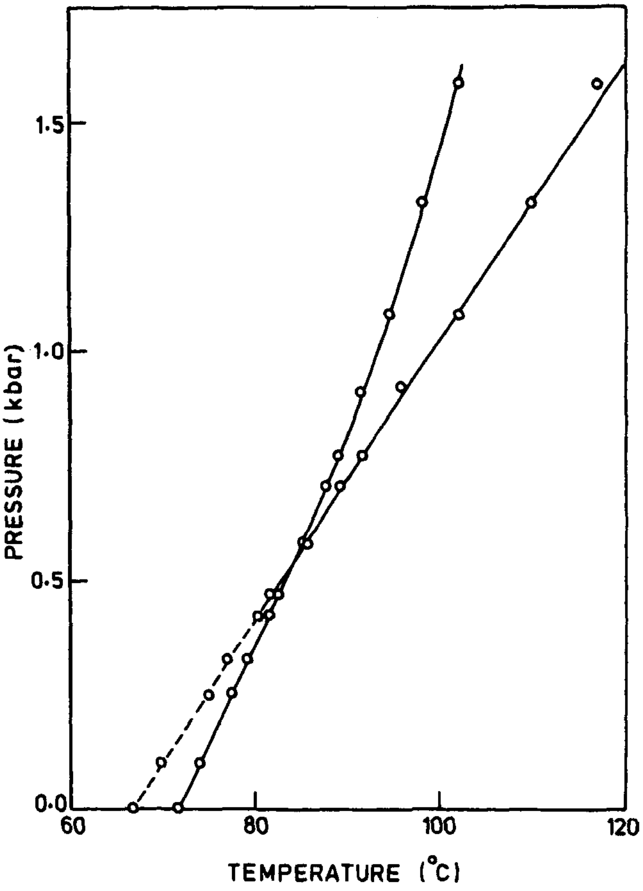


FIGURE 6 Phase diagram for trans-*p*-*n*-propoxy-α-methyl-*p*′-cyano phenyl cinnamate: the dashed line signifies that the transition is monotropic.

pressures. At all subsequent pressures, the nematic phase retains its enantiotropic character. From the phase diagram shown in Figure 6 it is seen that this change in the nature of the transition occurs at about 520 bars. Such a behaviour was first observed by Robberecht[1] in cholesteryl methyl carbonate.

3 *Cholesteryl nonanoate* This compound exhibits a monotropic smectic A phase in addition to the cholesteric phase at atmospheric pressure.[9] Its phase diagram presented in Figure 7 shows an interesting feature. It is seen that with increasing pressure, the range of the cholesteric phase diminishes and finally it is completely bounded. Therefore, there is a solid–cholesteric–isotropic triple point at ~2.85 kbar and 196°C. The cholesteric–smectic A

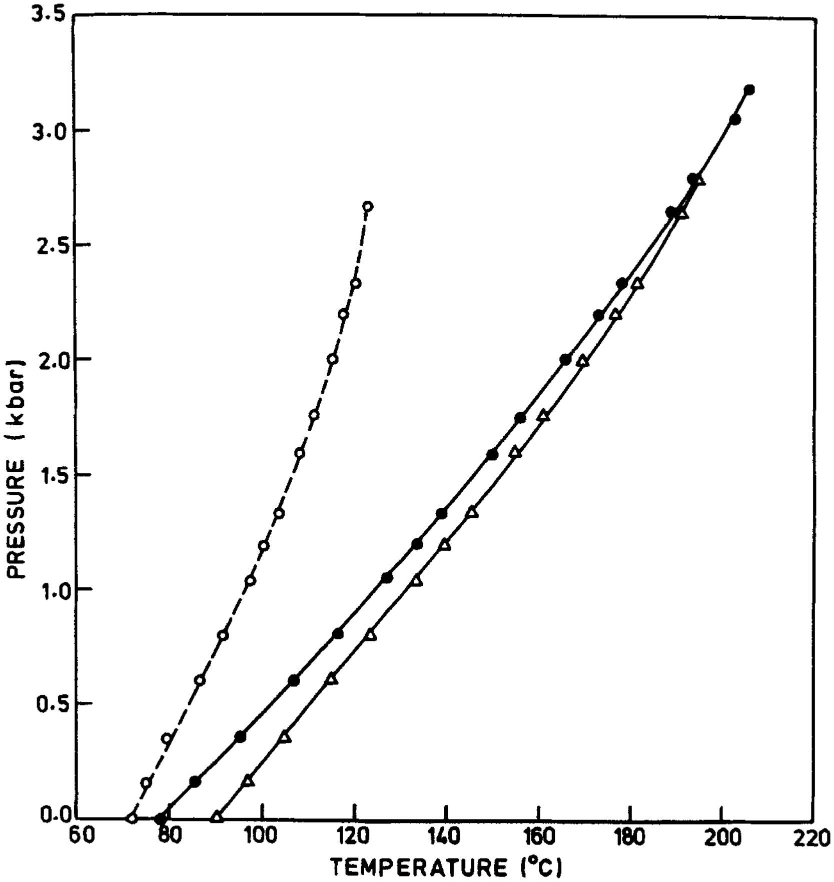


FIGURE 7 Phase diagram for cholesteryl nonanoate: ○, ● and △ correspond to smectic A-cholesteric, solid-cholesteric and cholesteric-isotropic transitions respectively. The dashed line signifies that the smectic A-cholesteric transition is monotropic.

transition remains monotropic at all pressures studied. After completing our study of this compound it was learnt that Keyes *et al.*[10] have also studied the same compound. Our results are in good agreement with their data.

4 *Cholesteryl myristate* The phase diagram for cholesteryl myristate is given in Figure 8. Experiments were conducted on this compound with a view to verifying whether the smectic A-cholesteric transition, which is first order at atmospheric pressure, becomes second order at high pressure as happens in cholesteryl oleyl carbonate[3,11] and in *p*-cyanobenzylidene-*p*′-nonyl analine.[12] But no such tricritical behaviour was observed here. Table I

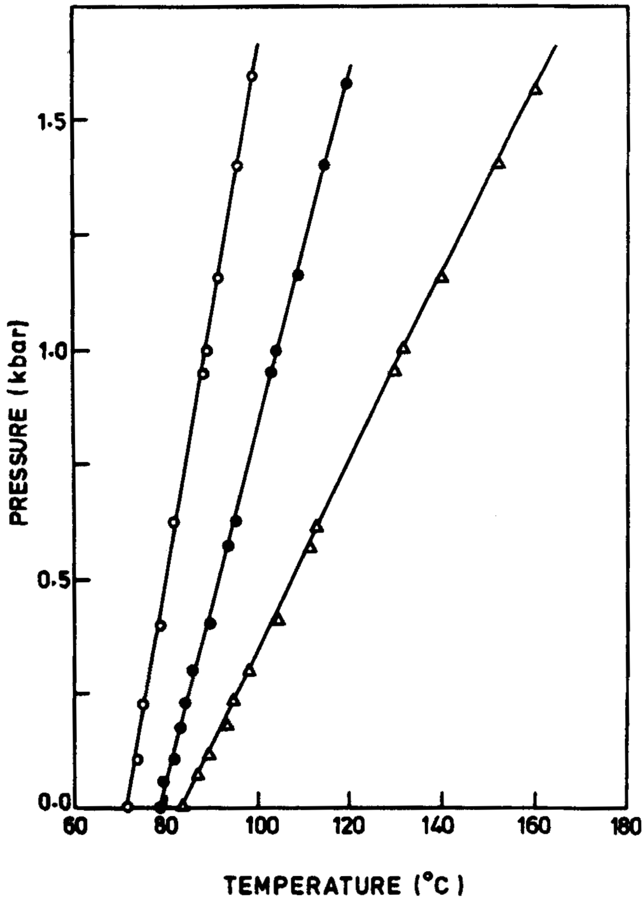


FIGURE 8 Phase diagram for cholesteryl myristate: ○, ● and △ correspond to solid smectic A, smectic A-cholesteric and cholesteric-isotropic transitions respectively.

TABLE I

dT/dp (in K/kbar) values for cholesteryl myristate

	Solid-smectic A	Smectic A-nematic	Nematic-isotropic
Present work	17.4	26.5	47.8
Calculated from Clausius-Clapeyron equation	21.8[13,14]	27.3[9,14]	51.7[9,14]

gives the slopes (dT/dp) for the solid–smectic A, smectic A–nematic and nematic–isotropic transitions obtained from the phase diagrams along with those calculated from the Clausius–Clapeyron equation using the known latent heat[9,13] and volumetric[14] data. It is seen that the agreement is quite good considering the relatively large errors involved in the measurement of volume changes.

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References

1. J. Robberecht, *Bull. Soc. Chim. Belg.*, **47**, 597 (1938).
2. S. Chandrasekhar, S. Ramaseshan, A. S. Reshamwala, B. K. Sadashiva, R. Shashidhar, and V. Surendranath, Proc. Int. Liquid Cryst. Conf., Bangalore, 1973, *Pramana Supplement*, **1**, 117.
3. R. Shashidhar and S. Chandrasekhar, *J. Physique*, **36**, C1-49 (1975).
4. A. S. Reshamwala and R. Shashidhar, *J. Phys. E.-Sci. Instruments*, **10**, 180 (1977).
5. J. Van der Veen, W. H. de Jeu, A. H. Grobben, and J. Boven, *Mol. Cryst. Liquid Cryst.*, **17**, 291 (1972).
6. R. Shashidhar, S. Ramaseshan, and S. Chandrasekhar, *Current Science*, **45**, 1 (1976).
7. B. K. Sadashiva (to be published).
8. B. K. Sadashiva, *Mol. Cryst. Liquid Cryst.*, **35**, 205 (1976).
9. W. L. McMillan, *Phys. Rev.*, **A6**, 936 (1972).
10. P. H. Keyes, H. T. Weston, and W. B. Daniels, *J. Chem. Phys.*, **63**, 5006 (1975).
11. P. H. Keyes, H. T. Weston, and W. B. Daniels, *Phys. Rev. Letters*, **31**, 628 (1973).
12. T. J. McKee and J. R. McColl, *Phys. Rev. Lett.*, **34**, 1076 (1975).
13. G. J. Davies and R. S. Porter, *Mol. Cryst. Liquid Cryst.*, **11**, 319 (1970).
14. F. P. Price and J. H. Wendhorf, *J. Phys. Chem.*, **75**, 2839 (1971).