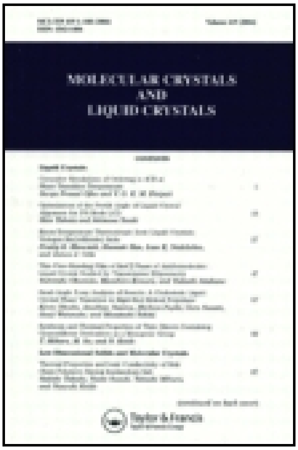

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Effect of Pressure on the Stability of Smectic C Phases[†]

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We have carried out pressure studies on three pure compounds, *viz.*, di-(4′-*n*-octyloxyphenyl)-trans-cyclohexane-1, 4-dicarboxylate), p-*n*-nonyloxybenzoic acid and *n*-pentyl-4 (4′-*n*-decyloxybenzylideneamino) cinnamate, each of which exhibits the smectic C phase but the nature of the temperature variation of the tilt angle being different in the three cases. It is found that for all the compounds the smectic C phase is suppressed at high pressures.

INTRODUCTION

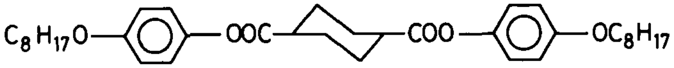
It has long been recognized[1–3] that the temperature variation of the tilt angle in the smectic C phase depends on the nature of the phase to which it transforms on heating. If the higher temperature phase is the nematic phase, then the tilt angle is rather large and independent of temperature.[3] On the other hand, if the C phase is followed by the smectic A phase, then the tilt angle is relatively small and temperature dependent.[3] However, more recently a third type of smectic C has been observed[4,5] in which the tilt angle is temperature independent even though the higher temperature phase is the A phase. We have carried out pressure studies on three pure compounds, *viz.*, di-(4′-*n*-octyloxyphenyl)-trans-cyclohexane-1, 4-dicarboxylate), p-*n*-nonyloxybenzoic acid and *n*-pentyl-4 (4′-*n*-decyloxybenzylidene amino) cinnamate, which exhibit these three types of smectic C to see if they behave differently at high pressures.

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.

THE COMPOUNDS

(i) di-(4′-*n*-octyloxyphenyl)-trans-cyclohexane-1, 4′-dicarboxylate (8 OPCDC)

This compound, which was first synthesized[6] with a view to studying the effect of replacing a benzene ring by a cyclohexane ring on the mesomorphic properties, has the following structural formula:



It exhibits two solid phases, two smectic B phases (biaxial and uniaxial) in addition to the smectic C and A phases. de Vries[7] has shown that the tilt angle in the smectic C phase of this compound is temperature dependent. The sample used in the present study was prepared by M. Neubert and J. P. Ferrato.

(ii) p-*n*-nonyloxybenzoic acid (NOBA)

This compound which belongs to a well known homologous seris, *viz.*, p-*n*-alkoxybenzoic acids, was first synthesized by Gray and Jones.[8] It exhibits 2 solid phases (one of which was newly observed by us) in addition to the smectic C and nematic phases. The tilt angle in the C phase has been measured by Chistyakov *et al*.[9] by X-ray diffraction technique and also by Taylor *et al.*[10] by optical methods. Both these studies show that the tilt angle is somewhat large (45°) and does not depend on temperature. The sample used in our study was prepared in our chemistry laboratory.

(iii) *n*-pentyl-4(4′-*n*-decyloxybenzylideneamino) cinnamate (PDOBAC)

This compound synthesized first by Demus *et al.*[11] exhibits three smectic phases B, C and A, but no nematic phase. The layer thickness in the smectic C and smectic A phases of PDOBAC has been measured by de Vries[4] who found that the tilt angle in the C phase which is about 15° remains constant throughout the C phase and does not change even at the C–A transition, the A phase also having the same tilt angle. The sample used in our experiments was prepared by Mary Neubert and Larry Maurer.

EXPERIMENTAL

The transition temperatures (at atmospheric pressure) of the compounds determined by optical microscopy are given in Table I. The values are in good agreement with the literature data.[8,11,12] The transition temperatures at high pressure were determined, using either a DTA cell or an optical cell depending on whether the transition was first order or second. The details regarding the high pressure cells used have been reported elsewhere[13–15] and will not be repeated here. The accuracies in the pressure and temperature measurements were ±7 bar and ±0.25°C respectively for the DTA cell, and ±10 bar and ±0.1°C for the optical cell.

RESULTS AND DISCUSSION

The P–T diagrams of 8 OPCDC, NOBA and PDOBAC are given in Figures 1–3. The dT/dP values for the various transitions of the three compounds are tabulated in Table I.

8 OPCDC: Though the two smectic B phases could be clearly detected in the DSC runs at atmospheric pressure, they could not be resolved in the high pressure DTA experiments. Hence, we have shown only a single

TABLE I

Transition temperatures (°C) of the compounds

Compound	Transition	Temperature
8 OPCDC	K II – K I	72.5
	K I – B (biaxial)	90.5
	B (biaxial) – B (uniaxial)	92.4
	B (uniaxial) – C	110.5
	C – A	119.1
	A – I	178.0
NOBA	K I – K II	92.3
	K II – C	93.6
	C – N	117.0
	N – I	140.0
PDOBAC	K – B	72.3
	B – C	99.8
	C – A	104.5
	A – I	140.0

K-crystal, B-smectic B, C-smectic C, A-smectic A, N-nematic, I-isotropic.

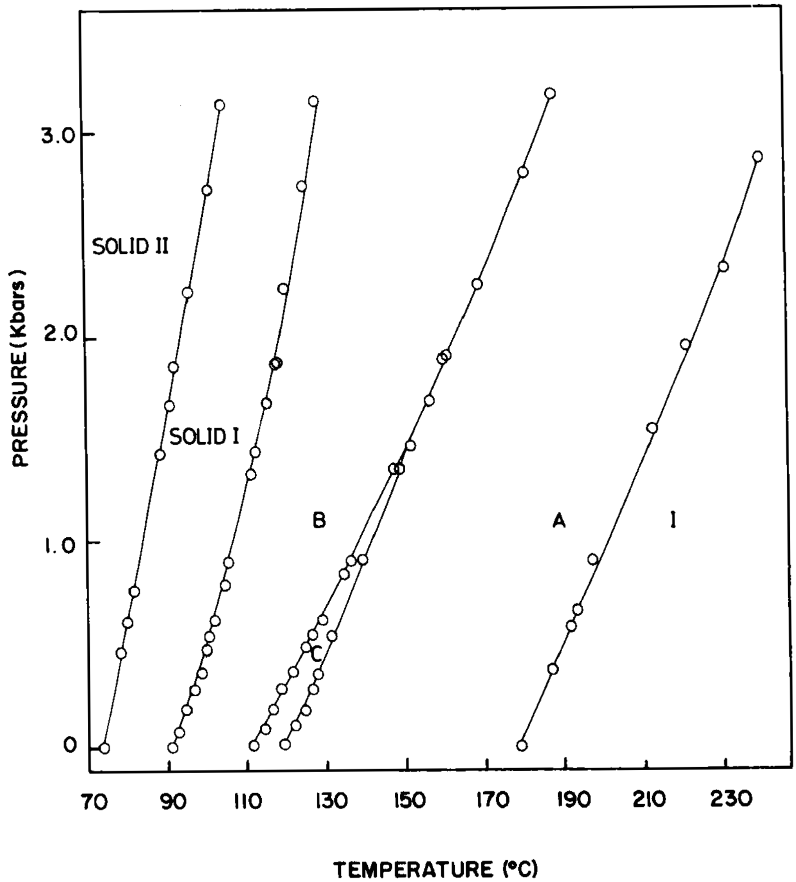


FIGURE 1 P–T diagram of 8 OPCDC.

smectic B phase in the P–T diagram (Figure 1). The different smectic phases behave differently under pressure. The range of the B phase increases with increasing pressure while that of the A phase remains practically constant. On the other hand, the range of the C phase decreases rapidly. This results in the suppression of the C phase with a smectic B-smectic C-smectic A triple point at 1.44 ± 0.05 kbar, 150 ± 0.5°C.

NOBA: All the transitions, *viz.*, solid I–solid, II, solid II–smectic C, smectic C–nematic and nematic–isotropic have been followed as functions of pressure. The feature of the P–T diagram (Figure 2) is again the bounding of the C phase at high pressures. The solid II–smectic C–nematic triple

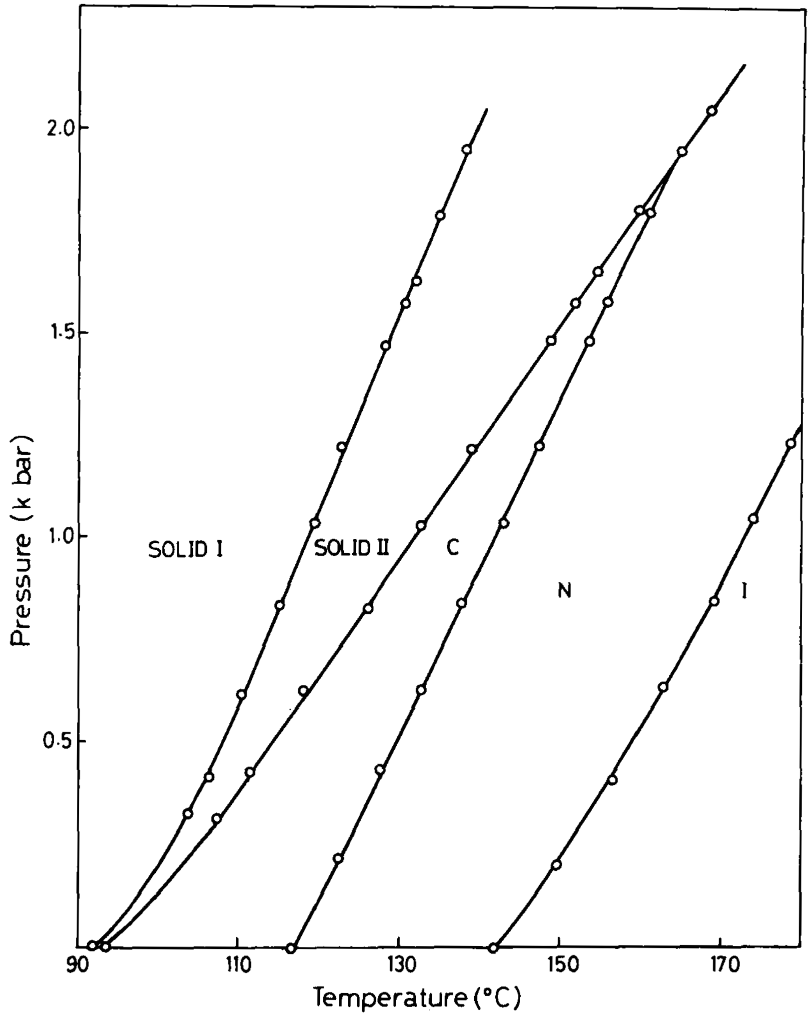


FIGURE 2 P–T diagram of NOBA.

point occurs at 1.92 ± 0.05 kbar, 164.0 ± 0.5°C. The stability of the nematic phase is, of course, increased at high pressures.

PDOBAC: Here again the smectic C phase is suppressed and the resulting smectic B–smectic C–smectic A triple point occurs at 1.57 ± 0.05 kbar, 157 ± 0.5°C. The rate at which the smectic C range decreases is much slower here compared to 8OPCDC or NOBA. Also both B–C and C–A phase boundaries show a pronounced curvature towards the pressure

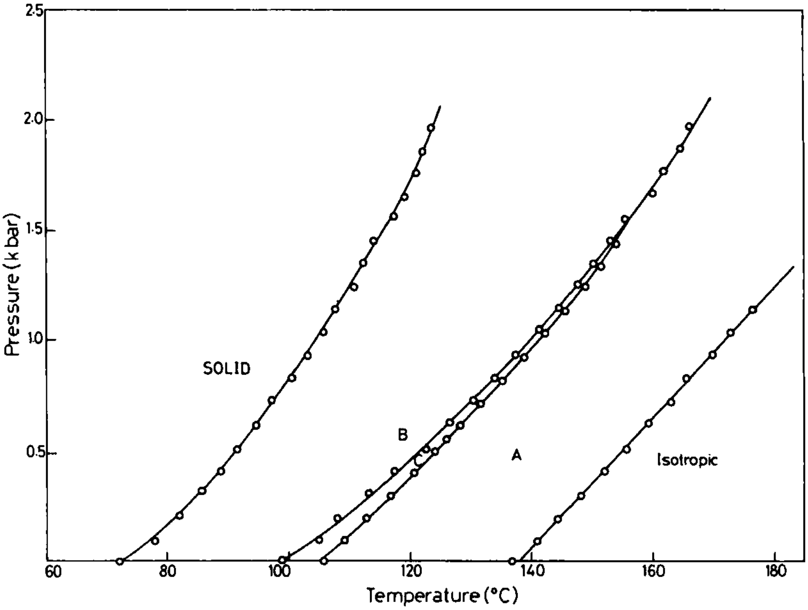


FIGURE 3 P–T diagram of PDOBAC.

axis. The A–I phase boundary on the other hand is, like the N–I boundary of 8 OPCDC and NOBA, practically straight.

Summarizing, it appears that pressure destabilizes the smectic C phase and results in its suppression. This suppression seems to occur whatever be the type of the C phase, i.e., regardless of the nature of the temperature variation of the tilt angle at atmospheric pressure. The exact correlation between the tilt angle and the maximum pressure of occurrence of the C phase should be an interesting problem. High pressure X-ray studies are envisaged to elucidate this point.

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