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# Pressure Studies of Liquid Crystalline Transitions

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# Pressure Studies of Liquid Crystalline Transitions†

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Some of the important results emerging from our recent pressure studies of liquid crystalline transitions are presented. In particular, the following topics are discussed: (i) The relation between $P_m$, the maximum pressure of smectic stability in reentrant mesogens, and the range of the nematic phase at atmospheric pressure vis-a-vis the molecular structure; (ii) Piezothermal studies in the vicinity of the A-N transition in 8 OCB; (iii) The influence of molecular ordering on the pressure behavior of the nematic-isotropic transition in reentrant nematic mixtures; and, (iv) The relation between the pressure behavior of the smectic A phase and the interdigitation of the molecules.

## I. INTRODUCTION

For sometime now we have been conducting high pressure studies on various types of phase transitions occurring in liquid crystalline systems and a number of new and interesting results have emerged from these investigations.[1-3] Of late, a problem that is attracting considerable attention is the phenomenon of reentrance in liquid crystals. The phenomenon was first observed in binary mixtures at atmospheric pressure[4] and later in pure compounds at high pressure.[5] Subsequently, it was also observed in pure compounds at atmospheric pressure.[6,7] We shall present here some important results of our recent pressure experiments on several substances which exhibit reentrant polymorphism.

†Invited paper, Ninth International Liquid Crystal Conference, Bangalore, 1982.

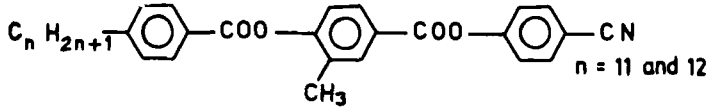
## II. VARIATION OF $P_m$, THE MAXIMUM PRESSURE OF SMECTIC STABILITY, WITH THE TEMPERATURE RANGE OF THE NEMATIC PHASE

We have studied the *P-T* diagrams of eight reentrant nematogenic compounds, these being the eleventh and twelfth homologues of four different homologous series. The molecular structures of these compounds which were synthesized in our chemistry laboratory[8,9] are given in Table I and their transition temperatures (at atmospheric pressure) measured by optical microscopy are given in Table II. All these compounds have three phenyl rings, a lateral methyl or methoxy group and a cyano end group. Two of

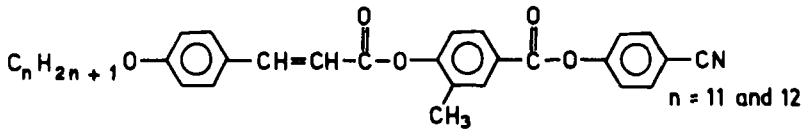
TABLE I

The compounds and their molecular structures

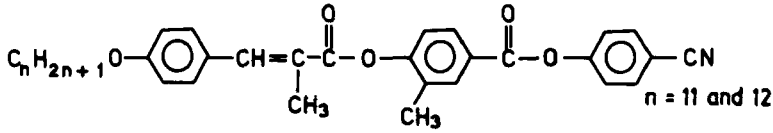
| Series number | Name of the compound |
|---|---|
| I | 4-Cyanophenyl-3′-methyl-4′-(4″-n-undecyl or dodecyl benzoyloxy)benzoate (11 CPMBB and 12 CPMBB) |




| | |
|---|---|
| II | 4-Cyanophenyl-3′-methyl-4′-(4″-n-undecyloxy or dodecyloxy cinnamoyloxy)benzoate (11 CPMCB and 12 CPMCB) |




| | |
|---|---|
| III | 4-cyanophenyl-3′-methyl-4′-(4″-n-undecyloxy or dodecyloxy-α-methyl cinnamoyloxy)benzoate (11 CPMαMCB and 12 CPMαMCB) |




| | |
|---|---|
| IV | 4-Cyanophenyl-3′-methoxy-4′-(4″-n-undecyloxy or dodeclyoxy-α-methyl-cinnamoyloxy)benzoate (11 CPMeOαMCB or 12 CPMeOαMCB) |

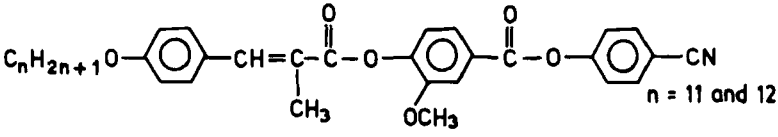


TABLE II

Transition temperatures and heats of transition of the compounds

| Series number | Compound | Transition | Transition temperature (°C) | $\Delta H$ (kJ/mole) |
|---|---|---|---|---|
| I | 11 CPMBB | *K-A* | 103.0 | 32.49 |
| | | *A-N* | 127.0 | 0.02 |
| | | *N-I* | 152.5 | 1.12 |
| | | *A-RN* | (78.5) | 0.02 |
| | 12 CPMBB | *K-A* | 102.0 | 35.55 |
| | | *A-N* | 138.5 | 0.26 |
| | | *N-I* | 148.0 | 1.26 |
| | | *A-RN* | (59.8) | 0.05 |
| II | 11 CPMCB | *K-RN* | 101.9 | 56.24 |
| | | *RN-A* | 105.1 | ~0† |
| | | *A-N* | 153.8 | 0.02 |
| | | *N-I* | 193.7 | 0.92 |
| | 12 CPMCB | *K-A* | 89.5 | 65.45 |
| | | *A-N* | 175.6 | 0.05 |
| | | *N-I* | 191.7 | 1.45 |
| | | *A-RN* | (82.1) | ~0† |
| III | 11 CPMαMCB | *K-RN* | 78.2 | 37.13 |
| | | *RN-A* | 101.1 | ~0† |
| | | *A-N* | 128.4 | 0.04 |
| | | *N-I* | 168.0 | 1.03 |
| | 12 CPMαMCB | *K-A* | 77.5 | 40.66 |
| | | *A-N* | 147.3 | 0.03 |
| | | *N-I* | 162.2 | 0.94 |
| | | *A-RN* | (69.2) | 0.02 |
| IV | 11 CPMeOαMCB | *K-A* | 82.9 | 38.80 |
| | | *A-N* | 125.2 | 0.02 |
| | | *N-I* | 138.2 | 1.16 |
| | | *A-RN* | (53.7) | 0.01 |
| | 12 CPMeOαMCB | *K-A* | 77.2 | 59.98 |
| | | *A-N* | 134.6 | 0.13 |
| | | *N-I* | 136.4 | 1.43 |
| | | *A-RN* | (42.8) | ~0† |

( ) denotes monotropic transition.
†The transition is very weak, no accurate estimation of $\Delta H$ can be made.
*K*–crystal, *A*–smectic A, *N*–nematic, *RN*–reentrant nematic.

the compounds, *viz.*, 11 CPMCB and 11 CPMαMCB, show enantiotropic smectic A-reentrant nematic transitions while in all the other cases the reentrant nematic phase appears as a monotropic phase.

The pressure dependence of the phase transitions were studied by the optical transmission technique. An optical high pressure cell equipped with sapphire windows was used. The liquid crystalline sample was sandwiched between two optically polished sapphire cylinders and enclosed inside a fluran tube. The transmitted light intensity was monitored by a photo cell. The experiments were always conducted along isobars, i.e., the transition temperature at any pressure was determined by keeping the pressure constant and varying the temperature at a rate of 1–2°C/min. The temperature at which there was an abrupt change in the transmitted light intensity was taken as the transition point. Pressures were measured to an accuracy of ±10 bars and temperatures to ±0.025°C. Further details of the experimental setup are described elsewhere.[10,11]

The *P-T* diagrams of all the eight compounds are essentially similar. Two representative plots are shown in Figures 1 and 2. The melting as well as the nematic-isotropic (*N-I*) boundaries are straight lines while the smectic A-nematic (*A-N*) phase boundary is elliptic in shape in all cases. $P_m$, the maximum pressure up to which the smectic A phase exists ($P_m$ is also commonly referred to as the maximum pressure of smectic stability), for the different compounds are listed in Table III.

It has been pointed out by Cladis, *et al.*[12,13] that for the substances studied by them, $P_m$ exhibits a monotonic dependence on the McMillan number.[14] For the compounds studied by us, we have attempted to relate $P_m$ with the

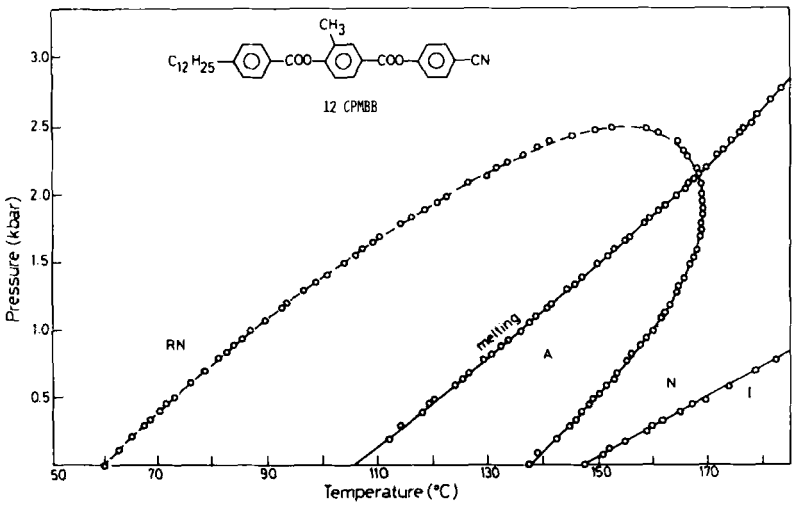



FIGURE 1 *P-T* diagram of 12 CPMBB. The dashed line indicates that the transition is monotropic.

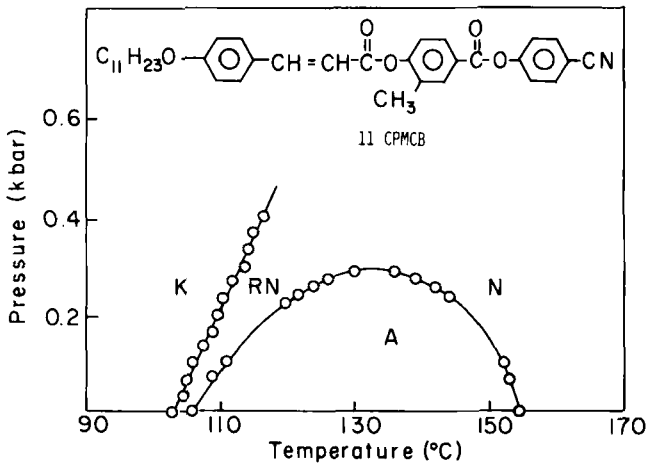



FIGURE 2 *P-T* diagram of 11 CPMCB.

range of the nematic phase $R = (T_{NI} - T_{AN})$ at 1 bar. Figure 3 shows a plot of log $P_m$ vs $R$ for all the 8 compounds. The data points fall on a straight line so that they can be represented by the expression

$$P_m = P_0 \exp(-mR)$$

The constants $P_0$ and $m$ evaluated from a least squares fit of the data to a straight line are 3769 bars and 0.071/°C. This result implies that with increasing nematic range $P_m$ should decrease.

Since the *P-T* data are known for several other reentrant nematogens, *viz.*, two pure compounds (8 OCB and CBOOA)[12] and many binary mixtures—8 OCB/6 OCB,[15,16] CBOOA/HBAB,[12] CBNA/CBHA[12] and 8 OCB/40.8,[17] it is worthwhile to see if such a relation is valid in these

TABLE III

$P_m$ of the reentrant nematogens

| No. | Compound | $P_m$ (kbar) |
|---|---|---|
| 1 | 11 CPMBB | 0.55 |
| 2 | 12 CPMBB | 2.50 |
| 3 | 11 CPMCB | 0.29 |
| 4 | 12 CPMCB | 1.05 |
| 5 | 11 CPMαMCB | 0.19 |
| 6 | 12 CPMαMCB | 1.35 |
| 7 | 11 CPMeOαMCB | 1.14 |
| 8 | 12 CPMeOαMCB | 3.45 |

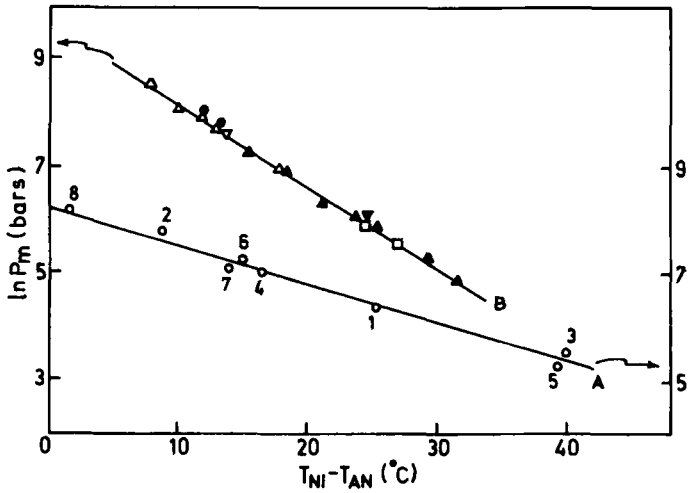



FIGURE 3 Plot of maximum pressure of smectic stability ($P_m$) versus the range of the nematic phase ($T_{NI} - T_{AN}$) at 1 bar. The data points 1, 2, 3, etc. on line A are for three phenyl ring compounds listed in Table III. The data on line B are for two phenyl ring compounds, *viz.*, ▽–8 OCB, ▼–CBOOA, △–8 OCB/6 OCB mixtures, □–CBNA/CBHA mixtures, ●–8 OCB/40.8 mixtures.

cases also. The plot of $P_m$ versus $R$ for these substances is also shown in Figure 3. These data again fall on a straight line (line B) but with a *different* slope. The constants for this line are $P_0 = 14050$ bars and $m = 0.140/°C$. It is interesting to note that all the substances whose $P_m$ data fall on line B have two phenyl rings while all the compounds whose data fall on line A have three phenyl rings. We, therefore, tentatively conclude that for a reentrant nematogen $P_m$ is uniquely related to the nematic range (and hence the stability of the nematic ordering) vis-a-vis the molecular structure. Also the values of $P_0$ for the lines A and B indicate that the smectic stability of compounds with two phenyl rings is higher than that of compounds with three phenyl rings. Hence the formation of the reentrant nematic phase is more favored in the latter compounds.

The shape of the *A-N* phase boundary for 8 OCB has been analysed by Clark[18] and independently by Klug and Whalley[19] who have also evaluated the various thermodynamic parameters determining the phase boundary. Also, Pershan and Prost[20] have shown that the smectic A-reentrant nematic phase transition follows from the Landau theory if one assumes the existence of an optimum density for smectic ordering. We have ascertained that the fit of an ellipse to the data for all the compounds studied by us is quite satisfactory. Figures 4 and 5 give two representative examples. The circles in these diagrams denote the data points while the solid curve represents the

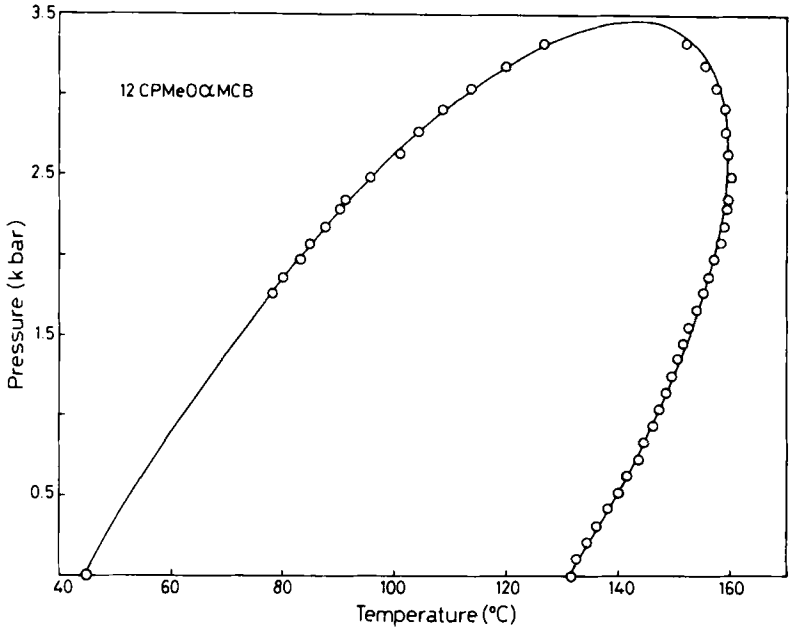



FIGURE 4 Computer fit of the data points for 12 CPMeO$\alpha$MCB to the equation of an ellipse. The circles are the experimental data points and the solid curve is the computer drawn curve.

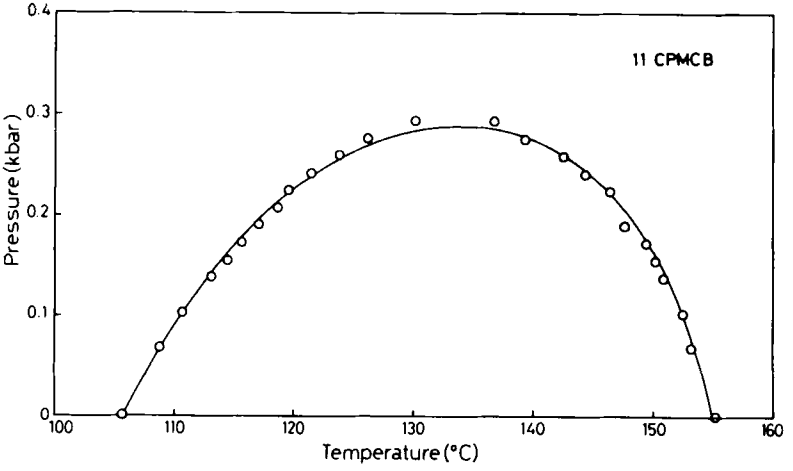



FIGURE 5 Computer fit of the data points for 11 CPMCB to the equation of an ellipse. See legend of Figure 4.

best fit for the data points to the equation to an ellipse and it can be seen that the fit is very good.

## III. PIEZOTHERMAL STUDIES IN THE VICINITY OF THE A-N TRANSITION IN 8 OCB

The thermal expansion of 4′-*n*-octyloxy-4-cyanobiphenyl (8 OCB) has been studied as a function of pressure in the vicinity of the *A-N* transition by the piezothermal method. The piezothermal or heat of compression method[21,22] essentially consists of a measurement of a quantity of heat Q liberated by a volume $V_s$ of the sample under a pressure variation $\Delta P$. This quantity of heat is directly related to the thermal expansion ($\alpha$) of the sample by the relation[23,24]

$$Q = -(\alpha - \alpha_r)TV_s\Delta P \tag{1}$$

where $\alpha_r$ is the thermal expansion of the containing material. The calorimeter used is a conventional flux calorimeter adapted for high pressure experiments.[21,22] The sample, contained in a pressure tubing and suspended inside the calorimeter, is compressed. The resulting heat liberated in the sample is measured as an e.m.f. by a set of 500 thermocouples which are electrically in series but thermally in parallel. The combined e.m.f. of the thermocouples is recorded and integrated as a function of time. The area under the 'thermogram'[21] gives the quantity of heat $Q$ caused by a change of pressure $\Delta P$. The values of $\alpha_r$ and $V_s$ being predetermined by calibration experiments, $\alpha$ of the sample can be determined using Eq. (1). The absolute pressures and temperatures were measured and maintained to accuracies of $\pm 0.5$ bar and $\pm 0.01$ K, respectively. The relative accuracy in the determination of $\alpha$ is reckoned to be about $\pm 2\%$.

The *P-T* diagram of 8 OCB (obtained using the optical high pressure cell described in Section II) is shown in Figure 6. The piezothermal experiment has been conducted along 4 different isotherms which are shown as dashed lines in Figure 6. Before commencing the experiment at any temperature, the system was allowed to attain thermal equilibrium for at least 24 hours. Then the pressure was increased very slowly to about 200 bars above the *A-N* transition pressure at that temperature. Pressure was then decreased by small steps (a few bars) and the area of the potential versus time curve integrated at each step. No experiments could be conducted on the reentrant nematic phase owing to the rapid crystallization of the supercooled smectic A phase.

Figures 7a–d show the thermal expansion versus pressure curves for the 4 different temperatures studied.[25] $\alpha$ exhibits an anomaly at the *A-N* transi-

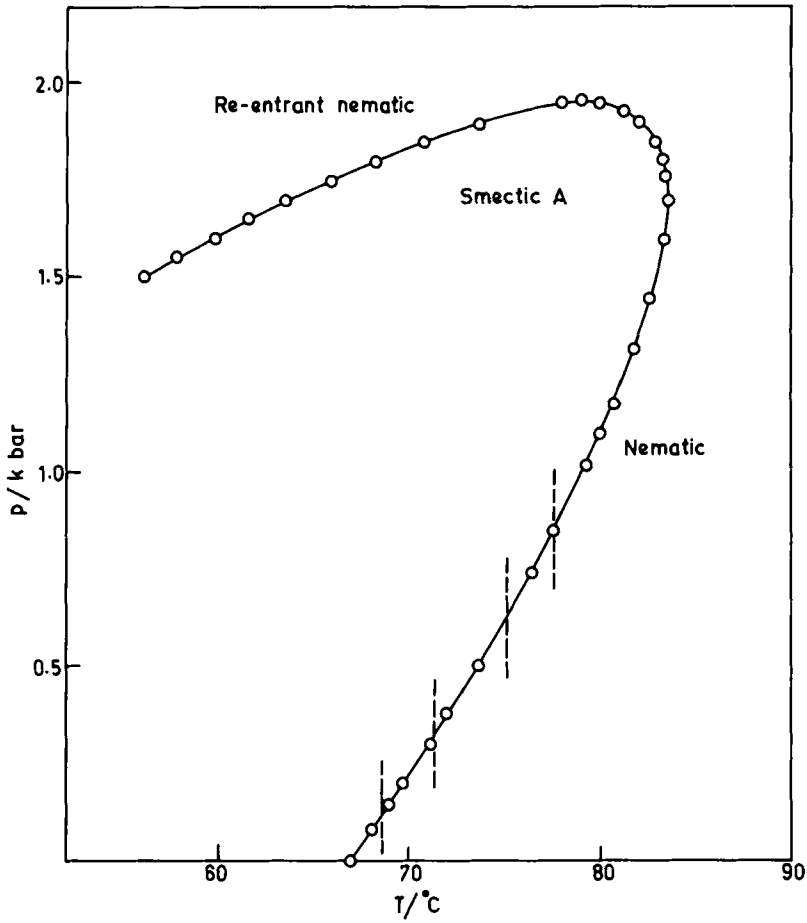



FIGURE 6 *P-T* diagram for the smectic A-nematic transition of 8 OCB. The dashed lines indicate the temperatures at which the piezo thermal measurements of $\alpha$ have been made.

tion. The strength of this peak decreases with increasing temperature and at the highest temperature studied, *viz.*, 77.6°C, there is hardly any anomaly (Figure 7d). It is well known that an integration of the $\alpha$ vs pressure curve essentially leads to a term which should be a function of entropy (see Ref. 21). Hence, it is not surprising that the trends of our $\alpha$ vs pressure curves with increasing temperature resemble generally the $C_P$ vs temperature curves with increasing pressure obtained for the same compound by Garland *et al.*[26,27]

It must also be mentioned that generally, it is far more difficult to achieve as fine a variation of pressure as of temperature. To that extent we would

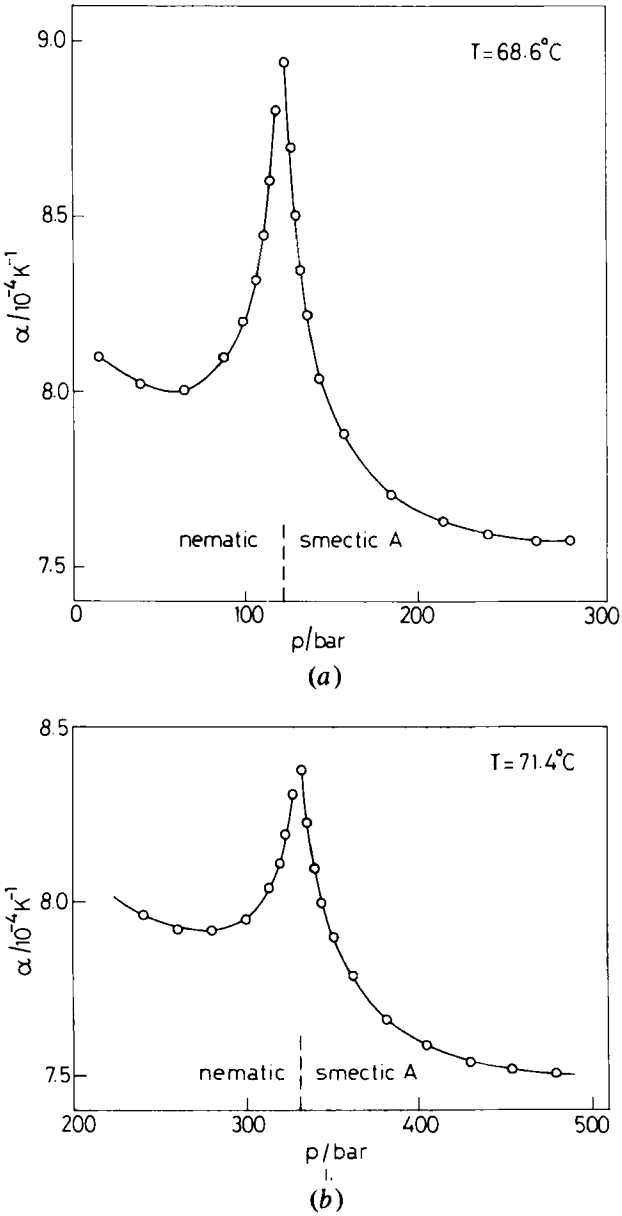
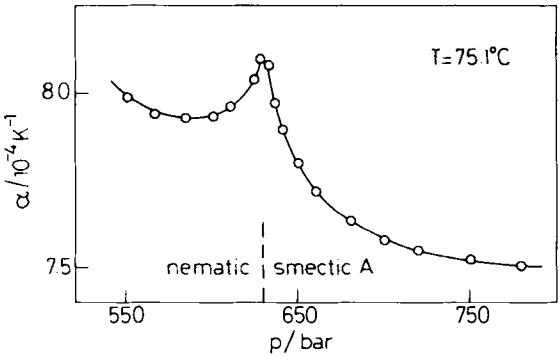
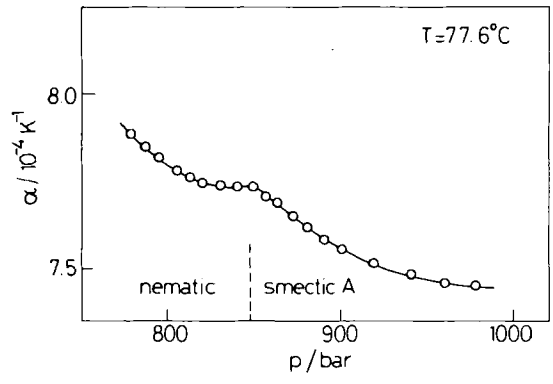



FIGURE 7 Variation of the thermal expansion ($\alpha$) of 8 OCB with pressure at 4 different isotherms: (a) 68.6°C (b) 71.4°C (c) 75.1°C and (d) 77.6°C.




(*c*)




(*d*)

like to emphasize that our experimental values of $\alpha$, particularly close to the *A-N* transition, do not have the precision required to make a good estimate of the exponent ($\beta$) associated with the pressure variation of $\alpha$. Nevertheless, an attempt has been made to fit all the data points for $T = 68.6$°C to equations of the type:

$$\alpha = a_0 + P_r a_1 + A|P_r|^{\beta}, \qquad \text{for } P < P_0,$$

and

$$\alpha = a_0' + P_r a_1' + A|P_r|^{\beta}, \qquad \text{for } P > P_0,$$

where $a_0$, $a_1$, $a_0'$ and $a_1'$ are all adjustable parameters, $P_0$ is the transition pressure for $T = 68.6$°C and $P_r = (P - P_0)/P_0$ is the reduced pressure.

The base line with respect to which the expansion coefficients have been evaluated for this fitting consists of two linear parts, one in the nematic and the other in the smectic A phase. This appears to yield a reasonably good fit over the entire range of pressure investigated, giving a value of 0.22 for the exponent $\beta$.

## IV. PRESSURE BEHAVIOR OF THE N-I TRANSITION IN REENTRANT NEMATIC MIXTURES

So far we have discussed the effect of pressure on the *A-N* phase boundary of reentrant nematogens. In order to see if any special features are observed for the *N-I* transition at high pressures, we have carried out, by differential thermal analysis (DTA), a detailed investigation of the *P-T* curves of the *N-I* transition in 6 OCB/8 OCB mixtures on which several experimental studies have already been made.[28–31] In the DTA experiments the sample was sealed in an indium capsule so that it was completely isolated from the pressure transmitting medium.[32] Pressures were measured to ±5 bar and temperatures to ±0.25°C.

The temperature-molar concentration ($X$) diagram evaluated at 1 bar for these mixtures is shown in Figure 8. The reentrant nematic phase exists for $0.18 < X < 0.30$. In all, we have studied the *N-I* phase boundary for mixtures of 12 different concentrations as well as for the pure compounds.

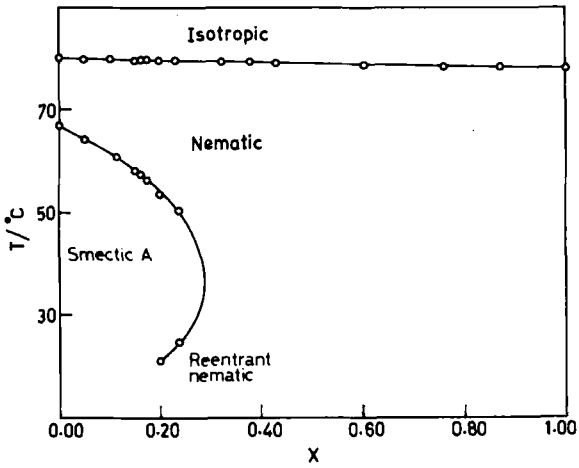



FIGURE 8 Temperature-concentration diagram of 6 OCB/8 OCB mixtures evaluated at 1 bar. $X$ is the mole fraction of 6 OCB in the mixture.

The $(dT/dP)_{1bar}$ was evaluated from each of the $P$-$T$ curves by a least square fit to the set of data points. The accuracy in the determination of $dT/dP$ is $\pm 0.2$ K kbar$^{-1}$. Figure 9 shows the plot of $dT/dP$ vs $X$.[33] Considering that the $N$-$I$ transition temperature at 1 bar evolves continuously (see Figure 8), one would intuitively expect the $dT/dP$ vs $X$ curve also to show a smooth variation. But, as seen in Figure 9, this is not the case and instead the curve exhibits an anomaly, the lowest value of $dT/dP$ occurring at $X \approx 0.18$. The maximum drop in $dT/dP$ (taken with respect to a smooth line joining the data points for the two pure compounds) is 2.1 K/kbar which is 10 times larger than the accruacy in the determination of $dT/dP$. Considering that these deviations occur only in the concentration range of occurrence of the reentrant nematic phase, it is natural to ascribe this anomaly to the presence of the smectic A and reentrant nematic phases at lower temperatures. This anomaly could also conceivably be due to kinetic effects. Subsequent experiments[34] carried out very carefully under different thermal conditions of the sample, have ruled out kinetic effects. Hence this anomaly is essentially due to the influence of molecular ordering—due to smectic-like ordering or due to the presence of the reentrant nematic phase at lower temperatures or due to a combination of both.

We have subsequently studied the $N$-$I$ transition in 8 OCB/CBOOA mixtures whose temperature-concentration diagram obtained at 1 bar is shown in Figure 10. In this case both the pure compounds exhibit the smectic A and nematic phases while the reentrant nematic phase is exhibited over a range of concentration, *viz.*, $0.26 < X < 0.78$, $X$ being the mole fraction of CBOOA in the mixture. The $dT/dP$ versus $X$ curve for the

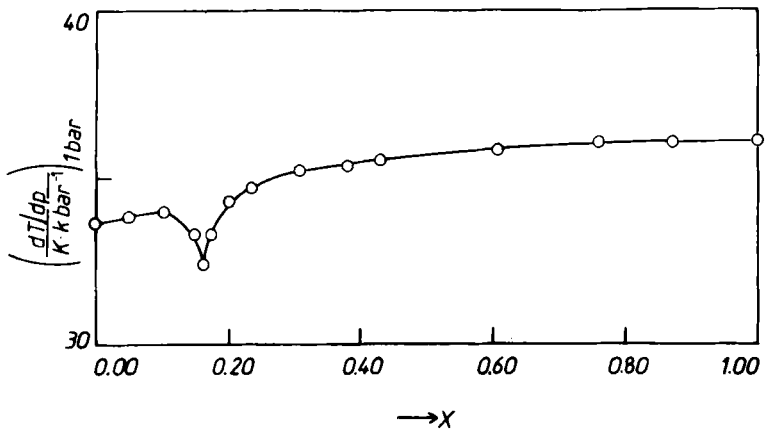



FIGURE 9 $(dT/dP)_{1\ bar}$ values for the nematic-isotropic transition in 6 OCB/8 OCB mixtures as functions of 6 OCB concentration.

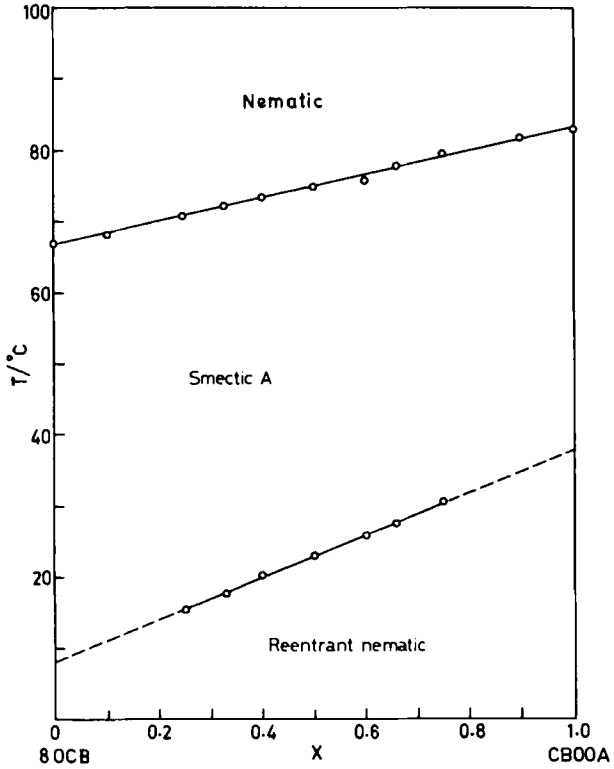



FIGURE 10 Temperature-concentration diagram of 8 OCB/CBOOA mixtures evaluated at 1 bar. $X$ is the mole fraction of CBOOA in the mixture.

*N-I* transition of the 8 OCB/CBOOA mixtures is given in Figure 11. It is seen that there are two minima in the curve. Interestingly, these minima occur almost exactly at those concentrations at which the reentrant nematic phase makes its appearance at atmospheric pressure (see Figure 10). It, therefore, appears that the changes in molecular ordering which accompany the formation of the reentrant nematic phase manifest at much higher temperatures and affect thereby the pressure behavior of the *N-I* transition.

## V. PRESSURE BEHAVIOR OF SMECTIC A AND ITS RELATION TO INTERDIGITATION OF MOLECULES

In this section we present results of our pressure studies on the 8th and 9th homologues of the series 4-alkoxy-benzoyloxy-4′-cyanoazobenzene

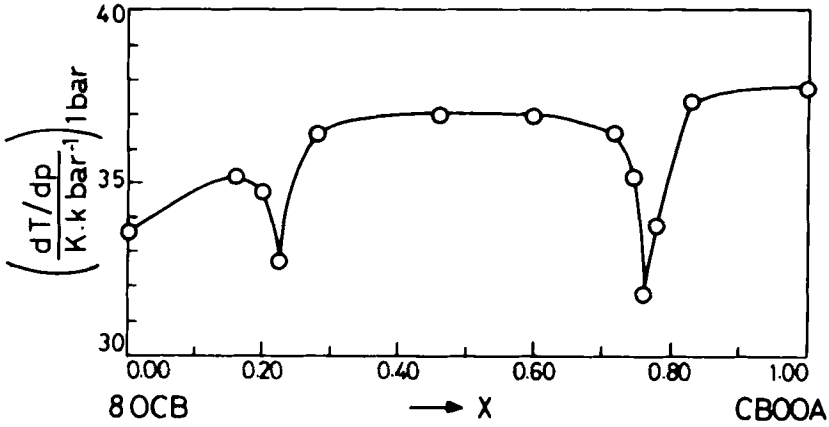



FIGURE 11 $(dT/dP)_{1\ bar}$ values for the nematic-isotropic transition in 8 OCB/CBOOA mixtures plotted as functions of CBOOA concentration.

($n$OBCAB):[35,36] The transition temperatures (at 1 bar) of these compounds are given in Table IV. 8 OBCAB exhibits a smectic A phase in addition to the nematic phase. X-ray studies[37,38] have shown that this is a monolayer smectic A with a $d/l$ ratio of 0.95, this ratio being independent of temperature ($d$ = smectic A layer spacing and $l$ the length of the molecule as measured in its most extended configuration using the Dreiding model). On the other hand, 9 OBCAB exhibits on cooling from the isotropic phase the nematic, smectic A, reentrant nematic and reentrant smectic A phases. The reentrant smectic A is, as in 8 OBCAB, a monolayer phase with a temperature independent $d/l$ ratio of 0.95 while the higher temperature smectic A is a partially bilayer phase ($A_d$) with a $d/l$ ratio which shows a decrease with

TABLE IV

Transition temperatures (at 1 bar) of 8 OBCAB and 9 OBCAB

| | Transition | Temperature (°C) |
|---|---|---|
| 8 OBCAB | crystal-smectic A | 93.0 |
| | smectic A-nematic | 97.0 |
| | nematic-isotropic | 257.5 |
| 9 OBCAB | crystal-reentrant nematic | 94.0 |
| | reentrant nematic-smectic A | 116.0 |
| | smectic A-nematic | 212.4 |
| | nematic-isotropic | 248.8 |
| | reentrant nematic-reentrant smectic A | (70.9) |

( ) denotes that the transition is monotropic.

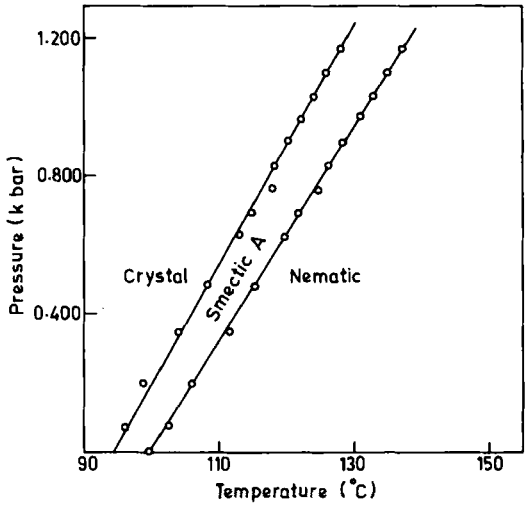



FIGURE 12 *P-T* diagram of 8 OBCAB.

decreasing temperature.[37,38] The *P-T* diagram of 8 OBCAB is shown in Figure 12. The range of the monolayer smectic A increases continuously with increase of pressure. In the case of 9 OBCAB (Figure 13) the two smectic phases behave very differently. The $A_d$-$N$ phase boundary has the expected elliptic-shape with $P_m = 520$ bars. This data also falls on line A of Figure 3 discussed in Section II. On the other hand, the reentrant (mono-

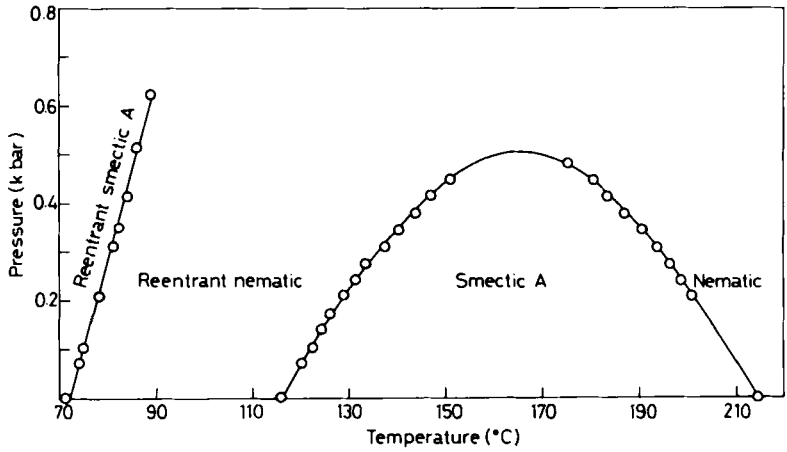



FIGURE 13 *P-T* diagram of 9 OBCAB.

layer) smectic A-reentrant nematic phase boundary is a straight line which has in fact the same slope as the *A-N* phase boundary of 8 OBCAB. Hence, we see that pressure has the effect of destabilizing the $A_d$ phase while it has the opposite influence on the monolayer A phase. One may infer from this that the pressure behavior of the smectic A phase should be related to the interdigitation of the molecules in the layer.

Summarizing therefore, high pressure studies have the potentialities to provide a clue to the understanding of the nature of the reentrant phenomenon at the molecular level.



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