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## High pressure studies on a nematogen with highly polar molecules: Evidence for a nematic–nematic transition\*

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**We have modified a high pressure optical set-up to enable measurements on the optical path difference of aligned liquid crystals. We present the phase diagram of a polar nematogen, viz. *p*-cyanophenyl *p*-*n* heptylbenzoate which is shown to exhibit a nematic ( $N_d$ ) to nematic ( $N_1$ ) transition in the bulk at elevated pressures. We have also measured the temperature variations of the orientational order parameter ( $S$ ) at various pressures to find that  $S$  has constant values at both the nematic to isotropic and  $N_d$  to  $N_1$  transitions at different pressures.**

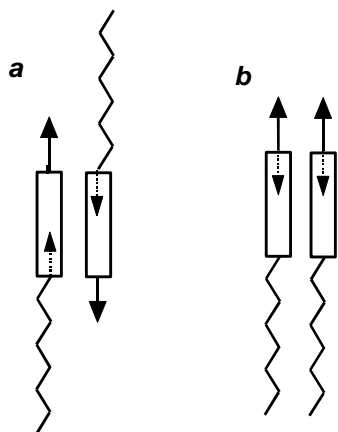
LIQUID crystals (LCs) made of rod-like molecules with polar end groups exhibit interesting phase sequences like smectic polymorphism, the reentrant nematic phase double reentrance, etc.<sup>1,2</sup>. Both phenomenological and molecular theoretical models have been developed to explain these phenomena<sup>1</sup>. In uniaxial nematics ( $N$ ), the long axes of the molecules are oriented on the average about the director  $\hat{n}$ , which is a dimensionless apolar unit vector. The apolar nature of the director in nematogens with highly polar end groups can be understood, as the molecules have an anti-parallel short-range order in the medium<sup>3</sup>. Smectic A ( $SmA$ ) LCs have a layering order, with the layer normal ( $\hat{z}$ ) being parallel to  $\hat{n}$ . In polar compounds which exhibit reentrant  $N$  and  $SmA$  phases, the high temperature smectic  $A_d$  ( $SmA_d$ ) phase has partial bilayer order with  $l < d < 2l$ , where  $l$  is the molecular length, and  $d$  the layer spacing. The low temperature smectic  $A_1$  ( $SmA_1$ ) phase has a layer spacing equal to the monomolecular length, i.e.  $d = l$ . The unusual phenomena exhibited by highly polar compounds have been successfully explained by Prost and co-workers using a phenomenological Landau theory. This model<sup>1</sup> takes into account the coupling between two smectic order parameters corresponding to the two lengths mentioned above. One of the consequences of this model is the prediction of an  $N_d$  to  $N_1$  transition line in continuation of the  $SmA_d$  to  $SmA_1$  transition line, the latter being characterized by an appropriate jump in the layer spacing. Indeed, such an  $N$ – $N$  transition has been found as a continuation of the  $SmA_1$ – $SmA_d$  transition line in the concentration–temperature phase diagram of a binary mixture of polar

\*Dedicated to Prof. S. Ramaseshan on his 80th birthday.

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compounds<sup>4</sup>. AC calorimetric and high resolution X-ray scattering studies on this system have revealed that the  $N_d-N_1$  transition is a weak first-order transition characterized by a sharp peak in the specific heat and a discontinuous jump in the correlation lengths associated with short-range smectic fluctuations. However, optical microscopic observations did not reveal any visible change at the  $N_d-N_1$  transition. This transition is a weak first-order transition as the macroscopic symmetry of the two nematics is identical. As in the liquid-gas transition under varying pressures, the  $N_d-N_1$  transition line can end in a critical point beyond which the two phases can evolve into each other as physical parameters such as concentration in a mixture or pressure and temperature are varied.

The physical origin of the two lengths corresponding to  $SmA_d$  and  $SmA_1$  phases has been explained in a molecular model proposed by Madhusudana and Jyotsna Rajan<sup>5</sup>. In highly polar compounds, the electrostatic interaction between the polar groups of neighbouring molecules favours an antiparallel association<sup>3</sup>. The aromatic cores of the molecules have large polarizabilities and the strong dispersion interaction between such cores of neighbouring molecules leads to an antiparallel association, as shown in Figure 1 *a*. In this configuration the effective dipole moment of the molecule is enhanced, as the neighbouring molecule induces a dipole moment which is parallel to the dipole moment of the polar group of the given molecule. The aliphatic chains are so far apart that the dispersion interaction between the chains of neighbours is negligible. When the neighbouring molecules are parallel to each other as in Figure 1 *b*, the dipolar interaction is repulsive but the net dipole moment of a molecule is reduced as the induced dipole due to the neighbouring molecule is in a direction opposite to that of the permanent dipole of the given molecule. In addition, the chains are in close proximity, adding to the attractive interaction.



**Figure 1.** Schematic representation of intermolecular associations of neighbouring molecules with highly polar cyano end groups. *a*, Antiparallel configuration favoured at low densities. *b*, Parallel configuration favoured at high densities. (The permanent and induced dipoles are indicated by solid and dashed lines with arrows respectively.)

The dipole-induced dipole interaction as well as the inter-chain dispersion interaction vary as  $1/r^6$ , where  $r$  is the intermolecular distance. On the other hand, the permanent dipole-dipole interaction varies as  $1/r^3$ . At low densities the permanent dipole-dipole interaction is dominant, leading to the antiparallel arrangement of neighbouring molecules. As the density is increased either by reducing the temperature or by increasing the pressure,  $r$  decreases and a change in the intermolecular configuration from antiparallel to parallel association of molecules can take place. This leads to a *polar short-range* order in the medium. Indeed, such a polar short-range order has been detected by Basappa and Madhusudana<sup>6</sup> in a strongly polar nematogen, viz. *p*-cyanophenyl *p*-*n*-heptylbenzoate (CP7B). This compound has the following phase sequence: crystal 43.5°C N 56°C Isotropic (*I*), and the *N* phase can be supercooled to room temperature. Basappa and Madhusudana<sup>6</sup> also noticed a sharp increase in the intensity of light scattered by twist fluctuations in the medium around 33°C, when a 10  $\mu$ m thick sample was cooled under a high electric field of  $\sim 600$  esu. They speculated that this indicated a nematic-nematic (*N-N*) transition in the compound. Indeed, an extension of the molecular theory of LC phases exhibited by highly polar compounds proposed by Govind and Madhusudana<sup>7</sup> has predicted the possibility of such an *N-N* transition which is not associated with the  $SmA$  phase. The model shows that the  $N_1-N_d$  transition temperature increases with pressure<sup>8</sup> and the first-order  $N_1-N_d$  transition line ends in a critical point. Experiments by Warriar *et al.*<sup>9</sup> on *planar, aligned, thin* samples of CP7B, with thickness lying between 1.9 and 3  $\mu$ m, revealed a jump in the optical path difference at some temperature in the nematic range. They identified the relevant event as an *N-N* transition. The transition temperature decreased with increase in sample thickness. In both thin cells, as well as samples subjected to high electric fields<sup>6,9</sup>, the orientational order parameter is enhanced compared to that in a field-free thick sample. It is hence likely that in CP7B the *N-N* transition occurs in the bulk at a temperature well below the ambient, when the order parameter increases to the required value. The transition point can be expected to increase above the ambient temperature at elevated pressures. To check this possibility, we undertook high pressure (HP) studies on this compound. The *N-N* transition is a weak first-order transition with about 1% jump in the orientational order parameter, when the latter has a sufficiently large value<sup>9</sup>. To detect such a small jump in the orientational order parameter, a convenient method is to measure the optical path difference of an aligned sample. In the earlier HP studies conducted in our laboratory<sup>10</sup>, phase transitions were detected by an optical transmission technique. We have modified the HP optical set-up so that the optical path difference of an aligned sample can be measured as a function of both temperature and pressure. Using such measurements on CP7B, the birefringence  $\Delta n$  has been evaluated as a func-

tion of temperature as well as pressure. We have found that indeed the  $N-N$  transition occurs in the bulk CP7B sample of thickness  $\sim 12 \mu\text{m}$  at high pressures.

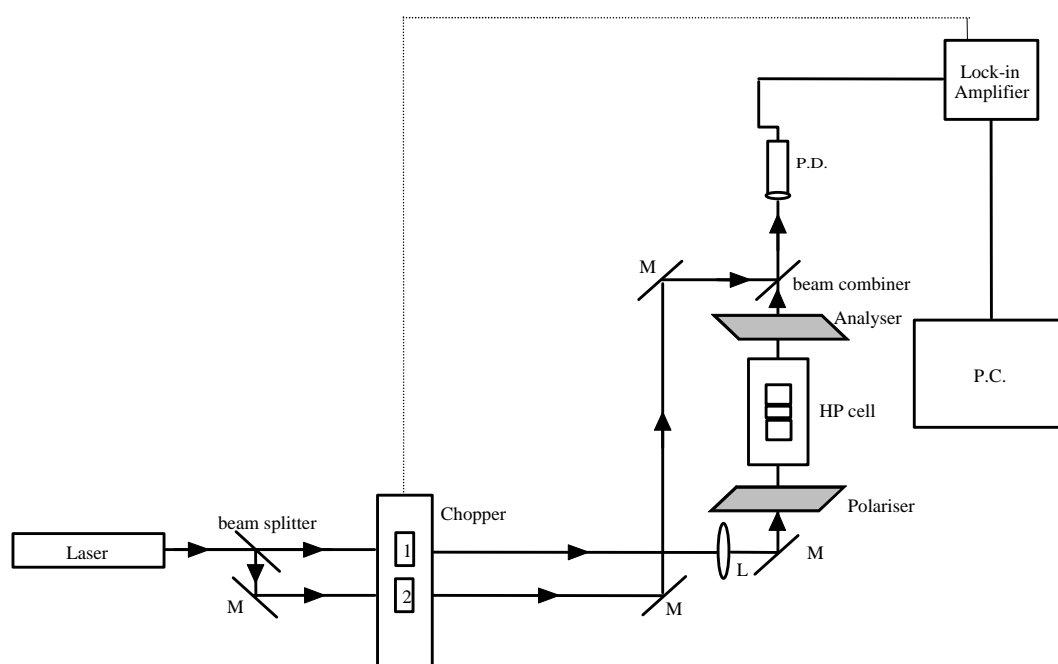
As mentioned earlier, we have modified the HP optical set-up so that optical path difference of an aligned sample can be measured. While tracing a weak transition such as the  $N-N$  transition which is associated with a minute jump in transmitted optical intensity, any source intensity fluctuations can be misleading. In the modified set-up, we use a lock-in amplifier (LIA; EG&G model 7260) in the dual reference mode, using which two different optical signals being chopped at two different frequencies are simultaneously measured using a single photodiode. A schematic diagram of the modified HP optical set-up is shown in Figure 2. A He-Ne laser beam of wavelength 633 nm is split into two beams using a beam-splitter. The two beams are made to pass through two different windows of the same chopper (EG&G model 198) operating at frequencies in the ratio of 11 : 18, with their sum frequency being fixed. One of the beams is treated as the reference beam and the other is allowed to pass through the sample placed between crossed polarizers. Both the beams are combined at a beam-combiner and detected using a single photodiode (Hamamatsu S1406, with a built-in amplifier). The ratio of the intensity of the beam transmitted through the sample to that of the reference beam is used in the further processing of data.

In the earlier HP optical studies<sup>10</sup>, the LC sample was sandwiched between optically polished sapphire windows which are birefringent. We use 5 mm thick fused quartz cylinders which are optically isotropic in the optical path difference measurements. The fused quartz cylinders are

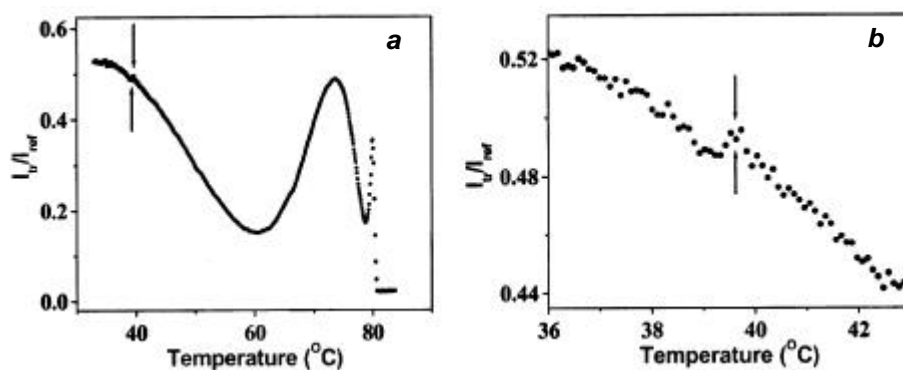
coated with polyimide and cured at 300°C for about an hour and then unidirectionally rubbed using soft tissue paper. The sandwich is prepared such that the directions of rubbing of both the cylinders are parallel to each other, allowing the sample to align homogeneously with the director lying along the rubbing direction. A mylar spacer is used to fix the thickness of the sample. The sandwich is enclosed in a Fluran tube, an elastomer which can transmit hydrostatic pressures very well from the pressure-transmitting medium.

The temperature is measured using a thermocouple placed in a radial hole near the body of the HP optical cell. A temperature controller (fabricated at the National Aerospace Laboratories, Bangalore) which has a built-in room temperature compensation for the cold junction of the thermocouple, is used to control the temperature. A suitable software program is used to control the temperature to an accuracy of 25 mK, and record the intensity signals at various temperatures. The accuracy of pressure measurement made using a Bourdon-type HEISE gauge is about 5 bars. The compound CP7B used in this study was obtained from Merck.

To make the path difference measurement, it is essential to know the optic axis or the rubbing direction. The HP cell is rigidly fixed and cannot be rotated to identify the rubbing direction of the sample. Instead, the crossed polarizers are rotated in tandem and the position of minimum intensity at which the rubbing direction of the cell is parallel to one of the crossed polarizers is located. Both polarizer and analyser are rotated by 45° from that orientation, such that the polarizers remain crossed. This corresponds to the position of maximum sensitivity. The



**Figure 2.** Schematic diagram of the modified high pressure optical set-up. M, Mirror; L, Lens; P.D., Photodiode.



**Figure 3.** Variation of ratio of transmitted intensity to reference intensity with temperature at a pressure of 650 bars in CP7B. *a*, Data over an extended temperature range, and *b*, Data in a small temperature range shown on an expanded scale. The  $N-N$  transition is indicated by arrows in both *a* and *b*.

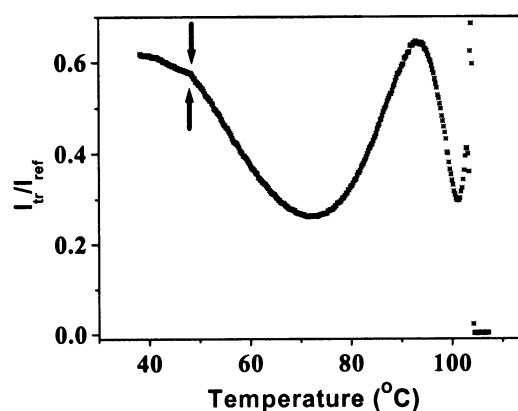
transmitted intensity is then given by

$$I_{\text{tr}} = I_0(1 - \cos \Delta f)/2, \quad (1)$$

where  $I_0$  corresponds to the maximum intensity and  $\Delta f = 2p\Delta n d/l$  is the optical phase difference,  $\Delta n = n_e - n_o$ , where  $n_e$  and  $n_o$  are the two principal refractive indices of the medium,  $d$  the sample thickness, and  $l$  the wavelength of the incident light (633 nm).

The profile of the ratio of transmitted intensity to reference intensity in the cooling run, made in steps of  $0.2^\circ\text{C}$  at atmospheric pressure is recorded from the isotropic phase down to room temperature using the automated program. The thickness  $d$  of the sample is determined using the known values of refractive indices at atmospheric pressure taken from the literature<sup>11</sup>. The variation of  $\Delta n$  over the entire nematic range from the present measurement at atmospheric pressure is in good agreement with the earlier measurements. The sample is pressurized up to 2 kbar in small pressure steps. At each isobar, the ratio of optical intensities as a function of temperature is recorded and the variation of  $\Delta n$  of the sample is calculated.

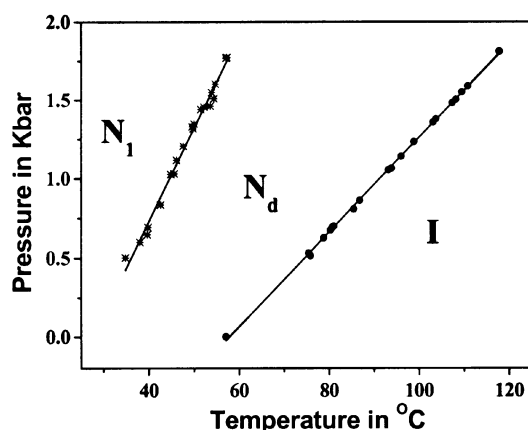
The profile of the ratio of transmitted to reference intensity signals at 650 bars is shown in Figure 3 *a*. The isotropic to nematic transition is characterized by a sharp jump in the intensity, reflecting the first-order nature of the transition. As mentioned earlier, the transmitted intensity is proportional to  $(1 - \cos \Delta f)$ . The value of  $\Delta n$  decreases with increase in temperature, and from eq. (1) the intensity is an oscillatory function with maxima and minima occurring for  $\Delta f = (2m + 1)\pi$  and  $2m\pi$  respectively, where  $m$  is an integer. Further, at 650 bars, a small jump in the measured intensity is seen at  $39.6^\circ\text{C}$ , i.e. well within the nematic range, as shown by arrows in Figure 3 *a*. For clarity, the intensity profile in a small temperature range around  $39.6^\circ\text{C}$  is shown in Figure 3 *b* on an expanded scale. Warriar *et al.*<sup>9</sup> had observed a similar jump in intensity of planar aligned, thin cells which they identified as corresponding to an  $N-N$  transition. Indeed, the temperature at which the jump in intensity occurs increases with increasing pressure, and we can identify



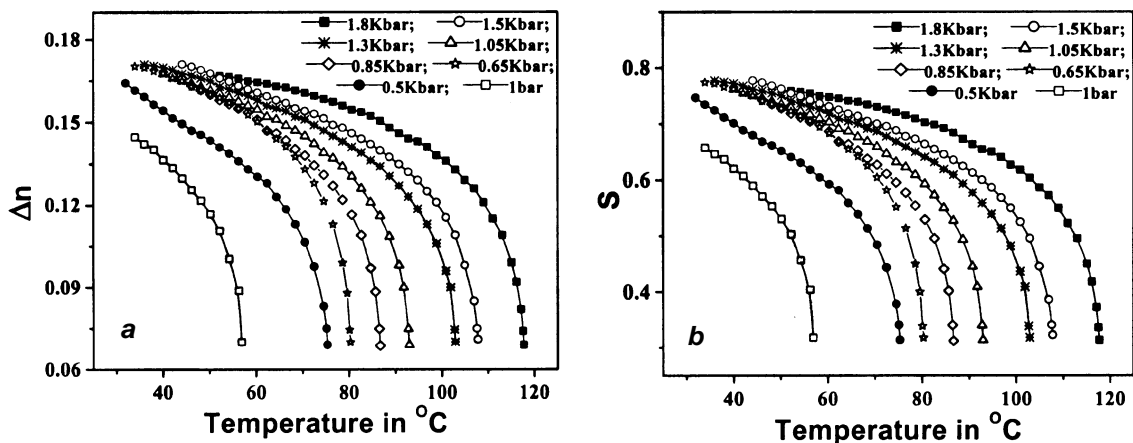
**Figure 4.** Variation of ratio of transmitted intensity to reference intensity with temperature at a pressure of 1.3 kbar. The  $N-N$  transition is indicated by arrows.

the jump with the  $N-N$  transition. At higher pressures,  $T_{NN}$  increases and the temperature gradient across the sample also increases. As a consequence, the small jump across the  $N-N$  transition gets smeared out, and the transition is seen as a slope change in the intensity. Data at 1.3 kbar are shown in Figure 4, where the slope change around  $49.2^\circ\text{C}$  is indicated by arrows. The pressure-temperature phase diagram is shown in Figure 5 in which both the  $N-N$  and  $N-I$  transition temperatures are plotted as functions of pressure. The  $N$  phase occurring above  $T_{NN}$  is denoted as  $N_d$ , and that occurring below  $T_{NN}$  as  $N_l$ , where the subscripts  $d$  and  $l$  indicate the type of short-range order favoured. Both  $T_{NI}$  and  $T_{NN}$  vary linearly with pressure with the corresponding slopes  $dP/dT$  being 30 and  $58.9 \text{ bar}/^\circ\text{C}$ , respectively. We do not show the melting transition temperature as a function of pressure, as the sample always supercooled at any given pressure. The values of the jump in the volume ( $\Delta V/V = 0.3\%$ )<sup>12</sup> and the heat of transition  $\Delta H (= 1 \text{ kJ/mol})$ <sup>13</sup> at the  $N-I$  transition for CP7B are available in the literature. Using the Clausius-Clapeyron equation, viz.  $(dP/dT) = \Delta H/(\Delta V \cdot T_{NI})$ , we obtain  $dP/dT_{NI} = 33 \text{ bar}/^\circ\text{C}$ , which agrees well with the experimental value. Of course, such data

are not available for the  $N-N$  transition. We have estimated the optical phase difference,  $\Delta f = 2 p \Delta n d / I$  of the sample using the measured optical intensity profiles at various pressures. Using the refractive indices data at atmospheric pressure available in the literature<sup>11</sup>, the sample thickness  $d$  and the absolute values of the phase difference corresponding to the maxima and minima of the measured optical intensity have been estimated. The birefringence  $\Delta n$  at various pressures can then be evaluated. The variations of  $\Delta n$  as functions of temperature along various isobars are presented in Figure 6 *a*. The orientational order parameter  $S$  of the nematic increases with increasing pressure, as the intermolecular distance  $r$  decreases at any temperature. Hence,  $\Delta n$ , which is a measure of  $S$ , is correspondingly enhanced with increasing pressure, as can be seen in Figure 6 *a*. The  $\Delta n$  value corresponding to  $T_{NN}$  at elevated pressures is  $0.165 (\pm 2\%)$ , which is in agreement with the  $\Delta n$  value measured by Warriar *et al.*<sup>9</sup> in a cell of thickness  $1.5 \mu\text{m}$  at the temperature corresponding to  $T_{NN}$ . To a good approximation, the orientational order parameter  $S \gg \Delta n / \Delta n_0$ , where  $\Delta n_0$



**Figure 5.** Pressure-temperature phase diagram of CP7B. The nematic phase occurring at temperatures above  $T_{NN}$  is indicated by  $N_d$  and that at lower temperatures by  $N_1$ .



**Figure 6.** Temperature variations of (a) Birefringence  $\Delta n$  and (b) orientational order parameter  $S$  of CP7B at various pressures.

is the value for the medium with perfect orientational order ( $S = 1$ ). The temperature variation of  $S$  can be fitted to Haller's extrapolation formula<sup>14</sup>, viz.  $S = (1 - T/T^*)^b$ , where  $T^*$  is a temperature at which  $S$  would have smoothly reduced to zero, if it did not jump to zero at the slightly lower, first-order transition temperature  $T_{NI}$ , and  $b$  is a constant. We have fitted the  $\Delta n$  values at atmospheric pressure to this formula to estimate the value of  $\Delta n_0$  ( $= 0.22$ ) and used it to calculate  $S$  values. The temperature variation of  $S$  at atmospheric pressure is in good agreement with the measurement of Balakrishnan *et al.*<sup>15</sup> using the NMR technique. The temperature variations of  $S$  along various isobars are presented in Figure 6 *b* in which it can be seen that the value at the  $N-I$  transition point, i.e.  $S_{NI}$ , is practically constant, and equal to  $0.32 (\pm 1.5\%)$  at all applied pressures. This is in agreement with the earlier results on paraazoxyanisole using NMR measurements at high pressures<sup>16</sup>. Wallis and Roy<sup>17</sup> have also found that the values of  $S_{NI}$  remain constant for several (but not all) nematogens at different pressures. Indeed, mean field theories such as the Maier-Saupe theory and the one outlined by Deloche and coworkers of  $N-I$  transition<sup>1,16</sup> predict that the value of  $S_{NI}$  should be independent of pressure along the transition line. It is indeed interesting to note that the value of  $S$  at the  $N-N$  transition ( $S_{NN}$ ) is also a constant and equal to  $0.75 \pm 0.01$  in the range of pressures from 0.6 to 1.8 kbar. Theoretical studies on this transition do not address this question. As seen in Figure 6, a much larger increase in temperature is needed to compensate for an increase in pressure to maintain a low value of the order parameter which occurs at a low density, than that for a high value of  $S$ . This is indeed reflected in the different slopes measured for  $dP/dT_{NN}$  and  $dP/dT_{NI}$ , as seen in Figure 5.

In conclusion, we have demonstrated that the compound studied, viz. CP7B exhibits a nematic-nematic transition at elevated pressures. This confirms the suggestions from earlier experimental investigations that the  $N-N$  transition occurs in this compound at a sufficiently large

value of the order parameter. Our experiments also show that both the  $N-I$  and  $N-N$  transitions occur at fixed values of the order parameters which are independent of pressure.

The HP studies on liquid crystals in Bangalore were initiated by S. Ramaseshan when he was in the National Aeronautical (now Aerospace) Laboratories<sup>18</sup>. It is indeed a pleasure to contribute this article to the special issue of *Current Science* which is being brought out in honour of his 80th birthday.

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## Twist grain boundary smectic A phase in compounds derived from cholesterol\*

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**The synthesis and characterization of four compounds of a homologous series of cholesteryl-2-fluoro-4-*n*-alkoxybenzoates is reported. The twist grain boundary smectic A phase was observed in three compounds which contain only one phenyl ring. All the compounds exhibiting this phase, also show blue phase, cholesteric, smectic A and smectic C\* phases. The mesophases were identified using polarizing optical microscopy, differential scanning calorimetry and helical pitch measurements.**

SINCE the discovery<sup>1</sup> of the liquid crystalline state in cholesteryl benzoate, chirality and optical activity have become an important topic for research in orientationally ordered fluids. Based on simple, but very clever symmetry arguments, Meyer *et al.*<sup>2</sup> discovered ferroelectricity in chiral compounds exhibiting the smectic C phase. This was followed by the demonstration of an electro-optical effect<sup>3</sup> that utilized this ferroelectric property exhibited by the chiral smectic C (SmC\*) phase. The SmC\* phase is the most fluid phase to offer such a property and hence has shown great potential for electro-optical device applications. During the centenary year of the discovery of the liquid crystalline state, two other significant discoveries were made. One is the antiferroelectric smectic C\* phase<sup>4</sup>, which shows electric-field-induced tristable switching characteristics and the other is the twist grain boundary smectic A (TGB<sub>A</sub>) phase<sup>5</sup>, which was discovered serendipitously. In the TGB<sub>A</sub> phase, small blocks of molecules which have a local smectic A structure, are rotated with respect to one another by screw dislocations, which results in the formation of a helical structure. In this helical macro structure, the smectic A blocks rotate such that the helical axis is parallel to the layer planes and the screw dislocations are periodic.

Though a theoretical model for the existence of TGB<sub>A</sub> phase was developed by Renn and Lubensky<sup>6</sup>, the first experimental confirmation for its occurrence was made by Goodby *et al.*<sup>5</sup> in a series of 1-methylheptyl-4'-(4''-*n*-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates. These materials had high optical purities with their chiral centers located adjacent to the rigid molecular cores containing three phenyl rings. Since then, a fairly large number of compounds exhibiting the TGB<sub>A</sub> phase have been synthesized<sup>8–10</sup>. It was believed for some time that a relatively

\*Dedicated to Prof. S. Ramaseshan on his 80th birthday.

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