Pramāṇa, Suppl. No. 1, 1975, pp. 117–129

Pressure induced mesomorphism

S CHANDRASEKHAR *, S RAMASESHAN †
A S RESHAMWALA†, B K SADASHIVA *
R SHASHIDHAR * and V SURENDRANATH *

* Raman Research Institute, Bangalore 560006

† Materials Science Division, National Aeronautical Laboratory, Bangalore 560017.

Abstract. The paper reports the discovery of mesomorphism induced by pressure in materials that do not exhibit the liquid crystalline phase at atmospheric pressure. This observation verifies a prediction of the theory of melting of molecular crystals.

Experiments were conducted on the first two members of the *p–n*–alkoxybenzoic acid series. These two compounds, the methoxy– and ethoxybenzoic acids, do not form liquid crystals at atmospheric pressure whereas the third and higher homologues do. However, as the pressure is raised both compounds exhibit mesophases, initially a nematic phase and then, at higher pressures, a smectic phase as well. Experimental phase diagrams are presented which establish for the first time the existence of the solid–nematic–isotropic and solid–smectic–nematic *triple points* in single component systems.

Introduction

Under what circumstances can the solid–liquid crystal–isotropic liquid triple point be observed experimentally? A study of the phase diagrams given by the theory of melting of molecular crystals discussed by Chandrasekhar *et al.*[1] provides an answer to this question. Two representative *P–T* diagrams evaluated from the theory are shown in figure 1. In figure 1(a) the orientational barrier of the molecule is large enough for the nematic phase to occur at zero pressure. As the pressure increases, both the solid-nematic and the nematic–isotropic transition temperatures increase, the slope dT/dP for the latter being greater in accordance with the experimental data available for *p*–azoxyanisole (PAA)[2–6] and *p*–azoxyphenetole (PAP)[2]. Figure 1(b) represents a more interesting case. Here the barrier is just below the critical value for the nematic phase to occur at zero pressure, As the pressure increases there is initially only a single transition, namely, the solid–liquid melting transition, but at higher pressures branching takes place and there are two transitions, the solid–nematic and the nematic–isotropic. Thus the theory makes the important prediction that the liquid crystalline phase can be induced by pressure in materials that are non–mesomorphic at atmospheric pressure, and also that at a certain pressure

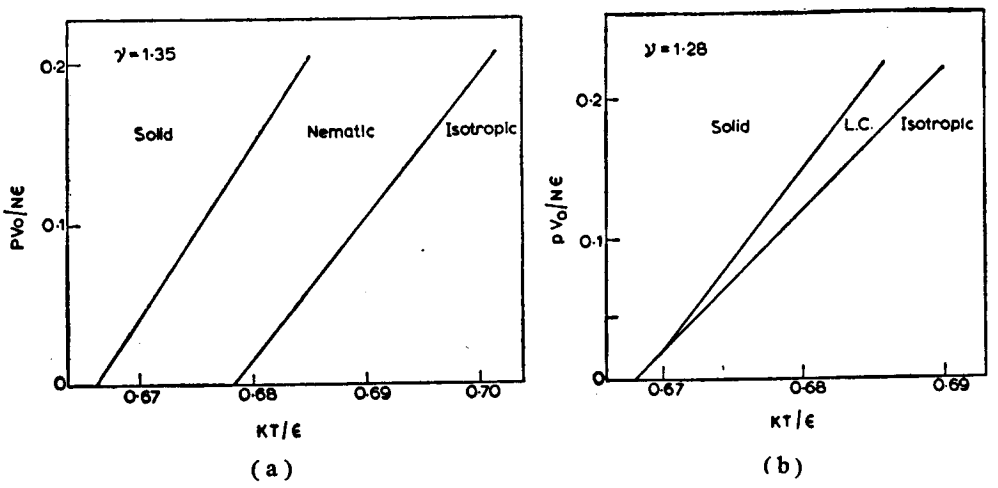

Figure 1 Theoretical phase diagrams evaluated for two values of ν, where ν is a measure of the relative barriers for the rotation of a molecule and for its diffusion to an interstitial site, (a) $\nu = 1.35$ (b) $\nu = 1.28$.

and temperature there should exist a solid–liquid crystal–isotropic liquid triple point. Experiments were undertaken to verify these conclusions.

After surveying various possible materials, it was decided to choose for these studies the first two members of the *p–n*–alkoxybenzoic acid series. These two members, methoxy– and ethoxybenzoic acids, do not show any mesomorphism whereas propoxybenzoic acid and the higher homologues exhibit at least one liquid crystalline phase[7]. Moreover, a mixture of the first two members shows a nematic phase, indicating that mesomorphism may be latent in each of them. It therefore appeared that the chances of observing liquid crystallinity in either of these two compounds at pressures easily attainable in the laboratory might be quite favourable.

Experimental

A 100-ton single acting hydraulic press (figure 2) was employed for the experiments. A schematic diagram of the press is shown in figure 3. The press has a 4″ diameter movable ram which can be worked upwards by a hydraulic pump. The high pressure cell, containing the encapsulated sample, the pressure transmitting medium and the heater, is held inside a binding ring (B) to prevent extrusion. A cooling jacket (J) used in series with a heat exchanger serves to prevent the pistons from getting overheated. A stainless-steel piston (SP) presses the cell from above. This piston has a central bore for taking out the thermocouple leads. As the movable ram is raised, the entire assembly moves up and presses against a stationary plate fixed to the body of the press. The amount of fluid that is pumped was accurately controlled by a manual pump so that the pressure could be built up very gradually.

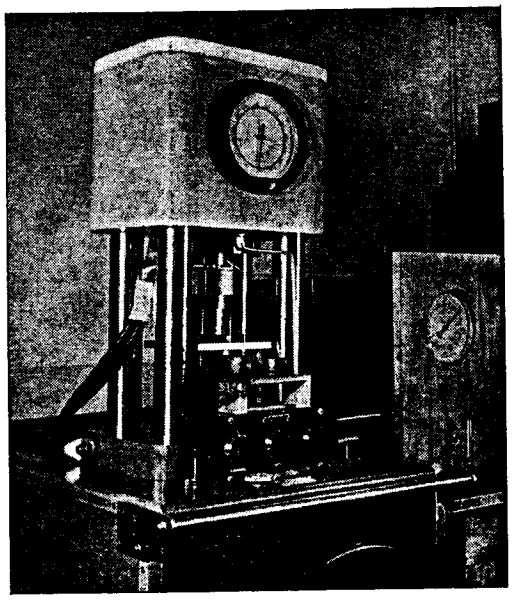

Figure 2 Photograph of the 100 ton press used for the experiments.

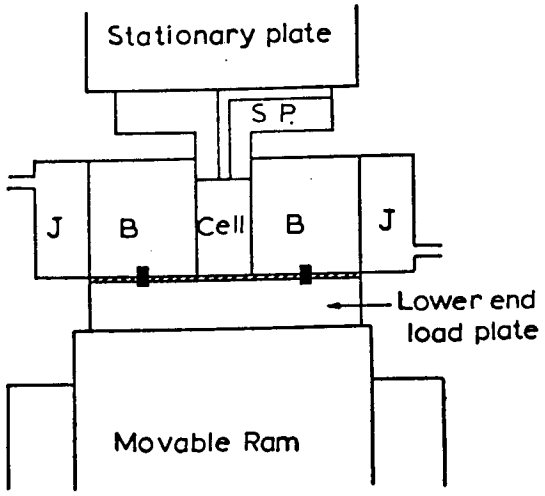

Figure 3 Schematic diagram of the press.

Since the nematic–isotropic transition is usually weakly first order, it was necessary to select a probe of high sensitivity. The obvious choice was DTA in which the difference between the reference and sample temperatures is plotted versus the sample temperature. Ideally the curve should be a horizontal line except when a transition occurs. However, in the present experiments, because of limitations of space – the pressure cell was only 1″ in diameter and contained the encapsulated sample, the heating element and the pressure transmitting medium – and also because of the

poor thermal conductivity of the sample holder and the natural temperature gradient set up by the graphite heater, a major problem that was encountered initially was the 'drift', which resulted in a base line that was very steeply inclined. To offset this the recorder pen had to be brought back to zero whenever it reached full scale, which was not a satisfactory procedure as there was every possibility of missing a sharp transition. The problem was overcome finally by experimentation with the design of the cell which required precise machining of its components and critical positioning of the sample and reference junctions of the thermocouple. A suitable geometry of the cell was arrived at which minimised this drift.

The sample was contained in a capsule made of glass filled teflon (supplied by Fluoro Carbon Industries, USA) which was sealed using a teflon plug. The advantages of using teflon are that it does not react with any of the compounds and that it flows under pressure thereby providing an airtight seal. The pressure transmitting medium was talc which surrounded the sample capsule on all sides. A thin graphite sleeve was used as the heater. A high current, low voltage source supplied power to the heater. By varying the current at a controlled rate any desired rate of heating could be achieved. Chromel–alumel thermocouples were used for temperature measurements. The correction due to pressure for these thermocouples is extremely small in the pressure range studied and was neglected. The temperature difference (ΔT) was fed to a Keithley nanovolt amplifier and the output of the amplifier to the Y–axis of a Moseley X–Y recorder. The sample temperature was fed to the X–axis. An amplification of 1000 was used for ΔT for all experiments. This amplification was enough to drive a 10 μV signal to full scale of the recorder. The linearity of the amplifier under experimental conditions was checked beforehand. In series with the differential (ΔT) was a zero–suppression unit which could suppress upto 40 mV of the thermocouple signal with a resolution of 1 μV. The line pressures were measured by a calibrated transducer (Type G 1–366 of Groseby Instruments, Surrey, England) reading to an accuracy of 1%. In order to evaluate the true pressure as seen by the sample, a small correction has to be applied. By measuring the resistance variation with pressure of a standard manganin gauge[8] immersed in silicone oil in the sample capsule, the true pressures were calibrated against the line pressures. The correction was found to be less than 2% over the entire range of pressures investigated.

Results and discussion

p–Azoxyanisole (PAA): To test the experimental set up, we first conducted experiments on PAA for which some data are available[3–7]. For each pressure, DTA runs were recorded for at least two heating rates and the average of the transition temperatures taken. All the transition temperatures were recorded during heating as there was always some supercooling

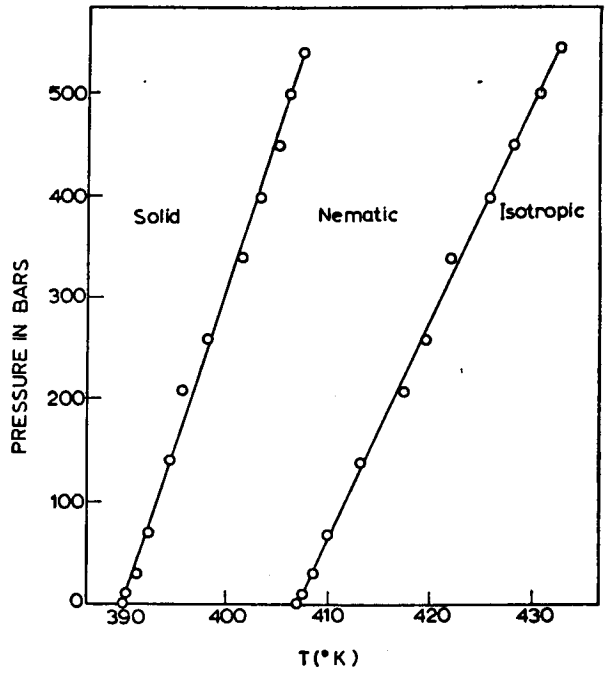

Figure 4 Experimental variation of the transition temperatures with pressure for *p*–azoxyanisole.

Table 1. dT/dP for PAA in °/kbar

	Solid–nematic	Nematic–isotropic
Hulett[2]	32·0 up to 300 bars	48·6 up to 300 bars
Pushin and Grebenschtschikow[3]	25·6 up to 2 kbars	39·4 up to 1 kbar
Robberecht[4]	32 up to 850 bars	48 up to 935 bars
Deloche, Cabane and Jerome[5]	23·7 up to 3 kbars	25·7 up to 3 kbars
McColl and Shih[6]	—	46 up to 640 bars
Present work	32 up to 540 bars	47 up to 540 bars

during the cooling part of the cycle. The results obtained for different pressures for PAA are plotted in figure 4. The slopes dT/dP evaluated for the solid–nematic and nematic–isotropic transitions are 32°/kbar and 47°/kbar respectively. Table 1 gives a comparison of these values with the other experimental data available for PAA. We see that our slopes agree very well with those of Hulett[2], Robberecht[4] and McColl and Shih[6].

The values of Deloche *et al.*[5] are rather different, probably because, as the authors themselves point out, helium gas which served as the pressure transmitting medium contaminated the sample.

p-*Azoxyphenetole (PAP):* Experiments were done for PAP up to a pressure of ~ 590 bars. Figure 5 shows the phase diagram. The slopes of the solid–nematic and nematic–isotropic transitions are 36°/kbar and 46° / kbar. They agree well with the only other available set of data on PAP, *viz.*, 37°/kbar and 47·6°/kbar obtained by Hulett[2]. Thus having tested the reliability of the experimental set up, studies on methoxy– and ethoxybenzoic acids were undertaken.

p-*Methoxybenzoic acid:* Figure 6 shows the DTA runs taken for methoxybenzoic acid at four different pressures (only the portions of the DTA records near the peaks are shown). The first record was taken at a pressure of 1 bar, *i.e.*, at atmospheric pressure. There is a single transition, the peak giving the solid–liquid transition temperature. In the next record, taken at 12 bars we see another small kink just separated from the main peak. This in fact shows that there are now *two* first order transitions separated on the temperature axis by about 1°. This new pressure induced phase has been identified (as will be described later) as the nematic phase. In the third record obtained at 24 bars, the separation between the two transitions has increased to ~ 2·2°. At 61 bars, they are nearly 5° apart. When the pressure is increased even further, an interesting

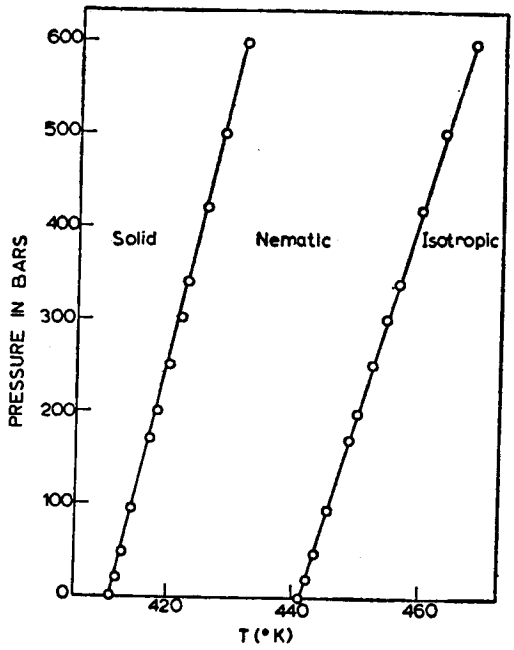

Figure 5 Experimental variation of the transition temperatures with pressure for *p*-azoxyphenetole.

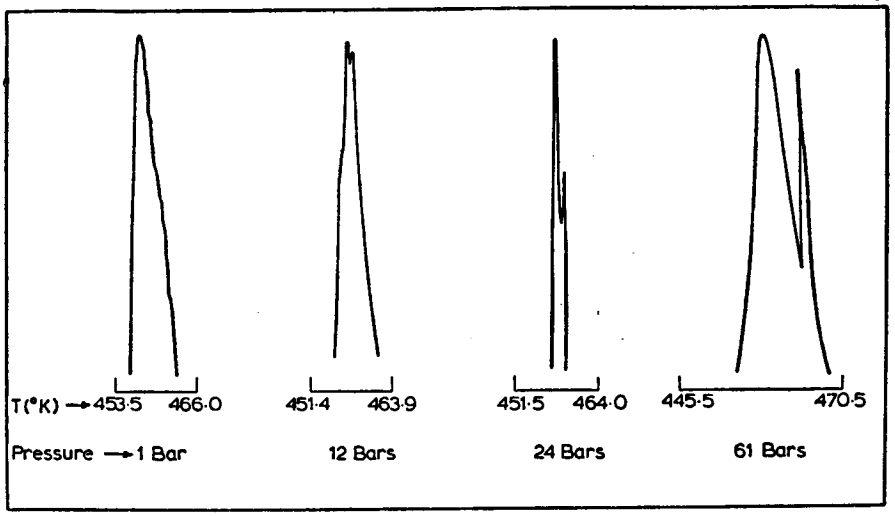

Figure 6 DTA records taken for methoxybenzoic acid at different pressures.

situation develops as can be seen in figure 7, which gives the DTA run at 145 bars. Here the nematic–isotropic transition is nearly 12° away from the first transition, but in addition, there is evidence that the first transition itself has started to split. There are now two distinct peaks separated by about 1·5°. As we shall see later, this new phase has been identified as the smectic phase. The complete data obtained for methoxybenzoic acid are plotted in figure 8. Measurements were made up to a pressure of 252 bars at which the nematic–isotropic transition is 21° away from the solid–smectic transition. The limitation of the experiment was set primarily by the temperature rather than by pressure. Teflon which was used to encapsulate the sample starts softening around 260° C and it was not safe to go to much higher temperatures. It shows clearly the solid–nematic–isotropic triple point at ~ 6 bars and 457·4 K and the solid–smectic–nematic triple point at ~ 96 bars and 458·4 K.

It should be emphasized that

(i) Each experimental point marked in the diagrams is the average of at least 2 runs taken at 2 different heating rates (the rates were between 0·5 to 2·5°/min.)

(ii) After completing the set of measurements with increasing pressure, the pressure was brought back to atmospheric pressure when a *single transition* was again observed. This transition temperature was the same as that obtained at the beginning of the experiment proving that the sample was completely free from any contamination.

p–*Ethoxybenzoic acid:* The phase diagram for ethoxybenzoic acid is given in figure 9. The behaviour is similar to that of methoxybenzoic acid. There is a single transition till 3 bars. At 8 bars the nematic phase has just appeared. At 96 bars the smectic phase also starts appearing. The maximum pressure that we could go to was 233 bars because of the temperature limitation mentioned earlier. Here again we have the two triple points at ~ 5 bars and 467·2 K and ~ 87 bars 468·5 K respectively. As before, it was verified that the sample was completely free from contamination by noting the reproducibility of the temperature of the single transition at atmospheric pressure before and after the experiment.

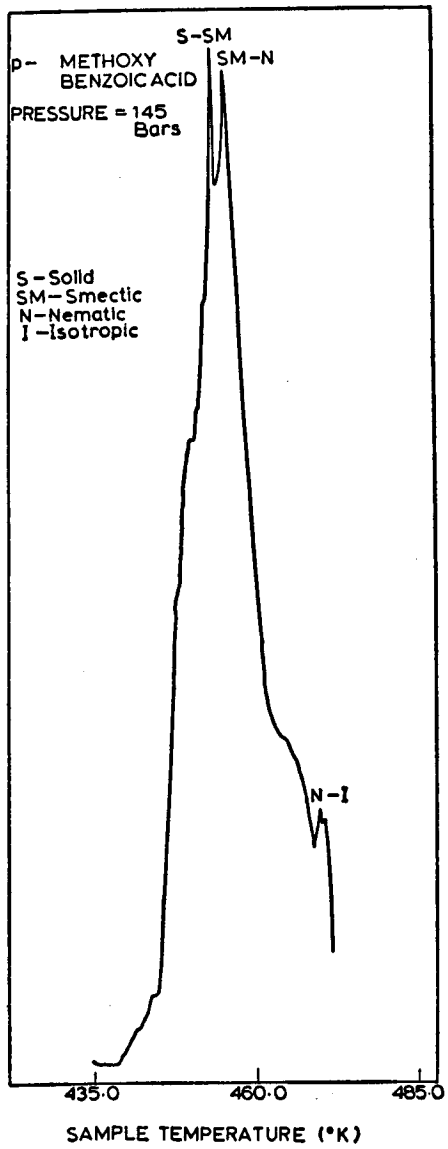

Figure 7 DTA run taken for methoxybenzoic acid at a pressure of 145 bars.

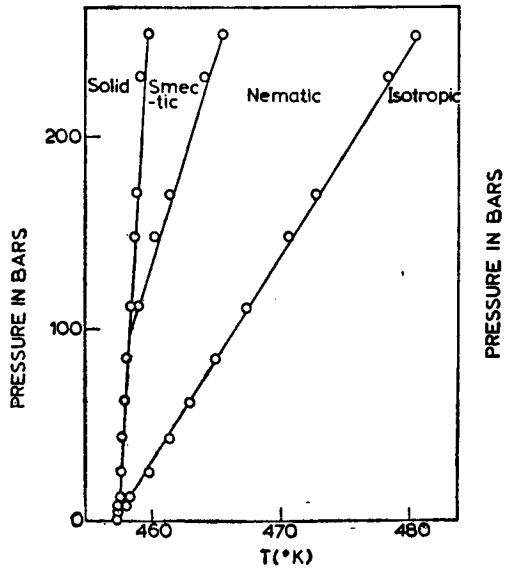

Figure 8 Experimental phase diagram for methoxybenzoic acid showing the solid–nematic–isotropic and solid–smectic–nematic triple points at ~6 bars and 457.4 K and ~94 bars and 458.4 K respectively.

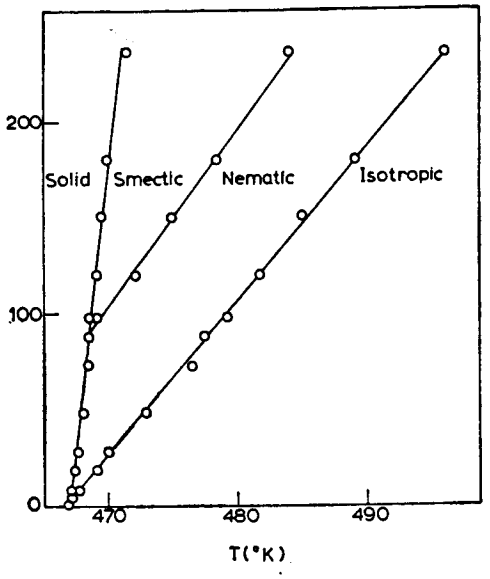

Figure 9 Experimental phase diagram for ethoxybenzoic acid showing the solid–nematic–isotropic and solid–smectic–nematic triple points at ~5 bars and 467.2 K and ~87 bars and 468.5 K respectively.

Identification of the phases

To identify the pressure induced phases an optical cell was constructed. A schematic diagram of the cell is given in figure 10.

The apparatus consists of a stainless steel stationary base plate (SP) in which is fitted a fused silica anvil (A). A thin stainless steel ring (R) is shrunk fitted to this anvil by heating both of them to 400°C. The inner diameter of this ring is slightly greater at the top to enable the other anvil, also made of fused silica and fixed to a top plate (TP), to just rotate inside the ring. The two anvils can be pressed against each other by screwing the top plate. The sample ($\sim$ 100 μ thick) is contained between the anvils in a hole in a teflon spacer as shown in figure 10. The teflon spacer requires very accurate machining on both sides so as to match the anvils perfectly. Only then was it possible to contain the sample without leaks. The top and bottom plates are provided with windows for optical observations. The entire assembly is inside a heater and the temperature of the sample is probed by a chromel-alumel thermocouple. All observations were made in transmitted light using a Leitz polarizing microscope equipped with a camera. The pressure developed was very roughly estimated using the known values of dT/dP for PAA.

At lower pressures ethoxybenzoic acid shows a single intermediate phase which exhibits the typical schlieren texture of a nematic liquid crystal

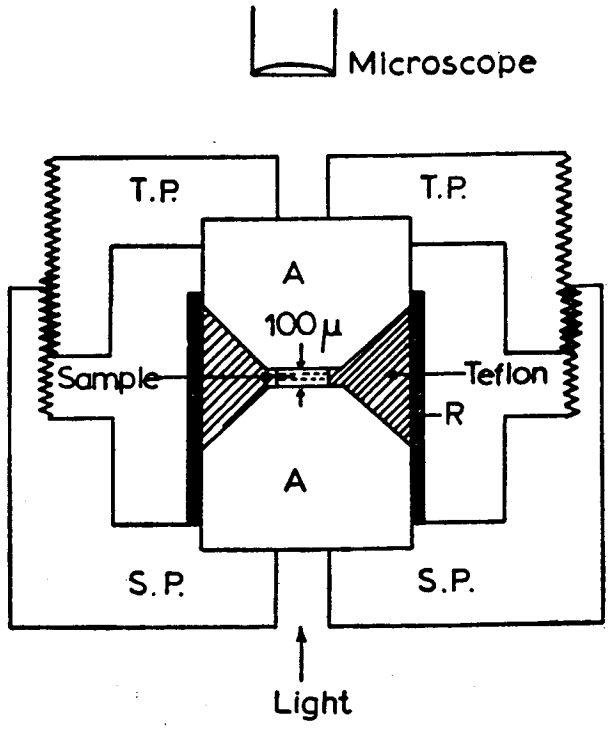

Figure 10 Schematic diagram of the optical cell.

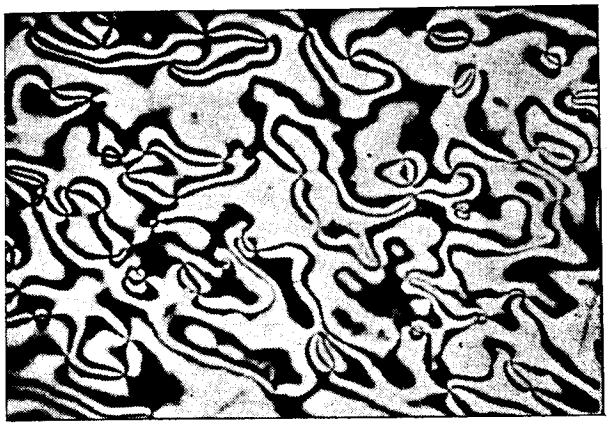

Figure 11 Schlieren texture exhibited by ethoxybenzoic acid (crossed polars, x 90).

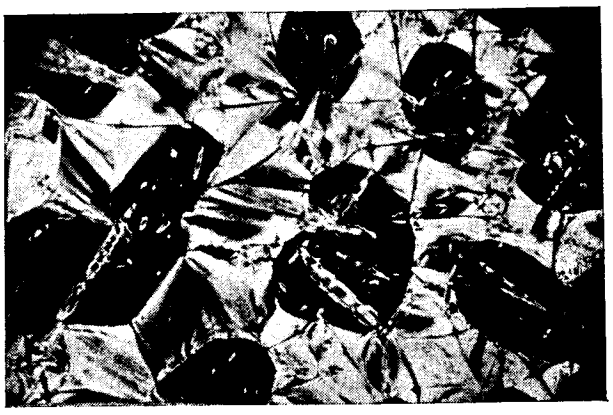

Figure 12 Focal conics and batonnets formed by ethoxybenzoic acid (crossed polars, x 90).

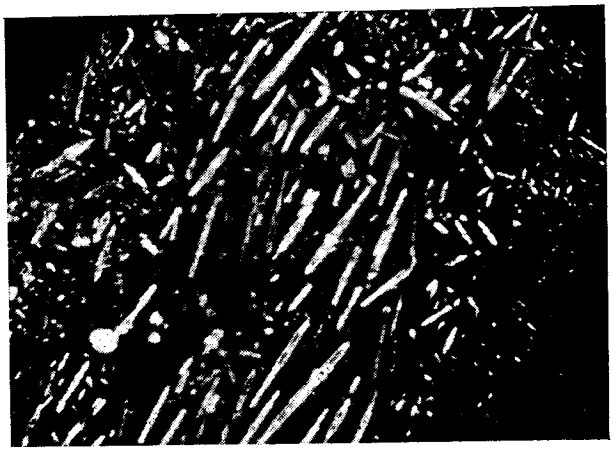

Figure 13 Batonnets shown by methoxybenzoic acid (crossed polars, x 90).

(figure 11). At higher pressures, it was found that on cooling the isotropic liquid a nematic phase (with a schlieren texture) appeared first, which then transformed at a lower temperature to another phase showing the focal conic texture and batonnets (figure 12) characteristic of a smectic. On further cooling it went over to the solid phase making the field of view completely opaque. The pressure induced phases of methoxybenzoic acid also exhibit similar textures. Figure 13 shows batonnets formed by the smectic phase of this compound. Thus the pressure induced phases in both methoxy- and ethoxybenzoic acids have been identified as the nematic and smectic phases.

Conclusions

Methoxy- and ethoxybenzoic acids, which are non-mesomorphic at atmospheric pressure, have been found to exhibit nematic and smectic phases at higher pressures. The transitions were detected by DTA and the phases were identified by optical microscopy. The phenomenon of pressure induced mesomorphism and the occurrence of solid–nematic–isotropic and solid–smectic–nematic triple points in single component systems have been established experimentally for the first time.

Acknowledgements

We are extremely thankful to Mr M T Srivatsa for his assistance in making the zero suppression unit and to Mr K Jagannath Rao and Mr V Venu for precise machining of the components of the cell.

References

1 CHANDRASEKHAR S, SHASHIDHAR R and TARA N, *Mol. Cryst. Liquid Cryst.* **10** 337 (1970); **12** 245 (1971); CHANDRASEKHAR S and SHASHIDHAR R *Mol. Cryst. Liquid Cryst.* **16** 21 (1972)
2 HULETT G A *Z. Phys. Chem.* **28** 629 (1899)
3 PUSHIN and GREBENSCHTSCHIKOW W *Z. Phys. Chem. (Leipzig)* **124** 270 (1926)
4 ROBBERECHT J *Bull. Soc. Chim. Belge* **37** 597 (1936)
5 DELOCHE B, CABANE B and JEROME D *Mol. Cryst. Liquid Cryst.* **15** 197 (1971)
6 MCCOLL J R and SHIH C S *Phys. Rev. Lett.* **29** 85 (1972)
7 BENNET G M and JONES B *J. Chem. Soc.* 420 (1939)
8 BRIDGMAN P W *Proc. Am. Acad. Arts Sci.* **74** 1 (1940); JAYARAMAN A, HUTSON A R MCFEE J H, CORIELL A S and MAINES R G *Rev. Sci. Instrum.* **38** 44 (1967)

DISCUSSION

Schnur: Have you checked for PAA, for which all the numbers are known, whether the *P–T* diagram is in accordance with the Clausius–Clapeyron equation ?

Shashidhar: Several measurements of ΔH are available, but the most detailed and systematic studies appear to be those of Arnold *. Using his values of ΔH, and the $\Delta V/V$ values of Maier and Saupe †, we get dT/dP for the solid–nematic and nematic–isotropic transitions to be 32·1 and 47·8°/kbar respectively. The experimental values are 32 and 47°/kbar, confirming that the Clausius–Clapeyron equation is obeyed.

Schnur: Have you checked if the smectic–nematic transition also fits the Clausius–Clapeyron equation?

Shashidhar: As we have no idea of the volume change and heat of transition for the smectic–nematic transition, it is not possible to check this.

Bulkin: Are you sure that you have ruled out solid–solid phase transitions?

Shashidhar: We are quite sure that what we have observed is not a solid–solid transition. Usually a solid–solid transition has a lower heat of transition than the melting transition, but we see from our DTA runs that the opposite is the case — the second transition is much weaker than the first one, a feature which is characteristic of mesophase transitions in general. But a more direct proof comes from an examination of these phases in a high pressure optical cell. The intermediate phases exhibit textures characteristic of liquid crystals. I have shown photographs of some of these textures.

Boccara: 1. Do you know the value of the discontinuities of the specific volume near the triple points?

2. What are the values of the slopes of the various transition lines at the triple points?

Shashidhar: 1. No, we have not carried out any measurements of the specific volume.

2. The values of the slopes (dT/dP) at the triple points are as follows:

	Methoxybenzoic acid	Ethoxybenzoic acid
Solid–smectic	10°/kbar	17°/kbar
Smectic–nematic	45°/kbar	109°/kbar
Nematic–isotropic	94°/kbar	126°/kbar

* Arnold H *Z. Phys. Chem.* (DDR) **226** 146 (1964)

† Maier W and Saupe A *Z. Naturforsch.* **15a** 287 (1960)

Dave : Have any calculations been made by extrapolation as to where the nematic phase should appear for pure methoxy– and ethoxy–benzoic acids at atmospheric pressure ?

Shashidhar : We have not made any such calculations.

Schnur : Have you observed the monotropic solid II phase in PAA on cooling in your pressure experiment ?

Shashidhar : No, we have not. In fact all the DTA runs were taken on heating only as cooling invariably resulted in supercooling of the nematic phase.

Rustichelli : You said you changed the pressure. Did the value of the temperature also change ?

Shashidhar : The experiment was done in the following way : The pressure was kept constant and the DTA run was taken by changing only the temperature. This gave the transition temperatures for that pressure. The procedure was repeated for different pressures.

Rustichelli : Is it possible to fix the temperature and increase the pressure ? It will be nice to see if the effect can be observed this way.

Shashidhar : It is possible, but there are some experimental difficulties which have to be overcome to do this.