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R. Shashidhar [a b], J. Herrmann [a] & H. D. Kleinhans [a]
[a] Department of Chemistry, Physical Chemistry Laboratory University of Bochum, 4630, Bochum, FRG
[b] Humboldt Fellow, on leave of absence from the Raman Research Institute, Bangalore, 560 080, India
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OBSERVATION OF A SMECTIC A - SMECTIC A TRANSITION AT HIGH PRESSURES: OPTICAL MICROSCOPY AND DTA STUDIES ON 6OPDOB

R.SHASHIDHAR*, J.HERRMANN and H.D.KLEINHANS
Department of Chemistry, Physical Chemistry Laboratory, University of Bochum,
4630 Bochum 1, FRG
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ABSTRACT. On the basis of DTA and textural studies at high pressure we report here the observation of a smectic A - smectic A transition at pressures exceeding 2.2 kbar in 4-n-hexyloxyphenyl-4'-n-decyloxybenzoate.

INTRODUCTION While studying the pressure - temperature diagram of 4-n-hexyloxyphenyl-4'-n-decyloxybenzoate (6OPDOB) two pressure induced phases were observed, one above 1.4 kbar and the other above 2.2 kbar[1]. Preliminary DTA studies indicated that the phase at lower pressures is a pressure induced solid phase while that at higher pressures is a pressure induced mesophase. The question arose as to what could be this mesophase which exists below the smectic A phase in the P-T

*Humboldt Fellow, on leave of absence from the Raman Research Institute, Bangalore - 560 080, India

plane and which is not the smectic C phase either. It was conjectured that this could be another form of the smectic A phase. To identify this phase we have studied by optical microscopy at high pressures the textures exhibited by the various phases. Also, we have carried out some high sensitivity DTA experiments to determine the exact pressure at which the pressure induced mesophase starts appearing.

EXPERIMENTAL The optical microscopy studies were made using an opposed diamond anvil cell and a polarizing microscope (Ortholux, Leitz, Germany). The cell is essentially similar to that developed by Piermarini and Block[2] at the National Bureau of Standards, Washington. It may be recalled that a diamond anvil cell has been used earlier for X-ray and optical transmission studies on liquid crystals at high pressures[3,4]. In these experiments a rather thick ($\sim$ 1 mm) aluminium gasket was used, while in the present study we have used, to get good textures, a 0.1 mm thick gasket made of hardened steel. (See references 5 and 6 for details concerning the construction of the cell as well as the pressure calibration procedure used). In the case of the DTA experiments the sample was sealed in an indium capsule[7].

RESULTS Figure 1 shows the P-T diagram of 6OPDOB[1]. The pressure induced mesophase is designated as S_X in the figure. (See reference 1 for further descriptions of this diagram). The

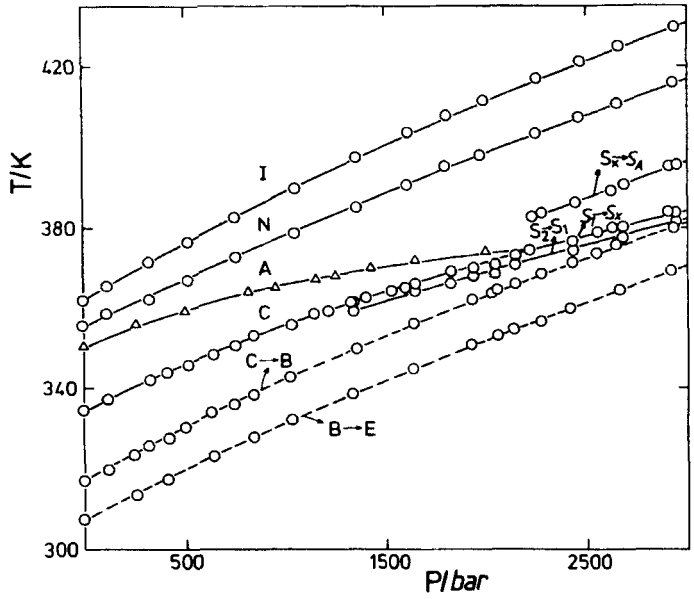

FIGURE 1. P-T diagram of 6OPDOB. The dashed lines indicate monotropic transitions.

optical microscopy experiments were conducted by keeping the pressure at about 2.8 kbar and decreasing the temperature from the isotropic phase. As the nematic phase was formed, the schlieren texture was clearly seen. On further cooling, this schlieren texture changed to a focal conic texture with ellipses (Fig. 2) characterizing the smectic A phase. The texture with ellipses remained unchanged even on cooling the sample into the S_X phase (Fig. 3), i.e., there was no textural change on crossing the S_A-S_X phase boundary. The dark regions seen in Figs 2 and 3 are homeotropically aligned regions. On further cooling, the monotropic smectic B phase with a mosaic texture was seen. (The solid phase S_1 supercools to a very

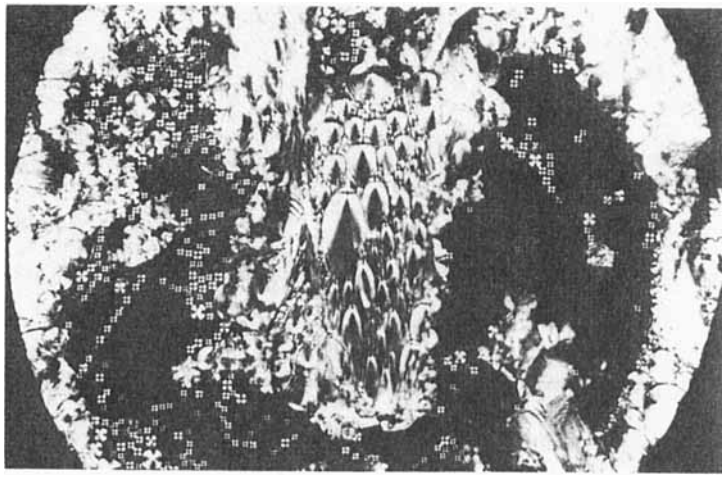

FIGURE 2. Ellipses and the focal conic texture of the smectic A (S_A) phase of 6OPDOB. P ∿ 2.8 kbar, temperature = 130°C, X125, crossed polarizers.

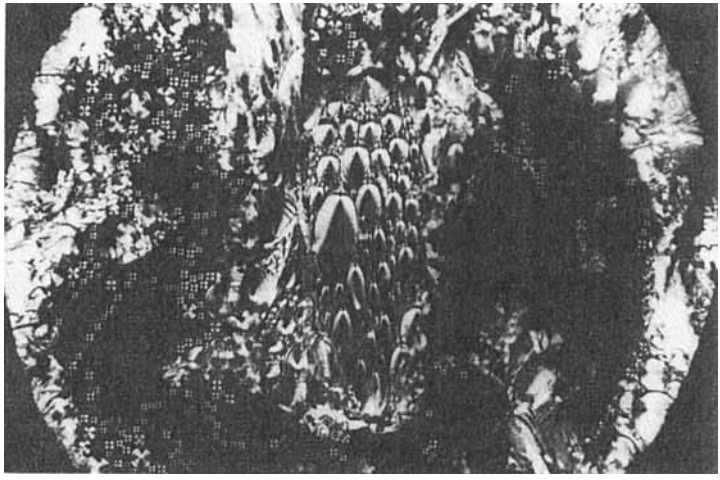

FIGURE 3. Same texture as in Fig. 2, but of the S_X phase of 6OPDOB. P ∿ 2.8 kbar, T = 115°C, X125, crossed polarizers.

large extent and is formed, during the cooling mode, only below the monotropic smectic B and E

phases. Therefore, the evidence, viz, a first order like transition (as seen by DTA) with no textural change, strongly indicates that this is a smectic A - smectic A (or A-A) transition. It may be recalled that the A-A transition was first observed by Sigaud et al in mixtures and later by Hardouin et al[9] in a pure compound, both these observations being at atmospheric pressure. This is however the first observation of an A-A transition at high pressures.

The question arises as to whether we can identify the high pressure A phase with any particular modification, eg A_1, A_2 or $\tilde{A}$, as defined by the Bordeaux group[10,11]. High sensitivity DTA studies were made to locate the exact pressure at which the high pressure A phase makes its appearance and there by ascertain if the A-A transition has a critical end point, a possibility which was theoretically postulated by Prost[12]. It was not possible to detect the high pressure A phase below about 2.2 kbar. The run taken only 50 bars below 2.2 kbar failed to show this phase[13]. This could be for several reasons, viz, (i) the transition might start as a second order transition and acquire first order contributions at higher pressures or (ii) the transition A-A, with a heat which is much smaller than that of the solid-smectic A transition, may well be masked by the latter owing to the close proximity of the two transitions in the temperature scale. In any case, the experimental resolution in the DTA set up is not sufficient for us to arrive at any definite

conclusion. High pressure X-ray studies are being taken up to probe the structure of the high pressure A phase.

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