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High Pressure Studies on HOAB: Pressure Dependence of the Smectic C Layer Spacing

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High Pressure Studies on HOAB: Pressure Dependence of the Smectic C Layer Spacing†

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Using an opposed diamond anvil cell, an X-ray investigation has been made of the pressure dependence of the layer spacing in the smectic C phase of 4,4′-bis(heptyloxy)azoxybenzene (HOAB) up to 3.8 kbar. It is found that the layer spacing is independent of pressure to within the experimental limits. It is concluded therefore that the suppression of the smectic C phase of this compound at higher pressures is not due to a tilt angle variation with pressure.

INTRODUCTION

In an earlier paper[1] it was shown that in 4,4′-bis(heptyloxy)azoxybenzene (HOAB) the range of the smectic C phase diminishes with increasing pressure and finally disappears altogether at high pressures, the resulting solid-smectic C-nematic triple point occurring at 6.67 kbar, 164°C. The suggestion was made that the suppression of the C phase may conceivably be due to a progressive increase of the tilt angle with increasing pressure until the layering is completely lost and the solid transforms directly to the nematic phase. We have undertaken an X-ray investigation of the pressure variation of the layer spacing in the C phase to test this point.

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EXPERIMENTAL

The sample of HOAB used in this study was purchased from Eastman Kodak and was recrystallized several times from *n*-heptane till the nematic-isotropic transition temperature was constant (123.7°C). The high pressure X-ray studies were carried out using an opposed diamond anvil cell constructed in this laboratory. It was essentially of the same type as that designed at the National Bureau of Standards, Washington, by Piermarini and Block[3] for X-ray high pressure studies of solids. The anvils were brilliant cut gem quality diamonds whose culets were removed by grinding and the faces were then polished. They were used in a gasketed configuration. By using a suitable gasket material, and suitably manipulating the areas of the anvil faces, it was possible to achieve two important functions: (i) the liquid crystalline sample could be encapsulated for long periods without leaks and (ii) the cell, which is normally useful for pressures beyond a few tens of kilobars only, was found applicable to quite low pressures.

Pressures were measured using an indirect but nevertheless quite accurate method; an *in situ* determination of the transition temperatures of the sample in the cell was made by the optical transmission technique and knowing the accurate P-T diagram of the sample obtained by DTA[1] (or differential thermal analysis) the pressure could be directly read out. Pressures are estimated to be accurate to ±15 bars while the transition temperature at any pressure could be determined to a reproducible accuracy of ±0.2°C. (For further constructional details of the cell as well as for the procedure adopted for pressure calibration see Ref. 4 and 5).

The X-ray diffraction maxima were recorded photographically using Nickel-filtered copper K_α radiation. The duration of each exposure was about 60 h and it was ascertained that during the exposure the sample temperature was constant to within the limits of experimental error. The sample to film distance was accurately calibrated using *p*-decanoic acid as the standard. The relative accuracy in the determination of the layer spacing at different pressures is reckoned to be ±0.1 Å.

RESULTS

The P-T diagram of HOAB obtained earlier using the DTA technique is reproduced in Figure 1. The layer spacing in the smectic C phase has been measured up to 3.8 kbar. Since it is not possible to study the pressure variation of the layer spacing at a constant temperature (the smectic C

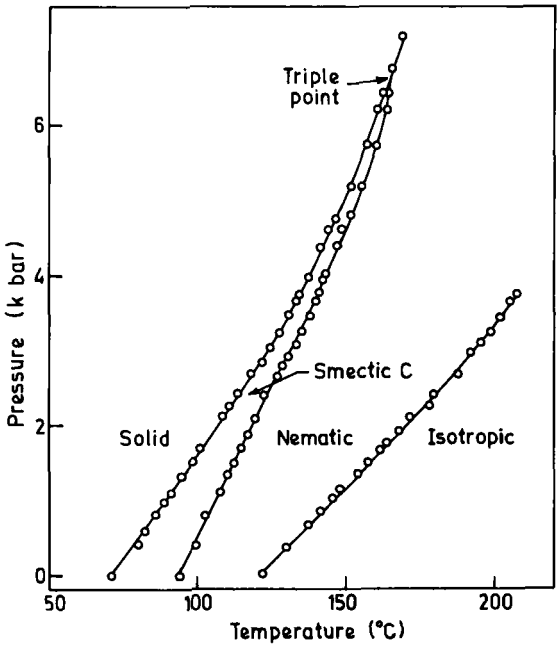

FIGURE 1 P-T diagram of HOAB.

would then transform to the solid phase at higher pressures), the layer spacing at every pressure was determiend at a common relative temperature of 2°C below the smectic C-nematic transition point.

A plot of the layer spacing (d) vs pressure is shown in Figure 2. Our value of d at atmospheric pressure is 23.5 Å. Taking the length of the HOAB molecule, measured in its most extended conformation using the Dreiding model, as 32.1 Å the tilt angle turns out to be 43°. This value of the tilt angle is in good agreement with the earlier determinations.[6–8] It is seen that the spacing is, within the limits of experimental error, independent of pressure right up to 3.8 kbar. Thus one may conclude that the suppression of the C phase of HOAB which occurs at 6.67 kbar is not due to a tilt angle variation with pressure. A similar conclusion has been drawn very recently by Guillon *et al.*[9] who have carried out X-ray measurements on this compound (using a different type of pressure cell) up to about 1.5 kbar.

It may also be recalled that recent pressure studies[10] have shown that pressure has the effect of destabilizing the smectic C phase, eventually leading to its suppression, regardless of the nature of the temperature

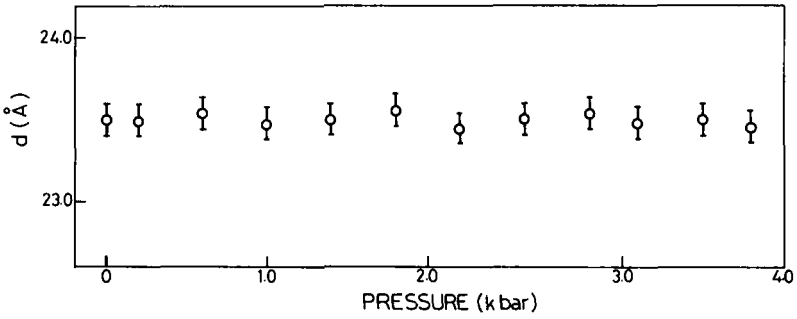

FIGURE 2 Variation of the layer spacing in the smectic C phase of HOAB with pressure.

variation of the tilt angle at atmospheric pressure. The exact reason for the suppression of the smectic C phase at high pressures is still to be understood.

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