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Volume and X-Ray Diffraction Study of Cyanobenzylidene *p,n* Octyloxyaniline (CBOOA)

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Using X-ray diffraction and dilatometry, we have studied the evolution of the layer spacing and of the volume of CBOOA with decreasing temperature. The results show a small change of behavior in the smectic A phase at about 70°C, which could indicate that the lateral contraction of the molecules is stopped at that temperature. The values of the molecular area we obtained from our data led us to propose a model of bilayer in which the molecules of CBOOA are tilted with respect to the normal plane.

I INTRODUCTION

Recently, some measurement of thermo-mechanical instability of layers in a smectic A phase have shown for some liquid crystals an unexpected inversion in the variation of the layer thickness as a function of temperature.[1] These observations have been performed on two compounds: cyanobenzylidene *p,n*-octyloxyaniline (CBOOA) and butoxybenzylidene *p,n*-anilinoacetophenone (BBAA); they have been supplemented by some direct measurement of the layer thickness obtained by X-ray diffraction.[1] However, there were not enough crystallographic experiments to give a definite proof of the phenomenon. A more systematic X-ray diffraction study complimented by a dilatometric analysis was needed.† In the present paper, we will describe

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† We thank Dr. Ribotta for having pointed out this phenomenon to us and his encouragement during the course of these experiments.

the results of the work we have done on one sample only, CBOOA. In addition, we will consider the implications of our results on the organization of the molecules inside the smectic layers.

II X-RAY DIFFRACTION STUDY

1 Diffraction chamber and experimental method

The experimental apparatus has been described elsewhere.[2] We only recall we have used a diffraction chamber of the Guinier type which has a monochromator with a bent quartz crystal. The chamber is under vacuum and we have used the $K\alpha_1$ copper radiation. All the patterns have been taken with a linear proportional counter coupled to a multichannel analyser. The diffraction patterns have been registered and the results printed automatically.

The different experiments of this study have been performed by decreasing the temperature from the nematic phase. We have chosen a very slow temperature scan: 3°C/hour. The exposure time for each pattern was 10 min.; so the temperature of the sample has been determined in a range of 0.5°C for each pattern.

2 Results

The thermal evolution of the layer thickness (Figure 1) shows that the smectic phase can be supercooled to a temperature of about 58°C (by increasing the temperature, the smectic A phase appears only at 73°C). At this temperature (58°C), the layer thickness changes from 34.5 Å to 45 Å, then at about 40°C, it changes again to 25 Å. It has to be noted that the lamellar phase which appears between 40°C and 58°C, occurs always with the presence of a small quantity of the phase which exists at room temperature.

From this figure (Figure 1), we are not able to distinguish any kind of anomaly in the evolution of the layer thickness as a function of temperature. However, a more precise observation of the experimental data (Figure 2) shows two regions of dilation, which can be detected on the scale of tenths of Å. When the temperature is decreasing, we see first of all a slight increase of the layer thickness, then a stabilization at about 70°C. Clearly, it is difficult to be very affirmative about this phenomenon, because of the very small difference between the layer thickness close to the nematic phase and far from it (0.3 Å; the experimental error is about 0.2 Å). In any case, the change in the layer thickness is different from the one which has been suggested recently,[1] where the layer spacing decreases with increasing temperature, then increases in the vicinity of the smectic–nematic transition. It has also to be

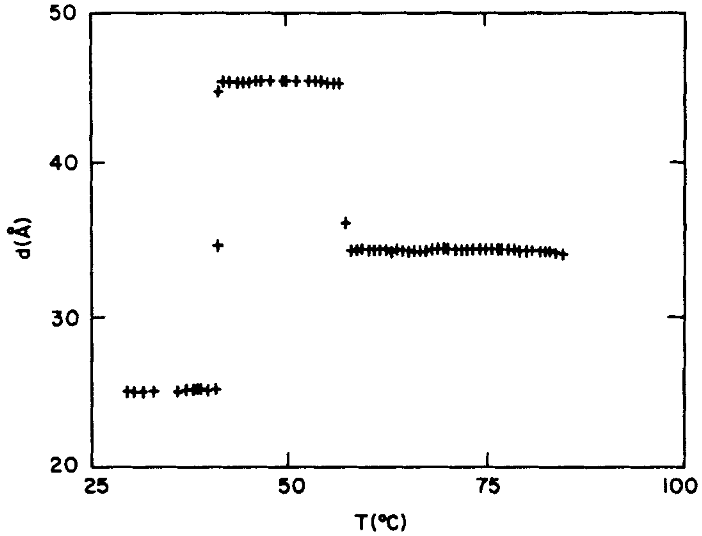

FIGURE 1 Evolution of the layer spacing by decreasing temperature.

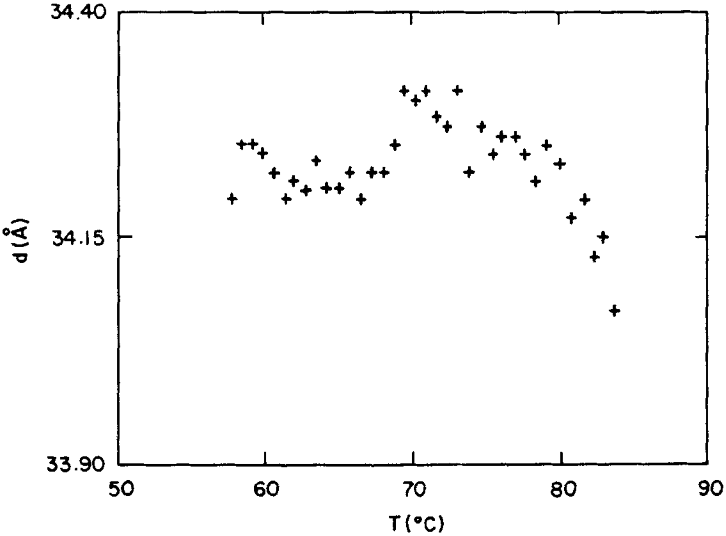

FIGURE 2 Evolution of the layer spacing by decreasing temperature in the smectic A phase.

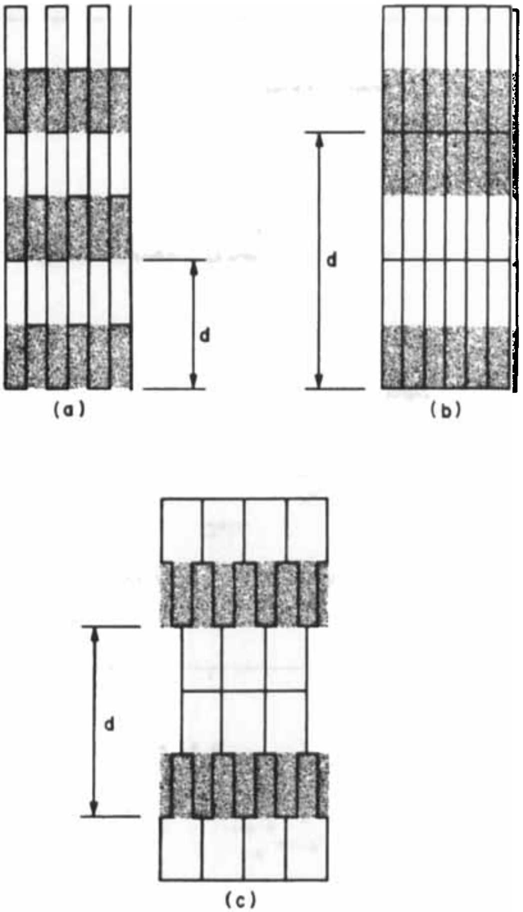

FIGURE 3 Different types of packing of molecules in layers. (3a) Alternatively superposed monolayers. (3b) Packing of molecules in bilayers. (3c) Packing of molecules with overlapping in a partial bilayer.

noted that we have observed some diffraction patterns in the vicinity of this transition which correspond to a Bragg spacing larger than the usual smectic layering; but these peaks are broader and show, in our opinion, the presence of smectic fluctuations in the nematic phase.

The layer thickness in the smectic A phase corresponds to about 1.5 times the length of the molecule: we have to deal with a bilayer system. We will come back to this observation later, when we will discuss our results.

The transition between the supercooled smectic phase and the crystalline phase is in fact very complicated and depends on the experimental conditions which are used to decrease the temperature. By decreasing the temperature from the smectic phase, we have identified two types of crystalline packing; and, very recently, Vani and Vijayan[3] have described the complete structure of a third crystalline kind which was obtained by slow evaporation of a CBOOA-heptane solution.

The crystalline state we have observed at room temperature is characterized by lamellae 25 Å thick, which corresponds almost exactly to the length of the fully extended molecule (~25 Å, measured from the crystallographic data of Vani and Vijayan[3] on the length and the angle of the bonds). In this state, the aromatic stems and the aliphatic chains of the molecules are organized in monolayers which are alternatively superposed (Figure 3a). The crystalline state observed at higher temperatures is characterized by lamellae of 45 Å thickness, which corresponds to a packing of molecules in bilayers (Figure 3b). In the crystalline state described by Vani and Vijayan the molecules are imbricated, without building very clear lamellae. Apparently, the way in which the dipolar moments of the azomethine and nitrile groups orient themselves, is at the origin of these different structural arrangements.

III VOLUME STUDY

1 Experimental method

We have used a classic dilatometer of Bekkedahl type.[4] The way to obtain such a dilatometer has been described elsewhere.[5]

The experiments have been performed in a liquid bath. We have also chosen in this case to impose on the system a scan of 0.3°C/min. The change in volume of CBOOA has already been studied as a function of temperature.[6,7] We have only focused our interest on the volumetric behavior of CBOOA by decreasing temperature, to be in the same experimental conditions as the diffraction study described above.

2 Results

The results are gathered in Figures 4 and 5. The values of the specific volume have been determined by taking as reference the value found by White *et al.*[7] for a precise temperature in the smectic phase.

In the Figure 4, we show the volume of CBOOA as a function of temperature in the smectic phase. Apparently, there is no singularity in this evolution; we can only note a very small change in the slope at about 70°C. However, the difference between the values of the thermal expansion coefficients is very small: above 70°C, we find it is equal to 6.85×10^{-4} cm^{3}g^{-1}K^{-1}, and

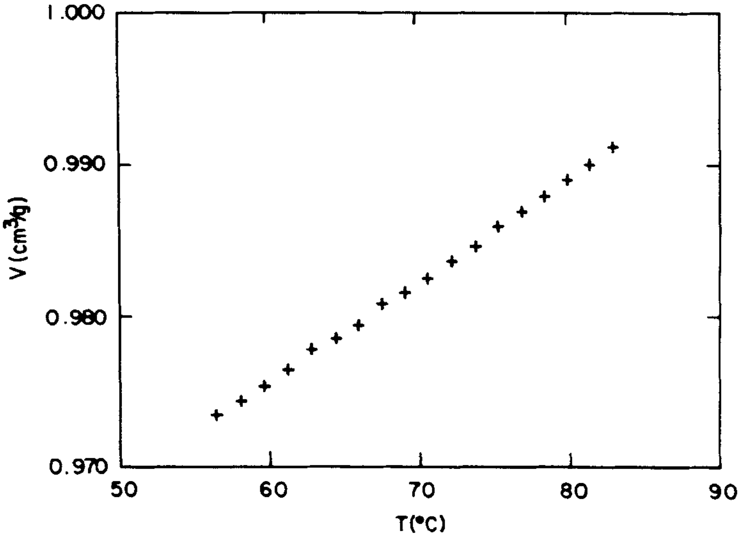

FIGURE 4 Evolution of the specific volume with decreasing temperature in the smectic A phase.

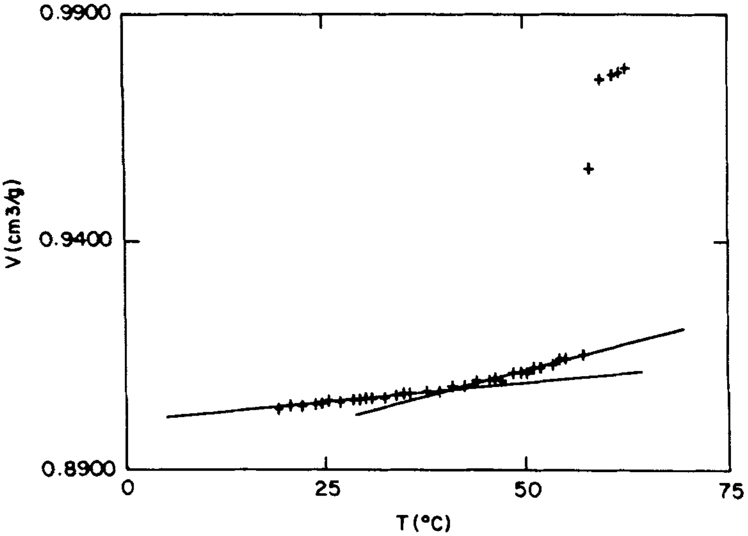

FIGURE 5 Evolution of the specific volume with decreasing temperature.

below 70°C we find it is equal to 6.50×10^{-4} cm^{3}g^{-1}K^{-1}. This very slight difference has to be correlated with the small change of behavior in the evolution of the lamellar spacing at about the same temperature.

The Figure 5 shows the evolution of the volume when we go from the smectic phase to the crystalline phase. We observe a sudden decrease of the volume of 7% which in fact corresponds to the crystallization of the paraffin chains. Then we observe a distinct change in the evolution of the volume at about 40°C. The values of the two expansion thermal coefficients which correspond to these two regions are 4.75×10^{-4} cm^{3}g^{-1}K^{-1} for temperatures above 40°C, and 1.98×10^{-4} cm^{3}g^{-1}K^{-1} for temperatures below 40°C. This change in behavior has to be correlated with the one observed for the lamellar spacing when we can distinguish two regions also: the phase above 40°C corresponds in fact to the one where there is a mixture of two lamellar phases, the spacing of which are 45 Å and 25 Å, while the phase below 40°C corresponds to the one in which the lamellar spacing is unique and equal to 25 Å.

IV DISCUSSION

In this study, we have been able to show that the change observed in the evolution of the layer thickness and of the volume by decreasing temperature within the domain of the smectic phase, is very small, a little bit larger than the experimental error. We will come back to this point later.

We will try now to discuss the organization of the molecules within the smectic layers. The lamellar spacing (~34.5 Å) is significantly larger than the total length of the molecules (~25 Å). Only models of structure with bilayers have been considered. Lydon *et al.*[8] have already proposed several molecular arrangements which show a head-to-head organization of the molecules in a clean bilayer, or an organization in a partial bilayer with overlapping of the paraffin chains (speckled parts in Figure 3c). Very recently P. Cladis *et al.*[9] have proposed a model of partial bilayer with an overlapping of the aromatic stems for several cyano compounds of the same type as CBOOA; the same authors suggest also the molecules are associated by pairs.[10] A similar model with an overlapping of the aromatic parts was simultaneously proposed by Leadbetter *et al.*[11]

To analyze these models, we have calculated, from our experimental values of the layer spacing, d, and of the specific volume $\bar{v}$, the parameter S we have defined elsewhere.[12]

$$S = \frac{2M\bar{v}}{Nd}$$

where M is the molecular weight and N the Avogadro number. In the case of a clear bilayer (Figure 3b), this parameter represents the molecular area which is the area occupied by any part of the molecule in the plane of the lamellae—the aromatic stem or the aliphatic chain. In the case of a partial bilayer (Figure 3c), this parameter represents either the molecular area of the non-overlapping parts of the molecules (unspeckled parts of the Figure 3c), or twice the molecular area of the overlapping parts (speckled parts of the Figure 3c). It is obvious that the value of this area is an upper limit of the lateral extent,[13] σ, of the molecules in a plane normal to their molecular axis ($\sigma = S \cos \theta$); this limit is reached when the molecules are oriented normal to the plane of the lamellae ($\theta = 0$).

a Crystalline phase

We have calculated S for the two crystalline phases we have identified at low temperature. In the case of the lamellar structure observed at 25°C, the calculation is easy, as we know the values of d and $\bar{v}$ with a good precision: $S = 40$ Å^2. The calculation is quite different for the lamellar structure which occurs between 40 and 58°C; this structure which has been observed with a small quantity of the crystalline phase identified at 25°C, cannot be characterized by a well defined specific volume. However, if we are satisfied with an uncertainty of about 2%, we find $S = 22$ Å^2. We know that the layer spacing, d, of the sheets (25 and 45 Å) corresponds in fact to the length of the molecules (~25 Å) or to twice it; so we can think the molecular orientation is very close to the normal to the sheets ($\cos \theta \sim 1$) and then the molecular area, S, (or the half of it) measures quite well the real lateral bulkiness of the molecules: $\sigma \simeq 20$ Å^2.

b Smectic phase

Let us consider now the smectic phase. The molecular area S varies as a function of the temperature between 31.5 and 32.5 Å^2 (Figure 6). It has to be noted that the small change which was observed in the thermal evolution of d and $\bar{v}$ is also seen of course in the evolution of S; this evolution of S as a function of the temperature could indicate that the lateral contraction of the molecules was stopped at about 70°C.

In the smectic A phase we find $S = 32$ Å^2. Assuming the partial bilayer arrangement, this implies that either the aromatic stems are packed extremely closely (16 Å^2) and the paraffin chains very loosely (32 Å^2)[9–11] or the paraffin chains are intolerably squashed together and the aromatic stems are the loosely packed elements.[8] Since the paraffin chains alone take up 30 Å^2 it seems we can exclude the latter arrangement on the basis of this result alone.

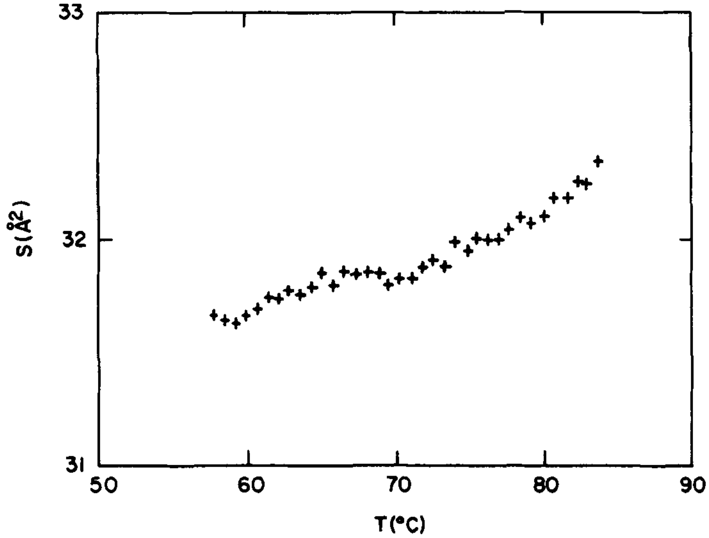

FIGURE 6 Evolution of the molecular area with decreasing temperature in the smectic A phase.

Even the former arrangement appears an uncomfortably tight packing to allow a very fast rotation of the aromatic stems which we know occurs in the smectic A phase.

As it is shown in the volumetric study (Figure 5), the aliphatic chains are disorganized and must occupy a lateral space which should not be much smaller than 30 Å^2. Moreover, even if they were crystallized, for example in the orthorhombic A lattice,[14] they would have a latent bulkiness σ of 18.6 Å^2 which is 15% bigger than the area available in the smectic layers.

For the aromatic stems, we can estimate that the latent bulkiness σ could not be smaller than 20 Å^2 (Appendix 1). We have seen, moreover, that σ is about 20 Å^2 in the two crystalline phases at low temperature.

It seems therefore that the model which can describe the packing of the molecules in the smectic layers is the one with a real bilayer (Figure 3b). Even if the model with the pair of molecules could conceivably fit our values of S, it was not substantiated in CBOOA, because in the wide angle X-ray diffraction we see only one diffuse ring corresponding to a distance of 4.3 Å.

If we assume the true bilayer model, then we need to tilt the molecules in the plane by 45 degrees in order to account for the layer thickness. This is compatible with the molecular area measurements since taking $\sigma = 22$ Å^2 (see Appendix 1), $S = 32$ Å^2, then $\theta = \cos^{-1}(\sigma/s) \cong 46$ degrees.

This model, which is suggested by our data of the diffractometric and the volumetric study sets a delicate problem. The smectic phase of CBOOA has been described as a smectic A phase, since all the observations with the microscope show a uniaxial texture.[8] In general, in the smectic A phases, the molecules are assumed to be oriented on average normal to the plane of the layers. Now, in this case, we propose the aromatic stems are tilted through a large angle with respect to the plane normal.

In a recent letter,[15] de Vries proposed a model of a smectic C–smectic A transition in which the molecules would keep their tilt with respect to the normal, but the layers would loose their orientational coherence by rotation in their plane. Leadbetter at the same time[16] proposed the same model for another compound, in which the molecules would be tilted with an angle of 28° in the smectic A phase. The same model has also been proposed by de Jeu and de Poorter.[17] It is assumed in this model we can find smectic A uniaxial phases, with tilted molecules; it is similar in fact to the model to which we have led for the case of CBOOA, although in our case, the tilt of the molecules is considerably larger. From a point of view of thermodynamics, such a situation is possible only if the coupling between adjacent layers is low and does not extend very far.† Below a certain temperature, the orientational order (smectic) appears although it does not exist at a higher temperature (smectic C).

Other experiments, in particular X-ray diffraction on oriented samples, are needed to test this model and to bring more information about the models which are proposed for the different smectic layers.

Acknowledgement

One of us (D. Guillon) wishes to thank P. E. Cladis for many helpful discussions.

Appendix

A value higher than 20 Å^2 for the molecular area of the aromatic stems normal to their axis, can be obtained with two methods.

In the first, we calculate directly in the smectic state the molar volume of the aromatic stem (by difference between the molar volume of CBOOA which is measured experimentally and the molar volume of seven methylenique groups calculated from a recent work on a similar smectic phase, S3[12]. The ratio between the volume and the length of the stem measured on model from the crystallographic data of Vani and Vijayan[3] gives a good

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† We thank Prof. F. Gautier for stimulating discussions on this point.

estimation of the molecular bulkiness. At 75°C for example, we find a global molar volume of 329 $\text{cm}^3\ \text{mole}^{-1}$, a molar volume for the aromatic part of 211 $\text{cm}^3\ \text{mole}^{-1}$, and a molecular area of $\sigma = 22 \pm 2\ \text{Å}^2$.

With the second method we do the same calculation for the crystalline phase which is observed at 25°C in this work. We find a global molar volume of 301 $\text{cm}^3\ \text{mol}^{-1}$, a molar volume for the aromatic stem of 198 $\text{cm}^3\ \text{mole}^{-1}$, and a molecular area $\sigma = 21 \pm 2\ \text{Å}^2$.

It has to be noted in this context that the molecular area σ of the aromatic stem of the dialcoxybenzylidene aminobiphenyl (which is also a Schiff base) is about 22–23 Å^2 for the smectic S1 phase (rectangular centered packing of the molecules in the smectic layers) and 23–24 Å^2 for the smectic S2 phase (hexagonal packing[12]). In the case of the smectic A phase of TBBA,[18] this area is 24–25 Å^2. At last, in the case of crystalline biphenyl,[19] $\sigma = 20\ \text{Å}^2$.

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