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Polymorphism of the Mesomorphic Compound Terephthal-*bis*-Butylaniline (TBBA)

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On the basis of x-ray monodomain and powder patterns, the structure of new identified terephthal-*bis*-butylaniline phases is described. These phases present a relatively high degree of order and appear as intermediate states between the smectic mesophases and the crystalline state.

TBBA (terephtal-*bis*-butylaniline) is known to present four stable liquid crystalline modifications, three of them being smectic mesophases: S_A, S_C, S_B.[1] Recently, it has been pointed out[2,3] that two metastable phases appear when the S_B phase is cooled below 84°C, and before reaching the crystalline state. Moreover, we have identified two different crystalline states. The various transitions are shown here:

$$\begin{tikzcd}
\begin{pmatrix}\mathrm{IX}\\ Cr\end{pmatrix} \arrow[r, shift left, "-42^\circ\mathrm{C}"] & \begin{pmatrix}\mathrm{VIII}\\ Cr\end{pmatrix} \arrow[l, shift left] \arrow[r, "113^\circ\mathrm{C}"] & \begin{pmatrix}\mathrm{V}\\ S_B\end{pmatrix} \arrow[r, shift left, "144^\circ\mathrm{C}"] \arrow[d, shift left, "84^\circ\mathrm{C}"] & \begin{pmatrix}\mathrm{IV}\\ S_C\end{pmatrix} \arrow[l, shift left] \arrow[r, shift left, "172^\circ\mathrm{C}"] & \begin{pmatrix}\mathrm{III}\\ S_A\end{pmatrix} \arrow[l, shift left] \arrow[r, shift left, "200^\circ\mathrm{C}"] & \begin{pmatrix}\mathrm{II}\\ N\end{pmatrix} \arrow[l, shift left] \arrow[r, shift left, "236^\circ\mathrm{C}"] & \begin{pmatrix}\mathrm{I}\\ L\end{pmatrix}. \arrow[l, shift left] \\
 & \mathrm{VII} \arrow[u, "52^\circ\mathrm{C}"] \arrow[r, shift left] & \mathrm{VI} \arrow[l, shift left, "68^\circ\mathrm{C}"] \arrow[u, shift left] & & & &
\end{tikzcd}$$

The different phases have thus been classified: TBBA I is the isotropic liquid and TBBA IX the low-temperature crystalline phase. The structure of TBBA V has already been described in a previous paper[4] and it appears to be very similar to the structure of some of the plastic crystals: In short, no long-range order exists in the direction of the molecular axes; however, each smectic layer is relatively well ordered and the mass centers of the molecules build a "local" monoclinic lattice,[5] with the c axis parallel to the molecules and a centered C face. It has also been shown that the difference between the two reticular spacings (110) and (200) is, in fact, very small, and the intersections of the molecular axes with a plane perpendicular to their directions approximately form a hexagonal lattice. From this experimental observation, and since a critical change in the lateral order of the parallel adjacent molecules occurs,[6] it was suggested that the transition from the solid phase into the S_B phase was directly connected with a correlated motion of the molecules around their long axes. This motion, which explains the pseudohexagonal symmetry, has recently been observed in the S_B phase by means of NMR experiments.[2]

In this Letter, we report new results concerning the structures of TBBA VI and VII modifications, yielded by x-ray experiments which were performed by using both powder and single-domain samples. It was relatively easy to obtain single domains of the different phases: A single crystal of the crystalline phase VIII, at room temperature, was progressively transformed into a single domain of modifications V, VI, VII, by successive heating and cooling.

Powder patterns were recorded by using a Guinier camera equiped with a heating stage[7] and a focused monochromatic beam (crystal-reflected Cu $K\alpha_1$ radiation). The results of the analysis of the powder patterns performed with a Joyce microdensitometer MK III C are given in Fig. 1.

The main results are here reported: (a) The crystalline state is characterized by a large number of diffraction rings and mostly by large-angle rings which do not exist in patterns corresponding to the phases V, VI, and VII. The three phases present a "local" order rather than a long-range order. (b) These rings have been indexed on the basis of a monoclinic lattice suggested by

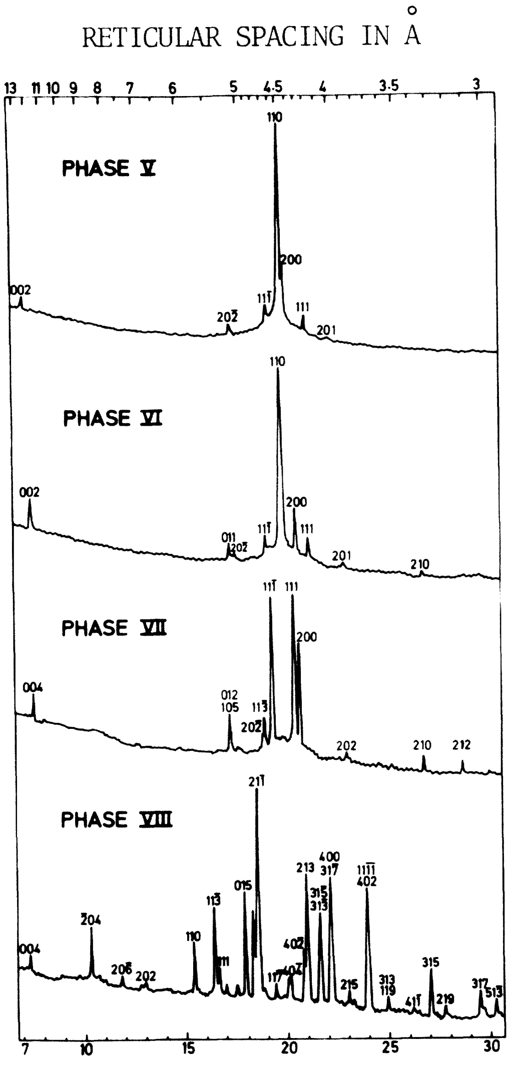

FIG. 1. Debye-Scherrer patterns of TBBA V to VIII.

single-domain patterns.[8] Miller indices are reported in Fig. 1; the monoclinic parameters are given in Table I for phases V to VIII.

As usual, b is the twofold symmetry axis and c is always approximately parallel to the long axes of the molecules. Table I indicates the values of (110) and (200) reticular spacings as well as the observed extinction rules. It is clearly seen that phase VII presents a great difference from both modifications V and VI: The c value is almost double the molecular length. The molecular packing seems more complex and requires further experiments to be solved. On the contrary, the structures of phases V and VI differ little (the major difference concerns the extinction rules). Indeed, phase VI has no centered C face and its structure is compatible with a *Pa* group, implying a herringbone-type arrangement of the molecules in one layer as described in Fig. 2, as opposed to phase V which provides a more symmetrical case. Such a structure is characterized by a larger distortion from the pseudohexagonal layer lattice: Phase VI allows a bigger difference between the reticular spacings (110) and (200) as shown in Fig. 1 and Table I.

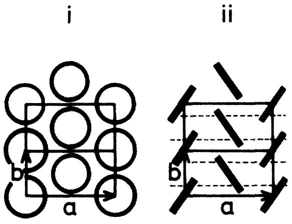

FIG. 2. (a,b) plane showing the positions of the TBBA molecules. (i) Phase V: The positions are equivalent. (ii) Phase VI: The positions are no longer equivalent, but related by a glide mirror (represented as dashed lines).

From such experimental results, it appears that the transformation of the S_B phase into the TBBA VI phase produces the freezing of the motion of the TBBA molecules around their axes. This assumption is in agreement with the observation of diffuse x-ray scattering spots, on supercooled S_B single domains. The diffuse scattering is localized around hkl $(h+k=2n+1)$ forbidden

TABLE I. Monoclinic lattice parameters for intermediate phases of TBBA.

Phase	a (Å)	b (Å)	c (Å)	β (deg)	d_{110} (Å)	d_{200} (Å)	Extinction conditions
V	10.15	5.18	28.60	119°00	4.467	4.428	$(h+k)=2n+1$
VI	10.38	5.24	28.31	123°6	4.484	4.325	$(h0l)h=2n$
VII	10.17	5.27	55.24	122°3	4.496[a]	4.300	No conditions
VIII	17.54	5.75	53.20	115°00			$(k+l)=2n+1$

[a] Calculated value; 110 reflection is not observed in phase VII.

reflections (reflections found in phase-VI structure). This observation supports the assumption of a rotational motion of the molecules in phase V. The motion is cooperative, and on a local scale the molecular structure is the same as in phase VI. The S_B structure then appears as a mean structure owing to a rotational disorder of the molecules jumping to different possible positions. The same diffuse spots have also been observed by de Vries and Fishel[9] for the S_B phase of BEA. These authors proposed as a solution that the molecules in each layer form a herringbone-type packing, but they did not point out that such an order only extends to very short distances, whereas the mean structure of the quasi-long-range order in each layer is more symmetrical (i.e., pseudohexagonal). Therefore, the herringbone local array does not appear on the Bragg spots which are characteristic of the three-dimensional order.

We come to the conclusion that the different phases of TBBA (V, VI, VII) which successively appear when cooled down and before reaching the long-range order crystalline state develop structures less and less symmetrical and more and more complex. Because of the layer structure and the absence of long-range three-dimensional order, we can assume that these phases are all smectic. Nevertheless, the order extent is sufficient to define a "local" lattice. Despite the considerable difference between the molecular packings, the x-ray powder patterns happen to be very similar. Therefore, without any further information, the distinction between phases V and VI would have been very difficult if not impossible. This example then emphasizes the difficulty of a classification of smectic compounds[10]: The problem of the identification of TBBA VI and VII with some of the numerous smectic modifications already described remains open. Furthermore, some questions on the distinction between such phases and some crystalline states are still to be solved.

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Phonon-Assisted Jump Rate in Noncrystalline Solids*

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An exact calculation of the acoustic-phonon–assisted jump rate has been carried out. It is found that while the Miller-Abrahams (single-phonon) approximation is adequate for the study of shallow-impurity conduction at helium temperatures, it is typically inappropriate for the study of hopping between deep states in noncrystalline solids. In particular, the multiphonon jump rate will display a nonactivated temperature dependence below the Debye temperature which is similar to the often-seen exp[$-(T_0/T)^{1/4}$] behavior.

Recently, considerable attention has been directed toward understanding the temperature dependence of the electrical conductivity associated with the hopping motion in noncrystalline solids. Much of this interest is related to the suggestion that the conductivity arising from the hopping of carriers between very shallow impurity states (such as those of Sb in Ge) should vary with temperature as $\exp[-(T_0/T)^{1/4}]$ near liquid-helium temperatures.[1] In particular, a similar temperature dependence has been reported at very much higher temperatures (of the order of 100 K) in a