Crystallography

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Abstract

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POLYMORPHISM IN ORGANIC MOLECULAR CRYSTALS

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By the method of X-ray photography and optical microscopy, polymorphic transformations in three organic substances—octahydroanthracene, orcin, and carbon tetrabromide—were investigated. It is shown that the transformation mechanism previously found in *n*-dichlorobenzene, whose main features are: (a) the growth of bounded single crystals of the new phase inside crystals of the nonequilibrium phase, and (b) the absence of a crystallographic relationship between the orientations of the two lattices, is typical, at least, for the majority of organic substances.

Introduction

Studies of the mechanism of the polymorphic transitions $\alpha \rightleftarrows \beta$ in *n*-dichlorobenzene ($^{1-3}$) showed that the process of polymorphic transformation is nothing other than the growth of a bounded single crystal (or several single crystals) of the new phase within the single-crystalline medium of the nonequilibrium phase. In this case there is no orientational relationship whatever between the lattices of the two phases. The crystallization centers are located at defective sites of the crystal. The single-crystal → single-crystal transition corresponds to sufficiently equilibrium growth of a crystal of the new phase from a single center. The single-crystal → polycrystal transition differs from the preceding one only in that the growth of single crystals of the new phase occurs from a large number of randomly oriented crystallization centers. An intermediate case is the transformation of a single crystal into several large crystalline blocks of the new phase, randomly oriented with respect to one another.

Since the mechanism of polymorphic transformation possessing the indicated features was discovered and, to a certain extent, studied only in *n*-dichlorobenzene, the question naturally arises as to whether it is an exception for organic crystals or a general rule. To this end, a search was undertaken for other organic substances convenient for investigation. The following requirements were imposed on these substances:

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

1. The substance must exhibit a temperature polymorphic transition into a new crystalline phase, preferably (but not necessarily) enantiotropic.

Fig. 1. Octahydroanthracene. a, b—microphotographs of successive stages of a $\beta \rightarrow \alpha$ transformation of the s-s type; flat faces of the growing crystal of the α-phase are visible; v, g—$\beta \rightarrow \alpha$ transition of the s-s type (v—Laue photograph of the β-phase, g—Laue photograph of the α-phase); d, e—transition of the β-phase from a single crystal (Laue photograph d) into an imperfect polycrystal (Laue photograph e) as a result of the transformations $\beta \rightarrow \alpha \rightarrow \beta$.

Fig. 2. Orcin. a, b—microphotographs of successive stages of an $\alpha \rightarrow \beta$ transformation of the s-s type; v, g—$\beta \rightarrow \alpha$ transition of the s-p type (v—Laue photograph of the β-phase, g—Laue photograph of the α-phase).

Fig. 3. Laue photograph of β_3 after a series of transformations ($\beta_1 \rightarrow \alpha_1 \rightarrow \beta_2 \rightarrow \alpha_2 \rightarrow \beta_3$) in the initial single crystal of CBr_4. Intermediate case between transitions of the s-s and s-p types.

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Fig. 1

Fig. 2

Fig. 3

2. The transition temperature must be above room temperature, but not very high (up to $\sim 100^\circ$), so that no unnecessary experimental difficulties arise in optical and X-ray studies.
3. It is desirable that the selected substances include both substances that do not form structures with hydrogen bonds and substances that do form structures with hydrogen bonds. In addition, among those selected there should be substances that exhibit a transition from the crystalline (c) to the rotational-crystalline state (r.c.s.).* Below are presented the results

Figure 3

Figure 3: Figure 3

of a study of the polymorphism of some substances selected according to these criteria.

Experimental Part

The following two methods were used primarily.

1) Laue X-ray photography of a single crystal fixed immovably on a goniometer head in an X-ray camera installed inside an air thermostat. By suitably changing the temperature regime of the thermostat, a series of X-ray photographs is obtained from each crystal:

$$\beta \to \alpha \to \beta \to \alpha \to \ldots$$

Such photography makes it possible to draw conclusions about the presence or absence of a regular relation between the orientations of the crystal lattices of the two phases.

2) Observation of the transformation process in an optical polarizing microscope with a heating stage.

In all cases the high-temperature phase is denoted by α, and the low-temperature phase by β.

Octahydroanthracene

The β-phase crystallizes well from solution in ethyl alcohol. The crystal structures of the phases are unknown. The melting point is 73°. The transformation temperature is subject to very large hysteresis: the $\beta \to \alpha$ transitions usually occur at 61–64°, and $\alpha \to \beta$ at 40°, but sometimes much lower, down to 20°. Experiments with arrest of the phase boundary show that the phase-equilibrium temperature is $T_0 = 56 \pm 3°$. Phase transformations are usually accompanied by the appearance in the crystal of large stresses, sometimes leading to cracking of the crystal exactly along the phase boundary.

X-ray photography has established that, depending on the individual characteristics of the crystal and also on the experimental conditions, transitions may be either of the single-crystal → single-crystal type (s–s), or single-crystal → polycrystal (s—p), or of an intermediate type. As in the case of *n*-dichlorobenzene, there is no fundamental difference between these types of transition, apart from the number of crystallization centers that arise. There is no crystallographic relation between the orientations of the lattices. In the case of s—s transitions this is demonstrated by the superposition of Laue photographs of one and the same phase, and in the case of s—p transitions by the very fact of the existence of such a transition. The latter case is illustrated in Figs. 1d and 1e. In Figs. 1a—1c are shown microphotographs and Laue photographs of transitions of the s—s type. The presence of very perfect faces on the growing crystal is obvious.

Orcin

It crystallizes well from solution in water or in ethyl alcohol. The transformation is observed only in crystals grown from water-containing solvents and is essentially a chemical reaction, during which water is released or incorporated. The crystal structures of the phases are unknown, but the presence of hydrogen bonds in them appears almost beyond doubt. The melting point

* R.c.s. is a state in which, because of the thermal motion of molecules, long-range order in their orientations is absent, but the centers of the molecules are arranged in three-dimensional long-range order. In connection with this state, in foreign literature the terms "plastic crystals,""crystals with rotational freedom of molecules," etc., are sometimes used.

~97°. The phase-equilibrium temperature is $T_0 = 58 \pm 1°$. The existence of hysteresis in the transformation temperature is noticeable: $\beta \to \alpha$ transitions usually occur at 60°, and $\alpha \to \beta$ at 40–57°. X-ray Laue photography and microscopic investigation of the polymorphic transitions in orcin show that this substance behaves quite analogously to *n*-dichlorobenzene and octahydroanthracene: depending on the quality of the single crystal and the experimental conditions, transitions of the single-crystal–single-crystal type, single-crystal–polycrystal type, and transitions of an intermediate type were again found. The presence of transitions of the single-crystal–polycrystal type proves that there is no crystallographic relationship between the lattices of the two phases. The process of polymorphic transformation in orcin proceeds as the growth of one or several faceted single crystals of the new phase inside a nonequilibrium host crystal. Figures 2 and 2 show Laue photographs illustrating the single-crystal–polycrystal transition, and Figs. 2 and 2 show microphotographs illustrating the single-crystal–single-crystal transition. The crystal surface in the microphotographs is damaged. This is probably connected with the release (addition) of water of crystallization, and also with the fact that, on heating, the crystal sublimates slightly. It is still not clear through which channels crystallization water is supplied to the growth faces (or removed from them).

Carbon tetrabromide (CBr_4). The melting temperature is 92.3°; the transformation temperature is

$$\text{c} \rightleftarrows \text{r.k.s.} \sim 47\text{–}48°.$$

The structure of the low-temperature phase has not been determined. The high-temperature phase is a typical example of a rotational-crystalline state. Superheating and supercooling during the transformations are small and do not exceed tenths of a degree. For both the $\beta \to \alpha$ and the $\alpha \to \beta$ transformations, the most typical case is the transition of a single crystal into several large, arbitrarily oriented blocks (Fig. 3). However, some Laue photographs indicate the existence of single-crystal–imperfect single-crystal transitions, while others indicate the existence of single-crystal–imperfect polycrystal transitions. In the latter case the Laue photographs contain many small spots tending to group into rings. Observations of polymorphic transitions in very perfect single crystals of CBr_4, grown by sublimation in a hermetically sealed jar during prolonged storage of this substance, revealed the presence, in the crystal of the new phase, of flat growth faces.

Discussion of the Results

From the experimental data presented and from the previously published results of the study of *n*-dichlorobenzene, it may be concluded that all four substances exhibit transformations of one and the same type, the characteristic features of which are: a) growth of faceted single crystals from the solid medium of a nonequilibrium phase, and b) absence of a crystallographic relationship between the orientations of the lattices of the two phases. It is of interest to determine how the type of polymorphic transition under consideration is related to the attempts found in the literature to classify transformations according to their mechanism.

In physical metallurgy, phase transformations are classified as martensitic and diffusional. Transformations in organic crystals are not martensitic, if only because the latter presuppose the existence of a crystallographic relationship between the orientations of the lattices of the two polymorphic modifications; nor are they diffusional, since diffusion processes of molecules in a solid body consisting of large particles (organic molecules) cannot provide such a comparatively high transformation rate as was found in *n*-dichlorobenzene ([3]).

Burger ([4],[5]) proposed a "crystallographic" classification, according to which polymorphic transformations are divided mainly into **reconstructive** and **displacive**. By the former are meant—

are transformations with complete rearrangement of the lattice (rupture of bonds between particles and their recombination in a new combination), and under the second—transformations occurring by "distortion" of the lattice. According to Buerger, reconstructive transformations require the overcoming of high potential barriers and therefore proceed slowly, whereas displacive transformations are barrier-free and therefore proceed very rapidly. This author asserts that his classification is close to the classification into transitions of first and second order, but does not coincide with it.

In view of the existence of a strict classification of polymorphic transformations into first- and second-order transformations, the above-mentioned "crystallographic" classification hardly seems expedient. There is no doubt that phase transitions of the second order can only be displacive. As for phase transitions of the first order, which are possessed by all four substances we have investigated, in principle they may be divided into two types, depending on the answer to the following question: is there, or is there not, a genetic relationship between the ideal crystal lattices of the two polymorphic modifications? In other words, does the polymorphic transformation take place by molecules occupying new positions that are strictly determined with respect to the old lattice, or not? A clear criterion in resolving this question may be the presence or absence of a crystallographic relationship between the orientations of the lattices. Giving Buerger' s terminology a somewhat different content, one could call transformations with preservation of the orientational relationship displacive, and, in the absence of such a relationship, reconstructive. In this sense, all the organic substances we have investigated have exhibited polymorphic transformations of the reconstructive type, despite differences in the character of the interaction of the molecules in their crystals. Whether there exist organic crystals with another mechanism of polymorphic transformation will be shown by further investigations.

In conclusion, let us point to the recently published study of polymorphism in *n*-nitrophenol ([6]), which is in complete agreement with the results presented, since it was established that in this substance there is no orientational correspondence between the lattices of the phases. In addition, in the earlier works of Hartshorne and co-workers (see ([7]) and the literature cited there) there are indications of the absence of such an orientational relationship in the polymorphic transformations of sulfur and azoxybenzene.

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