POLYMORPHIC TRANSFORMATIONS IN ORGANIC CRYSTALS

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Abstract

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POLYMORPHIC TRANSFORMATIONS IN ORGANIC CRYSTALS

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In the laboratory of A. I. Kitaigorodskii, several years ago a systematic study was begun of polymorphic transformations in molecular crystals. From the very beginning it was unclear what specific features characterize the mechanism of rearrangement of a crystal lattice composed of large organic molecules.

As a result of the investigation of the polymorphic transformation in paradichlorobenzene ([1,2]), and then in other crystals ([3,4]), the view was formed that there is no crystallographic relation between the orientations of the axes of single crystals of the low-temperature (β) and high-temperature (α) phases participating in the transformation.

However, attention is drawn to the fact ([2,4]) that the orientations of single crystals of the low-temperature β-phase, obtained each time after repeated cooling and recrystallization of the high-temperature α-phase, coincide with one another and with the orientation of the crystal in the initial state. This apparently indicates an orienting influence of the crystal lattice of the high-temperature phase on the growth of the low-temperature phase.

A natural question arises: has the reverse relationship not escaped notice because of imperfections in the method, i.e., the influence of the mother crystal of the β-phase on the growth of the high-temperature α-phase?

To solve this question, in the present work a method was used involving optical observation of birefringence in single crystals during the phase transformation and after it. The mother crystal was placed on the heating stage of an MIP-8 polarizing microscope in such a way that, between crossed nicols, it gave maximum extinction. (As usual, complete extinction was absent because of double refraction in the optics.) Thus the position of the optical, as well as the crystallographic, axes was fixed. A single crystal of the β-phase, transformed by heating into a single crystal of the α-phase, ceases to extinguish polarized light. In order again to obtain maximum extinction, the crystal has to be rotated through a certain angle relative to the initially fixed position. This difference in angles $\Delta\varphi$ characterizes the change in the orientation of the crystallographic axes in the course of the phase transformation. The accuracy of measuring the difference in angles does not exceed 2–3° (Table 1). Thus, $\Delta\varphi$ was measured for 43 crystals of paradichlorobenzene. As is seen from Table 1, the angles $\Delta\varphi$ are grouped around four mean values: 8.6°, 17.2°, 32.1°, and 54°. For the 4th and 3rd groups, the angles $\Delta\varphi_4 + \Delta\varphi_3 = 86.1°$, i.e., groups 4 and 3 coincide. As is seen from Table 1, the angles of disorientation of the crystallographic axes of the mother and daughter phases are by no means arbitrary. Let us note that the values of the angles $\Delta\varphi$ do not depend on the habit of the initial crystal, but are determined only by the arrangement of its crystallographic axes.

Since the structure of both phases of paradichlorobenzene is known ([6,7]), it was not difficult to establish that the obtained values of the angles $\Delta\varphi$ correspond in the unit cell of the mother crystal to directions with simple indices (111), (121), (141). Let us note that in a paradichlorobenzene crystal the developed face is the (100) face.

Table 1

Values of the angles $\Delta\varphi$ in degrees between the angles of extinction of light in crossed nicols for single crystals

β- and α-modifications of paradichlorobenzene	β- and α-modifications of paradichlorobenzene	β- and α-modifications of paradichlorobenzene	β- and α-modifications of paradichlorobenzene	β- and α-modifications of octahydroanthracene	β- and α-modifications of octahydroanthracene	β- and α-modifications of octahydroanthracene	β- and α-modifications of octahydroanthracene
1st group of angles	2nd group of angles	3rd group of angles	4th group of angles	1st group of angles	2nd group of angles	3rd group of angles	4th group of angles
11	17	30	56	28	34	57	17,5
9,5	15,5	32	50	28	33	52	19
9,5	17,5	30,5	55,5	26,5	34,5	56	18,5
7,5	19	32	Av. 54 (l 11)	28	32	50	16,5
6,5	18	33		25	36	55	20
7,5	18,5	33		28	36,5	56	19,5
6,5	22	32,5		28,5	36	55	19
8	17	36		25	33	56	18
8	19	31		28	33	56	18,5
11	17,5	30		27	30,5	55	18
12	14,5	29		28	36	56	14,5
Av. 8,6 (l 14)	15	34		28	35	56	16,5

Fig. 1

Figure 1: Fig. 1

β- and α-modifications of paradichlorobenzene	β- and α-modifications of paradichlorobenzene	β- and α-modifications of paradichlorobenzene	β- and α-modifications of paradichlorobenzene	β- and α-modifications of octahydroanthracene	β- and α-modifications of octahydroanthracene	β- and α-modifications of octahydroanthracene	β- and α-modifications of octahydroanthracene
	16	35		Av. 27,4 (31 l)	33,5	Av. 55,0 (11l)	15
	17	Av. 32,1 (l 11)			33		13
	Av. 17,2 (l 12)				34		13
					Av. 33,9 (11 l)		13
							15 Av. 16,8 (12 l)

The structure of **octahydroanthracene** is unknown. The author and T. L. Khotsyanova determined the space group and the parameters of the unit cell of the β-phase of octahydroanthracene. The monoclinic crystal with space group $P2_1/a$ has the following parameters: $a = 9.88$; $b = 6.76$; $c = 9.96$ Å; $\beta = 123°30'$; the parameters of the α-modification are unknown.

The assumption of a crystallographic correspondence between the axes of the low-temperature and high-temperature phases was also confirmed for octahydroanthracene (Fig. 1). Similarly to what was observed in paradichlorobenzene, in octahydroanthracene the boundary of the growing α-phase corresponds to planes of the parent crystal with indices: $(11l)$, $(12l)$, $(31l)$. (As in the case of paradichlorobenzene, the third index could not be determined, and the letter l has been put in its place.) The crystals have the form of thin plates developed along the plane (001) (see Fig. 1 and Table 1). In Table 1 are given

Fig. 1. A –unit cell of the low-temperature phase of octahydroanthracene. The directions corresponding to the extinctions of the crystal after its transformation

into the high-temperature phase are shown. The angle 123°30′ is the monoclinic angle β. **B** –schematic representation of a real crystal of octahydroanthracene grown in the form of a rhombus. The long diagonal of the rhombus corresponds to the *a* axis, the short diagonal to the *b* axis. The (ab) plane of the unit cell is coincident with the plane of the crystal. The arrows show the extinction directions of the α-phase; the dashed lines show the corresponding directions in the unit cell.

the results of measuring $\Delta\varphi$ for 55 crystals of octahydroanthracene. The angles of the 2nd and 3rd groups complement one another to 90°. It is also noteworthy that $2\Delta\varphi_1 = \Delta\varphi_3$ and that $2\Delta\varphi_4 = \Delta\varphi_2$.

In Fig. 2 the habit of the crystal and of the unit cell are superposed. The flat crystalline plates have the form of rhombi with diagonal lengths 9.88 and 6.76. These diagonal lengths correspond to an angle at the vertex of $68°22' = 2{\cdot}34°11'$. Extinction of the crystal occurs when the Nicol axis is directed along one of the diagonals of the rhombus. The plane *ab* of the unit cell of the crystal is also shown in the same figure. The unit cell itself is shown in Fig. 1. In Fig. 1B the extinction directions of the crystal of the α-phase are shown for all three types of formation of new phases. It should be noted that, under the microscope, the faces of the new phase of type 2 (and 3) grow parallel to the edge of the rhombus, and the extinction of the new crystal occurs parallel to this same edge of the rhombus. For the other two cases I found no such simple regularity. As in the case of paradichlorobenzene, so also for octahydroanthracene, in the case of the so-called "multicenter" transition, when a single crystal of one phase is transformed into a block crystal of another phase, the orientation of the crystallographic axes of these blocks relative to the axes of the original crystal repeats that set of angles $\Delta\varphi$ which is obtained in transformations of the single-crystal $\rightleftarrows$ single-crystal type. I artificially created (by pricking with a needle) one or several centers of growth of the new phase–and in this case the orientations of the daughter phases did not introduce diversity into the previously obtained set of angles. Cases are observed when, in thick octahydroanthracene crystals about 0.5 mm thick, the $\beta \rightleftarrows \alpha$ transformation occurs in two layers of the crystal from different centers. However, in this case as well, the orientation of the crystallographic axes in these layers coincides, as can be judged after complete transformation of the crystal–it gives maximum extinction. From the foregoing it follows that growth of the daughter phase proceeds by no means independently. The direction of growth and the orientation of the crystallographic axes are determined by the structure of the parent crystal, and not by a "potential nucleus," still less by the habit of the initial crystal. The parent crystal "provides" the growing phase only with certain, quite definite directions in its crystal lattice, ensuring the best contact between the phases.

During the phase transformation in the crystals studied, a temperature hysteresis of the transformation is observed. The transition $\beta \rightleftarrows \alpha$ does not begin immediately upon reaching the temperature of phase equilibrium T_0; rather, a certain supercooling (or overheating) is required in order for growth of the new

Fig. 3. Schematic representation of a crystal of octahydroanthracene in the low-temperature phase: a—initial, and b—after another recrystallization of the high-temperature phase. The elongation of the crystal along the large diagonal of the rhombus and the appearance of an additional face are shown.

Figure 2: Fig. 3. Schematic representation of a crystal of octahydroanthracene in the low-temperature phase: a—initial, and b—after another recrystallization of the high-temperature phase. The elongation of the crystal along the large diagonal of the rhombus and the appearance of an additional face are shown.

phase to begin in a crystal that is nonequilibrium at the given temperature T. Thus, the high-temperature phase of paradichlorobenzene may remain in a metastable state at room temperature for several days; its supercooling down to 0° is possible (^{8}).

The growth of a new phase, having begun at some temperature $T > T_0$, may stop. In such a state a partially transformed crystal may remain for a very long time. To continue the growth it is necessary additionally to heat or cool the crystal (depending on the direction of the process). For octahydroanthracene, a mechanical action is sometimes sufficient to stimulate the growth of the arrested phase (slamming the door in the room, tapping with the tip of tweezers on the table on which the small crystal is located). The longer the phase boundary is kept immobile, the greater a temperature difference is required to resume its growth. In the crystals investigated, arrest of the growing phase is observed also under the following circumstances: having begun to grow at temperature $T_1 > T_0$ from the center O_1, the phase reaches a certain size at a certain temperature T_2, at which growth of the new phase begins from another center O_2, and moreover at a higher rate than the first. Growth of the phase from O_1 ceases. The phase growing from the center O_2 fills the entire remaining part of the parent crystal. Orienta- tion of the two blocks thus formed may coincide, or may assume one of the values of $\Delta\varphi$ indicated above.

Fig. 2. Crystal of ammonium rhodanide in the low-temperature phase in the initial state (a) and after another recrystallization (b) of the high-temperature phase. A change in faceting is observed. c, d —crystal of tetrabromomethane: c —in the initial state, β-phase; d —in the high-temperature α phase after the third reversible transformation $\beta \rightleftarrows \alpha$ in it.

Deformation of crystals. In the course of a phase transformation, and especially after its completion, an irreversible change in the shape of the transformed crystal is noticeable. Thus, in octahydroanthracene, after several reversible transformations $\beta \rightleftarrows \alpha$, an additional face may even appear.

Fig. 3. Schematic representation of a crystal of octahydroanthracene in the low-temperature phase: a—initial and b—after a further recrystallization of the high-temperature phase. The elongation of the crystal along the large diagonal

of the rhombus and the appearance of an additional face are shown.

A crystal of octahydroanthracene, on cooling ($\alpha \to \beta$), becomes strongly elongated along the long diagonal (the axis of the $\alpha\beta$-phase) (Fig. 3); moreover, cases are observed in which this reverse transformation $\alpha \to \beta$ is accompanied by considerable residual deformation, so that the orientation of the resulting low-temperature phase may not change relative to the high-temperature α phase that was its starting phase.

Crystals of carbon tetrabromide in the form of thin needles are also strongly deformed in the course of the transformation (Fig. 2). Considerable residual deformation also accompanies the phase transformation in ammonium rhodanide (Fig. 2). We see how the dimensions are redistributed in two directions in the single-crystal plate of the initial crystal. The phenomena of hysteresis and plastic deformation are consequences of one and the same cause—namely, changes in the specific volume and internal stresses and, probably, cracks due to distortion of the crystal lattice in the course of the phase transformation. The presence of considerable internal stresses in the crystal during a phase transformation is indicated by the fact that crystals of octahydroanthracene, if they are not allowed to "rest" after 6–7 successive transformations $\beta \rightleftarrows \alpha$, fly apart into pieces; this is often accompanied by a click. If, during one of these transitions, the phase boundary was stopped and held immobile for some time, the crystal invariably cracks along the trace left by this phase boundary. A crystal of paradichlorobenzene also cleaves readily exactly along the phase boundary. The fracture surfaces are smooth and resemble the cleavage planes of twinned crystals.

Thus, during a phase transformation in the organic crystals studied, there occurs an oriented, strictly regular growth of the new phase in the parent single crystal. The temperature hysteresis and plastic deformation of the transformed crystal testify to considerable internal stresses in the crystal lattice "distorted" during the phase transition. The transformation in crystals resembles in many respects elastic twinning and, possibly, proceeds by a dislocation mechanism.

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Note: Figure translations are in progress. See original paper for figures.