

An X-ray Study on the Phase Transition of Aniline Hydrobromide, $C_6H_5NH_3Br$

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Crystal structures of amine halides can be divided into two groups. To the first group belong methylammonium chloride¹⁾ and *n*-propylammonium halides²⁾, in which the nitrogen atoms are surrounded by four halogen atoms. To the second group belong adenine hydrochloride³⁾, hexamethylenediamine dihalides⁴⁾, aniline hydrochloride⁵⁾ and cyclohexamine hydrochloride⁶⁾, in which the nitrogen atoms are surrounded by three halogen atoms. It is interesting to note that those crystals belonging to the first group always exhibit a phase transition at low temperature, whereas no report has ever been made of any phase transition in crystals belonging to the second group.

A preliminary report on the crystal structure of aniline hydrobromide, $C_6H_5NH_3Br$, has been published⁷⁾, in which it is shown that the nitrogen atom in this crystal is surrounded by four bromine atoms. During the course of refinement, it was found that the crystal exhibits a peculiar type of phase transition in the neighbourhood of room temperature. Detailed structure analyses of the crystal below and above the transition temperature will soon be reported⁸⁾. In the present paper, an account of an X-ray study on the phase transition of aniline hydrobromide will be given.

Outline of the Phase Transition.—Large crystals of aniline hydrobromide in the form described by Groth⁹⁾ are easily obtained by evaporation from methanol, ethanol or acetic acid solutions. Preliminary X-ray examinations showed that most of these crystals contained stacking disorder as revealed by diffuse scattering. Crystals free from stacking disorder were found to be obtainable by slow evaporation

from methanol solutions. The crystals obtained are long along the [010] axis, and the planes (001) and (100) are predominant. A sharp cleavage is found parallel with (001).

Using these 'single crystals', a series of oscillation and Weissenberg photographs were prepared, using Cu K radiations, about the three principal axes. It was found that not all but many reflections are split into two closely separated spots, appearing more or less blurred. If we ignore these splittings, all the reflections could be indexed based on an orthorhombic unit cell, in accord with the axial ratios given by Groth. It is suggested that these crystals are not really single crystals, but that they consist of repeated twins or polysynthetic twins¹⁰⁾, such as are found in orthorhombic pyroxene¹¹⁾. All the reflections appearing on oscillation photographs are split into two along the same ζ -lines, except those of (*hk*0) and (00*l*). These can be interpreted, if we assume that the twin components or domains are oriented to two different directions, and that each domain is in fact monoclinic with an axial angle β slightly deviated from 90° , and that all the domains have their *b*- and *c*-axes in common directions. All the reflections appearing on oscillation and Weissenberg photographs were satisfactorily indexed without any ambiguity by two axial systems, as schematically shown in Fig. 1.

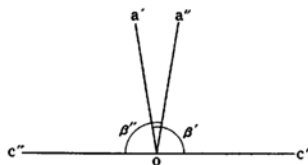


Fig. 1. Schematic representation of the orientations of the principal axes of the two components of the domains.

It was noticed that Weissenberg photographs prepared at different seasons of the year, using one and the same crystal, showed differences in detail. We were led to an assumption that these differences might be caused by a slight

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8) I. Nitta, T. Watanabé and I. Taguchi, to be published in this Bulletin.

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10) I. Ito, "X-ray Studies on Polymorphism", (1950) p. 122.

11) T. Ito, *Z. Krist.*, **90**, 151 (1935).

variation of temperature. A series of Weissenberg photographs were taken at various temperatures, using a carefully designed temperature control camera¹²⁾, and confirmed the fact that they are really sensitive to temperature in the neighborhood of room temperature. Split reflections observed at 18°C became degenerated into a single one at 25°C, and blurred reflections at 18°C became more or less distinct. These changes were more marked at 50°C. From these observations, it was concluded that the crystal would undergo a phase transition in this temperature range, the splitting and blurring of reflections being associated with the formation of domains. The crystal does not shatter on passing the transition range.

Variation of the Axial Angle β with Temperature.—From the preliminary experiments stated in the preceding paragraphs, it became clear that the splitting distances of reflections depend upon temperature, implying that the axial angle β varies gradually with temperature. The variation of the axial angle β with temperature was determined from the splitting distances of the reflection (002), which is the largest and most intense. The results are shown in Fig. 2. It was also found that the

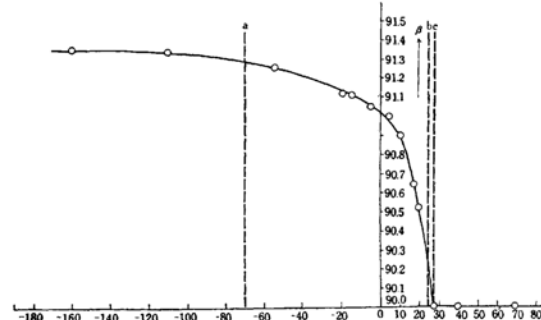


Fig. 2. Variation of the axial angle β with temperature.

relative intensities of reflections vary with temperature, parallel with the variation of β with temperature. The intensity variation ceases practically outside the range from +30°C to -160°C. The axial angle β also remains unchanged outside this region. There was found to be no other phase transition down to -160°C as far as X-ray methods were employed.

The temperature variations of the axial angle β , of the relative intensities and of the fine structure of reflections were found to be reversible. Photographs taken after cooling or heating are practically the same as those taken before heat treatment.

Now, in order to investigate the variation of the axial angle β with temperature more precisely and to determine the transition temperature of the high temperature side, experiments at smaller temperature intervals were carried out at temperatures, ranging from 15°C to 30°C. Measurements for cooling were made after keeping the temperature of the crystal at 30°C for twenty hours. The results are shown in Fig. 3, where crosses and small circles are the values obtained for heating and cooling respectively. From all the observations and results obtained therefrom the following conclusions are made. (1) The transition temperature range is as wide as 100°C, i. e., from 27.5°C to ca. -70°C. (2) The phase change is perfectly reversible within the experimental error. (3) The phase transition is of a higher order. It was suggested that the specific heat curve would show the λ type anomaly. The temperature range between -40°C and 24.5°C, as is shown by dotted lines a and b, might correspond to the ascending part of the specific heat curve, and the range between 24.5°C and 27.5°C as is shown by curves b and c might correspond to the declining part of the same curve. This view was recently verified by a calorimetric measurement¹³⁾.

The Unit Cell Dimensions and Space Groups of the High and Low Temperature Modifications.

—Above 27.5°C, the crystal is orthorhombic, and below this temperature it is monoclinic. The unit cell dimensions and space groups of the two modifications, determined at 70°C and at -110°C, respectively, are given in Table I. There are four formula units in each unit cell.

TABLE I. THE UNIT CELL DIMENSIONS AND SPACE GROUPS OF THE HIGH AND LOW TEMPERATURE MODIFICATIONS

	70°C	-110°C
<i>a</i>	$16.77 \pm 0.06 \text{ \AA}$	$16.725 \pm 0.06 \text{ \AA}$
<i>b</i>	6.05 ± 0.03	5.95 ± 0.03
<i>c</i>	6.86 ± 0.03	6.81 ± 0.03
β	90°	91°22'
Space group	D_{2h}^{19} -Pnaa	C_{2h}^2 -P2 ₁ /a

Nature of the Domain Structure.—It was found that the axis [010] and the plane (001) are in common with the two modifications and remain unaltered on passing the transition temperature. These features are illustrated schematically in Fig. 4. Since there are no appreciable changes in the axial parameters, the change of the axes can be taken as a kind of shear, which can be expressed by $\Delta\beta$ as is shown in Fig. 4.

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13) H. Suga, *This Bulletin*, 34, 426 (1961).

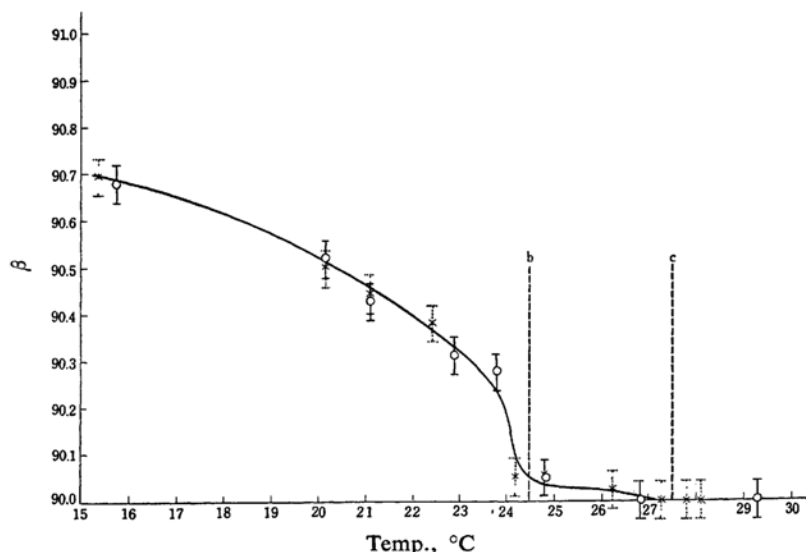


Fig. 3. Details of the variation of the axial angle β with temperature.

○ : heating

× : cooling

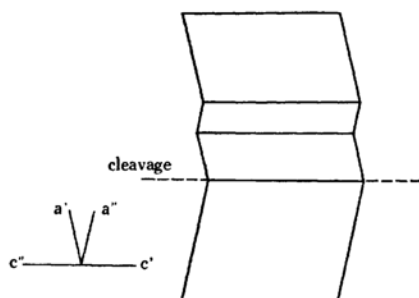


Fig. 4. Cleavage planes and the domain structure.

Below the transition temperature, the crystal is built up by domains which are oriented to the two directions, as shown in Fig. 4. These domains can be seen under a polarized microscope in certain specimens¹⁴⁾.

It was found that the ratios of the intensities within a pair of split reflections vary from specimen to specimen. For numerous specimens these ratios are found to be nearly at unity, as the formation of the two orientations of the domains is expected to occur with equal probability, though we have once found a specimen which is made of nearly a single domain.

Quite independent of these intensity ratios, or the abundance of the two orientations of the domains, each of a pair of split reflections shows a similar fine structure. There were found no complementary features in intensity in these split reflections, suggesting that these domains are interpenetrated.

On passing the transition temperature, no

line broadening was ever found. This is in contrast to the observations reported for cobalt oxide¹⁵⁾, CoO, or potassium dihydrogen phosphate¹⁶⁾, KH_2PO_4 . Thus the lower limit of the size of domains is of the order of 10^{-6} cm. No diffuse scattering associated with the splitted reflections was found, hence the domains are distributed in such a way that they are incoherent to X-ray. In this connection, it must be mentioned that in the cases of ferroelectric crystals there has never been reported any polysynthetic twinning associated with the domain formation.

As stated earlier, the (001) plane gives a perfect cleavage. The (100) plane also gives a cleavage at low temperature. It was observed that this latter cleavage becomes poorer as temperature increases, and finally vanishes at 30°C. This cleavage plane is the twinning plane between the two adjacent domains, as shown in Fig. 4. The vanishing of cleavage can be taken as a measure of the coalescence of the domain structure.

The Mechanism of the Phase Transition.—It will be interesting to discuss the structural change taking place during the transformation from symmetry considerations. There are four formula units in the unit cell, both of the high and low temperature modifications. The space group, D_{2h}^{10} -Pnaa, to which the high temperature modification belongs, requires that the anilinium ion, or more precisely the axis of anilinium ion passing through $\text{N}-\text{C}_1 \cdots \text{C}_4$ atoms, should lie on a digonal axis. This

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16) A. R. Ubbelohde and I. Woodward, *Proc. Roy. Soc., A*188, 358 (1947).

14) T. Iwai, to be published.

implies that the three hydrogen atoms bound to the nitrogen atom are arranged in a statistical way so that the anilinium ion assumes a digonal symmetry in a statistical sense. In the low temperature modification, the anilinium ion is no more restricted by the digonal symmetry by virtue of the low symmetry of the crystal, $C_{2h}^5-P2_1/a$. Above the transition temperature, the $-NH_3^+$ group assumes two (or a multiple of two) equally stable orientations with respect to the C-N bond, or it may be flipping among different orientations. When the crystal is cooled down and passes the

transition temperature, all the atoms move onto new equilibrium positions and the flipping ceases. These will be the most essential features of this phase transition.

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