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The Crystal Structure and the Molecular Behaviour of 2,3-Dibromo-2,3-dimethylbutane at Room Temperature

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The crystal structure of 2,3-dibromo-2,3-dimethylbutane at room temperature has a disordered nature. In the crystal, *trans*-form molecules have at least four orientations of equal statistical weight around the axes parallel to the [001] direction. Therefore, in spite of the low symmetry of the molecule, the crystal belongs to the tetragonal system and has the space group of $I4/mmm$, while $a=7.38$ Å, $c=8.12$ Å and $Z=2$.

The crystal of 2,3-dibromo-2,3-dimethylbutane has three modifications, phase I (high-temperature modification) appearing above 80°C,[1] phase II (room-temperature modification) existing between −90°C and 80°C, and phase III (low-temperature modification) appearing below −90°C.[2] An X-ray investigation of the room-temperature modification (phase II) has already been carried out by Yardley,[3] who has given useful crystal data and suggested some possible crystal structures. Yamada and Taguchi[4] have pointed out that phase I is cubic, the molecules rotating as a whole in the crystal.

A reexamination of the structure of phase II will be described in this paper.

Experimental

The material was synthesized by mixing hydrogen bromide and pinacol at 0°C (Thiele's method[5]). It was purified by several vacuum sublimations. Single crystals were obtained from an ethanol solution. They were colourless needles which were elongated along the [001] axis and were flexible. The crystals, enclosed in thin-walled terex-glass capillary tube to protect them from sublimation and contamination, were used in the X-ray investigations.

The unit-cell dimensions were determined from Weissenberg photographs superimposed on a powder pattern of pure sodium chloride. The density was measured by the floatation method. Laue photographs were also taken to determine the crystall class.

Crystal data:
2,3-dibromo-2,3-dimethylbutane, $C_6H_{12}Br_2$
mol wt 243.9, mp 182°C.

Tetragonal, $a=7.38$Å, $c=8.12$Å. $U=442.2$Å^3. Density (observed) 1.82 g/cm^3, Density (calculated) 1.83 g/cm^3, $Z=2$. Laue symmetry: $4/mmm$.*1

The absent spectra are:

$$hkl\colon\ h+k+l=2n+1,$$
$$hk0\colon\ h+k=2n+1,$$
$$hhl\colon\ l=2n+1,$$
$$0kl\colon\ k+l=2n+1.$$

Thus, the space group was selected as one of the following: $I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$, or $I4/mmm$.

The intensity data were obtained from equi-inclination Weissenberg photographs, $hk0$, $hk1$, $hk2$, and $hk3$, taken by means of CuK_α radiation filtered through nickel foil. The multiplefilm technique was used, and the intensities were estimated visually by comparison with a calibrated scale. The intensities were corrected for the Lorentz and polarization factors to obtain the relative values of $|F|^2$.

Structure Determination

Since the body-centered unit cell contains two molecules, the centers of the molecules must be placed at 0,0,0 and 1/2, 1/2,1/2.

Even though the crystals belong to one of the possible space groups mentioned above, the point symmetry of these positions must at least contain a four-fold rotation axis or a four-fold inversion axis. On the other hand, when the configuration of a free molecule is considered, the *trans*-form is taken as the highest symmetric one, for it possesses the symmetry C_{2h}. This symmetry does not, however, satisfy requirement of a high symmetrical nature such as C_4 or S_4 for the molecules in the crystal. This inconsistency in symmetry consideration proves some disordered character in the crystal.

1) A. H. White and W. S. Bishop, *J. Amer. Chem. Soc.*, **62**, 8 (1940).
2) H. Suga, K. Nakatsuka, T. Shinoda and S. Seki, *Nippon Kagaku Zasshi*, **82**, 29 (1961).
3) K. Yardley (Mrs. Lonsdale), *Proc. Roy. Soc., Ser. A*, **118**, 485 (1928).
4) Private communication. See also Ref. 2.
5) Thiele, *Ber.*, **27**, 455 (1894).

*1 It is to be noted that these crystal data are in harmony with those of Yardley.

To obtain preliminary knowledge on the structure, a Patterson map, $P(u,v)$, was synthesized. As is shown in Fig. 1, there is no predominant peak except at the point of origin and at 1/2,1/2, indicating that the Br–Br axis in the molecule is oriented almost parallel to the c-axis. Hence, it is reasonable that the *trans* molecules placed at 0,0,0 and at 1/2,1/2,1/2 with their Br–Br axis parallel to the [001] axis remain some disordered orientation about the [001] axis, thus having, on the average, a symmetry higher than 4 or $\bar{4}$.

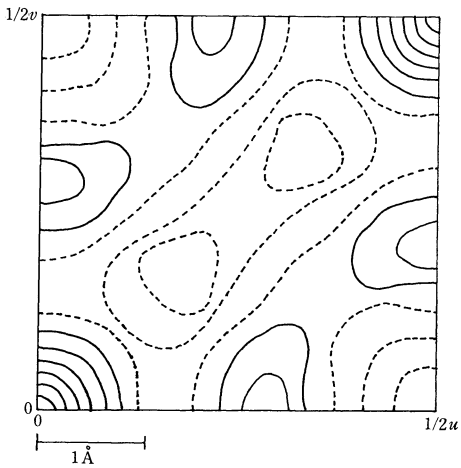

Fig. 1. Patterson map: $P(u,v)$.

Let us now proceed with the structure analysis using the trial-and-error method.

The configuration of molecule used in the trial calculations is an ordinary *trans* one; that is to say, the bond lengths used are 1.54 and 1.91 Å for C–C and C–Br bonds respectively, while normal tetrahedral bonds are taken for the carbon atom. For convenience in calculating, we used the value of $3/2f_c$ for the scattering factor of carbon atoms belonging to methyl groups, moreover, the precise contribution of hydrogen atoms was not calculated, as it is thought to be small.

The adopted arrangements of the molecules in the crystal and the results of the calculated structure factors are as follows:

Case I. Axial Rotation. As the first example in this case, let us consider a model in which the "axial rotation" of the molecule about its Br–Br axis is taking place freely, the Br–Br axis coinciding with the [001] direction. This is called model I. The calculated values of the structure factors are compared with the observed values in Fig. 4a. The general correspondence seems to be satisfactory. However, the aspects in (220), (310), (400), and especially in (hk1) do not give sufficient agreement.

In order to improve this inconsistency in the case of model I, a slightly modified model was considered. That is, in the second model, we assumed that the bromine atoms also rotate about the axis parallel to [001]. This model is shown in Fig. 2b. However, this treatment produces no remarkable improvement, as may be seen in Fig. 4b.

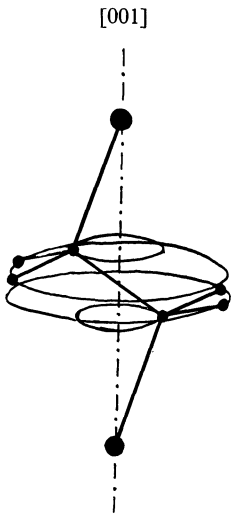

Fig. 2a. Model I.

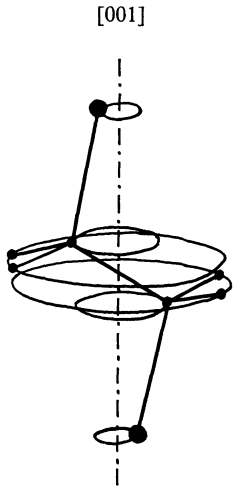

Fig. 2b. Model II.

Case II. Static Statistical Structure. Now, we can also assume static statistical structures in which the *trans* molecules with their Br–Br axis in the direction of the [001] axis occupy laterally four orientations about [001], with an equal statistical weight of 1/4, resulting in a four-fold nature of the [001] axis.

The atomic parameter values selected for this model, III, were as follows:

Br: $x = y = 0.00$, $z = 0.28$;

C: $x = y = 0.06$, $z = 0.05$;

C (methyl group): $x=0.26$, $y=0.016$, $z=0.018$.

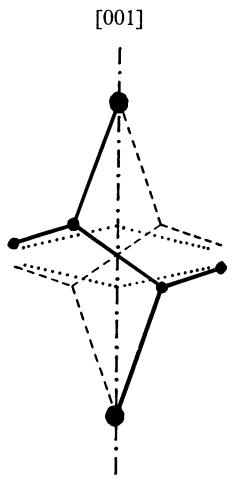

Fig. 3a. Model III.

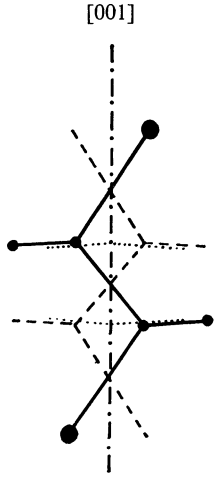

Fig. 3b. Model IV.

The calculated structure factors are shown in Fig. 5a. The correspondence of F_c and F_o is fairly good. This structural model may be said to represent well the structure of the present crystal.

Now, in this case, the central C–C bond of each molecule is on the plane on the (110) type. The methyl groups are, then, lying nearly on the plane of the (100) type. Speaking only on the basis of a consideration of the statistical symmetry, another arrangement of molecules is also possible, one where the central C–C bond is not on the (110)-type plane but on the (100)-type plane. However, in this model the agreement of F_c and F_o is far less than with the model III.

In model III, the Br–Br axis of a molecule has been taken as parallel to the [001] direction. In this arrangement, the intermolecular Br–Br distance along the [001] direction is calculated as 3.73 Å. This value can be seen to be slightly shorter than the normal distance, 3.90 Å, of Van der Waals contact. In view of this, we further assumed the model IV, in which the Br–Br axis of the molecule is slightly inclined to the [001] direction. In this case, four statistical positions must be considered for bromine atoms, also.

The atomic parameter values used were as follows:

Br: $x=y=0.029$, $z=0.278$;

C: $x=y=0.051$, $z=0.068$;

C (methyl group): $x=0.014, y=0.257, z=0.051$.

The calculated structure factors are shown in Fig. 5b. In this case the coincidence of F_c and F_o is better than in the case of model III.

In the analyses hitherto described, the *trans* configuration has been adopted as that of the free molecule. We have also tried an analysis using the *gauche* form of the molecule. However, such a form does not explain the observed values of the structure factors. Therefore, the *gauche* configuration can be disregarded.

Conclusion

The results obtained above for the present crystal structure can explain the mechanism of the transitions at about 70°C and at −120°C. When the temperatures are raised from room temperature, the thermal motion of the *trans* molecules possessing an orientational or rotational disorder around the Br–Br axes almost parallel to the [001] axis is more and more enhanced, and at 70°C the crystal is transformed to its cubic phase, in which the molecules rotate spherically as a whole, their Br–Br axes being randomly oriented. In this high-temperature modification, it may be possible for the molecules to take the *gauche* configuration.

When the temperatures are lowered from room temperature, the cessation of the axial rotation of the molecules around their Br–Br axes occurs below −120°C, the crystal taking an ordered structure.

Furthermore, it is of interest to compare the present structure with that given for the dichloroethane crystal above its transition temperature at −70°C. It has been reported by Reed and Lipscomb[6] that the molecules in that phase rotate axially about their Cl–Cl axes, the molecules also possessing the *trans* configuration. This structure is quite similar to the present one given for the 2,3-dibromo-2,3-dimethylbutane crystal at room temperature.

However, the 2,3-dibromo-2,3-dimethylbutane crystal shows a high-temperature transition at 70°C, whereas there is no corresponding transition in the case of dichloroethane crystals.

The onset of the spherical rotation of the molecules as a whole in the high-temperature modification

6) T. B. Reed and W. N. Lipscomb, *Acta Crystallogr.*, **6**, 45 (1953).

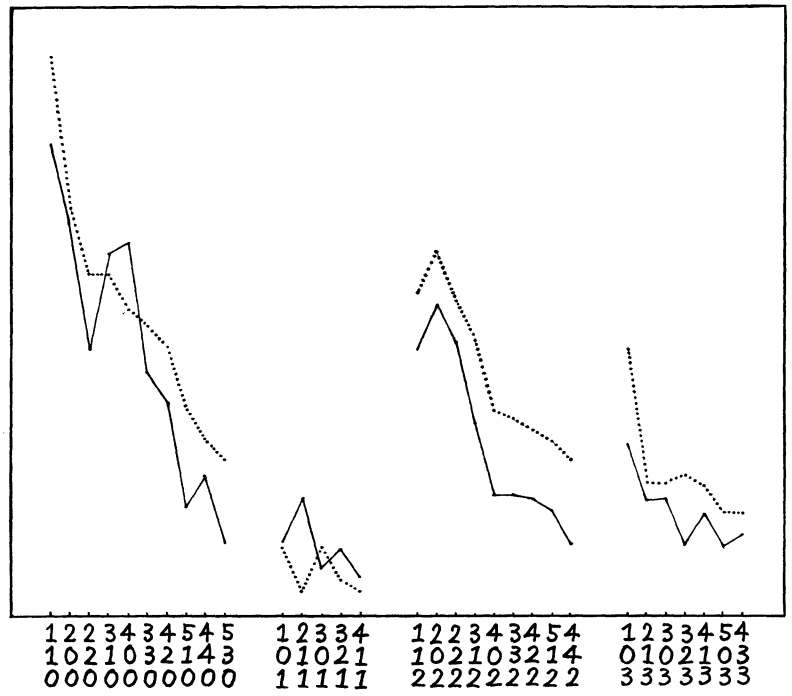

Fig. 4a
F_o —— F_c ……

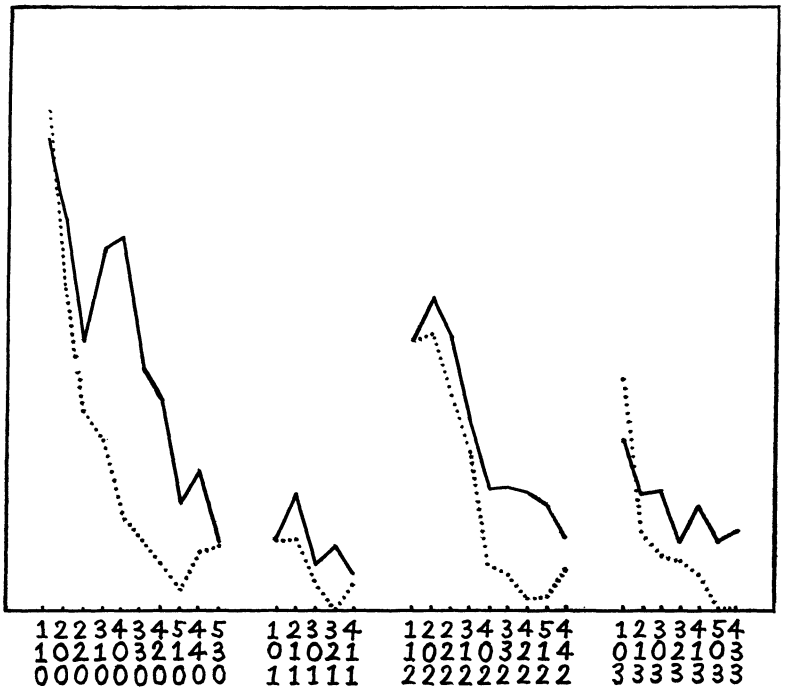

Fig. 4b
F_o —— F_c ……

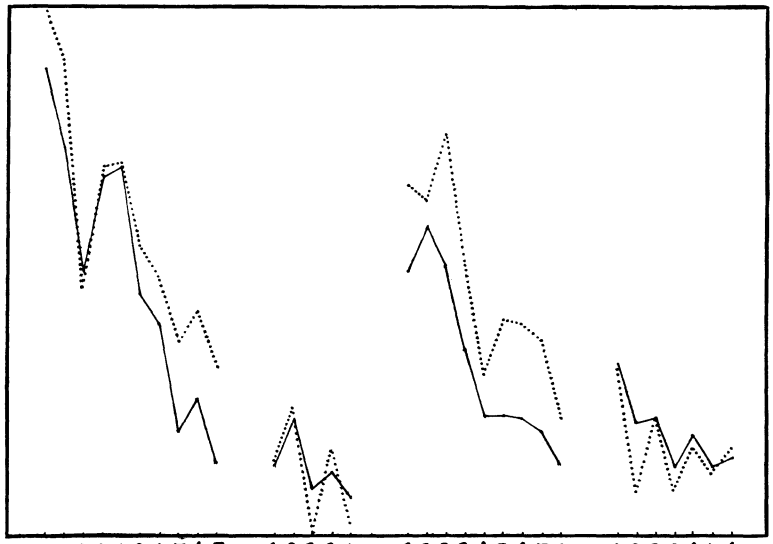

Fig. 5a

F_o —— F_c .....

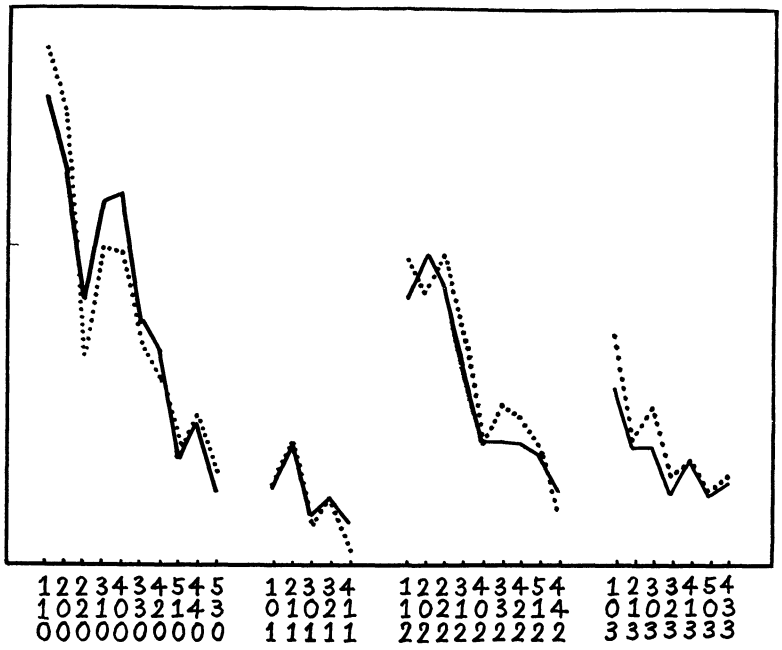

Fig. 5b

F_o —— F_c .....

in the case of 2,3-dibromo-2,3-dimethylbutane may be closely related to the "ellipsoidal" shape of the molecules in contrast to the elongated "rectangular" shape of dichloroethane.

Turning to the low-temperature transition, it is desirable to investigate the crystal structure below −120°C in order to give a precise explanation of the mechanism of the low-temperature transition.

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