*Physical Properties and Crystal Structure of 2-Bromo-2, 3, 3-trimethylbutane**

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It has been shown that the haloethane derivatives such as 1, 1, 1, 2-tetrachloro-2-methylpropane[1] and other compounds whose molecules are similar to hexamethylethane[2] in shape possess polymorphism and for any temperature range below their melting points they possess molecular orientational or rotational freedom. This freedom in the high temperature modification, which is cubic, seems to be responsible for their relatively high melting points.

Since the van der Waals radius of bromine atom is nearly equal to that of chlorine[3], it is of interest to investigate the behavior of molecules in the solid state for bromo-derivatives of ethane in comparison with the same state of its chloro-derivatives[1,4]. As an example, the authors have studied the crystal structure and the behavior of molecules of 2-bromo-2, 3, 3-trimethylbutane by means of optical, X-ray and differential thermal analysis methods.

Experimental and Results

Materials. — The sample of 2-bromo-2, 3, 3-trimethylbutane was prepared by passing gaseous hydrogen bromide through an ethereal solution of pentamethylethanol, which had been obtained by the Grignard reaction of pinacolone with magnesium bromide in ethereal solution. The final product was twice purified by recrystallization, followed by sublimation in high vacuum (10^{-5} mmHg).

The melting point is found to be 151°C in a sealed capillary tube. The liquid phase vaporizes immediately after melting. The solid is soft and shows plasticity. The density is found to be 1.31 g./cc. at 13°C by the flotation method using an aqueous solution of calcium carbonate.

Optical Observation.—Under the polarized microscope, the room temperature phase was found to be isotropic, indicating the crystal to be cubic. Observations were extended to the liquid air temperature. The cryostat for this purpose is shown in Fig. 1. Cooling was made by heat conduction through a copper rod dipped in liquid air. The temperature was measured with a copper-constantan thermo-couple and a millivoltmeter. By cooling, it was observed that the crystal transformed at about -117°C into a different crystalline phase which was optically anisotropic.

X-ray Measurements.—*The Crystal Structure of the High Temperature Modification.*—Owing to its extremely high volatility, a single crystal of this substance, sealed in a capillary tube for X-ray measurement, sublimes gradually in few days into a number of smaller crystals in the cooler part of the tube. Therefore, in order to prevent this loss of sample due to sublimation, a glass rod just fitting the glass capillary was inserted to make the remaining free space as small as possible.

Using Cu-K_α radiation ($\lambda=1.54$ Å) filtered through nickel foil, we prepared a series of 20° oscillation photographs covering a range of about 90° with [011] as the axis of rotation.

Laue photographs were taken with X-ray beams parallel to [100], [110] and [111]. All of the Laue spots were split into two or three parts, but the same crystal showed no splitting in its oscillation photographs when rotated through [110]. Thus the crystal used was not a single crystal, but was composed of several crystallites which were slightly different in orientation. All the efforts to get a single crystal have been unsuccessful, as was the case of 2-chloro-2, 3, 3-trimethylbutane[5]. All the Laue spots were successfully indexed, based upon a cubic lattice having holotesseral symmetry. The point group symmetry of the crystal was found to be T_d-$\bar{4}3m$, O-43 or O_h-$m3m$.

The observed spectra in oscillation photographs can be indexed satisfactorily with a body-centered cubic lattice having a unit cell of the side $a=7.66$ Å. The observed value of density, 1.31 g./cc., is almost equal to the calculated value, 1.32 g./cc., assuming that two molecules are contained in the unit cell.

Differential Thermal Analysis (D. T. A.).—The apparatus used for the D. T. A. was described elsewhere[1]. The temperature range of the measurement was from 90°C to the liquid air temperature. Fig. 2 shows the result of the D. T. A. measurement for warming. The time-temperature curve of Fig. 2 shows the temperature of the used reference substance (sodium chloride) and the differential curve shows the temperature difference between the reference

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[1] T. Koide, T. Oda and I. Nitta, This Bulletin, 29, 738 (1956).

[2] D. W. Scott, D. R. Doulsin, M. E. Gross, C. D. Oliver and H. M. Huffman, *J. Am. Chem. Soc.*, 74. 883 (1954).

[3] L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca (1948), p. 189.

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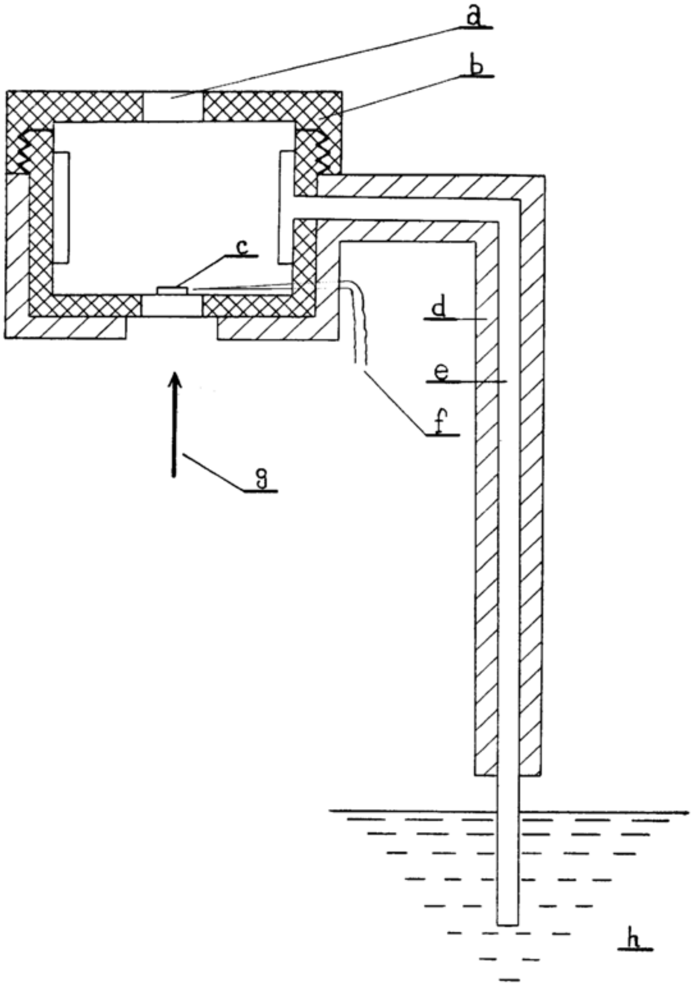

Fig. 1. The cryostat for the optical measurement at low temperature.
a) window (glass), b) bakelite, c) sample, d) thermal insulator, e) copper rod,
f) thermocouple, g) polarized light, h) liquid air

substance and the sample. The temperature differences are plotted on an arbitrary scale. There is an anomalous thermal effect at about −114°C (the peak of the differential curve in Fig. 2) for warming and at about −117°C for cooling. This result is in good agreement with the optical observation.

Discussion

Since there are two molecules in each unit cell with the body-centered cubic lattice, it is reasonable to place the centers of mass of the molecules at the lattice points 0, 0, 0 and 1/2, 1/2, 1/2. The proper symmetry of these points is T_d-$\bar{4}3m$, O-43 or O_h-$m3m$, so that the symmetry of the molecule should have one of these cubic point groups. On the other hand, if we assume that the molecule has the skew configuration (Fig. 3), the highest symmetry that the molecule could have is C_s-m, the central C–C bond lying on the plane of symmetry. In order that the molecule, which has the symmetry C_s-m, attains the cubic symmetry, it is necessary to take into consideration some statistical arrangements for explaining the structure of the crystal, as was done in the X-ray studies of other plastic crystals⁶⁾.

One of the possibilities that the statistical symmetry of the molecule is as high as T_d-$\bar{4}3m$ is that the molecule orientates its central C–C axis parallel to each one of the four body-diagonals statistically equally, so that the C–C axis acquires at least a statistical symmetry

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6) C. D. West, *Z. Krist.*, **88**, 195; C. Finbak, *Tids. Kjem, Bergv.*, **17**, 2 (1937); M. Atoji, T. Oda and T. Watanabe, *Acta Cryst.*, **6**, 868 (1953); I. Nitta and T. Watanabe, This Bulletin, **13**, 28 (1938); T. Oda and T. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **65**, 154 (1944); T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 108 (1958).

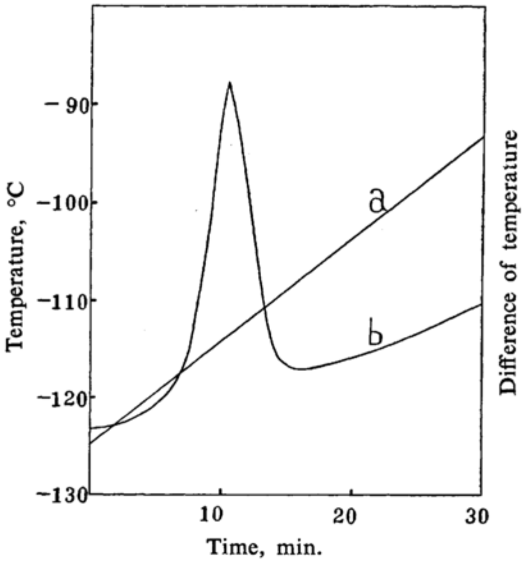

Fig. 2. Differential thermal analysis curve for 2-bromo-2,3,3-trimethylbutane $Br(CH_3)_2C \cdot C(CH_3)_3$.
a) time-temperature curve
b) differential curve

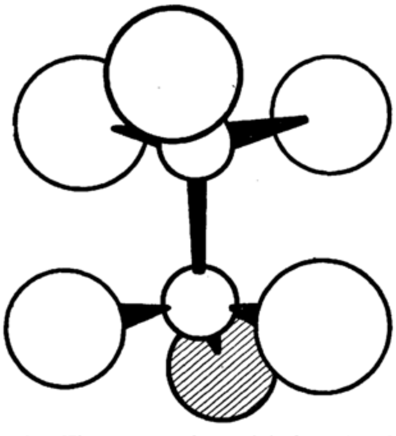

Fig. 3. The assumed model for the free molecule of 2-bromo-2,3,3-trimethylbutane. The small circle represents the carbon atom, the large circle the methyl group and the hatched one the bromine atom.

of $3m$. Following such a statistical configuration, a calculation of structural factors was carried out, using two models, Ia (Fig. 4) and Ib, which are slightly different from each other. Namely in Ia, the two bromine atoms were assumed to lie statistically on the twenty-four equivalent positions, 24 (g)⁽⁷⁾ near the three principal axes, and the ten CH_3 groups on another set of the same equivalent positions. In Ib the bromine atoms and the methylic carbon atoms lie separately on two sets of forty-eight equivalent positions, (h) with a weight 1/24 for bromine and 5/24 for C. It is to be added here that in these calculations the molecule was assumed to possess the skew form with the C–C and C–Br bond distances, 1.54 and 1.94 Å, and the tetrahedral valency angle.

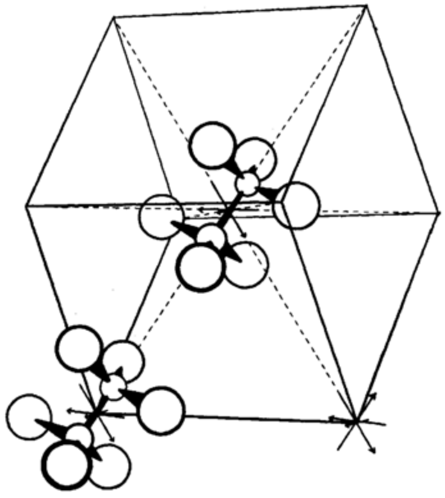

Fig. 4. The model for a statistical configuration, Ia.

If half of the molecules, in a statistical sense, rotate their molecular axes around the principal crystal axes through 90°, then the polar molecular axes will be found in eight different directions parallel to the body-diagonals of the crystal. If we add this operation to model Ia, the symmetry of the crystal will become O^{9}_{h}–$Im3m$. We shall call this model IIa. In this model, the polar axes of the molecules will be found in antiparallel orientations, whereas the bromine atoms and methyl groups will remain in almost the same positions as in model Ia. In these two models Ia and IIa, methyl groups and bromine atoms belonging to any two neighbouring molecules are found in trans configuration. By twisting the molecular axis from the positions given by model IIa, we have model IIb (angle of twist ±15°), model IIc (angle of twist ±40°) and model IId (angle of twist ±60°). The symmetry of these three models remains as in IIa.

In addition to these models, which are statistically static, we have also considered model III, in which molecules are rotating spherically around their centers of mass. The crystal will also assume the symmetry of O^{9}_{h}–$Im3m$.

The calculated $|F|$-values based on these models are plotted in Fig. 5, together with the observed data. Curve III is quite different

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7) "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham (1952), p. 326.

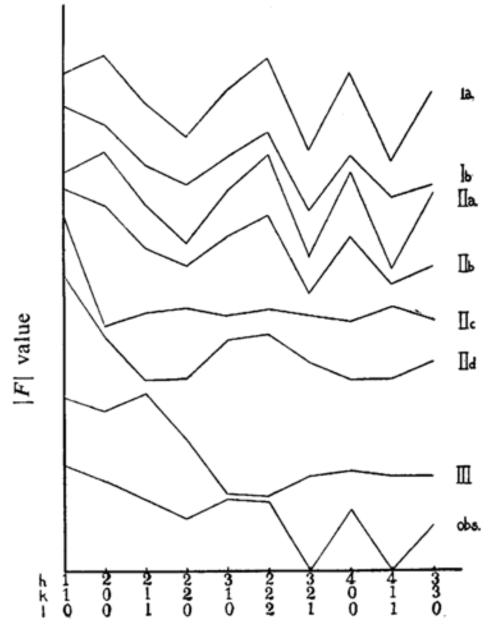

Fig. 5. Observed and calculated values of $|F|$.

from the observed one, suggesting that the free rotation of molecules as a whole in the crystal is ruled out. As a matter of fact, the domain required for the free rotation of the molecules at each lattice point overlaps not only with those of the first neighboring molecules but also with the second neighboring molecules as shown in Fig. 6. The curves for the models IIc and IId also do not agree with the observed one.

The curve Ia agrees fairly well with the observed one. In this model, though there is no appreciable overlap between the first neighboring molecules, there remains the possibility of colliding between the second neighboring molecules (Fig. 6). The agreement between the intensities calculated by model IIb, Ib and the observed ones is the best among all the models so far investigated. In these models, none of the shortest distances between atoms in neighboring molecules exceeds appreciably the sum of the van der Waals radii. It is difficult to decide which one of models, Ib or IIb, is really the case in point. The actual configuration may be expressed by a combination of Ia, Ib, IIa and IIb with appropriate weights.

This statistical structure may throw light on the explanation of the plasticity and rapid decrease of intensity with the increase of diffraction angle.

The orientational disorder of the arrangement of molecules may disappear below the transition temperature. This view is supported by the thermal differential analysis. The change of the optical property from isotropic to anisotropic in passing the transition temperature means that the crystal assumes the lower symmetry. This may imply that the arrangement of the molecules becomes more ordered than that of the room temperature phase.

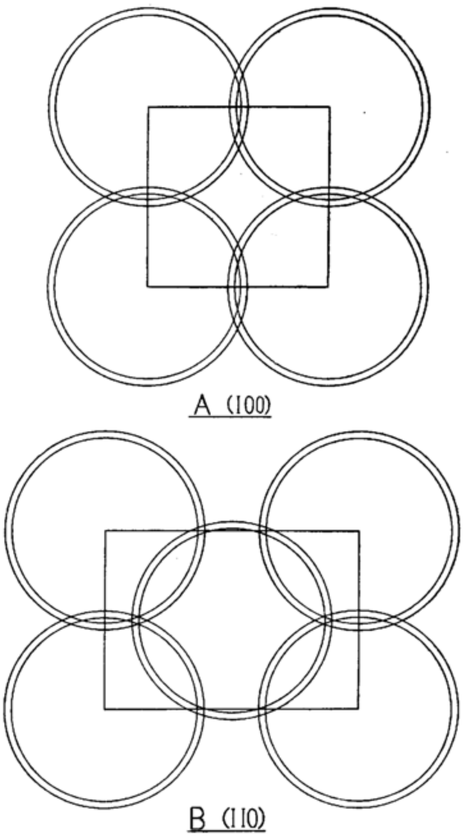

Fig. 6. The required domain for the free rotation of molecule at each lattice point. The radii of these circles are calculated using assumed molecular configuration and van der Waals radii for bromine (outer circles) and methyl groups (inner). A shows the section parallel to (100). B shows the section parallel to (110).

It has been reported that 1, 1, 1, 2-tetrachloro-2-methylpropane[1] and 2-chloro-2, 3, 3-trimethylbutane[4] also give plastic crystals at high temperature. Both of these also belong to the body-centered cubic lattice and the fact that their unit cell dimensions (7.4 and 7.62 Å) are close to the value of the present substance indicates that the free volumes of these molecules are similar.

Summary

2-Bromo-2, 3, 3-trimethylbutane gives a plastic crystal, which is optically isotropic and has a density of 1.31 g./cc. at 13°C. The X-ray data

can be interpreted on the bases of a body-centered cubic lattice, having $a=7.66\,\text{Å}$ with two molecules in the unit cell. The symmetry interpretation gives a structure of disordered orientation of molecules. It was found, by means of optical and differential thermal analysis methods, that there is a phase transition at about $-114°\text{C}$, below which the crystal is of a lower symmetry.

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