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The Physical Properties and Crystal Structure of 2-Bromo-1, 1, 1-trichloro-2-methylpropane

By Tsutomu KOIDE, Tsutomu ODA, Osamu WASHIO* and Kazuo FUJITA**

Laboratory of Chemistry, Osaka University of Liberal Arts and Education, Tennoji, Osaka

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2-Bromo-1, 1, 1-trichloro-2-methylpropane gives a plastic crystal, named by Timmermans (*J. Chim. Phys.*, **35**, 331 (1938)), which is optically isotropic and which has a density of 1.97 g./cc. at 25°C. The X-ray data can be interpreted with a body-centered cubic lattice, with 7.42 Å for the unit cell length containing two molecules. The symmetry interpretation gives a crystal structure of a disordered orientation of molecules. It was found, by means of optical measurements and differential thermal analysis, that there is a phase transition at about −62°C, below which the crystal is in a lower symmetry.

In our previous papers,[1-5] several hexasubstituted ethane derivatives expressed by the formula

* Present adrress, Gojo High School, Gojo, Nara.
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1) T. Oda and T. Koide, This Bulletin, **29**, 208 (1956).
2) T. Koide, T. Oda and I. Nitta, ibid., **29**, 738 (1956).
3) T. Koide, T. Oda and I. Nitta, ibid., **30**, 119 (1957).
4) T. Koide, S. Takeuchi, T. Oda, Y. Yamada and I. Taguchi, ibid., **30**, 683 (1957).
5) T. Koide, Y. Kato and T. Oda, ibid., **33**, 1572 (1960).

$X_{3-n}(CH_3)_nC-C(CH_3)_mX_{3-m}$ were studied from the point of view of crystal chemistry. It was observed that all the investigated substances undergo a phase transition in the solid state and that their high temperature modifications belong to the cubic structure, in which the molecular arrangement is in a disordered state.

It seems that it would be interest to see what effect may occur in the molecular behavior in the crystal, when substitution is extended to three species of atoms and groups such as chlorine, bromine and methyl groups, since they have nearly equal van der Waals radii.[6] In the present paper, the authors have studied 2-bromo-1, 1, 1-trichloro-2-methylpropane by means of X-ray diffraction, differential thermal analyses and optical measurements.

Experimental and Results

Material.—2-Bromo-1, 1, 1-trichloro-2-methylpropane was prepared by the bromination of chloreton with phosphorus pentabromide, following the method of Willgrerodt and Dürr.[7] The material obtained was purified by fractional melting and further by recrystallization three times from ether. The final purification was effected by fractional sublimation in a high vacuum (about 10^{-5} mmHg). The crystal shows plasticity and high volatility, its fumes irritating the eyes and nose.

Physical Properties.—The melting point was to be 160°C, and it sublimes at almost the same temperature. The density was found to be 1.97 g./cc. at 25°C by the flotation method using an aqueous solution of zinc chloride.

Optical Observation.— Under a polarized microscope, the optical properties of the crystal were observed at room and at lower temperatures. The cryostat used for the low-temperature measurements is described in Ref. 5. In the temperature range between room temperature and about −60°C, the crystal was found to be optically isotropic, indicating that the crystal is cubic. At about −60°C, it was suddenly transformed into a birefrigent polycrystal.

X-Ray Study.—A single crystal was sealed in a thin-walled Pyrex glass capillary tube. Within the capillary tube, a Pyrex glass rod almost filling the space was inserted to prevent the loss of crystal by sublimation.

Using Cu$K\alpha$ radiation ($\lambda=1.54$ Å) filtered through a nickel foil and adjusting [110] as the axis of rotation, we prepared a series of 30° oscillation photographs, covering a range of about 90°.

Laue photographs were also taken with X-rays parallel to [100], [110] and [111]. They show that the point-group symmetry of the crystal is T_d-$\bar{4}3m$ or O-43 or O_h-$m3m$. All the spectra appearing in oscillation photographs were extinguished except those of $h+k+l=2n$, they can be indexed with a body-centered cubic lattice with a unit cell of the side of $a=7.42$ Å.

The density indicates that two molecules are present in the unit cell, giving the calculated density to be 1.59 g./cc.

Differential Thermal Analysis (D. T. A.).—The apparatus and procedure of D. T. A. have been described elsewhere.[2] The investigated temperature range was from about −80°C to the melting point, 160°C. Two thermal anomalies were observed. One of them occurs at about −62°C on cooling, and at −35°C on heating. It is in accordance with the anomlies observed by a polarized microscope. Another anomaly was found at 160°C, corresponding to the melting point.

Discussion

The unit cell length of the cubic crystal of 2-bromo-1, 1, 1-trichloro-2-methylpropane, 7.42 Å, is comparable with the value of 7.43 Å given for hexachloroethane and that of 7.46 Å given for 1, 1, 1, 2-tetrachloro-2-methylpropane, even though the substance under investigation contains a bromine atom which has a larger van der Waals radius, 1.9 Å, than that of the chlorine atom, 1.8 Å.[6]

Since the unit cell contains two molecules, it is reasonable to place the centers of the mass of molecules at the lattice points, 0, 0, 0 and 1/2, 1/2, 1/2. The proper symmetry of these points is T_d-$\bar{4}3m$ or O-43, or O_h-$m3m$, so that the molecular symmetry in the crystal should have one of these cubic point groups. On the other hand, if we consider that the free molecule has the skew configulation (Fig. 1), the highest symmetry that the molecule

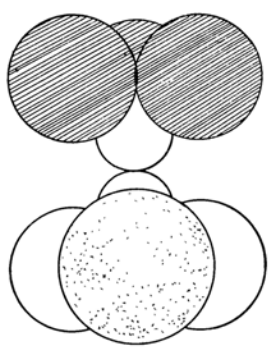

Fig. 1. The assumed skew configuration for the free molecule of 2-bromo-1, 1, 1-trichloro-2-methylpropane, $Br(CH_3)_2C-CCl_3$. The small circles represent carbon atoms, the larger circles the methyl groups, the dotted circle the bromine atom and the hatched one the chlorine atoms.

6) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cronell Univ. Press, Ithaca, New York (1960), p. 260.

7) C. Willgrerodt and F. Dürr, *J. prakt. Chem.*, **2**, 39, 284 (1889).

could have is C_s-m. In order for such a molecule of low symmetry to aquire an apparent high symmetry, it is necessary to take into consideration some statistical arrangements of molecules, as we have done in the cases of several other plastic crystals.[1-5,8]

Such a statistically-disordered molecular arrangement may disappear at lower temperatures. Thus the phase transition occuring at about $-62°C$ is perhaps the extreme temperature, below which the arrangement of the molecule is in an ordered state. The optical observation indicates that the crystal below the transition point possesses a lower crystal symmetry.

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8) C. D. West, *Z. Krist.*, **88**, 195 (1934).