On the Crystal Structure of 2,2-Dichloro-3,3-dimethylbutane

By Tsutomu Koide, Tsutomu Oda
and Isamu Nitta*

(Received December 4, 1956)

Hexachloroethane and hexamethylethane are characterized by relatively high melting points, 185°C and 100.6°C, respectively; by polymorphism in the solid state, the transition points being 43°C and 71°C for hexachloroethane[1] and −125°C for hexamethylethane[2]; and by high symmetry of the high temperature modifications, as shown by optical isotropy and confirmed by x-ray studies[3,4]. Recently, it has been confirmed[5] that hexabromoethane is also isotrimorphous[6] with hexachloroethane. It seems of interest to examine what will occur in the phase just below the melting point of a hexa-substituted ethane of the type of $(CH_3)_xCl_{3-x}CC(CH_3)_{x'}Cl_{3-x'}$. We have carried out an x-ray diffraction study of 2,2-dichloro-3,3-dimethylbutane, which was reported[7] to have high volatility and a relatively high melting point such as 151–152°C.

This compound was prepared by the method of P. D. Bartlett and L. J. Rosen[7]. Pinacolone was added to powdered phosphorus pentachloride with mechanical stirring, the reaction being maintained at about 5°C. The time of addition was about three hours, after which stirring was continued for ten hours. This mixture was poured on ice. The solid was removed by filtration, washed with water, and air-dried. It was recrystallized twice from ether and then subjected to sublimation twice under abuot 20 mmHg. The solid is volatile and plastic, its vapour having a camphoric odour. A melting point of 151°C was observed in sealed tubes. The crystals were found to be optically isotropic.

Using Cu K_α radiation and materials sealed in thin-walled capillary tubes, we prepared x-ray powder photographs, in which seven lines appeared. The reflections were indexed with a body-centered cubic lattice, the edge length being 7.58 Å. By suspension in a solution of sodium chloride in water, the density of the solid was measured as 1.17 g./cc. at 23°C. Hence it was found that the unit cell contains two molecules, yielding the calculated density as 1.18 g./cc.

Since the lattice is body-centered and the unit contains two molecules, we may place them at the lattice points 0, 0, 0 and 1/2, 1/2, 1/2, of which the symmetry should be at least T-23. On the other hand, as the rigid molecule of $(CH_3)_3C\text{-}C(CH_3)Cl_2$ can have at the highest only one plane of symmetry which contains the central C-C bond axis, it becomes necessary to consider some statistical explanation of the structure, as is always so in plastic crystals[3,4,5,8]. In order that the statistical symmetry of the molecule be higher than T-23 at 0, 0, 0 and 1/2, 1/2, 1/2, the molecule of the symmetry C_s-m should orientate its central axis C-C parallel to each one of the four body-diagonals statistically equally and at

---

* Faculty of Science, Osaka University.

[1] I. Nitta and S. Seki, *J. Chem. Soc. Japan*, **62**, 581 (1941); K. J. Ivin and F. S. Dainton, *Trans. Faraday Soc.*, **43**, 32 (1947); S. Seki and M. Momotani, This Bulletin, **23**, 30 (1950). See also O. Lehman, *Z. Krist.*, **1**, 106 (1877); ibid., **6**, 584 (1882).

[2] G. S. Parks, H. M. Huffman and B. Thomas, *J. Am. Chem. Soc.*, **52**, 1032 (1930).

[3] C. D. West, *Z. Krist.*, **88**, 195 (1934).

[4] C. Finbak, *Tids. Kjem. Bergv.* **17**, No. 9, 2 (1937). M. Atoji, T. Oda and T. Watanabé, *Acta Cryst.*, **6**, 868 (1953).

[5] G. J. Snaauw and E. H. Wiebenga, *Rec. Trav. Chim. Pay-Bas.*, **61**, 3 (1942).

[6] B. Goszner, *Z. Krist.*, **38**, 151 (1904).

[7] P. D. Bartlett and L. J. Rosen, *J. Am. Chem. Soc.*, **64**, 543 (1942).

[8] J. Timmermans, *J. Chim. Phys.*, **35**, 331 (1938); I. Nitta and T. Watanabé, This Bulletin, **13**, 28 (1938); T. Oda and T. Watanabé, *J. Chem. Soc. Japan.* **65**, 154 (1944); T. Oda and I. Nitta, ibid., **65**, 621 (1944); R. S. Schwartz, B. Post and I. Fankuchen, *J. Am Chem. Soc.*, **73**, 4490, 5113 (1951); T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 108 (1953).

the same time laterally so that the C-C axis acquires a statistical symmetry of 3 at least. It is also conceivable that the observed feature of x-ray diffraction can be explained by molecules in free rotation about the central C-C axis. Which one is the case of the present statistical structure seems almost entirely indiscriminable from consideration of intensity data, since the lines are so few as mentioned above. However, it may be said that this structure is statistically isomorphous with cubic hexamethylethane at room temperatures and hexachloroethane above 71°C. The edge length 7.58 Å is between those[3] of 7.69 Å for $C_2(CH_3)_6$ and 7.43 Å for C_2Cl_6 at 80°C. In the diffraction of x-rays by the present crystal, we have observed, similarly to those hexa-substituted ethanes stated above, very rapid decrease of intensity with increasing angles of scattering, which is evidently in close relationship with the disordered orientation of the molecule in intense thermal motion.

It will be expected that such "rotational" mode of the molecule in the crystal will change at lower temperatures. We have undertaken a differential thermal analysis and observed, on its heating curve from liquid air temperature, anomalous heat effect at about −94.9°C and a small effect at −75.1°C. As a result, x-ray studies of single crystals of probably ordered phase below the transition point must await techniques for the growth of the single crystals below this temperature.

In conclusion, we should express our hearty appreciation to Doctor S. Seki, Faculty of Science, Osaka University for his gracious interest during this work. We also wish to thank Mr. H. Chihara for his kind aid. The cost of this research was defrayed from the Scientific Research Grant from Ministry of Education, to which the thanks of the present authors are due.

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