SHORT COMMUNICATIONS

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

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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 haxachloroethane[1] and −125°C for hexamethylethane[2], and by high symmetrys of the high temperature modification as shown by optical isotropy and confirmed by X-ray studies[3,4]. Recently, it has been reported[5] that hexabromoethane is also isotrimorphous with hexachloroethane. In order to examine what occurs in the high temperature modifications by symmetrical replacement of methyl group pair or pairs by Cl pair or pairs (resulting in substances such as $(CH_3)_2ClCCCl(CH_3)_2$ and $(CH_3)Cl_2CCCl_2(CH_3)$), we have carried out an X-ray diffraction study of 2, 3-dichloro-2, 3-dimethylbutane crystal, which has been also reported to have relatively high melting point, 161°C, in a sealed tube[6].

This compound was perpared by treating[6] pinacol with phosphorus trichloride and was subjected to sublimation under about 30 mm Hg. The solid is very volatile and plastic, its vapour having a camphoric odour. A melting point of 158°C was observed in a sealed tube. The crystals were found to be optically isotropic at room temperatures. Using Cu K_α radiation and samples 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 an aqueous solution of sodium chloride, the density of the solid was measured as 1.14 g./cc. at 30°C. Hence, it was found that the unit cell contains two molecules, yielding the calculated density of 1.18 g./cc. Since the lattice is body-centered and the unit contains two molecules, we may place the two centers of them at the lattice points 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, of which the symmetry should be at least T–23. On the other hand, as the symmetry of the rigid molecule of $(CH_3)_2ClCCCl(CH_3)_2$ can be at highest $C_{2h}-2/m$[7], it becomes necessary to consider some statistical explanation of the structure, as is always the case in plastic crystals[3,4,8]. In order that the statistical symmetry of the molecule be higher than T–23 at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the molecule of the symmetry $C_{2h}-2/m$ should orientate its axis C–C parallel to one of the four body-diagonals statistically equally, and at the same time with its two-fold axis oriented parallel to one of the three similar azimuthal directions also equally so that the axis C–C acquires three-fold symmetry statistically. Such statistical high symmetry is similarly gained with a model of molecule of the "*gauche*" form[7], the other rotational isomer having the symmetry C_2-2, or with another model of molecule which is in free rotation about the C–C axis. Which one is the case of the present statistical structure seems, almost entirely undiscriminable from the presents 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 of 7.58 Å is between those[3] of 7.69 Å and 7.43 Å for $C_2(CH_3)_6$ and C_2Cl_6 at 80°C respectively. In the diffraction of X-rays by the present crystal, we have observed, similarly to the hexa-substituted ethanes stated above, a 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 a "rotational" mode of the molecules in the crystal will change at lower temperatures. We have undertaken a differential thermal analysis, and observed, on its heating curve from low temperatures, anomalous heat effect at about −112°C. Therefore, X-ray studies of single crystals of the probably ordered phase below the transition point must await techniques for the growth of single crystals below the temperature.

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1) O. Lehman, *Z. Krist.*, **1**, 106 (1877); ibid., **6**, 584 (1882); 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).

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. Bergvesen*, **17**, No. 9, 2 (1937); M. Atoji, T. Oda and T. Watanabe, *Acta Cryst.*, **6**, 868 (1953).

5) G.J. Snaauw and E.H. Wiebenga, *Rec. Trav. Chim. Pays-Bas*, **61**, 253 (1942). See also B. Goszner, *Z. Krist.*, **38**, 151 (1904); K. Yardley, *Proc. Roy. Soc., London (A)*, **118**, 449, 485 (1928).

6) F. Couturier, *Ann. Chim. Phys.*, **26**, 433 (1892).

7) Y. Morino, I. Miyagawa, T. Haga and S. Mizushima, This Bulletin, **28**, 165 (1955).

8) J. Timmermans, *J. Chim. Phys.*, **35**, 331 (1938); I. Nitta and T. Watanabe, This Bulletin, **13**, 28 (1938); T. Oda and T. Watanabe, *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).