An X-Ray Study on the Crystal Structure of 2-Chloro-2, 3, 3-trimethylbutane[*]

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Crystals of hexamethylethane undergo phase transition at −125°C.[1] The phase between the transition and the melting point (m. p. 100.6°C) is characterized by the softness and the high volatility. The crystal structure was investigated by West,[2] who vaguely pointed out that the molecules in the crystal are in orientational or rotational disorder. In order to see what will occur in the high temperature modification by replacement of a methyl group by chlorine, we have carried out an X-ray examination of 2-chloro-2, 3, 3-trimethylbutane, which has relatively high melting point, 134–135°C.[3]

Following the method used by Butlerow,[3] we prepared 2-chloro-2, 3, 3-trimethylbutane by adding powder of phosphorus pentachloride to pentamethylethanol hydrate, which had been obtained by the Grignard reaction[4] of pinacolone with methyl magnesium bromide in ether. The final product, $Cl(CH_3)_2C—C(CH_3)_3$ was recrystallized from its ethereal solution and then subjected to sublimation under low pressure.

It was observed that the solid sealed in a thin-walled melting point tube melts at 134–135°C. It recrystallizes readily in a closed vessel to give transparent aggregates. The solid is very soft and plastic. We have found it to be optically isotropic. The vapor has a camphoric odor. These properties are similar to those of cubic hexamethylethane. By the suspension method in the dilute aqueous solution of sodium chloride, the density of the solid was determined as 0.999 g./cc. at 15°C.

As the solid is volatile, we used single crystals sealed in thin-walled glass capillary tubes for X-ray examination. Such a sample was placed on a goniometer-head of an X-ray camera. Using Cu-radiations, we took several Laue photographs and a series of 20° oscillation photographs over a range of 75° about [001] as the axis of rotation. Laue photographs taken with the X-ray beam parallel to [100] and [110] showed holotesseral symmetry, and thus the point group of the crystal should be $T_d-\bar{4}3m$, $O-43$ or O_h-m3m. All reflections appearing on the oscillation photographs were indexed satisfactorily by a cubic reciprocal lattice corresponding to $a=7.62$ Å. All spots were extinguished except those for which $h+k+l=2n$. This indicates that the lattice is of the body-centered cubic. Thus the space group should be $T_d^3-I\bar{4}3m$, O^5-I43 or O_h^9-Im3m. The density indicates two molecules per unit cell, the densities being calculated, 1.01 g./cc.; observed, 0.999 as mentioned above.

Since there are two molecules in the unit cell with the body-centered translation, it is reasonable to place the centers of molecules at the positions 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, of which the symmetry should be $T_d-\bar{4}3m$, $O-43$ or O_h-m3m. On the other hand, as the rigid molecule of $(CH_3)_2ClC—C(CH_3)_3$ can have at the highest only one plane of symmetry C_s-m, which contains the central C—C bond axis, it becomes necessary to consider some statistical explanation of the structure, as is always so[2,5] in organic plastic crystals. In order that the statistical symmetry of the molecule be as high as $T_d-\bar{4}3m$ at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, the molecule should orientate its central C—C bond axis parallel to each one of the four body-diagonals statistically equally and at the same time laterally so that the C—C axis acquires a statistical symmetry $3m$ at least. Such a statistical symmetry can also be gained by a model of molecules in rotation about the C—C axis. In the cases of O^5-I43 and O_h^9-Im3m, it is necessary to add the anti-parallel orientations of the polar C—C axis along the four body-diagonals, these directions having the symmetry of 3 or $3m$. It is also conceivable that the observed feature of the X-ray diffraction can be explained by assuming molecules in free spherical rotation. Which one of

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these possibilities is the case for the actual statistical structure seems indiscernible from the consideration of intensity data, since the observable reflections are few. However, it may be said that the structure found for the present crystal is statistically isomorphous with that of the high temperature modification of $C_2(CH_3)_6$[2].

The rapid decrease in intensity of the X-ray reflections with increasing angle of scattering is evidently due to the disordered orientation of molecules with violent thermal motion. In accordance with these X-ray observations, the crystal is soft, plastic and highly volatile.

With a view that such a "rotational" mode of the molecules in crystals will cease at lower temperatures, we have undertaken a differential thermal analysis, and observed an anomalous heat effect at about −146°C on cooling, and at about −139°C on heating, showing hysteresis phenomenon. We have also taken X-ray oscillation photographs at about −160°C, which give a number of reflections showing that the structure below the thermal transition point is of low symmetry and probably has a more ordered structure.

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