SHORT COMMUNICATIONS

An X-ray Study on Thiacyclohexane

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McCullough and his collaborators[1] reported that thiacyclohexane (pentamethylene sulphide) has three modifications in the solid state and the molal entropy of fusion is 2.002 cal./deg. A chair form having the point group symmetry Cs is suggested for the molecule from the infrared and Raman spectroscopy.

The highest temperature modification of this crystal, stable between the transition point, 240.02°K, and the melting point, 292.25°K, is found to be optically isotropic and shows plastic behavior. These facts, together with the very low value of molal entropy of fusion, suggest that this modification falls into the category of plastic crystal.

The dipole moment of this molecule is estimated to be about 1.7 D.U., assuming the bond moment of C–S to be 1.4 D.U., (obtained from the dipole moments of diethyl and diphenyl sulphides[2,3]), and the valence angle C–S–C, 105°[1,4]. It is of interest to see that the physical properties of this compound in the highest temperature modification such as the entropy of fusion, plasticity and isotropy are quite similar to those of the non-polar compound cyclohexane[5], in spite of the difference in the molecular symmetry and polarity, which would give rise to different types of intermolecular correlation in the solid state. Furthermore, another related compound pentamethylene oxide having the molecular form analogous to that of thiacyclohexane does not seem to give plastic crystals. It would be because of the difference between the electronegativity of oxygen and sulphur atoms. The highest temperature modification has been studied by means of X-rays.

(A) The material used for this investigation was prepared and purified by the American Petroleum Institute research project 48 at the Laramie Station of U.S. Bureau of Mines, Wyoming. The material received was claimed to be 99.92% pure. It was again purified by drying and sublimation and was sealed in a thin wall capillary made of borosilicate glass. Single crystals can be grown very easily in a capillary by slow cooling of the melt. It is likely to occur that the [110] direction of the crystal lies nearly parallel to the capillary axis.

Laue, rotation, and oscilation photographs were taken with filtered Cu Kα and Mo Kα X-rays, at 14°C.

(B) The symmetry of the crystal is determined as face centered cubic with four molecules in the unit cell. The six Bragg reflection spectra observed are indexed as 111, 200, 220, 311, 222 and 331. The lattice constant is found to be 8.69±0.02 A at 14°C. With this value, the density of the crystal is calculated to be 1.036, which seems to be reasonable compared with the measured value, 0.985, of the liquid at 21°C. The spectral intensities are much like those of other plastic crystals such as trimethylacetic acid[6].

Considered from the standpont of the crystal and molecular symmetry, molecules will be in highly disordered orientation, including some sort of rotational motion, keeping presumably the center of the mass of the molecule fixed at the lattice site. We have observed very pronounced X-ray diffuse scattering. Spot-like diffuse scattering is appearing on Laue photographs, the intensity of which is strongest around the reciprocal lattice points 200 and 111, and there are also weaker ones around 100. The general appearance of those diffuse scatterings are very similar to those of other plastic crystals like cyclohexane[5].

From these observations we conclude that the highest temperature modification of thiacyclohexane belongs to the plastic crystal.

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