On the Phase Transitions of 1,2-Dibromo-1,1,2,2-tetrachloroethane

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The three solid phases of C_2Cl_6 have been well studied from the standpoint of crystal structure and molecular motion by the methods of X-ray diffraction,[1] heat capacity measurement,[2] nuclear quadrupole resonance,[3] *etc.* Similar studies have also been reported in the case of C_2Br_6.[4]

For the case of $BrCl_2C\text{-}CCl_2Br$, the interest is not only in the polymorphism[5] but in the isomerism between trans- and gauche-forms of the molecule in the solid state. From such standpoint, the polymorphism and the crystal structure are studied and the results will be described in this paper.

The material was prepared by bromination of tetrachloroethylene with bromine under the sun light.[6] Crude crystals were recrystallized three times from ethyl alcohol and sublimed twice at about 10^{-2} mmHg at about 50°C. The crystals melt at about 200°C in a sealed tube with decomposition.

A differential thermal analysis examination between about −190°C and about 230°C showed three phase transitions at 75, 101, and 108°C on heating. However, in the cooling direction transition occurred at 59, 99, and 105°C, indicating at large thermal hysteresis with regard to the lowest transition. The rate of temperature change was controlled to be at about 1/4 degree per minute.

The sample began to melt at about 200°C with decomposition, and the color of free bromine was observed.

The transition at 101°C was not reported by Gossner,[5] who described only two transitions at 80°C and at 108—109°C under a polarized microscope. Two transition temperatures, 75 and 108°C, agree with his optical results. Our reexamination of Gossner's experiment revealed that the transition at 101°C caused no detectable change in the optical properties, this explains the apparent discrepancy in the number of solid phase transitions reported. The solid phase above 108°C is optically isotropic.

The existence of these four solid phases was acertained also by X-ray diffraction method with powder samples.

The X-ray diffraction pattern of the phase above 108°C was consistent with a body-centered cubic lattice, the unit cell having a dimention of 7.7 Å at 130°C and containing two molecules (d_{cal}= 2.34 g/cc). This result suggests that the molecules undergo molecular rotation about the lattice points, taking the statistically high symmetry.

The lowest solid phase (IV), below 75°C, is orthorhombic with the crystal parameters a= 11.81, b=10.25, and c=6.51 Å, and these values are in accordance with the results given by Yardley.[7] The phase (III) in the temperature range of 75—101°C is of lower symmetry, possibly triclinic. The phase II between 101 and 108°C resembles the phase III but is different from the other three.

The crystal structure below 75°C will be studied in detail in future using single crystals.

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