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THE CRYSTAL STRUCTURE OF HIGH CYCLOBUTANE

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The Crystal Structure of High Cyclobutane*

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According to Rathjens and Gwinn (1953), cyclobutane melts at 182°K and has a transition point at about 145°K . We have investigated the structures of the two solid forms by the X-ray diffraction method.

Samples provided by Dr. Rathjens were sealed in Pyrex capillaries, mounted in the camera, and cooled in the usual way with a stream of cold nitrogen gas. Powder patterns of the low temperature form contain many lines. The structure is not cubic and has not been solved. Powder patterns of the high form show only a single line which is assigned to 110 on the basis of the single crystal work.

Slow freezing resulted in single crystals of the high form whose orientations seemed to be random in the capillary. Rotation photographs of four such crystals at about 173°K (axes of rotation approximately [100], [311], [531], and [441], respectively) show the unit cell to be body-centered cubic, with $a = 6.06 \pm 0.03 \text{ \AA}$ ($\lambda \text{ Cu K}\alpha = 1.542 \text{ \AA}$). Though only reflections of the forms {110} and {200} are observed, the interpretation is unique because the crystals were misaligned enough to permit independent observation of "coincident" reflections in nearly every case so that the multiplicities of the forms were determined. The distribution of the spots

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among the various layer lines was also checked in each case. This unit cell, with two molecules, corresponds to a calculated density of $0.84 \pm 0.01 \text{ g cm}^{-2}$.

If the origin is chosen at the center of gravity of one molecule, then the second molecule must be at the body center. To achieve cubic symmetry, these molecules must have rotational disorder, either static or dynamic. Structure factors were calculated on the basis of complete spherical symmetry, using molecular dimensions consistent with the electron diffraction results of Dunitz and Schomaker (1952) for the gas. No correction was made for temperature or absorption. The results, listed in Table 1, explain the rapid decrease of intensity with increasing Bragg angle and the absence of the higher order reflections. However, it is impossible to get perfect agreement with the observed ratio of $F(110)$ to $F(200)$ unless the absorption error is more serious than is estimated. This fact is interpreted as evidence that the rotational disorder is not spherically symmetric. Indeed, since the intermolecular distance, 5.25 \AA between centers, is substantially smaller than the largest van der Waals diameter of cyclobutane, the rotations are expected to be hindered appreciably.

These data yield no information concerning the planarity of the carbon skeleton, since reasonable deviations from planarity have a trivial effect on the form factor of the rotating molecule.

Table 1
Structure Factors for High Cyclobutane

hk ℓ	F _{obs}	F _{calc}
110	2.8	2.8
200	1.5	1.0
211	<0.9	<0.2

References

Dunitz, J. D., and Schomaker, V., (1952). J. Chem. Phys. 20,
1703-7.

Rathjens, G. W., and Gwinn, W. D., (1953). To be published.