

Short Communications

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On the crystal structure of cubic hexachloroethane. By MASAO ATOJI,* TSUTOMU ODA† and TOKUNOSUKÉ WATANABÉ, Faculty of Science, Osaka University, Nakamoshima, Osaka, Japan

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Hexachloroethane is trimorphous. At 45° C. the orthorhombic form becomes monoclinic, and at 71.4° C. the monoclinic form becomes cubic with an entropy change of 5.7 e.u., which is comparable with the 5.5 e.u. change at the melting-point of 185° C. (Seki & Momotani, 1950; Nitta & Seki, 1941; Ivin & Dainton, 1947). Powder diffraction studies of the cubic phase have vaguely suggested a disordered structure (West, 1934; Finbak, 1937). In an attempt to study this disorder in some detail we have obtained single-crystal data, and compared them with various models.

Hexachloroethane (Schering-Kahlbaum A. G.), recrystallized from ether-alcohol, was sealed into thin-walled borosilicate glass capillaries. Single crystals were readily grown, and, with the use of Cu K radiation, oscillation photographs indicated lattice dimensions of

$$a = 7.51 \text{ \AA} \text{ at } 105^\circ \text{ C. and } 7.6 \text{ \AA} \text{ at } 145^\circ \text{ C.,}$$

in agreement with the previous authors. The Laue symmetry, O_h-3m , and extinctions indicate the space groups T_d^2-I43m , $O-I43$ or O_h-Im3m . The site symmetry at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (the molecular centers) is T_d-43m , $O-I43$ or O_h-3m , but the isolated molecule has symmetry $D_{3d}-3m$ (Morino & Iwasaki, 1949). Hence some disorder is indicated. Because the molecule is centrosymmetric the space group O_h-Im3m has been selected as most probable for all models.

For twelve models comparisons of observed and calculated structure factors and Patterson functions were made. Three models gave values of

$$R = \Sigma |F_o| - |F_c| \div \Sigma |F_o| \text{ less than } 0.25.$$

These models are as follows:

- (1) The C-C axis is statistically distributed along the four body-diagonals. The Cl atoms undergo hindered rotation, with $V/2kT = 1$ (King & Lipscomb, 1950). The three potential minima for each rotator correspond to the positions 48(k) of O_h-Im3m (*Internationale Tabellen*, 1935).
- (2) Free rotation of the longest Cl...Cl axes of the molecule, the axes through the molecular center. These axes are chosen parallel to [100], [010] and [001] with equal probability.
- (3) A static statistical model ($V = \infty$), with C-C as in Model (1) and with the Cl distributed over positions

96(l) in O_h-Im3m . The minima of this distribution are 23° away from the minima of Model (1).

The values of R are 0.15 for (1), 0.19 for (2) and 0.17 for (3), after choice of the temperature factor constant, $10 \leq B \leq 12 \text{ \AA}^2$, to give the lowest R values. This ambiguity in the choice of a satisfactory model arises, with little doubt, from the small number (11) of observations. The choice of the most nearly correct one must be made on such grounds as the physical reasonableness of the model, and the appearance of our three-dimensional Fourier series. Chiefly on physical grounds we prefer Model (1), which also gave the best agreement with the observed data (Table 1). Although this comparison is

Table 1. Observed and calculated structure factors.*

	F_o	F_c	F_o	F_c
110	49	49	321	0
200	25	31	400	24
211	35	-32	411	8
220	25	-21	330	12
310	16	21	420	9
222	24	-32		8

* All three models gave the same set of signs.

quite satisfactory in comparison with other investigations of similar crystals, a slightly different type of disorder, or some more complex composite disorder, might well give as good or slightly better agreement.

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