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THE MOLECULAR STRUCTURE OF PERCHLORO-(4,8-DIMETHYLENE-TRICYCLO[3.3.2.0^{1,5}]DECA-2,6-DIENE), $C_{12}Cl_{12}$

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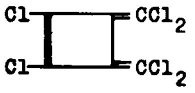
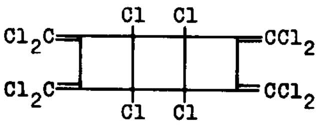
It has been found recently that at least four isomeric compounds of the formula $C_{12}Cl_{12}$ have been obtained by pyrolytic reaction of perchloro-(3,4-dimethylenecyclobutene) (I).$^{1)}$ The crystal and molecular structure of one of these isomers, perchloro-(3,4,7,8-tetramethylene-tricyclo[4.2.0.0^{2,5}]octane) (II), was reported already.$^{2)}$ The present paper will describe the structure determination of another isomer, m.p. 273°, obtained on the pyrolysis of (I) at about 250°.



(I)



(II)

It was difficult to determine the molecular structure of this isomer by means of chemical reactions since it was impossible to obtain the substance in sufficient quantity because of its very poor yield in the pyrolytic reaction.

Since fortunately this substance is obtained as sufficient large single crystals for X-ray determination, the three-dimensional structure analysis has been carried out for the purpose of elucidating the molecular structure of the compound Single crystals, suitable for the structure determination, were kindly supplied by Dr. A. Fujino, Osaka City University.

The crystal is monoclinic, with four molecules in a unit cell of the dimensions, a = 16.78, b = 6.80, c = 17.10 A and β = 116.5°. From the systematic absences, the space group is Cc or C2/c, the latter being more probable considering the positive result of Wilson statistics for centrosymmetry. The calculated density is 2.17 g.cm^{-3}. The three-dimensional data of intensities were measured visually from integrating Weissenberg photographs around the b and c axes taken with Ni-filtered Cu Kα radiation. The Lorentz and polarization corrections were made in the usual way. Though the crystals, used for the intensity measurement, were not small enough, no correction was applied for the absorption effect. Thus, the structure factors of 1432 independent reflections were obtained out of 1824 possible ones.

The crystal structure was elucidated by the minimum function method[3)] and the Fourier synthesis by Sim's method[4)]. In consideration of the fact that this crystal should have at least a symmetry of Cc, three of the vectors among two sets of two chlorine atoms, related with each other by a c-glide plane, were used for the minimum function. In this manner, the positions of all the chlorine atoms could be obtained, but those of the carbon atoms could not. The arrangement of the chlorine atoms, thus obtained, showed that there are two-fold rotation axes in the crystal, and hence the space group C2/c is reasonable as the corresponding one. After several cycles of the least-squares refinement with chlorine atoms alone, the three-dimensional Fourier synthesis was carried out by Sim's method. This Fourier map revealed the whole appearance of the molecule, giving peaks of the carbon atoms. The approximate coordinates, obtained from the Fourier map, were refined by the least-squares method. The discrepancy factor R at the present stage is 15.8 %.

The molecular framework thus obtained is shown in Fig. 1. Judging from the bond lengths and angles, calculated with the present atomic coordinates, it is concluded that the compound under the present investigation is perchloro-(4,8-dimethylene-tricyclo[3.3.2.0^{1,5}]deca-2,6-diene) as shown in Fig. 2.

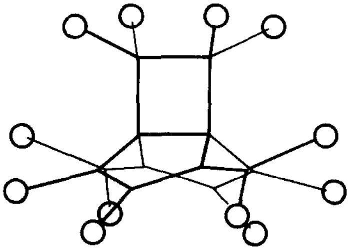


Fig. 1.

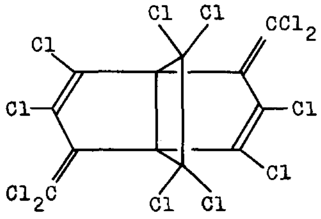


Fig. 2.

The molecule has a symmetry of C_2, the two-fold rotation axis being a crystallographic one. The rotation axis runs through the middle points of the two sides, opposite to each other, of the four-membered ring in the molecule, and relates the two five-membered rings of the same molecule with each other.

The four-membered ring is slightly distorted, and consequently the conformation of the two adjoining dichloromethylene groups is about 8° deviated from the eclipsed form. The five-membered ring is also somewhat puckered, and the dichloromethylene group, attached to the ring, is fairly deviated from the mean plane of the ring. The dihedral angle of the two five-membered rings in a molecule is about 123°.

In the course of the present study, the calculations necessary to derive the structure factors on an absolute scale from the intensity data were carried out on Bendix G-20 at C. Itoh Electronic Computing Service Co., Ltd. using a program written by Y. Utsumi and Y. Tomiie of this university, while the Fourier syntheses and the least-squares method were carried out on HITAC 5020 using our programs.

References

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4. G. A. Sim, Acta Cryst., **12**, 813 (1959).