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THE CRYSTAL AND MOLECULAR STRUCTURE OF PERCHLORO-(3,4,7,8-TETRAMETHYLENE-TRICYCLO[4.2.0.$0^{2,5}$]OCTANE), $C_{12}Cl_{12}$

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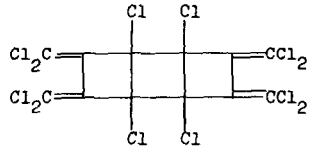
Four different isomeric compounds of the formula $C_{12}Cl_{12}$ were obtained by pyrolytic reaction of perchloro-(3,4-dimethylenecyclobutene).[1] One of these isomers, hereafter (I), was found to have the following structural formula,[1]

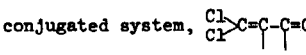


Since two bulky dichloromethylene groups are in adjacent positions of the molecule, the part of the conjugated system, $\begin{matrix}Cl\\Cl\end{matrix}\!\!>\!C\!=\!C\!-\!C\!=\!C\!<\!\!\begin{matrix}Cl\\Cl\end{matrix}$, may be distorted to a considerable extent owing to the expected contact of the groups too close with each other. This may be looked upon as an example of overcrowded molecules. In such a case, the whole molecule may show a fairly complicated appearance. In order to obtain more detailed information about the stereochemistry of this molecule, the X-ray investigation has been carried out.

Small single crystals of (I) suitable for the structure determination

were kindly supplied by Dr. A. Fujino, Osaka City University. From the present X-ray experiment, the crystal was found to be triclinic with the unit cell of the dimensions, a = 9.35, b = 7.45, c = 8.44 Å, α = 111.8°, β =117.6° and γ =96.0°. The space group has been taken to be PI throughout the present work. This assumption turns out reasonable because no contradiction has yet been encountered. The calculated density, with one molecule of (I) in the unit cell, is 2.07 g/cm^3. The three-dimensional data of intensities were measured visually from integrating Weissenberg photographs around a and c axes taken with filtered Cu K_α radiation. To these intensities, Lorentz and polarization corrections were applied, thus the structure factor of 1643 independent reflections being obtained.

A three-dimensional Patterson function was calculated. By superposing two sets of the Patterson maps using only one Cl-Cl vector, there could be found out not only the positions of all chlorine atoms but also those of all carbon atoms. The structure thus obtained was refined immediately by the least squares method. The value of R-factor is 20.0 % at the present stage.

Figs. 1 and 2 show the molecular framework projected along the a and b axes, respectively. This corresponds to the very structure concluded in the preceding paper. The bond lengths and angles are all reasonable considering the present accuracy. So far the molecule has a centre of symmetry, and hence the central four-membered ring should be exactly planar. The part of the conjugated system,  , appears almost planar in spite of very close contact between the two adjacent dichloromethylene groups of the same molecule. The conformation of the three four-membered rings as a whole is such that the molecule is of chair-like form, with one end definitely up and the other down. It may be said that the molecule has an approximate symmetry of C_{2h}.

In the course of the present investigation, the calculations necessa-

ry to derive the three-dimensional structure factors were carried out on IBM 7090 using a program written by Tomiie and Utsumi, the Patterson function using ERFR-2 programmed by Sly, Shoemaker and Van den Hende,[2] and the least squares method using ERBR-1 programmed by Van den Hende.[3]

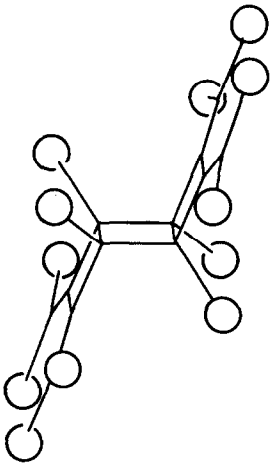


Fig. 1

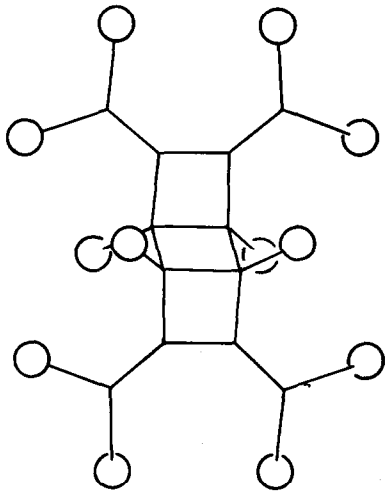


Fig. 2

REFERENCES

1. K. Mano, K. Kusuda, A. Fujino and T. Sakan, preceding paper.
2. W. G. Sly, D. P. Shoemaker and J. H. Van den Hende, (1962). ERFR-2: ESSO Research and Engineering Co.
3. J. H. Van den Hende, (1961). ERBR-1: ESSO Research and Engineering Co.