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THE CRYSTAL AND MOLECULAR STRUCTURE OF PERCHLORO-(1,4-DIMETHYL-5,8-DIMETHYLENECYCLOOCTA-1,3,6-TRIENE), $C_{12}Cl_{14}$

A. Furusaki and I. Nitta
Faculty of Science, Kwansei Gakuin University,
Nishinomiya, Japan

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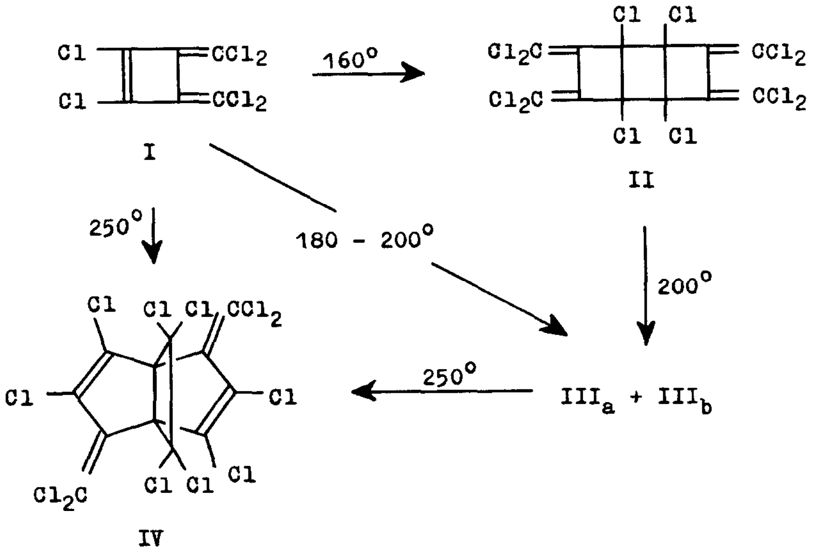
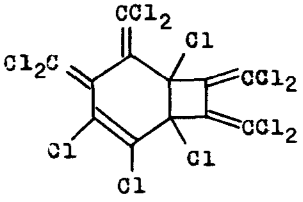
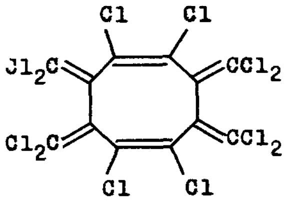
It has been recently found that the pyrolytic reaction of perchloro-(3,4-dimethylenecyclobutene) (I) gives at least four isomeric compounds of the molecular formula $C_{12}Cl_{12}$.$^{1)}$ The relation among these compounds is shown in the following chart.$^{1)}$





V



VI

The molecular structures of II[1, 2)] and IV[3)] out of the isomeric compounds have been already determined as shown in the chart. Before the structure of IV has been determined, it was proposed on the basis of the chemical evidences available at that time that III_a and III_b might have the same structural formula corresponding to perchloro-(2,3,7,8-tetramethylenebicyclo[4.2.0]octa-4-ene) (V). However, judging from the fact that III is the precursor of IV in the course of the successive isomerization, another structure (VI), instead of (V), seems to be adequate as that of III. Thus, the X-ray structure analysis has been undertaken for the purpose of elucidating the molecular structure of III. Unfortunately, as described later, it was revealed during the course of the present study that the crystals supplied were not those of III_b, but the dichloride of III_a, with the formula $C_{12}Cl_{14}$. Therefore the present paper will describe the structure of the dichloride of III_a, which is still useful to discuss the reaction mechanism of the isomerization.

The samples, suitable for the X-ray measurement, were supplied by Prof. Akira Fujino, Osaka City University. From oscillation and Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation, it has been found that the crystal is monoclinic with four molecules in the unit cell of the dimensions $a = 17.16$, $b = 9.31$, $c = 13.73$ Å and $\beta = 91.8^{\circ}$. From the systematic absences, the space group was found to be either C2/c or Cc. As the final result of the present analysis, the former has been concluded to be the corresponding space group.

The intensities of reflections were measured visually from integrating

Weissenberg photographs around the a and b axes taken with Cu Kα radiation. Due to the rule of absences corresponding to C2/c, the intensities of (hkl) reflections with h and k even and those with h and k odd cannot be compared directly with each other only using the intensity data from the a and b axes. Therefore the (hkk) photographs were taken around the [011] axis to obtain the intensity ratio between such two types of reflections. Thus the structure factors of 1683 reflections were uniquely derived, which were converted into an absolute scale by Wilson's method4).

The minimum function method5) was carried out three-dimensionally in order to seek for the positions of the chlorine atoms. To obtain the diagram, the peaks due to the three independent vectors among the two sets of two chlorine atoms, related with each other by a c-glide plane, were superposed at the origin, since there should be c-glide planes in the crystal whichever of the two possible space groups, C2/c and Cc, may be the real one. The minimum function diagram thus obtained contained twenty-four significant peaks per quarter of the unit cell. As it was believed at this stage that the compound under the present study had the molecular formula $C_{12}Cl_{12}$, the twelve peaks were chosen as the chlorine atoms out of the twenty-four peaks only on condition of satisfying the Patterson map. The arrangement of these twelve peaks showed the presence of two-fold rotation axes. Therefore, the space group was concluded to be C2/c. The coordinates of the chlorine atoms were refined with the diagonal-matrix least squares method. However, the refinement lowered the R factor from its initial value 0.46 only by 0.05. In order to ascertain the correctness of the structure obtained from the minimum function, the three-dimensional electron density distribution was calculated with Sim's method6). From the electron density diagram, the positions of the six independent chlorine atoms already obtained were found to be essentially correct. Besides, the diagram revealed not only the positions of the six independent carbon atoms but also the presence of an additional chlorine atom per asymmetric unit. Consequently the molecular formula of the compound under investigation might not be $C_{12}Cl_{12}$ but should be $C_{12}Cl_{14}$. This is also supported by the fact that, for the formula $C_{12}Cl_{12}$, the calculated density is 1.73 g/cm^3; this value seems too small as compared with those of II and IV, 2.07 and 2.17 g/cm^3 respectively. The atomic coordinates of the seven chlorine and six carbon atoms were refined with the diagonal-matrix least squares method with individual isotropic temperature factors using the 1319 data around the b axis. Further, these coordinates were refined by the block-diagonal-matrix least squares method assuming anisotropic thermal motions of all the atoms using 827 data except very weak reflections. The R factor at the present stage is 10.0 %.

The molecular framework thus obtained is shown in Fig. 1. Judging from the bond lengths and angles calculated with the final atomic coordinates, it is concluded that the compound under investigation is perchloro-(1,4-dimethyl-5,8-dimethylenecycloocta-1,3,6-triene) as shown in Fig. 2. Consequently it has become almost certain that the structure of III$_a$ corresponds to perchloro-(3,4,7,8-tetramethylenecycloocta-1,5-diene) (VI).

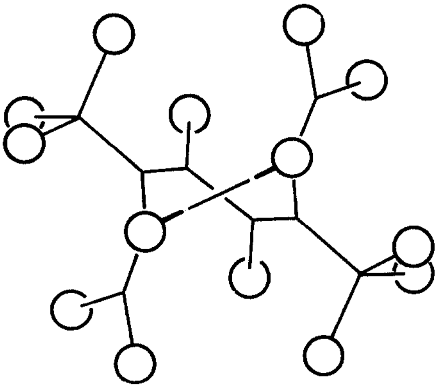


Fig. 1

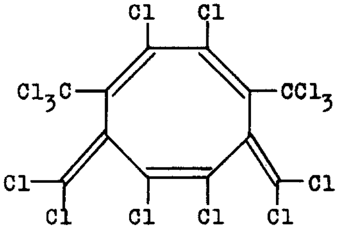


Fig. 2

The molecule has a site symmetry of C_2. The cyclooctatriene ring in the molecule has a somewhat distorted tub form, which is compared with that of cyclooctatetraene. In the molecule, any two adjacent double bonds among five do not lie in a plane, and hence there may be only weak conjugation between them. The conformation of the trichloromethyl group is such that one of the three mirror planes of the methyl group is almost coplanar with the plane of the ethylenic group, to which the methyl group is attached, and that one of the three C-Cl bonds is in a trans position with respect to the same ethylenic group.

All the calculations necessary for the present investigation were carried out on HITAC 5020 using our programs.

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