BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2518—2525 (1967)

The Crystal and Molecular Structure of Perchloro-(4, 8-dimethylene-tricyclo[3. 3. 2. $0^{1,5}$]deca-2, 6-diene)

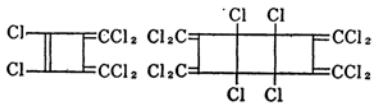
Akio Furusaki

Faculty of Science, Kwansei Gakuin University, Nishinomiya

(Received May 12, 1967)

The molecular structure of the compound of the formula $C_{12}Cl_{12}$, mp 273°C, obtained on the pyrolysis of perchloro-(3, 4-dimethylenecyclobutene) at about 250°C, has been determined by a three-dimensional X-ray crystal analysis. The crystal of the compound is monoclinic with four molecules in the unit cell of the dimensions $a=16.78$, $b=6.80$, $c=17.10$ Å and $\beta=116.5°$; the space group is $C2/c$. The positions of all the chlorine atoms were elucidated by using the minimum function method, and then those of all the carbon atoms were obtained from an electron density distribution calculated with the phases of chlorine atoms alone. The positional parameters of all the atoms thus obtained were refined by the block-diagonal matrix least-squares method with anisotropic temperature factors. The final discrepancy factor R is 0.094 excluding zero intensity data. As a result of the present study, it is concluded that the compound is perchloro-(4, 8-dimethylene-tricyclo[3.3.2.$0^{1,5}$]deca-2, 6-diene). Except the contacts between the chlorine atoms attached to the same carbon atom, there are several intramolecular Cl···Cl contacts with distances smaller than twice the ordinary van der Waals radius of the chlorine atom; *i. e.*, 3.06, 3.12, 3.13, 3.18 and 3.32 Å. However, it is found that these very close contacts do not seriously affect the bond lengths and angles in the molecule.

It has recently been reported that the pyrolytic reaction of perchloro-(3, 4-dimethylenecyclobutene) (I) gives at least four isomeric compounds of the formula $C_{12}Cl_{12}$.[1] The molecular structure of one of these isomers, perchloro-(3, 4, 7, 8-tetramethylene-tricyclo[4.2.0.$0^{2,5}$]octane) (II), has already been determined on the basis of chemical evidences.[1] The structure has also been confirmed by the X-ray crystal analysis.[2]



I II

It did not seem easy to determine by means of chemical reactions the molecular structure of another isomer, mp 273°C, obtained on the pyrolysis of I at about 250°C, since it was difficult to obtain the compound in sufficient quantity because of its very poor yield in the pyrolytic reaction.[1] However, since a number of single crystals suitable for X-ray measurement could fortunately be prepared,[1] the three-dimensional structure analysis has been carried out for the purpose of elucidating the molecular structure of the compound.

Experimental

Small single crystals, suitable for the structure determination, were kindly supplied by Professor Akira Fujino, Osaka City University. The crystals are colorless prisms, rather elongated in the direction of the monoclinic b axis. The crystal data were obtained from oscillation and Weissenberg photographs taken with Ni-filtered Cu$K\alpha$ radiation. The results are summarized in Table 1. From the systematic absences of reflections, hkl with $h+k$ odd and $h0l$ with l odd, the space group is concluded to be either Cc or $C2/c$. A statistical test[3] of the $h0l$ zone indicates centrosymmetry

1) K. Mano, K. Kusuda, A. Fujino and T. Sakan, *Tetrahedron Letters*, **1966**, 489.
2) A. Furusaki, This Bulletin, **40**, 758 (1967).
3) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

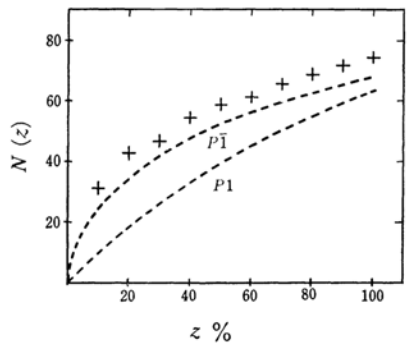


Fig. 1. $N(z)$ plot for $h0l$ reflections.

TABLE 1. CRYSTAL DATA

Monoclinic

$a = 16.78 \pm 0.04$ Å
$b = 6.80 \pm 0.02$
$c = 17.10 \pm 0.04$
$\beta = 116.5° \pm 0.3°$

Space group $C2/c$
Z 4
$\rho_{calcd.}$ 2.17 g cm^{-3}

as shown in Fig. 1. Therefore, the space group of this crystal is probably $C2/c$.

Equi-inclination integrating Weissenberg photographs were taken with Cu$K\alpha$ radiation for the zeroth to the fourth layer around the b axis and for the zeroth to the twelfth layer around the c. The intensities were estimated visually with the multiple-film technique and were corrected for the Lorentz and polarization factors. Though the cross-sections of the samples used were not small enough (about 0.15×0.2 mm for the b axis and 0.15×0.3 mm for the c), no correction was applied for the absorption effect. The partial resolution of α_1-α_2 doublets was not taken into account and only the α_1 spot intensities were measured where the doublets were completely resolved, since for the purpose of the present study the thermal vibrations of the atoms were not very important. Thus, the structure factors of 1432 independent reflections were obtained out of about 1800 possible reflections. Tentative scale and mean temperature factors were obtained by Wilson's method,[4] the latter being 3.25 Å^2.

All the calculations necessary to derive from the intensity data the structure factors in an absolute scale were carried out on Bendix G-20 at C. Itoh Electronic Computing Service Co., Ltd. using a program written by Yoshihisa Utsumi and Yujiro Tomiie of this University.

Structure Determination

The three-dimensional Patterson function $P(u, v, w)$ was calculated for u=0/60—30/60, v=0/30—15/30 and w=0/60—30/60 on the computer mentioned above using a program written by Y. Utsumi and Y. Tomiie.

Then, the following consideration was made on the Patterson map. It is certain that there are c-glide planes in the crystal in any case whether for the space group $C2/c$ or for Cc. If two independent chlorine atoms A(1) and A(2) are situated at (x_1, y_1, z_1) and (x_2, y_2, z_2) respectively, two chlorine atoms A(1′) and A(2′), related with A(1) and A(2) by a c-glide plane at $y=0$, should be placed at $(x_1, -y_1, 1/2+z_1)$ and $(x_2, -y_2, 1/2+z_2)$ respectively. The independent vectors among these four chlorine atoms are thus as follows,

$\boldsymbol{V}_1$ $(0, -2y_1, 1/2)$
$\boldsymbol{V}_2$ $(0, -2y_2, 1/2)$
$\boldsymbol{V}_3$ $(x_2-x_1, -y_2-y_1, 1/2+z_2-z_1)$
$\boldsymbol{V}_4$ $(x_2-x_1, -y_2+y_1, z_2-z_1)$

It is an important relation that the u components of the vectors $\boldsymbol{V}_3$ and $\boldsymbol{V}_4$ are identical, and the w components are different from each other just by 1/2. By comparing peaks with each other, making use of this relation, it becomes easy to pick up correctly a pair of peaks corresponding to $\boldsymbol{V}_3$ and $\boldsymbol{V}_4$ from the Patterson map.

The two peaks, both of which seemed to be a single peak judging from their height and shape, were chosen as $\boldsymbol{V}_3$ and $\boldsymbol{V}_4$. These are (5/60, 6/30, 33/60) and (5/60, 15/30, 3/60) respectively. Hence, $\boldsymbol{V}_1$ should be (0, −9/30, 1/2) and $\boldsymbol{V}_2$, (0, 21/30, 1/2). Thus the presence of the peaks corresponding to $\boldsymbol{V}_1$ and $\boldsymbol{V}_2$ was recognized, though they did not seem to be a single peak. In the case of the only presence of c-glide planes, x_1 and z_1 parameters can be arbitrarily chosen as $x_1=0$ and $z_1=0$. The relative coordinates of the four atoms mentioned above become as follows,

$A(1)$ (0, 4.5/30, 0)
$A(2)$ (5/60, −10.5/30, 3/60)
$A(1')$ (0, −4.5/30, 1/2)
$A(2')$ (5/60, 10.5/30, 33/60)

Only the y coordinates are conditioned to be so by the presence of the c-glide plane at $y=0$.

Using these four sets of coordinates, the minimum function method[5] was carried out on HITAC 5020 at the University of Tokyo with a program written by the author. The minimum function map thus drawn had a centrosymmetry. This is due to the use of the special vector $\boldsymbol{V}_4$ whose v component is 15/30. From this map with such extra symmetry, the twelve peaks corresponding to the chlorine atoms could be selected by examining whether the peaks could satisfy the Patterson map. The arrangement of the chlorine atoms thus obtained showed the presence of two-fold rotation axes, and hence it became certain that the corresponding space group is $C2/c$.

4) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

5) M. J. Buerger, *Acta Cryst.*, **4**, 531 (1951).

Table 2

(a) The final atomic coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cl(1)	0.2121	−0.1512	0.3168	C(1)	0.0468	0.0129	0.2909
Cl(2)	0.1070	−0.2723	0.1201	C(2)	0.1043	−0.0987	0.2582
Cl(3)	−0.0859	−0.2237	−0.0289	C(3)	0.0553	−0.1528	0.1724
Cl(4)	−0.2004	0.0089	0.0136	C(4)	−0.0364	−0.0865	0.1341
Cl(5)	0.0556	0.3641	0.3829	C(5)	0.0486	0.2356	0.2895
Cl(6)	0.1326	0.3338	0.2664	C(6)	−0.0997	−0.0973	0.0517

(b) The anisotropic temperature factors in form of $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{23}kl-_{31}lh)$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
Cl(1)	0.00186	0.02535	0.00305	0.00218	−0.00106	0.00144
Cl(2)	0.00323	0.01831	0.00271	0.00330	−0.00038	0.00336
Cl(3)	0.00369	0.02421	0.00229	0.00050	−0.00434	0.00202
Cl(4)	0.00256	0.02103	0.00261	0.00280	0.00155	0.00099
Cl(5)	0.00460	0.01483	0.00272	0.00161	−0.00217	0.00273
Cl(6)	0.00308	0.01784	0.00439	−0.00262	0.00257	0.00391
C(1)	0.00241	0.00954	0.00231	−0.00005	0.00063	0.00222
C(2)	0.00259	0.01967	0.00278	0.00018	−0.00227	0.00295
C(3)	0.00229	0.01257	0.00267	0.00129	0.00037	0.00242
C(4)	0.00245	0.01500	0.00217	0.00145	0.00227	0.00234
C(5)	0.00251	0.01347	0.00248	0.00045	0.00060	0.00214
C(6)	0.00302	0.01861	0.00233	0.00102	−0.00215	0.00204

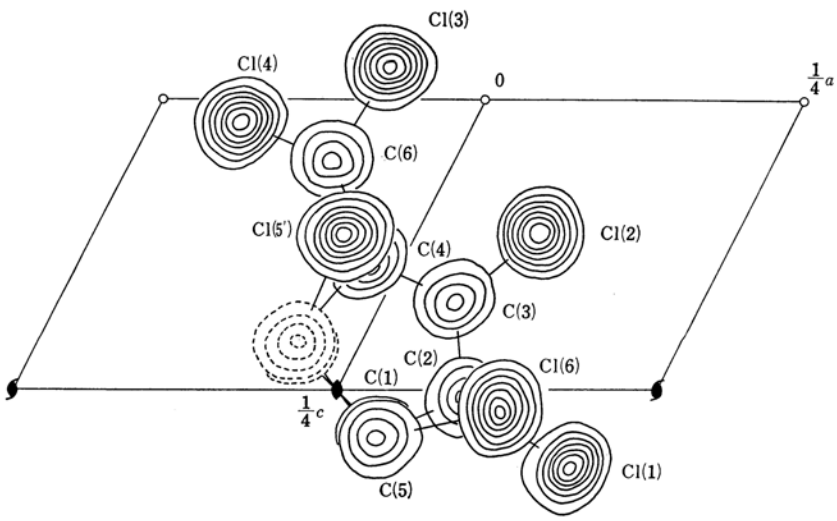


Fig. 2. A composite diagram of the (010) sections, taken through the atomic centers, of the final electron density distribution.
For carbon atoms, contours are drawn at intervals of 2e. Å^{-3}, beginning with 2e. Å^{-3}.
For chlorine atoms, contours are at intervals of 4e. Å^{-3}, beginning with 4e. Å^{-3}.

The atomic parameters of the six independent chlorine atoms were refined by the diagonal-matrix least-squares method with individual isotropic temperature factors on HITAC 5020 using a program written by the author. This treatment might be said to be more or less far from thoughtfulness. However, it has actually been revealed that the least-squares method shows unexpectedly good convergence and hence can be used in such a case as a very convenient method for a sort of structure test.[6] After three cycles of the refinement, the discrepancy factor R dropped from the

6) Y. Tomiie, I. Nitta, A. Furusaki, N. Sakabe, Y. Hirata, H. Matsuda, M. Nishikawa, K. Kamiya and M. Asai, Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

initial value 0.419 to 0.297.

At this stage, the positions of the carbon atoms has not been found yet, and hence the molecular structure of the compound under the present study remained unknown. In order to look for the coordinates of the light atoms, the Fourier synthesis was carried out by using Sim's method. In case of centrosymmetry, the statistical weight for each structure factor, W, is given by the following equation[7];

$$W = \tanh(|F||F_H| / \sum f_L^2)$$

where F is the observed structure factor in an absolute scale, F_H is that calculated with heavy atoms alone, and $\sum f_L^2$ is the sum of the squares of the atomic scattering factors of light atoms in a unit cell. From the three-dimensional electron density map thus obtained, the peaks corresponding to the six independent carbon atoms could be picked out easily owing to the distinct difference in height between these and ghost peaks.

The atomic parameters of all the atoms were refined by the diagonal-matrix least-squares method mentioned above on HITAC 5020. After five cycles of the refinement, R dropped from the initial value 0.184 to 0.158. After additional five cycles, the R factor reached a value of 0.144. The positional parameters were further refined by the block-diagonal matrix least-squares method with anisotropic temperature factors of the form

$$\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{23}kl-B_{31}lh).$$

After three cycles of the refinement, the R factor dropped to 0.094 excluding zero intensity data. The final atomic coordinates and temperature factors are listed in Table 2. Figure 2 shows the composite diagram of the (010) sections, taken as through the atomic centers in the molecule, of the final three-dimensional electron density distribution.

Discussion

The molecular framework obtained and the bond lengths and angles calculated with the final coordinates are shown in Figs. 3 and 4 respectively. The mean standard deviations of the atomic coordinates are 0.0038 and 0.013 Å for the chlorine and carbon atoms respectively. Accordingly the estimated standard deviations of the distances between the two mutually independent atoms are 0.005 for Cl–Cl, 0.014 for Cl–C and 0.018 Å for C–C distances, while those of the distances between the two atoms, related by a center of symmetry or a two-fold rotation axis, are 0.008 for Cl–Cl and 0.026 Å for C–C distances. Judging from the bond lengths and angles, it is concluded that the compound under the present investigation is per chloro-(4, 8-dimethylene-tricyclo[3.3.2.0^{1,5}]deca-2, 6-diene), the structural formula being as follows; The numbering of the carbon atoms in the present

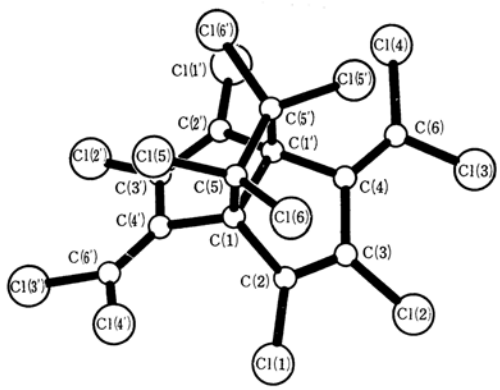


Fig. 3. The molecular framework of perchloro-(4, 8-dimethylene-tricyclo[3. 3. 2. 0^{1,5}]deca-2, 6-diene).

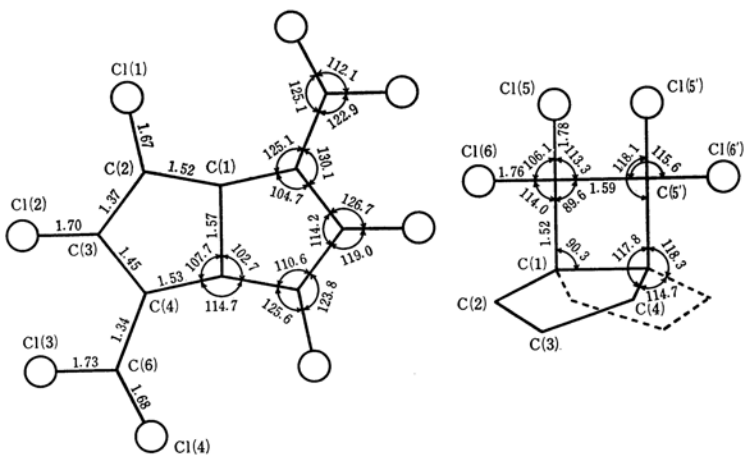
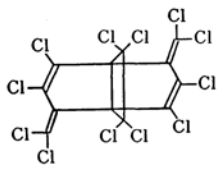


Fig. 4. The bond lengths (Å) and angles (°).

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



paper is somewhat different from that ordinarily used in organic chemistry. The correspondence of these two numbering systems is given in Table 3.

Table 3. The correspondence of the two numbering systems

Organic	Present	Organic	Present
C_1	C(1)	C_7	C(3′)
C_2	C(2)	C_8	C(4′)
C_3	C(3)	C_9	C(5)
C_4	C(4)	C_{10}	C(5′)
C_5	C(1′)	C_{11}	C(6)
C_6	C(2′)	C_{12}	C(6′)

The molecule has a site symmetry of C_2. The two-fold 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 internal angles of the four-membered ring (C(1), C(5), C(5′) and C(1′)) are all nearly 90°, but the ring is slightly deviated from a regular square. The lengths of the bonds C(1)–C(1′) and C(5)–C(5′) are 1.57 and 1.59 Å respectively, which are somewhat larger than those of the bonds C(1)–C(5) and C(1′)–C(5′), 1.52 Å. The two bonds C(1)–C(1′) and C(5)–C(5′) are both perpendicular to the *b* axis, and make an angle of about 3.6° with each other around the rotation axis. The azimuthal angle of the bonds C(1)–C(5) and C(1′)–C(5′) around the bond C(5)–C(5′) is nearly 3.4°, while the bonds C(5)–Cl(5) and C(5′)–Cl(6′) make an azimuthal angle of about 7.4° around the same bond C(5)–C(5′) and are somewhat deviated from the complete eclipsed conformation. The distance between the chlorine atoms Cl(5) and Cl(6′) is 3.06 Å, showing the very close approach between them. The sense of the deviation from the eclipsed form is such that the nearest of the contacts between one of the chlorine atoms of the dichloromethylene group and another chlorine atom in the same molecule, *i. e.*, the Cl(5)···Cl(4′) contact, becomes more or less apart. The lengths of the bonds C(5)–Cl(5) and C(5)–Cl(6) are 1.78 and 1.76 Å respectively, these values corresponding to those found in ordinary chlorinated paraffinic compounds.

The five-membered ring is also somewhat puckered. However, the six atoms C(1), C(2), C(3), C(4), Cl(1) and Cl(2) are nearly coplanar, and the best plane, determined as through these six atoms by the least-squares method, is described by the equation;

$$-0.4148X-0.8665Y+0.2777Z-1.765=0$$

where X, Y and Z are rectangular coordinates in Å unit; $X=x+z\cos\beta$, $Y=y$ and $Z=z\sin\beta$. The deviations of the atoms from this plane are given in Fig. 5. This figure shows that the dichloro-

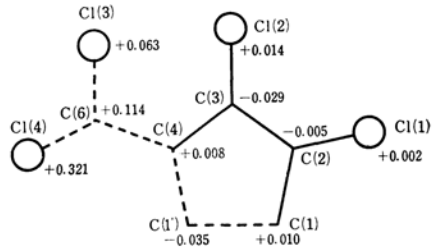


Fig. 5. Deviations of the atoms from the mean plane through C(1), C(2), C(3), C(4), Cl(1) and Cl(2).

methylene group (Cl(3), C(6) and Cl(4)) is fairly deviated from this plane toward the four-membered ring. In other words, the two conjugated double bonds C(2)–C(3) and C(4)–C(6) are about 6.5° twisted from the ideal trans-conformation around the bond C(3)–C(4). A more interesting fact is that the plane of the dichloromethylene group and that of the three atoms C(1′), C(4) and C(3) of the five-membered ring are fairly twisted around the double bond C(4)–C(6). Figure 6 shows such a twisting viewed along the bond C(4)–C(6). As shown in this figure, the bond C(6)–Cl(4) makes an azimuthal angle of about 4.2° with the bond C(4)–C(1′) around the bond C(4)–C(6) and the bond C(6)–Cl(3) does about 7.0° with the bond C(4)–C(3). Moreover, the angle of the bonds C(4)–C(1′) and C(4)–C(3) around the bond C(4)–C(6) is about 3.2° deviated from that which would be found if the atoms C(1′), C(3), C(4) and C(6) would lie on the same plane. On the other hand, the four atoms Cl(3), Cl(4), C(4) and C(6) are almost coplanar.

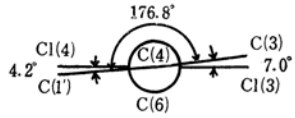


Fig. 6. The configuration of the atoms C(3), C(1′), Cl(3) and Cl(4) around the double bond C(4)–C(6).

The distortion of the double bond C(4)–C(6) mentioned above seems to be due to the strong repulsions between one of the chlorine atoms of the dichloromethylene group and another chlorine

atom in the same molecule, in particular between Cl(4) and Cl(1′) and between Cl(3) and Cl(2). These interatomic distances are 3.18 and 3.12 Å respectively, and are comparable to that between the chlorine atoms Cl(1) and Cl(2) attached in the cis-configuration to the ethylenic group, that is, 3.13 Å. The intramolecular Cl···Cl distances smaller than twice the van der Waals radius of chlorine atom are listed in Table 4.

Table 4. The intramolecular Cl···Cl distances shorter than 3.60 Å (in Å).

Cl(3)···Cl(4)	2.82
Cl(5)···Cl(6)	2.82
Cl(6)···Cl(5′)	3.06
Cl(2)···Cl(3)	3.12
Cl(1)···Cl(2)	3.13
Cl(4)···Cl(1′)	3.18
Cl(4)···Cl(5′)	3.32
Cl(1)···Cl(6)	3.52

The three bonds C(1)–C(2), C(1)–C(1′) and C(1′)–C(4) in the five-membered ring are respectively 1.52, 1.57 and 1.53 Å in length, approximately corresponding to the ordinary C–C single bond. The lengths of the three C–C bonds in the conjugated system (C(2), C(3), C(4) and C(6)) are 1.37 Å for C(2)–C(3), 1.34 Å for C(4)–C(6) and 1.45 Å for C(3)–C(4); these values are in agreement with those in buta-1, 3-diene, 1.35 and 1.46 Å.[8]

The lengths of the C–Cl bonds of chloroethylene-type are 1.67 Å for C(2)–Cl(1), 1.70 Å for C(3)–Cl(2), 1.73 Å for C(6)–Cl(3) and 1.68 Å for C(6)–Cl(4). In the present molecule, the average C–Cl bond distance, 1.69 Å, of chloroethylene-type is fairly smaller than that of chloromethane-type, 1.77 Å. The shortening of the bond may be partly explained by the change of carbon covalent radius due to the hybridization effect.[9] However, in order to explain further such remarkable shortening, we should take into consideration the conjugation effect between the carbon 2pπ and chlorine 3pπ orbitals. Similar bond shortening has been reported in chloroethylene,[10] chlorobenzene[11] and so on. It may be of interest to recognize that the distortion in the present molecule, due to the overcrowded chlorine contacts, does not seriously affect the bond shortening due to such conjugation effect.

Since the bond C(1)–C(1′) is held in common by the four-membered and the two five-membered rings, the conformation around this bond is interesting. The bonds C(1)–C(5) and C(1′)–C(5′)

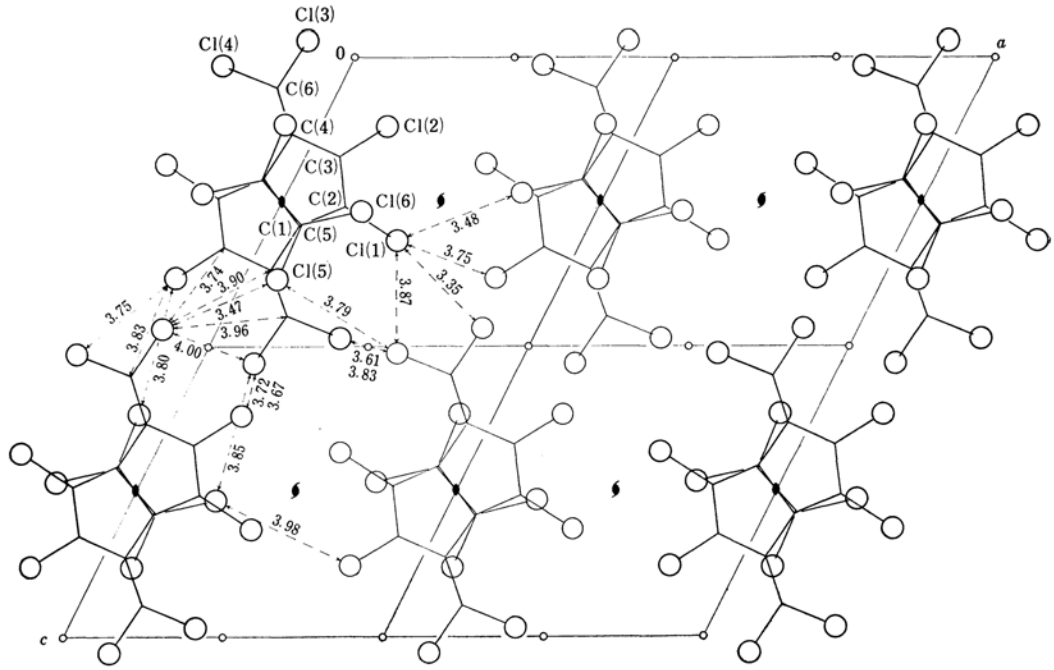


Fig. 7. The crystal structure viewed along the *b* axis.

8) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).
9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca (1960).
10) L. O. Brockway, J. Y. Beach and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2693 (1935).
11) L. O. Brockway and K. J. Palmer, *ibid.*, **59**, 2181 (1937).

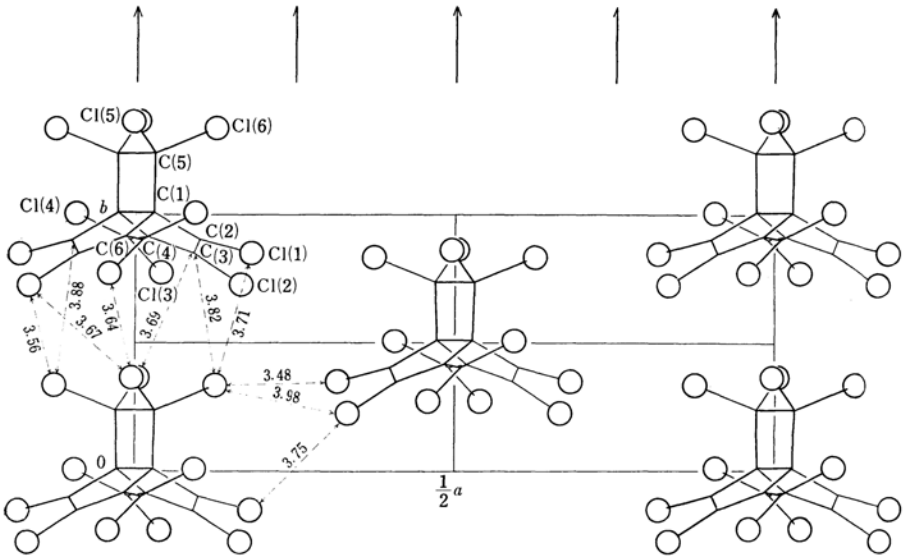


Fig. 8. The molecular layer at $z=0$, parallel to the (001) plane.

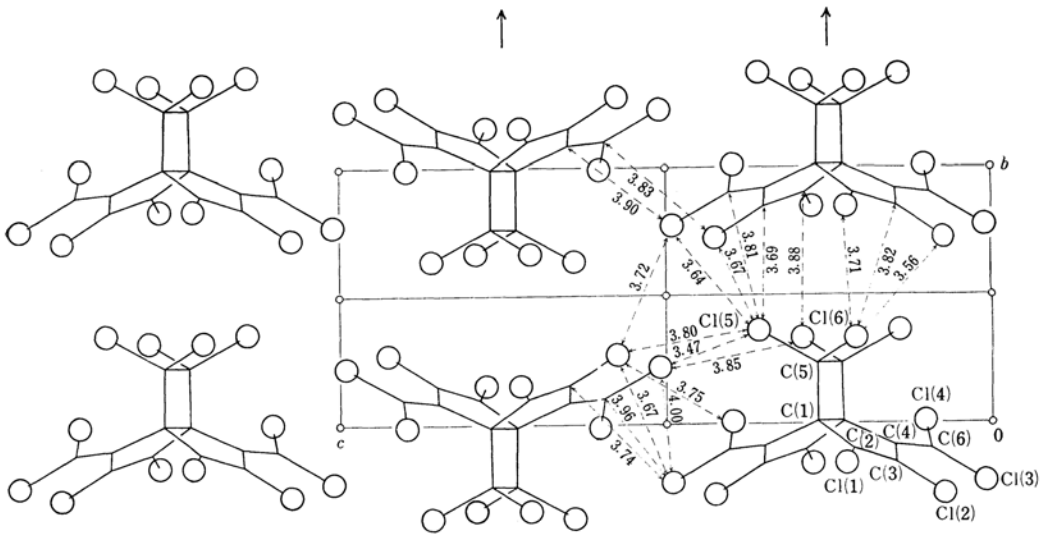


Fig. 9. The molecular layer at $x=0$, parallel to the (100) plane.

are about 3.5° twisted from the ideal cis-conformation, while the bonds C(1)–C(2) and C(1′)–C(4) are also about 3.1° twisted in the same sense. The average plane through the atoms C(2), C(1), C(1′) and C(4) makes the dihedral angle of 121.5° with that through the atoms C(2′), C(1′) C(1) and C(4′). Similarly the former makes the dihedral angle of 119.3° with that through the atoms C(5), C(1), C(1′) and C(5′).

The crystal structure viewed along the b axis is given in Fig. 7. It may be said that the present crystal, being a sort of racemic crystal, is composed of alternating molecular layers of D- and L-types, parallel to the (001) plane. The molecules of the same stereochemical type, related by two-fold screw axes or by translations, are arranged to form a two-dimensionally extended molecular layer parallel to (001) as shown in Fig. 8. Such molecular layers of the two types are alternately piled up in such a way that two adjacent layers are related with each other by a center of symmetry and a c-glide plane.

The intermolecular distances within such molecular layer, smaller than 4.0 Å, are given in Fig. 8. All these distances except two Cl···Cl pairs are larger than the sum of the van der Waals radii of

the atoms. One of these two close contacts occurs with a distance of 3.56 Å between the atom Cl(2) and the corresponding atom of the adjacent molecule, Cl(6′), related with Cl(6) by a translation along the b axis, while the other does with a distance of 3.48 Å between the atom Cl(1) and that, Cl(2′)′, related with Cl(2′) by a translation along the [110] or [$\bar{1}$10].

The distances between the molecular layers parallel to (001) are given in Figs. 7 and 9, the latter showing an arrangement of the molecules in a molecular layer parallel to (100). Two close Cl···Cl contacts are found here again. One of them is an approach between the atom Cl(1) and that of the next molecule, Cl(3)′, related with Cl(3) by a *n*-glide plane, the distance being 3.35 Å. The other contact occurs with a distance of 3.47 Å between the atom Cl(5) and that, Cl(3′)′, related with Cl(3′) by a center of symmetry.

It has already been suggested that the effective radius of chlorine atoms of chloroethylene-type may be fairly smaller than the usual van der Waals radius, 1.80 Å.[12] Of the four close intermolecular Cl···Cl contacts mentioned above, the two Cl(1)···Cl(2′)′ and Cl(1)···Cl(3)′ are contacts between the chlorine atoms of chloroethylene-type. On the other hand, the two remaining contacts Cl(2)···Cl(6)′ and Cl(3′)′···Cl(5) are approaches between the chlorine atom of chloroethylene-type and that of chloromethane-type. If half the smallest distance between the chlorine atoms of chloroethylene-type, found in the present crystal, 1.67 Å, is taken as their effective radius, these chlorine atoms can be made approach to those of chloromethane-type at a distance of 3.47 Å. Both distances of the contacts Cl(2)···Cl(6)′ and Cl(3′)′···Cl(5) are equal to, or larger than this critical value.

The intermolecular closest Cl···Cl contact found in the present crystal is numerically precisely comparable to that found in the crystal of chlorine at about −160°C, 3.34 Å,[13] where adjacent chlorine molecules are said to be connected together partly by weak covalent forces due to the $p\pi^* \rightarrow p\sigma^*$ charge transfer. In the present case also, similar forces may be exerted between the chlorine atoms of chloroethylene-type and between such atoms and those of chloromethane-type. Or, otherwise the chlorine atom of chloroethylene-type may be actually contracted owing to the displacement of a portion of the electrons in the outermost shell of the chlorine atom toward the ethylenic group.

Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan.*

The author is grateful to Professor Akira Fujino and his co-workers, Research Institute for Atomic Energy, Osaka City University, for providing him with the samples and for valuable discussions. The author also wishes to express his sincere thanks to Professor Isamu Nitta and Professor Yujiro Tomiie for their kind guidance and helpful discussions during this work. Thanks are also due to the staff of C. Itoh Electronic Computing Service Co., Ltd., for allowing freely the use of Bendix G-20.

12) A. Furusaki, This Bulletin, **40**, 758 (1967).

13) R. L. Collin, *Acta Cryst.*, **5**, 431 (1952).

* The complete data of the $F_o - F_c$ table are kept as Document No. 6706 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting in advance, ¥400 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.