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On the Isomerization of Dimers of Perchloro-(3,4-dimethylenecyclobutene) as Revealed by X-ray Methods

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The isomerization of several dimers of perchloro-(3,4-dimethylenecyclobutene) (I) has recently been reported by Fujino *et al.* Of these dimers, one (II) is transformed to other isomers (IIIa) and (IIIb) by means of pyrolysis at *ca.* 200°C. When heated to *ca.* 250°C, IIIa and IIIb are further converted into a fourth isomer (IV). The present X-ray study has revealed that II corresponds to perchloro-(3,4,7,8-tetramethylene-tricyclo[4.2.0.0^{2,5}]octane), as supposed from the chemical evidence, and IV, to perchloro-(4,8-dimethylene-tricyclo[3.3.2.0^{1,5}]deca-2,6-diene). It has been further established, from the results of the X-ray analysis of the dichloride of IIIa with the help of the chemical information, that IIIa and IIIb have the same two-dimensional chemical structure, perchloro-(3,4,7,8-tetramethylene-cycloocta-1,5-diene), rather than perchloro-(2,3,7,8-tetramethylene-bicyclo[4.2.0]octa-4-ene) which was speculated by Fujino *et al.*, and that IIIa and IIIb are different from each other in the conformation of the cyclooctadiene ring. These structures for II, IIIa, IIIb, and IV give a reasonable explanation of the mechanism of the successive isomerization reactions mentioned above.

It has been reported by Fujino *et al.* that the pyrolysis of perchloro-(3,4-dimethylenecyclobutene) (I) affords, depending on the heating temperature applied, at least four different isomeric compounds, $C_{12}Cl_{12}$.[1] Of these isomers, one (II), mp 166°C, is obtained from I in a 30% yield by means of pyrolysis at *ca.* 160°C, as is shown in Fig. 1. When heated to *ca.* 200°C, either as it is or in the medium of nitrobenzene, II is further transformed to a mixture of other isomers, (IIIa) and (IIIb), in which IIIa with a mp of 215°C dominates IIIb, mp 262°C. These two isomers show very similar IR absorption spectra in spite of fairly different chemical behavior. With the exception of its melting point, which is close, IIIb is different from II in all respects. Lastly, the application of pyrolysis at *ca.* 250°C to III results in a low-yield formation of the fourth isomer (IV), mp 273°C. III and IV are also derived directly from I through pyrolysis at 180—200°C and 250°C respectively. The yields are, however, much lower than those in the step-by-step conversion, since the direct transformation is always accompanied by the production of perchlorobenzene (ordinarily the major product), perchlorofulvene, perchloro-4-methylenecyclopent-1-ene, and an uncharacterized glassy material with the composition of $(CCl)_x$, which is the major product, particularly in higher-temperature pyrolyses in a solution.

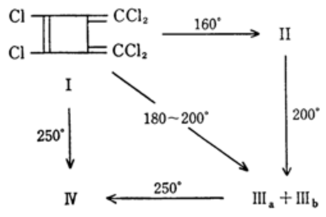
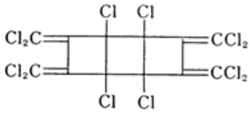


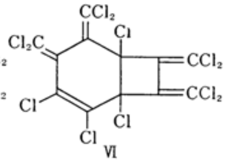
Fig. 1. The relationship among the four isomers of the formula $C_{12}Cl_{12}$.

Of the four isomers produced in the course of the pyrolytic transformation described above, II has been supposed, on the basis of the chemical analysis, to be perchloro-(3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane) (V).[1] Further, it has been tentatively proposed, on the basis of the chemical and IR data, that the two-dimensional chemical structure of IIIa and that of IIIb are both perchloro-(2,3,7,8-tetramethylene-bicyclo-[4.2.0]octa-4-ene) (VI).[1] On the other hand, the structure determination of IV by means of the chemical analysis did not seem feasible because of the poor yield of the compound in the pyrolytic reaction.

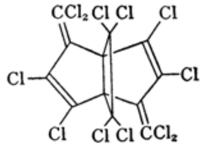
It is the purpose of the present study to confirm, or to determine by means of X-ray analysis, the molecular structures of II, III, and IV, and to elucidate the mechanism of the successive isomerization reactions. Of these substances, the molecular structures of II[2] and IV[3] have already been determined by such methods and found to correspond to V and VII respectively. Since, unfortunately, the sample supplied as IIIb was not such, but the dichloride of IIIa, the X-ray analysis has been carried out with this compound. However, the structure determination of the dichloride has enabled us to conclude unequivocally the structures of IIIa and IIIb.



V



VI



VII

All the samples used in the present experiment were kindly supplied by Professor Akira Fujino, Research Institute for Atomic Energy, Osaka City University. The calculations necessary for the present study were carried out on a Bendix G-20 computer at the C. Itoh Electronic Computing Service Co., Ltd., and on a HITAC 5020 computer at the University of Tokyo, using programs devised at this laboratory.

Structure Determination of th Dichloride of IIIa

Experimental. The crystals of the dichloride of the isomer IIIa were colorless and in the shape of thick rhombic plates. The samples used were cut out from thse crystals into adequate rod-shapes with a razor. The crystal data have been derived from Weissenberg photographs around the *a* and *b* axes, taken with Cu$K\alpha$ radiation; the results are summarized in Table 1. From the systematic absences, the space group was found to be either

TABLE 1. CRYSTAL DATA OF THE DICHLORIDE OF IIIa

Monoclinic	
	$a=17.16\pm0.04$ Å
	$b=9.31\pm0.03$
	$c=13.73\pm0.04$
	$\beta=91.8°\pm0.3°$
Space group	*C2/c*
Z	4
ρ_{calcd}	1.94 g/cm³

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[1] K. Mano, K. Kusuda, A. Fujino and T. Sakan, *Tetrahedron Letters*, **1966**, 489.

[2] A. Furusaki, This Bulletin, **40**, 758 (1967).

[3] A. Furusaki, *ibid.*, **40**, 2518 (1967).

*C*2/*c* or *Cc*. As a final result of the present analysis, the former has been concluded to be the corresponding group.

In order to collect three-dimensional intensity data, equi-inclination Weissenberg photographs were taken with Ni-filtered Cu$K\alpha$ radiation for the zeroth to the twelfth layer around the *a* axis and for the zeroth to the sixth layer around the *b* axis. The intensities were measured visually using a calibrated scale. Due to the rule of absences corresponding to *C*2/*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 in order to obtain an approximate intensity ratio between two such types of reflections. This intensity ratio was then revalued by a comparison of the observed and calculated structure factors in the course of analysis. Thus, the structure factors of 1683 reflections were uniquely derived; they were then converted into an absolute scale by Wilson's method. Though the samples used were not very small, no correction was applied with regard to the absorption effect.

Structure Determination. The crystal structure was successfully elucidated by using the same method as was applied to the structure determination of IV.[3] The three vectors used for the minimum function method were (3/60, 11/30, 7/60), (33/60, 12/30, 37/60), and (30/60, 23/30, 30/60). 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 presently being studied had the molecular formula $C_{12}Cl_{12}$, the twelve peaks were chosen as the chlorine atoms out of the twenty-four peaks solely 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 *C*2/*c*, as has already been mentioned.

The coordinates of the chlorine atoms were refined by the use of the diagonal-matrix least-squares method. However, five cycles of the refinement lowered the *R* factor from its initial value of 0.46 by only 0.05. In order to ascertain the correctness of the structure obtained from the minimum function, a three-dimensional electron density distribution was calculated using Sim's method.[4] 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 presently being studied might not be $C_{12}Cl_{12}$, but $C_{12}Cl_{14}$. This was also supported by the fact that, for the $C_{12}Cl_{12}$ formula, the calculated density is 1.73 g/cm^3; this value seems too small compared with those of II and IV, 2.07 and 2.17 g/cm^3 respectively, the crystal structures of which have already been determined.

The atomic parameters of the seven chlorine and six carbon atoms were refined by the use of the diagonal-matrix least-squares method with individual isotropic temperature factors using 1319 data around the *b* axis. After five cycles, the *R* factor dropped only to 0.207. This large value may be due to the weakness of the reflection intensities recorded on the Weissenberg photographs, or it may be attributed to the absorption effect, since the samples used were not small enough, as has been mentioned already. The electron density distribution, calculated at this stage using all the observed data, is given in Fig. 2. Further, the atomic coordinates were refined by the block-diagonal-matrix least-squares method assuming anisotropic thermal motions of all the atoms using 827 data around the *b* axis except for very weak reflections. After three cycles of the refinement, *R* was lowered to 0.100. The final atomic parameters thus obtained are listed in Table 2.

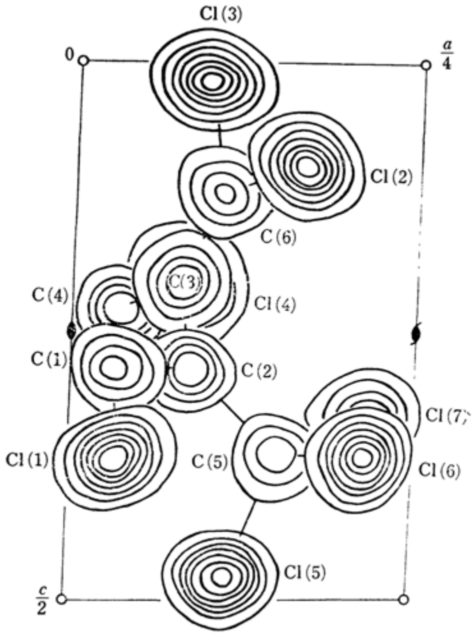

Fig. 2. The electron density distribution of the dichloride of IIIa.
A composite diagram of the (010) sections taken as through the atomic centers. Contours are at intervals of 2 e/Å^3 for carbon atoms and 4 e/Å^3 for chlorine atoms, beginning at 2 e/Å^3.

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

TABLE 2.

(a) The final atomic coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cl(1)	0.4676	−0.0553	0.1329	C(1)	0.4644	0.0821	0.2130
Cl(2)	0.3343	0.1296	0.4031	C(2)	0.4140	0.1861	0.2144
Cl(3)	0.4046	0.3834	0.4806	C(3)	0.4206	0.3043	0.2962
Cl(4)	0.4189	0.5938	0.2943	C(4)	0.4625	0.4332	0.2684
Cl(5)	0.3852	0.2339	0.0206	C(5)	0.3460	0.2042	0.1329
Cl(6)	0.2862	0.0486	0.1322	C(6)	0.3911	0.2752	0.3764
Cl(7)	0.2856	0.3508	0.1658				

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

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
Cl(1)	0.00313	0.00673	0.00472	0.00266	−0.00671	−0.00186
Cl(2)	0.00425	0.00948	0.00450	−0.00706	0.00042	0.00261
Cl(3)	0.00446	0.01045	0.00357	−0.00023	−0.00512	0.00101
Cl(4)	0.00344	0.00229	0.00746	0.00168	−0.00203	0.00363
Cl(5)	0.00396	0.01124	0.00307	−0.00097	0.00422	−0.00082
Cl(6)	0.00229	0.01263	0.00552	−0.00527	0.00070	−0.00157
Cl(7)	0.00436	0.01519	0.00825	0.01197	−0.01118	−0.00657
C(1)	0.00140	0.00473	0.00257	0.00047	−0.00183	0.00026
C(2)	0.00166	0.00534	0.00285	−0.00187	0.00014	0.00073
C(3)	0.00215	0.00330	0.00442	−0.00162	−0.00294	0.00121
C(4)	0.00206	0.00375	0.00366	−0.00089	−0.00309	0.00012
C(5)	0.00299	0.01413	0.00545	−0.00184	−0.01025	0.00160
C(6)	0.00237	0.00820	0.00382	0.00098	−0.00035	0.00529

Description of the Structure of the Dichloride of IIIa

The molecular framework thus obtained and the bond lengths and angles calculated with the final atomic coordinates are shown in Figs. 3 and 4 respectively. The standard deviations of the coordinates are 0.008 Å for chlorine atoms and 0.021 Å for carbon atoms; therefore, those of the distances between mutually-independent atoms are 0.022 Å for C–Cl and 0.030 Å for C–C. Judging from the present results, it may be concluded that the dichloride of the isomer IIIa corresponds to perchloro-(1,4-dimethyl-5,8-dimethylene-cycloocta-1,3,6-triene).

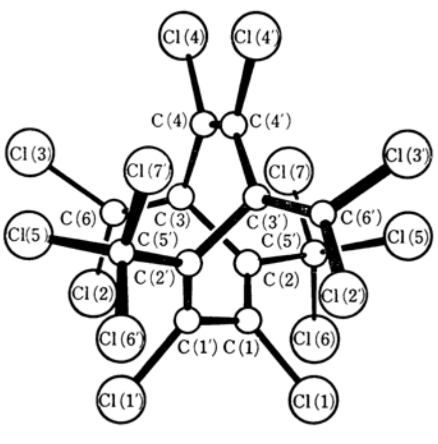


Fig. 3. The molecular framework of the dichloride of IIIa.

The molecule has a symmetry of C_2, the diad of which coincides with a crystallographic one and runs parallel to the mean plane of the cyclooctatriene ring. The ring has a somewhat distorted tub-form compared with that of cyclooctatetraene.

The mean plane through the six atoms, Cl(1), C(1), C(2), C(3), C(5), and C(1′), is determined by means of the least-squares method as the following equation:

$$0.5904X+0.5489Y-0.5916Z-3.374=0 \quad (1)$$

where X, Y, and Z are the rectangular coordinates in Å unit, where $X=x+z\cos\beta$, $Y=y$, and $Z=z\sin\beta$. As is shown in Fig. 5, four of the six atoms, Cl(1), C(1), C(2), and C(3), are nearly coplanar, but the C(5)–C(2)–C(1)–C(1′) segment is somewhat concave toward the center of the molecule. Such a deviation from planarity may be due to the close approaches between Cl(1) and the trichloromethyl group (Cl(5), Cl(6), Cl(7), or C(5)) and between Cl(1) and Cl(1′); Cl(1) is located at distances of 3.19 Å from C(5), 3.26 Å from Cl(6), 3.39 Å from Cl(5), and 3.37 Å from Cl(1′). As is shown in Fig. 6, the trichloromethyl group takes such a conformation around the C(2)–C(5) bond that one

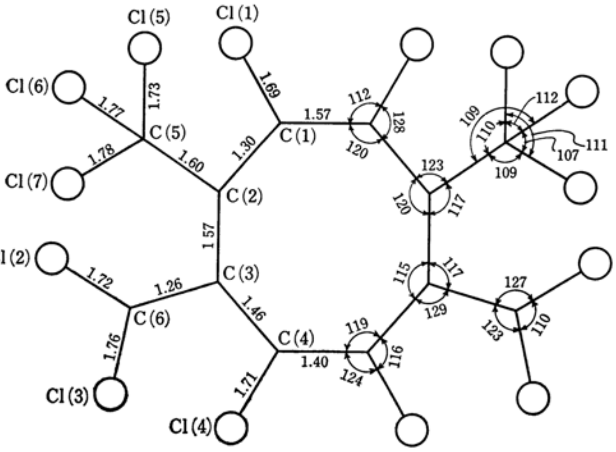


Fig. 4. The bond lengths (Å) and angles (°) of the dichloride of IIIa.

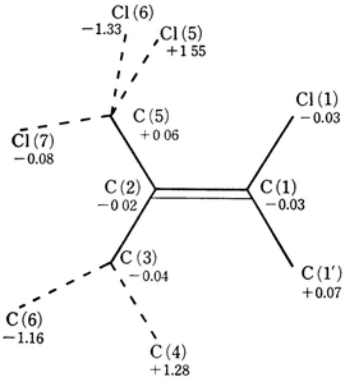


Fig. 5. The deviations of the atoms from the mean plane (1).

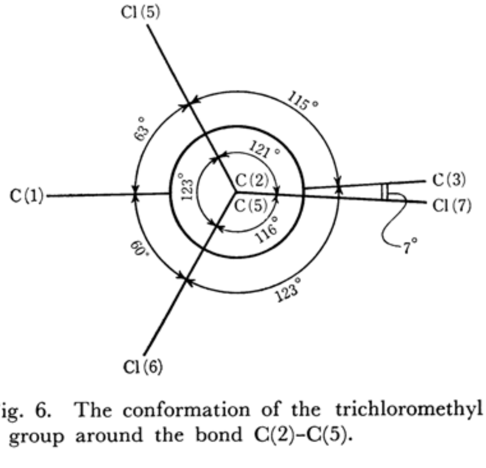


Fig. 6. The conformation of the trichloromethyl group around the bond C(2)-C(5).

of the three planes of the trichloromethyl group, through Cl(7), C(2), and C(5), is approximately coplanar with the plane (1) given above, Cl(7) being most remote from Cl(1). The adjacent endo-cyclic double bonds, C(1)–C(2) and C(1′)–C(2′), deviate by 62° from the virtual cis-conformation around C(1)–C(1′). Since, besides, the bond distance C(1)–C(1′) is about 1.57 Å, the conjugation between these two double bonds seems to be very weak.

The best plane, determined to run through Cl(2), Cl(3), C(2), C(3), C(4) and C(6), is described by the equation:

$$0.8305\,X-0.4715\,Y+0.2966\,Z-5.772=0$$

Figure 7 shows the deviations of the atoms from this plane. The double bond C(3)–C(6) is shown to be twisted to a considerable degree. Since, of these six atoms, two sets, Cl(2), Cl(3), C(3), and C(6), and C(2), C(3), C(4), and C(6), are almost coplanar, the angle of twisting around C(3)–C(6) is represented by the angle between the mean planes of these two sets of atoms; the twisting angle is estimated at about 8°. The sense of this twisting is just such that the chlorine atoms, Cl(3) and Cl(4), separate from each other, giving rise to an interatomic distance still with a value of 3.24 Å.

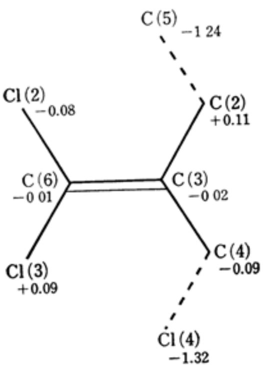


Fig. 7. The deviations of the atoms from the mean plane,
$0.8305X-0.4715Y+0.2966Z-5.772=0.$

Since the double bond C(3)–C(6) makes an azimuthal angle of about 96° with C(1)–C(2), these two double bonds seem hardly to be conjugated at all. This idea is supported by the fact that the bond, C(2)–C(3), between the two double bonds is about 1.57 Å long. As a result of the large azimuthal angle (about 81°) of the bonds, C(2)–C(5) and C(3)–C(6), around C(2)–C(3), the trichloromethyl group and the dichloromethylene group adjoining to it are sufficiently apart from each other; the nearest approach between their chlorine atoms occurs between Cl(2) and Cl(7), when the distance is 3.92 Å.

The six atoms, Cl(4), C(3), C(4), Cl(4′) C(3′), and C(4′) (the double bond of which is C(4)–C(4′)), are nearly coplanar in spite of the close approach between Cl(4) and Cl(4′) at a distance of 3.07 Å, their mean plane being described by the equation:

$$0.4020X + 0.9156Z - 6.546 = 0$$

The deviations of the atoms from this plane are shown in Fig. 8. The double bond C(4)–C(4′) makes an azimuthal angle of about 125° with C(3)–C(6) and C(3′)–C(3′). These three double bonds are closest to planarity among all the pairs of double bonds adjacent to each central single bond. The length of the C(3)–C(4) bond is 1.46 Å, and that of C(4)–C(4′), 1.40 Å. Thus, it may be concluded that the three double bonds are conjugated with one another to a certain extent.

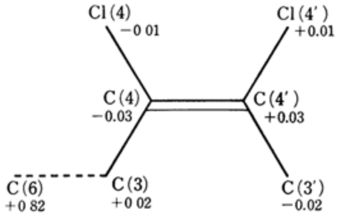


Fig. 8. The deviations of the atoms from the mean plane.
$0.4020X + 0.9156Z - 6.546 = 0.$

The projection of the crystal sturcture along the *a* and *b* axes are shown in Figs. 9 and 10 respectively, where all the intermolecular distances smaller than 4.0 Å are also given. It is of interest to note that the center of a molecule is located at $x=1/2$, $y \approx 1/4$, and $z=1/4$; therefore, those of the three remaining molecules in the unit cell are situated at approximately (0, 3/4, 1/4), (0, 1/4, 3/4),

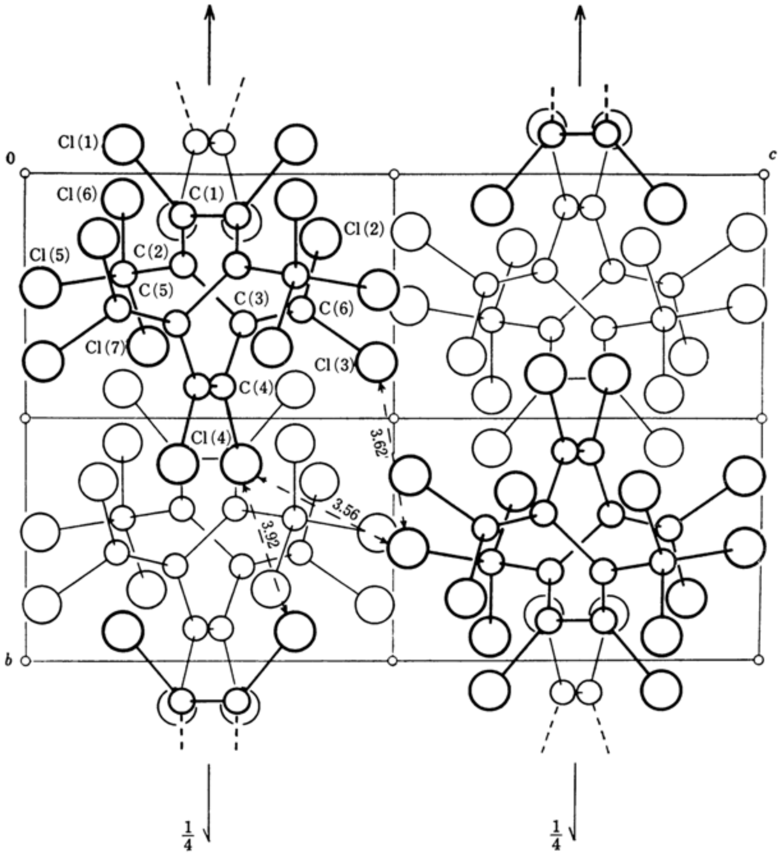


Fig. 9. The crystal structure of the dichloride of IIIa viewed along the *a* axis.

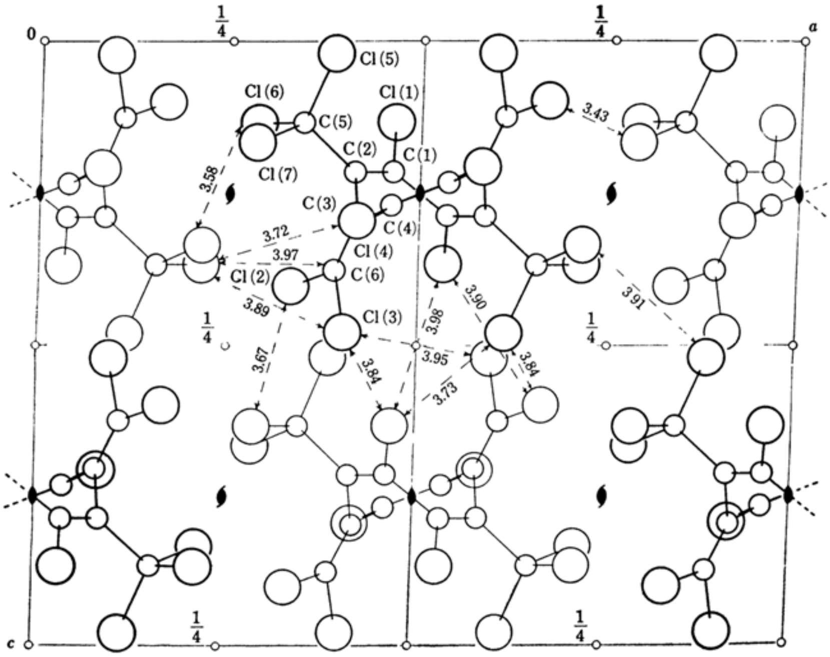


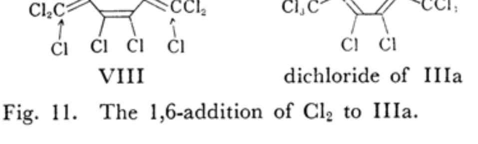
Fig. 10. The crystal structure of the dichloride of IIIa viewed along the *b* axis.

and (1/2, 3/4, 3/4); these four sets of coordinates correspond to those of lattice points in the face-centered cubic lattice. If adjacent molecules with intermolecular contacts of less than 4.0 Å are taken as nearest neighbors, each molecule is found to have twelve nearest neighbors. The central molecule at the height of $y \approx 1/4$ has two neighbors at the same height, four at the $y \approx -1/4$ height, four at $y = 3/4$, and two just above and below. Due to the deviation of the molecular form from an ideal sphere, the three principal axes, *a*, *b*, and *c*, are not equal in length, but are in the ratio 1.84 : 1.00 : 1.47, the β angle deviating from a right angle by 1.8°.

As in II and IV, in the present crystal also close intermolecular Cl···Cl contacts are found: 3.43, 3.56, and 3.58 Å. Of these three close contacts, the former two occur between the chlorine atoms, one of the chloroethylene type and the other of the chloromethane type. The last one is that between the chlorine atoms, both of the chloromethane type. The difference between this observed distance and twice the standard van der Waals radius, 3.60 Å, may not be significant considering the accuracy of the present determination. Thus, the closer approaches found in the present crystal may be looked upon as due to the chlorine atoms of the chloroethylene type.

Discussion

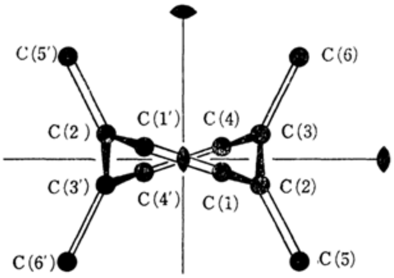
All the molecular sturctures of II, IV, and the dichloride of IIIa have now been elucidated by means of X-ray analysis. Judging from the facts that IIIa reacts with liquid chlorine to form its dichloride, while the dichloride loses two chlorine atoms in the presence of Raney nickel to form IIIa, IIIa should have a structure closely similar to that of its dichloride. Thus, it may be concluded that the two-dimensional chemical structure of IIIa is perchloro-(3,4,7,8-tetramethylene-cycloocta-1,5-diene) (VIII) rather than perchloro-(2,3,7,8-tetramethylene-bicyclo[4.2.0]octa-4-ene) (VI), which, as has already been mentioned, was proposed from the chemical analysis. For the former, the formation of the dichloride can be simply explained through the 1,6-addition of chlorine to IIIa, as is shown in Fig. 11, whereas, for the latter, any explanation has to assume a complicated structural change.

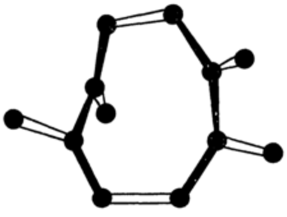


VIII dichloride of IIIa

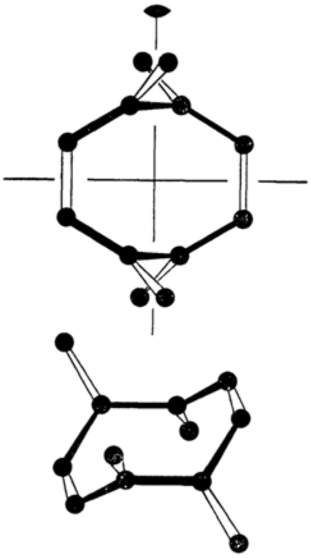
Fig. 11. The 1,6-addition of Cl_2 to IIIa.

As for the structure VIII, the conceivable molecular forms can be divided into two groups. Of these two, the one (VIIIa) with a twisted ring has a symmetry of D_2, but this molecular form can be easily changed into another with a lower symmetry C_2 by a conformational change around the single bonds. On the other hand, the other group (VIIIb) has a symmetry of C_{2h}, and the cyclooctadiene ring takes the very rigid frame of a chair-like form.





VIIIa



VIIIb

The molecular structure VIIIa makes possible a lucid explanation of the isomerization reaction of III into IV. In VIIIa, the two exo-cyclic double bonds, C(2)–C(5) and C(3)′–C(6′), or C(3)–C(6) and C(2′)–C(5′), which are to form a four-membered ring, stand out to the same side of the mean plane of the ring: moreover, because of the ring's flexibility, these bonds can approach each other without much bond distortion. Thus, the addition reaction of such two double bonds results in the formation of a four-membered ring, giving rise to IV, as is shown in Fig. 12. On the other side, neither VI nor VIIIb can give so adequate an explanation of the isomerization of III as VIIIa can. Thus, it is reasonable to consider that VIIIa is the molecular structure of either IIIa or IIIb.

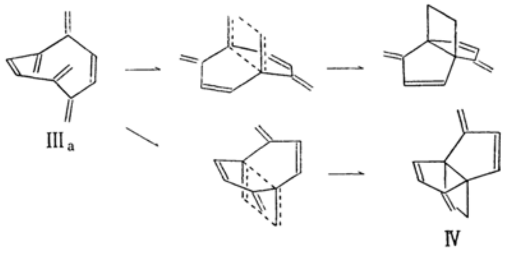


Fig. 12. The process of the isomerization of IIIa into IV.

From the similarity of the IR data, it has been proposed by Fujino *et al.* that two isomers, IIIa and IIIb, have the same two-dimensional chemical structure. According to them, it seems that either the molecular structure of IIIa corresponds to VIIIa and IIIb to VIIIb, or *vice versa*. The former possibility seems to be more probable judging from the following points. In the first place, the fact that IIIb resists the oxydization of nitric acid and the addition of chlorine, while IIIa does not, seems to favor the present conclusion that IIIb has an inflexible and rigid structure, VIIIb, while IIIa has a labile and deformable structure, VIIIa, which is more likely to be attacked by reagents. Further, the change in the π-bond location seems to be effected by the attack of chlorine more smoothly in VIIIa than in VIIIb, because the part which is concerned with the 1,6-addition of chlorine is closer to planarity in the former. The unchanged part of the 1,6-addition product found in the present analysis is more similar in conformation to the corresponding part of VIIIa than to that of VIIIb, as is shown in Fig. 13. Therefore, it may be concluded that the molecular structure of IIIa, the precursor of the 1,6-addition

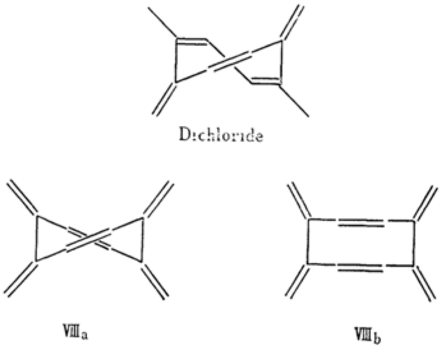


Fig. 13. The conformational resemblance of VIIIa to the dichloride.

product, corresponds to VIIIa rather than to VIIIb.

The transformation of IIIa into IV has already been explained. Thus, the only remaining problem is to elucidate how II is transformed into IIIa and IIIb. As has been mentioned above, the molecular structure of II has been found to be perchloro-(3,4,7,8-tetramethylene-tricyclo-[4.2.0.0^{2,5}]octane) (V) by the X-ray method. The three adjoining four-membered rings take a chair-like form, and the two pairs of alternating double bonds are both nearly planar. Thus, the whole molecule has a symmetry of C_{2h}. It seems reasonable to suppose that the transformation of II begins with the cleavage of the two single bonds which partition the eight-membered ring into three four-membered rings. As this cleavage proceeds, two dichloromethylene groups in the same conjugated system come to be unable to keep their planarity because these groups move on toward each other due to the relaxation of the considerable bond distortions in the three adjoining four-membered rings. Thus, two exo-cyclic double bonds, C(2)–C(5) and C(3)–C(6), or C(2′)–C(5′) and C(3′)–C(6′), are rotated around the single bond, C(2)–C(3) or C(2′)–C(3′), so as to avoid close approaches between the dichloromethylene groups. In this case, there are two different ways conceivable as to how the two pairs of the adjoining double bonds deviate from their planar conformation. One is that out of the molecular symmetry, C_{2h}, of II, a center of symmetry is preserved, as is shown in Fig. 14; the other is that a two-fold rotation symmetry is kept, as is shown in Fig. 15. Of course, such rotations around the single bonds, C(2)–C(3) and C(2′)–C(3′), are accompanied by a change in the conformation around the bonds, C(1)–C(1′) and C(4)–C(4′). Then new π-bonds begin to be formed, as the conformation around the latter bonds becomes favorable for the overlapping of the 2pπ-orbitals of these two pairs of atoms. Thus, one may assume two possible processes of the isomerization reaction; in the former, the isomer IIIb, with a molecular symmetry of C_{2h}, is formed, while in the latter the other isomer, IIIa, with C_2 or D_2 is formed.

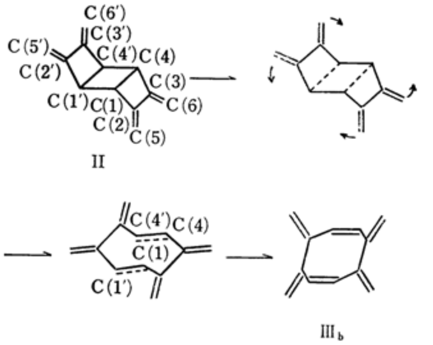


Fig. 14. The process of the isomerization of II into IIIb.

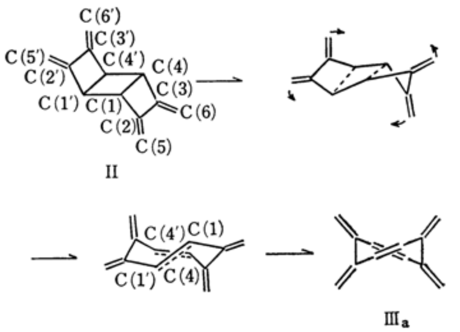


Fig. 15. The process of the isomerization of II into IIIa.

After all, the problems regarding the mechanism of the successive isomerization reactions posed in the introduction to the present paper may be looked upon as solved through the series of X-ray structure analyses made on the compounds II, the dichloride of IIIa, and IV.

Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan.[*1]

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[*1] The complete data of the F_o-F_c table are kept as Document No. 6804 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, ¥300 for photoprints. Pay by check or money order, payable to: Chemical Society of Japan.