BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 818—826 (1966)

The Crystal Structure of 1, 2, 3, 4-Tetrachlorobenzo[g]sesquifulvalene

By Yoriko Nishi, Yoshio Sasada, Tamaichi Ashida and Masao Kakudo

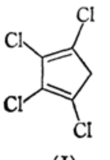
Institute for Protein Research, Osaka University, Joancho, Kita-ku, Osaka

(Received September 20, 1965)

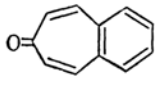
The molecular structure of 1, 2, 3, 4-tetrachlorobenzo[g]sesquifulvalene has been ascertained by X-ray crystal analysis. The crystal of this substance is monoclinic, with four molecules in a unit cell of dimensions: $a=21.31$, $b=16.88$, $c=3.83$ Å, and $\beta=93.3°$, the space group being $P2_1/a$. The crystal structure was determined by the Harker-Kasper inequality and the Sayer's method. The atomic coordinates and the anisotropic temperature factors of each atom were refined by the block-diagonal-matrix least-squares method. The average length of the C–Cl bonds is 1.705 Å, a value which is in good agreement with those of several chlorobenzenes. In the sesquifulvalene skeleton, longer and shorter bonds are disposed as may be expected from the conventional chemical formula. The average length of the longer bonds is 1.461 Å, while that of the shorter ones is 1.354 Å. The mean C–C bond length in the benzene ring is 1.413 Å. The whole molecule is not on a plane, although the component ring systems are nearly planar. The five-membered ring and the seven-membered ring twist to each other by an angle of about 31° around the bond connecting these two rings. This might be due to the repulsion forces between chlorine and hydrogen atoms which approach each other closely. The plane of the seven-membered ring makes an angle of about 5° with that of the six-membered ring.

In attempting to synthesize some derivatives of sesquifulvalene (cycloheptatrienylidenecyclopentadiene), Kitahara, Murata, Funamizu and Asano[1] have found that there action of tropone with 1, 2, 3, 4-tetrachlorocyclopentadiene (I) in methanol results in a mixture of 1, 2, 3-trichloro-6-(*o*-methoxyphenyl)fulvene and the corresponding para-isomer. This is an entirely new type of rearrangement reaction, in which the methoxy group enters the seven-membered ring (a six-membered ring after the rearrangement) and in which a chlorine atom in the five-membered ring is liberated. This chemical conclusion was confirmed by an independent crystal structure determination of an analogous product containing bromine atoms.[2]

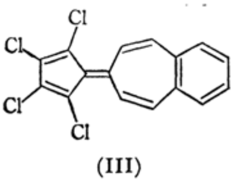
Such a kind of rearrangement could be avoided by using benzo[d]tropone (II) instead of tropone; the product, in the form of fine violet needles, may be supposed to be 1, 2, 3, 4-tetrachlorobenzo-[g]sesquifulvalene (III).[3]



(I)



(II)



(III)

The results of the elementary analysis of the substance also supported this formula. For an independent verification of the structure by means of X-ray analysis, a sample of the compound was supplied to us by Professor Yoshio Kitahara of Tohoku University.

The stereochemistry of this compound is also interesting. If the molecule is planar, or nearly so, as may be expected from the chemical formula, much steric hindrance should be exerted between Cl(1) and the hydrogen atom bonded to C(10), and between Cl(4) and the hydrogen bonded to C(5). In addition to the establishment of the chemical formula, this investigation has been carried out in order to clarify the molecular configuration and the features of the steric hindrance.

The present paper will describe the structure determination of this compound by the three-dimensional Fourier and least-squares methods.

Experimental

The crystals of 1, 2, 3, 4-tetrachlorobenzo[g]sesquifulvalene are deep violet needles elongated along the c axis.

The crystallographic and physical data found are as follows:

1, 2, 3, 4-Tetrachlorobenzo[g]sesquifulvalene, $C_{16}H_8Cl_4$.
M.p.: 234°C.
Monoclinic: $a=21.31\pm0.05$, $b=16.88\pm0.03$,
$c=3.83\pm0.02$ Å, $\beta=93.3\pm0.3°$.
Volume of the unit cell: 1375.3 Å^3.
Density observed by the floatation method; 1.64 g.cm^{-3}
Density calculated; 1.65 g.cm^{-3}
Number of molecules in the unit cell: 4

---

[1] Y. Kitahara, I. Murata, M. Funamizu and T. Asano, This Bulletin, **37**, 1399 (1964).

[2] Y. Kato, Y. Sasada and M. Kakudo, ibid., **38**, 1761 (1965).

[3] Y. Kitahara, I. Murata and S. Katagiri, *Angew. Chem.*, **77**, 345 (1965).

Absent spectra: ($h0l$) when h is odd,
($0k0$) when k is odd
Space group: $P2_1/a$.

The crystal was found to be twin; the X-ray photographs showed that the twinning occurred with a common (100) plane. The crystals were so thin along the c axis that it was impossible to obtain a single crystal. Therefore, we selected a few crystals in which one component of the twin was as small as possible.

Copper $K\alpha$ radiation was used with a nickel filter. The intensity data were collected only for the ($hk0$), ($hk1$) and ($hk2$) zones by means of equi-inclination Weissenberg photographs. In order to correlate strong and weak reflections, the multiple-film technique was applied, the relative intensities being ranged between 3300 and 1 for ($hk0$), between 5000 and 1 for ($hk1$), and between 350 and 1 for ($hk2$). The maximum ($2\sin\theta$)'s of the observed reflections were 1.98, 1.66 and 1.75 for ($hk0$), ($hk1$) and ($hk2$) respectively. 277 independent reflections out of 418 possible ($hk0$), and 428 out of 935 ($hk1$) and ($hk2$), were observed within the above-mentioned ranges.

Precession photographs were also taken for the ($h0l$) zone in order to determine the relative scale factors among the three layers of the Weissenberg photographs. The crystal used had a cross section of about 0.1×0.03 mm.

The intensities were estimated visually by comparison with a standard intensity scale prepared using the same crystal. Corrections for Lorentz and polarization factors were applied as usual, while the absorption effect was neglected because of the small size of the crystal used in the experiment. The observed structure factors were then put onto a tentative absolute scale by means of Wilson's statistics.[4)]

Structure Determination

Structure Projected along the c Axis.—Since the c axis of the crystal is short, the molecule was supposed to be approximately planar and almost parallel to the (001) plane. In order to locate the four chlorine atoms, the sharpened Patterson projections on the (001) plane were synthesized with several degrees of sharpening. It was difficult to interpret the maps so obtained, however, because of the heavy overlappings of peaks due to chlorine-chlorine and chlorine-carbon interactions.

In the next attempt, the direct sign-determination methods were applied to $F(hk0)$'s. The Harker-Kasper inequality[5)] was used;

$$(U_{\mathrm{H}}\pm U_{\mathrm{H}'})^2\leq(1\pm U_{\mathrm{H}+\mathrm{H}'})(1\pm U_{\mathrm{H}-\mathrm{H}'})$$

where U_{H} etc., are the unitary structure factors for the ($hk0$) plane. Signs for 76 out of 277 observed reflections were obtained by this method. Further sign-determinations were made by using Sayre's relation,[6)]

$$S_{\mathrm{H}}=S_{\mathrm{H}'}S_{\mathrm{H}+\mathrm{H}'}$$

where S_{H} denotes the sign of F_{H}. The relation gave signs of 50 more reflections. After the final refinement of the structure, it was found that only two out of the 126 signs determined by the direct methods were incorrect.

The projection of the electron-density distribution along the c axis was then synthesized using these 126 reflections. The map showed not only the four chlorine atoms, but also a rough layout of the carbon skeleton, as may be seen from Fig. 1. The structure was then refined by the usual Fourier technique, after which the anisotropic temperature factors in the form of $\exp\{-(h^2B_{11}+k^2B_{22}+hkB_{12})\}$ were assigned to each non-hydrogen atom, and the least-squares refinement method was applied with a block-diagonal-matrix approximation. The atomic scattering factors given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry and Veenendaal[7)] for carbon and chlorine and by McWeeny[8)] for hydrogen were used throughout this structure determination. After three cycles of refinement, the discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, decreased to 0.091 for all the observed reflections ($R=0.145$ if unobserved reflections were included).

Using the coordinates so determined, the (F_o-F_c) synthesis was computed. Several peaks of residual electron density were observed, as is shown in Fig. 2; some of these might be due to the hydrogen atoms. Among them, two peaks corresponding to H(5) and H(10) were also included; those two hydrogen atoms are involved in the steric hindrance mentioned above. Therefore, all the hydrogen atoms were located geometrically at a distance of 1.0 Å outward from the carbon atoms.

Three more least-squares refinement cycles, including those hydrogen atoms with isotropic temperature factors, were carried out. The final discrepancy factor was 0.081 for all the observed reflections ($R=0.133$ including the unobserved reflections). The final x- and y-coordinates and temperature factors are given in Tables I and II respectively, while the observed and calculated structure factors, $F(hk0)$, are listed in Table III. The final electron density projection along the c axis is shown in Fig. 3.

The Determination of the z-Coordinates.—Although no complete three-dimensional intensity data were collected, the Harker section, $P(u, 1/2, w)$, was synthesized, using $F(hk0)$, $F(hk1)$ and $F(hk2)$, in order to obtain the z-coordinates of the atoms. The peaks on the Harker section, as is shown in Fig. 4, were interpreted rather easily by assuming that the chlorine atoms attached to the five-membered ring are coplanar. As the y-coordinates of Cl(2) and Cl(4) are nearly

---

[4)] H. Lipson and W. Cochran, "The Determination of Crystal Structure," Bell, London (1953), p. 61.

[5)] Ibid., p. 250.

[6)] Ibid., p. 269.

[7)] J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. McGillavry and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

[8)] R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

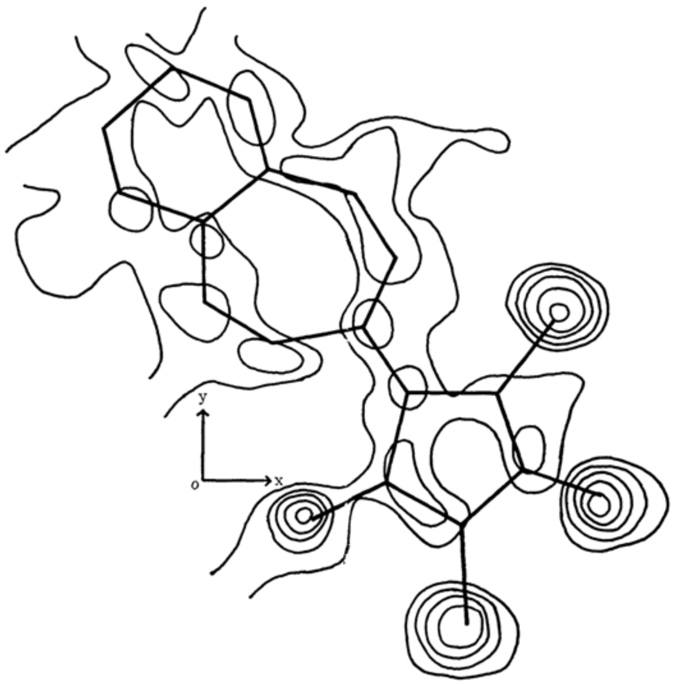


Fig. 1. The first electron density projection along the c axis. In Fourier summation, 126 reflections are included whose signs have been obtained by the direct methods. Contours are drawn at equal intervals on an arbitrary scale. The final skeleton of the molecule is superimposed.

TABLE I. THE FINAL ATOMIC COORDINATES

Atom	*x/a*	*y/b*	*z/c*
Cl(1)	0.2693	0.1691	0.0109
Cl(2)	0.3192	−0.0155	−0.0310
Cl(3)	0.2066	−0.1394	0.2110
Cl(4)	0.0793	−0.0364	0.3927
C (1)	0.2276	0.0882	0.1284
C (2)	0.2476	0.0139	0.0873
C (3)	0.1982	−0.0382	0.1680
C (4)	0.1443	0.0031	0.2154
C (5)	0.0509	0.1378	0.1426
C (6)	0.0008	0.1804	0.1874
C (7)	−0.0049	0.2594	0.3513
C (8)	0.0459	0.3089	0.4791
C (9)	0.1127	0.2921	0.4430
C (10)	0.1429	0.2267	0.3381
C (11)	0.1613	0.0895	0.1830
C (12)	0.1190	0.1511	0.2437
C (13)	−0.0684	0.2868	0.3777
C (14)	−0.0798	0.3583	0.5557
C (15)	−0.0298	0.4043	0.6876
C (16)	0.0306	0.3839	0.6453

TABLE II. THE FINAL TEMPERATURE FACTORS, USED FOR THE CALCULATION OF $F(hk0)$.

Atom	B_{11}	B_{22}	B_{12}
Cl(1)	0.00199	0.00399	−0.00084
Cl(2)	0.00238	0.00484	0.00160
Cl(3)	0.00369	0.00305	0.00040
Cl(4)	0.00238	0.00346	−0.00105
C (1)	0.00214	0.00365	−0.00152
C (2)	0.00267	0.00458	0.00280
C (3)	0.00247	0.00322	0.00124
C (4)	0.00283	0.00425	−0.00051
C (5)	0.00316	0.00367	−0.00152
C (6)	0.00314	0.00333	−0.00023
C (7)	0.00281	0.00237	−0.00158
C (8)	0.00186	0.00359	−0.00183
C (9)	0.00274	0.00445	0.00099
C (10)	0.00217	0.00389	−0.00017
C (11)	0.00187	0.00338	0.00053
C (12)	0.00267	0.00386	0.00230
C (13)	0.00225	0.00389	0.00056
C (14)	0.00301	0.00400	0.00051
C (15)	0.00335	0.00359	−0.00063
C (16)	0.00257	0.00328	0.00105

equal, the non-Harker peak due to these atoms should be placed at the mid-point of their Harker peaks,[9] the Harker peak of each chlorine being indicated in Fig. 4. Near this non-Harker peak, the Harker peak of Cl(3) appears accidentally. This is the reason why the peak corresponding to Cl(3) is higher than those of the other chlorine atoms.

A three-dimensional Fourier synthesis was carried out using the structure factors based on the four chlorine atoms. The electron density

---

[9] G. Albrecht and R. B. Corey, *J. Am. Chem. Soc.*, **61**, 1087 (1939).

Table III. Observed and calculated structure factors, $F(hk0)$

K	10FC	10FC
H,L=	0,	0
2	101	92
4	0	-1
6	264	283
8	110	107
10	45	-45
12	0	1
14	0	-6
16	40	-43
18	37	-38
20	8	-1
H,L=	1,	0
2	70	-73
3	110	111
4	150	148
5	0	-3
6	55	51
7	70	72
8	123	121
9	108	-102
10	158	162
11	62	-60
12	0	2
13	0	-15
14	62	-58
15	9	-19
16	52	52
17	15	-25
18	0	-4
19	14	-13
20	21	-24
21	13	8
H,L=	2,	0
0	119	-103
1	38	-39
2	177	-177
3	87	88
4	23	15
5	0	-7
6	186	-192
7	77	73
8	48	-44
9	96	88
10	19	17
11	11	-23
12	81	-76
13	33	-39
14	49	-48
15	32	-33
16	0	12

K	10FC	10FC
17	22	-25
18	0	-4
19	32	-31
20	8	9
21	21	-22
H,L=	3,	0
1	103	-102
2	0	2
3	133	135
4	36	40
5	183	186
6	197	207
7	64	61
8	38	42
9	60	-59
10	86	-83
11	76	72
12	107	104
13	23	-19
14	9	16
15	0	-7
16	64	-67
17	10	15
18	0	-5
19	0	5
20	8	10
21	31	-30
H,L=	4,	0
0	178	172
1	72	-68
2	97	-90
3	42	43
4	168	-177
5	325	322
6	55	55
7	39	43
8	22	-22
9	0	11
10	0	-15
11	85	83
12	59	58
13	76	75
14	43	-42
15	29	32
16	10	22
17	10	-19
18	0	-3
19	0	3
20	17	-13
21	0	0

K	10FC	10FC
H,L=	5,	0
1	104	-100
2	69	-73
3	218	-238
4	77	76
5	109	-114
6	0	12
7	33	-28
8	36	-35
9	0	12
10	41	44
11	38	-41
12	13	-10
13	0	18
14	45	-43
15	77	76
16	0	-10
17	25	-28
18	0	-15
19	0	-5
20	23	-22
21	18	18
H,L=	6,	0
0	77	-74
1	208	214
2	31	29
3	0	-4
4	54	75
5	88	-90
6	69	-65
7	56	55
8	93	96
9	65	64
10	79	76
11	53	53
12	61	58
13	24	-32
14	25	22
15	29	28
16	42	38
17	19	-24
18	0	3
19	23	-16
20	0	7
21	15	-13
H,L=	7,	0
1	91	-85
2	123	132
3	132	-135
4	71	-69

K	10FC	10FC
5	125	125
6	0	-3
7	41	-43
8	146	139
9	0	-9
10	8	13
11	117	115
12	36	37
13	37	46
14	38	33
15	14	-8
16	0	18
17	40	39
18	34	31
19	30	26
20	18	16
21	14	-23
H,L=	8,	0
0	103	-101
1	226	-230
2	208	-204
3	92	-89
4	15	-34
5	76	75
6	38	-31
7	119	-116
8	50	-55
9	115	-116
10	17	20
11	0	-2
12	102	94
13	0	0
14	0	-17
15	0	0
16	0	22
17	0	0
18	41	38
19	0	5
20	0	-3
H,L=	9,	0
1	62	59
2	168	-167
3	37	44
4	113	-104
5	0	7
6	118	-109
7	45	47
8	142	-139
9	50	46
10	71	-70

K	10FC	10FC
11	0	-0
12	14	-18
13	0	-1
14	48	-54
15	49	51
16	0	-5
17	10	-15
18	0	8
19	0	-3
20	23	23
H,L=	10,	0
0	13	23
1	0	-3
2	0	5
3	0	-5
4	0	-3
5	78	-81
6	0	12
7	0	6
8	49	33
9	0	-9
10	86	-86
11	27	-35
12	47	-48
13	56	54
14	0	-1
15	0	14
16	0	-4
17	24	20
18	29	-27
19	31	27
H,L=	11,	0
1	14	-14
2	111	110
3	112	-110
4	72	-73
5	0	6
6	40	-41
7	53	-53
8	8	-9
9	122	-126
10	23	21
11	0	13
12	32	-25
13	61	-71
14	10	-13
15	48	-45
16	30	30
H,L=	12,	0
0	37	33

K	10FC	10FC
1	53	-48
2	101	93
3	15	10
4	146	145
5	44	39
6	0	2
7	112	-109
8	9	-18
9	23	-38
10	9	14
11	14	-23
12	20	22
13	30	-34
14	41	-43
15	0	-6
H,L=	13,	0
1	87	87
2	11	-24
3	152	154
4	0	14
5	15	18
6	44	43
7	61	-58
8	0	-0
9	70	64
10	14	17
11	14	29
12	9	13
13	53	-49
14	0	10
15	12	-7
H,L=	14,	0
0	48	41
1	72	70
2	55	-51
3	12	-22
4	8	-18
5	15	-19
6	13	-12
7	105	92
8	0	-6
9	14	22
10	59	-65
11	9	-8
12	14	-24
13	10	27
14	0	-4
15	0	-14
H,L=	15,	0
1	94	91

K	10FO	10FC
2	0	3
3	52	-53
4	29	34
5	63	57
6	33	-27
7	64	67
8	43	50
9	20	-36
10	9	17
11	0	0
12	25	-23
13	13	-11
14	37	-30
15	9	-17
H,L=	16,	0
0	9	11
1	35	40
2	19	13
3	69	69
4	84	85
5	39	41
6	34	38
7	14	14
8	14	12
9	60	59
10	0	5
11	47	47
12	0	-7
13	26	-27
14	0	2
15	22	23
H,L=	17,	0
6	0	15
1	80	-79
2	27	37
3	9	-14
4	56	59
5	87	-91
7	9	-26
8	48	53
9	0	6
10	0	2
11	0	15
12	9	18
13	0	-4
H,L=	18,	0
0	14	-13
1	28	34
2	69	-70
3	20	-29

K	10FO	10FC
4	35	-39
5	0	-4
6	0	3
7	0	18
8	0	-16
9	31	-34
10	10	19
11	0	-9
12	39	41
13	9	11
H,L=	19,	0
1	41	41
2	54	-53
3	50	-53
4	17	22
5	0	-5
6	0	10
7	47	53
8	10	-16
9	19	4
10	29	22
11	15	20
12	9	9
13	19	18
H,L=	20,	0
0	39	-44
1	0	-7
2	32	-33
3	0	-13
4	0	-0
5	0	9
6	15	24
7	21	-19
8	0	5
9	15	19
10	10	-2
11	21	17
12	0	-10
H,L=	21,	0
2	0	20
3	0	6
4	40	-44
5	0	-7
6	34	-34
7	12	-14
8	0	-3
9	29	26
10	37	-34
11	0	-3
12	0	-21

K	10FO	10FC
H,L=	22,	0
0	33	31
1	0	1
2	0	-0
3	19	-14
4	0	17
5	9	-24
6	30	29
7	0	-6
8	0	-12
9	16	-20
11	15	-13
12	29	28
H,L=	23,	0
1	0	-4
2	30	-30
3	29	-22
4	0	17
5	0	-4
6	0	-0
7	13	-14
8	0	-17
H,L=	24,	0
0	9	-3
1	0	-12
2	0	12
3	0	-6
4	9	-3
5	0	-10
6	0	-7
7	20	-26
H,L=	25,	0
1	41	34
2	22	21
3	31	27
4	12	-23
5	11	10
6	0	-3
H,L=	26,	0
0	49	37
2	0	-4
5	16	13
6	16	8
H,L=	27,	0
2	17	-15

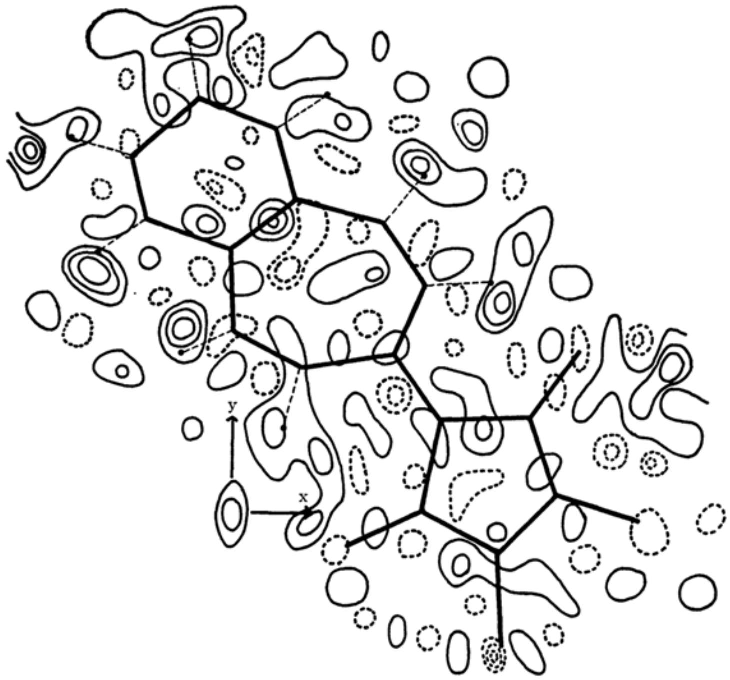


Fig. 2. The (F_o-F_c) synthesis projected along the c axis. Contours are drawn at intervals of 0.3 e. Å^{-2}. Negative contours are broken. The skeleton of the molecule is superimposed and the estimated positions of hydrogen atoms are shown by black circles.

TABLE IV. THE FINAL TEMPERATURE FACTORS USED FOR THE CALCULATION OF $F(hk1)$ AND $F(hk2)$

For chlorine atoms, temperature factors are in form of

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

Atom	B_{11}	B_{22}	B_{33}
Cl(1)	0.0026	0.0045	0.1294
Cl(2)	0.0031	0.0056	0.1298
Cl(3)	0.0046	0.0034	0.1730
Cl(4)	0.0030	0.0036	0.1303

Atom	B_{12}	B_{23}	B_{31}
Cl(1)	−0.0007	0.0039	0.0046
Cl(2)	0.0010	0.0008	0.0028
Cl(3)	0.0004	0.0008	0.0008
Cl(4)	−0.0010	0.0014	0.0032

Atom	B(Å^2)	Atom	B(Å^2)
C (1)	3.93	C (9)	5.17
C (2)	5.62	C (10)	6.04
C (3)	5.80	C (11)	4.49
C (4)	4.81	C (12)	5.25
C (5)	5.35	C (13)	6.25
C (6)	5.47	C (14)	6.79
C (7)	5.23	C (15)	6.01
C (8)	6.07	C (16)	6.25

distribution so obtained showed up all the carbon atoms clearly. After one more three-dimensional Fourier synthesis, the structure was subjected to the least-squares refinement. Since the three-dimensional intensity data were incomplete, not only in number but also in their accuracy, only the z-coordinates and temperature factors of non-hydrogen atoms were refined, while anisotropic temperature factors for chlorine and isotropic temperature factors for carbon atoms were assigned. The final R factor for the set of $F(hk1)$ and $F(hk2)$ is 0.136 for the observed reflections.

The final z-coordinates of all the atoms are included in Table I, while the final temperature factors are listed in Table IV. The observed and calculated structure factors, $F(hk1)$ and $F(hk2)$, are tabulated in Table V.

All the numerical computations in this study were done on the NEAC-2101 of the Institute, the NEAC-2206 of the Computing Center of Osaka University and the IBM 7090 of the "UNICON" project, with programmes written by the authors and their collaborators.

A Description of the Structure and Discussion

From the first electron density distribution, which was obtained without any assumption regarding the structure, it was concluded exclusively that the chemical formula deduced from the synthetic process was valid as a whole. This conclusion was confirmed by the subsequent refinement, which gives a fairly good agreement between the observed and calculated structure factors

TABLE V. OBSERVED AND CALCULATED STRUCTURE FACTORS, $F(hk1)$ and $F(hk2)$

K	10FO	10FC
H,L=	0,	1
0	192	103
2	150	157
3	190	178
4	26	-40
5	30	-38
6	180	174
7	23	22
9	94	96
12	112	106
13	29	-46
H,L=	1,	1
2	220	-207
3	187	-161
4	107	105
5	22	-27
6	97	93
7	102	-95
10	144	127
11	54	59
16	21	30
H,L=	2,	1
0	531	-796
1	58	-76
2	161	-165
3	20	-28
4	21	-36
5	26	20
6	172	-170
7	40	-56
8	38	-49
9	143	-130
H,L=	3,	1
1	98	98
2	56	-69
3	53	-63
4	89	-92
5	39	40
6	22	-12
7	54	68
8	88	-92
9	34	-26
10	97	-106
11	43	46
14	65	63
H,L=	4,	1
0	326	306
1	38	-37
2	59	-54
4	42	-47
6	82	94
7	78	-83
H,L=	5,	1
1	39	-40
2	71	-85
3	32	38
4	35	-40
5	92	-106
6	155	-145
7	68	-71
12	106	-99
H,L=	6,	1
2	77	83
4	189	188
5	169	-155
9	17	-42
10	47	45
H,L=	7,	1
1	56	72
2	58	-71
3	84	87
5	66	84
6	41	55
9	64	-60
11	35	39
14	37	41
15	57	-55
H,L=	8,	1
0	65	76
1	129	-126
4	98	-93
5	41	64
6	49	51
7	57	-53
8	48	-49
10	78	-71
12	36	-39
H,L=	9,	1
1	48	60
2	29	-43
3	120	109
4	61	55
11	56	-57
12	30	-39
H,L=	10,	1
1	146	147
2	42	55
3	74	78
4	33	46
7	115	104
9	89	93
H,L=	11,	1
1	60	-62
2	53	60
3	38	-56
4	98	89
7	58	-67
8	45	53
H,L=	12,	1
1	58	-64
5	18	48
10	65	63
H,L=	13,	1
9	53	56
H,L=	14,	1
0	39	-39
2	83	-88
4	88	-87
5	61	-61
7	47	47
9	37	39
H,L=	15,	1
3	46	-57
H,L=	16,	1
1	63	-69
H,L=	17,	1
5	43	-44
H,L=	18,	1
0	48	48
1	31	-32
H,L=	19,	1
5	42	50
H,L=	-1,	1
3	314	-292
4	34	-34
5	47	-51
6	125	130
8	50	53
9	46	39
10	17	-38
11	32	-37
H,L=	-2,	1
0	107	-116
1	107	-116
2	33	30
3	232	230
4	47	-54
5	222	186
6	53	-61
8	48	42
10	47	-37
11	60	72
12	34	-40
13	70	75
14	43	39
H,L=	-3,	1
10	54	63
15	21	-35
1	133	127
2	148	-144
3	36	52
4	130	130
5	162	172
6	132	128
8	34	-43
9	15	15
H,L=	-4,	1
0	65	78
1	133	143
3	62	72
5	90	-101
6	100	91
8	122	-108
9	68	69
10	25	-36
11	18	32
13	47	-56
14	53	-53
H,L=	-5,	1
2	184	165
3	34	38
4	58	-75
5	94	-84
8	181	164
11	76	-80
10	31	43
13	57	-61
H,L=	-6,	1
0	182	169
1	58	-66
2	243	210
5	33	33
6	43	43
7	68	-72
8	23	41
11	18	39
12	72	-78
16	29	-17
18	51	-46
H,L=	-7,	1
2	209	-205
6	145	-129
8	143	-133
9	45	-45
10	58	-63
15	21	-29
H,L=	-8,	1
0	25	-30
1	56	-61
2	36	-53
3	38	-43
5	75	-77
8	78	-81
9	62	-61
10	52	45
11	20	-23
H,L=	-9,	1
2	104	106
3	152	132
4	45	-56
5	42	36
6	73	-67
9	118	101
H,L=	-10,	1
1	88	-78
2	42	-56
3	34	33
4	42	-36
7	114	-105
H,L=	-11,	1
1	116	-97
3	222	-199
5	17	-41
7	37	48
8	48	-47
9	71	-72
H,L=	-12,	1
3	17	-24
6	26	34
7	90	86
10	57	53
H,L=	-13,	1
1	84	-70
3	88	87
5	18	-39
H,L=	-14,	1
0	73	-67
2	18	-34
3	54	56
4	47	-57
5	48	42
6	61	-60
8	52	-52
H,L=	-15,	1
1	48	51
2	44	49
4	87	84
6	20	18
8	30	36
H,L=	-16,	1
0	45	48
2	50	70
H,L=	-17,	1
2	42	-59
H,L=	0,	2
0	19	29
3	148	-149
4	71	78
6	63	75
7	46	-41
8	39	-41
10	17	22
11	17	-26
12	18	15
13	43	-42
14	18	-26
15	17	-0
H,L=	1,	2
1	99	-107
2	74	-80
3	97	90
4	70	68
5	18	-20
6	12	-17
7	49	-47
8	68	-63
11	18	-26
12	38	24
H,L=	2,	2
0	47	-57
2	25	-16
3	49	-50
6	49	-50
7	38	-30
9	49	-46
11	37	-35
12	61	-69
15	17	7
H,L=	3,	2
1	211	204
2	85	89
3	79	66
5	49	50
6	36	-26
7	45	41
10	41	-40
H,L=	4,	2
0	112	123
2	98	97
3	34	47
6	49	61
7	32	24
9	126	115
H,L=	5,	2
1	89	-79
4	61	58
5	29	-30
6	35	37
7	65	-68
10	42	43
11	26	-14
H,L=	6,	2
0	161	-152
2	56	58
3	12	-12
4	42	45
5	38	40
7	23	31
13	26	14
14	37	-2
H,L=	7,	2
2	44	31
3	61	-56
4	26	37
6	59	61
7	50	39
12	38	41
H,L=	8,	2
0	61	-59
2	63	-65
4	64	-62
5	41	40
6	38	-34
7	36	-39
9	42	41
H,L=	9,	2
1	58	-52
2	36	33
3	23	26
5	34	-31
6	36	-44
8	18	-0
9	42	41
12	26	-31
14	24	-17
H,L=	10,	2
0	53	-44
4	30	43
10	38	46
13	25	23
14	23	16
H,L=	11,	2
1	17	-22
3	57	-55
H,L=	12,	2
0	36	36
1	44	-53
2	17	20
3	41	-36
4	31	-30
7	70	-72
9	33	-27
14	31	22
H,L=	13,	2
11	40	-32
H,L=	14,	2
1	42	47
10	44	-36
H,L=	15,	2
2	18	-23
4	26	27
5	18	29
H,L=	16,	2
0	33	31
2	51	50
4	38	16
6	18	-7
H,L=	17,	2
8	38	28
H,L=	-1,	2
2	31	28
3	24	5
4	55	-59
5	89	-95
6	128	-121
10	31	-41
H,L=	-2,	2
0	57	-49
1	20	-25
3	77	-67
4	57	-62
5	54	62
6	40	-39
8	46	46
14	42	48
H,L=	-3,	2
1	34	44
2	100	-116
3	15	-28
4	103	105
6	46	-49
7	77	73
8	85	-86
13	47	47
H,L=	-4,	2
0	67	-74
1	18	-26
2	106	-118
3	31	-44
4	31	-29
9	56	-39
11	37	-35
12	51	47
H,L=	-5,	2
1	70	-75
2	92	103
3	21	-33
5	31	-45
6	34	39
7	22	-29
8	92	89
9	25	26
10	37	43
12	18	9
H,L=	-6,	2
1	35	41
2	25	33
3	60	58
5	44	50
6	14	-19
8	60	54
9	93	89
12	22	-31
H,L=	-7,	2
2	12	-26
3	79	-79
4	36	39
5	20	-38
9	55	-54
10	18	35
11	18	-35
H,L=	-8,	2
4	25	-34
7	38	44
9	25	25
10	18	-26
11	18	-4
12	26	-19
13	33	31
H,L=	-9,	2
1	47	54
2	14	-11
3	152	153
5	15	33
9	25	41
12	33	22
H,L=	-10,	2
2	66	77
6	30	-29
7	61	-65
11	18	10
13	25	-27
H,L=	-11,	2
3	44	-58
6	25	38
9	26	-40
H,L=	-12,	2
0	45	57
1	15	34
2	15	42
6	45	52
7	18	-14
8	38	40
10	26	-36
H,L=	-13,	2
2	25	-54
4	52	-63
10	26	-29
H,L=	-14,	2
0	52	-68
2	17	-30
6	38	-52
7	51	-60
H,L=	-15,	2
11	39	40
H,L=	-16,	2
11	33	-27
H,L=	-17,	2
5	38	-26
H,L=	-18,	2
5	46	47

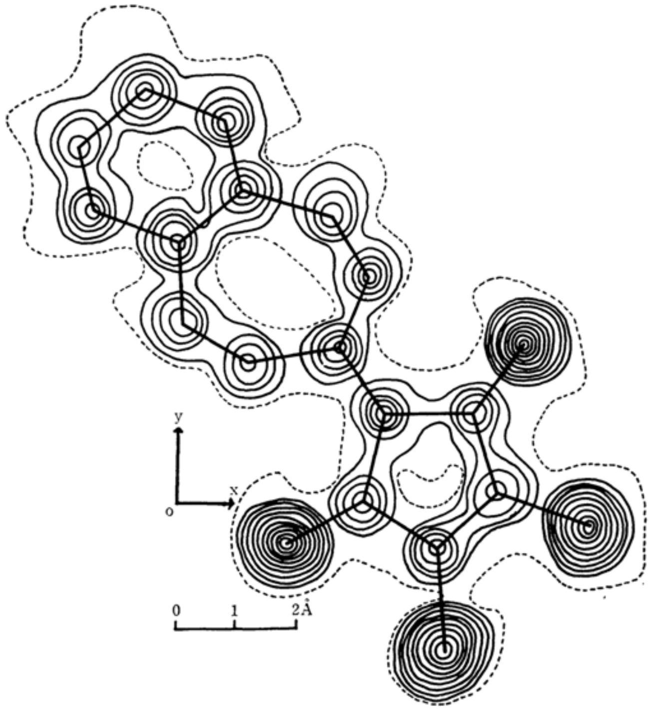


Fig. 3. The final electron density projection along the c axis. Contours are drawn at intervals of 1 e. Å^{-2} with broken contour of 1 e. Å^{-2}. For chlorine atoms, contours are drawn at intervals of 2 e. Å^{-2} beginning with 2 e. Å^{-2}.

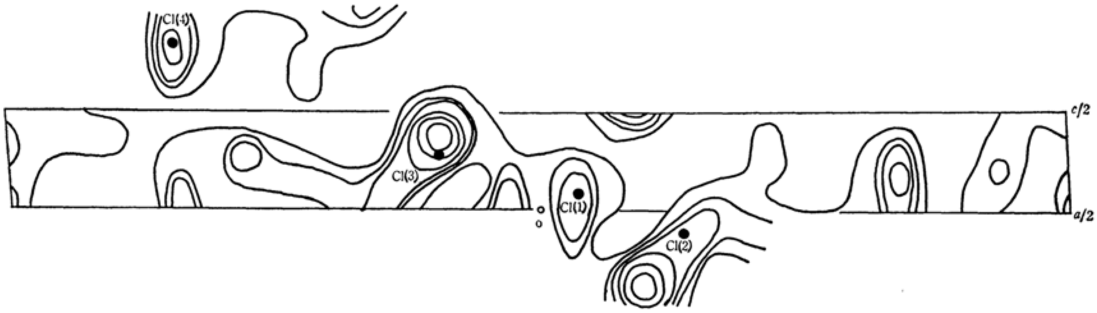


Fig. 4. Harker section $P(u, 1/2, w)$. Contours are drawn at equal intervals on an arbitrary scale. Harker peaks corresponding to the chlorine atoms are indicated.

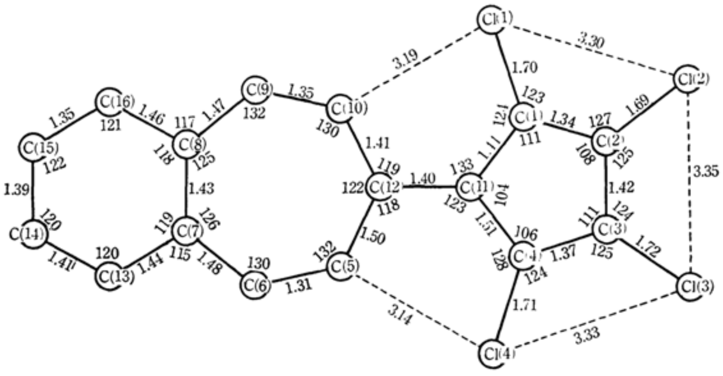


Fig. 5. Bond lengths (Å) and bond angles (°) in the molecule of 1,2,3,4-tetrachlorobenzo[g]-sesquifulvalene.

and which results in quite reasonable intra- and intermolecular distances.

All the bond lengths and angles are shown in Fig. 5. The average standard deviations of the atomic coordinates are 0.011 and 0.036 Å for chlorine and carbon atoms respectively. Therefore, the estimated standard deviation of a C–C bond length is 0.05 Å, while that of a C–Cl bond length is 0.04 Å.

The mean length of C–Cl bonds is 1.705 Å, a value which is in good agreement with the average value of those in several chlorobenzenes (1.70 Å).[10] In the benzene ring of the present molecule, the mean C–C length is 1.413 Å.

In the sesquifulvalene skeleton, longer and shorter bonds are disposed alternately, as could be expected from the chemical formula (III). The average of the longer bond lengths is 1.461 Å, while that of the shorter is 1.354 Å. These values may be compared with those observed in some similar compounds; 1.451 and 1.373 Å in 8,8-dicyanoheptafulvene,[11] 1.446 and 1.358 Å in 7,7,8,8-tetracyanoquinodimethane,[12] 1.477 and 1.322 Å in *p*-benzoquinone,[13] 1.477 and 1.342 Å in tetrachloro-*p*-benzoquinone,[14] and 1.470 and 1.322 Å in cyclooctatetraenecarboxylic acid.[15]

Murata[16] deduced the bond orders in benzo[g]-sesquifulvalene from a molecular orbital treatment by assuming the planarity of the molecule and the presence of a mirror plane perpendicular to the molecular plane through C(11)–C(12). Table VI shows the theoretical bond lengths converted from the bond orders. It can be said that the observed lengths of the bonds related to each other by the mirror do not differ significantly in the present molecule. Therefore, the average lengths of the equivalent bonds (Table VI) may be compared with the theoretical values. The agreement between them is fairly good, although the assumption of the planarity of the molecule does not hold, as will be described below .

TABLE VI. THEORETICAL AND OBSERVED BOND LENGTHS (Å)

Bonds	Theoretical	Observed
C(1)-C(2) and C(3)-C(4)	1.36	1.355
C(2)-C(3)	1.46	1.420
C(1)-C(11) and C(4)-C(11)	1.45	1.475
C(11)-C(12)	1.37	1.400
C(10)-C(12) and C(5)-C(12)	1.46	1.455
C(9)-C(10) and C(5)-C(6)	1.36	1.330
C(8)-C(9) and C(6)-C(7)	1.46	1.475
C(7)-C(8)	1.41	1.430
C(8)-C(16) and C(7)-C(13)	1.46	1.450
C(15)-C(16) and C(13)-C(14)	1.39	1.380
C(14)-C(15)	1.40	1.390

The equations of the best planes of the five-, seven- and six-membered rings (A, B and C respectively) were derived by the least-squares method. In the final evaluation of the coefficients of the equations, the C(1) and C(12) atoms were excluded, because they were significantly off the planes. The equations of these best planes are:

$$-4.786X-Y-16.984Z+26.139=0 \qquad (A)$$

$$-0.002X-Y+2.238Z+1.342=0 \qquad (B)$$

$$-0,008X-Y+1.842Z+1.947=0 \qquad (C)$$

where $X=x\sin\beta$, $Y=y$, and $Z=z+x\cos\beta$.

The perpendicular displacements of the atoms from each mean plane are shown in Table VII. The C(1) atom is shifted from the mean plane by 0.12 Å. Except for this, the five-membered ring might be thought to be planar. Some of the chlorine atoms are significantly off from the five-membered ring. In the seven-membered ring, the C(12) atom which is linked to the five-membered ring deviates from the mean plane by 0.22 Å. The other atoms in the ring lie on the plane. The six-membered ring also seems to be planar within the limit of error.

TABLE VII. DEVIATION OF THE ATOMS FROM THE MEAN PLANES (Å)

Atoms	From the plane A (The five-membered ring)	From the plane B (The seven-membered ring)	From the plane C (The six-membered ring)
Cl(1)	0.04		
Cl(2)	0.14		
Cl(3)	−0.11		
Cl(4)	−0.30		
C (1)	−0.12		
C (2)	0.01		
C (3)	−0.01		
C (4)	0.02		
C (11)	−0.02	0.39	
C (12)	−0.11	0.22	0.39
C (5)		0.04	0.24
C (6)		−0.04	0.11
C (9)		−0.04	−0.06
C (10)		0.01	0.08
C (7)		−0.01	0.03
C (8)		0.04	0.00
C (13)		−0.03	−0.03
C (14)		0.11	0.01
C (15)		0.20	0.02
C (16)		0.12	−0.03

---

10) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958), p. 15.

11) H. Shimauchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata and Y. Kitahara, This Bulletin, **38**, 1230 (1965).

12) R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Cryst.*, **18**, 932 (1965).

13) J. Trotter, *Acta Cryst.*, **13**, 86 (1960).

14) S. S. C. Chu, G. A. Jefferey and T. Sakurai, *Acta Cryst.*, **15**, 661 (1962).

15) D. P. Shoemaker, H. Kinder, W. G. Sly and R. C. Srivastave, *J. Am. Chem. Soc.*, **87**, 482 (1965).

16) I. Murata, Private Communication (1964).

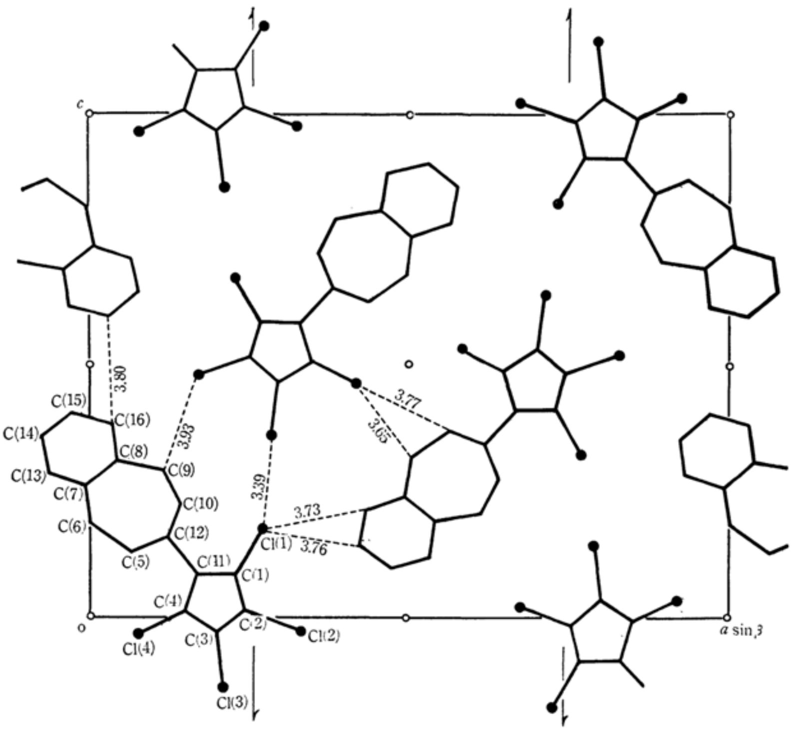


Fig. 6. Arrangement of the molecules in the crystal viewed along the c axis. Short intermolecular distances are indicated.

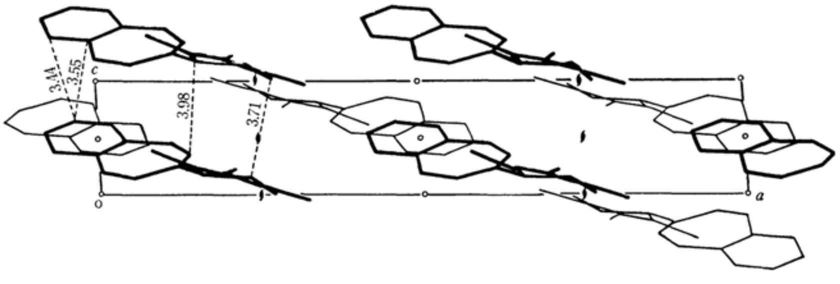


Fig. 7. Arrangement of the molecules in the crystal viewed along the b axis. Short intermolecular distances are indicated.

The five- and seven-membered rings twist around the C(11)–C(12) bond by an angle of about 31° to each other. This might be due to repulsion forces between Cl(1) and H(10) and between Cl(4) and H(5). If the hydrogen atoms are assumed so as to be located at a distance of 1.0 Å outward from the carbon atoms, the distances between the chlorine and hydrogen atoms may be computed to be 2.45 Å for the former and 2.57 Å for the latter.

The seven- and six-membered rings are not coplanar; these two planes make slight angles (of about 5°).

The arrangement of the molecules in the crystal is shown in Figs. 6 and 7, where the short intermolecular distances are given. There is observed one short intermolecular approach, 3.39 Å between Cl(1) in a molecule and Cl(3) in the neighboring molecule related by the screw axis to it. All the other intermolecular separations are equal to or larger than the sums of the van der Waals radii of the corresponding atoms.

As may be seen from Figs. 6 and 7, two molecules related by a center of symmetry to each other make a pair; the dipole moment of this compound (5.20 D)[3)] is compensated for by this pairing. Such pairs are packed together in the manner found in the crystals of typical aromatic molecules.

The authors would like to express their deep thanks to Professor Yoshio Kitahara and Dr. Ichiro Murata of Tohoku University for supplying material and for their continued interest. Thanks are also due to the staff of the University Computing Center for their kind help. The computing time of the IBM 7090 was made available to the authors through the "UNICON" project.