

print of their paper on a three-dimensional structural determination of (C₃H₅PdCl)₂ at room temperature (Dahl & Oberhansli, 1965). Both structure determinations are in agreement within the limit of experimental error. The standard deviations in bond lengths and angles for the low temperature work are, as expected, somewhat lower, *i.e.* only about one-third those of the room temperature determination. In addition it was possible to locate the H atoms approximately in the low temperature determination.

The author is indebted to W. R. Busing and H. Levy for making their least-squares and error programs available and to A. Zalkin for his Fourier synthesis program. He is also indebted to W. F. Birka for the design and construction of the constant level device and for aid with some of the calculations. He also wishes to thank J. L. Van Winkle for the preparation of the complex and for valuable discussions.

References

BALLHAUSEN, C. J. (1962). *Introduction to Ligand Field Theory*. New York: McGraw-Hill.
 BUSING, W. R. & LEVY, H. A. (1959a). Oak Ridge National Laboratory Report 59-4-37.

BUSING, W. R. & LEVY, H. A. (1959b). Oak Ridge National Laboratory Report 59-12-3.
 CHATT, J. & DUNCANSON, L. A. (1953). *J. Chem. Soc.* p. 2939.
 CRUICKSHANK, D. W. J. (1960). *Acta Cryst.* **13**, 774.
 DAHL, L. F. & OBERHANSLI, W. E. (1965). *J. Organometallics*. In the press.
 DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
 DAWSON, B. (1960). *Acta Cryst.* **13**, 403.
 DEHM, H. C. & CHIEN, J. C. W. (1960). *J. Amer. Chem. Soc.* **82**, 4429.
 DEWAR, M. J. S. (1951). *Bull. Soc. Chim. Fr.* **18**, C79.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-Ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 LEVDIK, V. F. & PORAI-KOSHITS, M. A. (1962). *J. Struct. Chem.* (p. 455, Trans-Consultants Bureau 1963).
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 MOISEEV, I. I. *et al.* (1959). *J. Inorg. Chem. (USSR)*, **4**, 2641.
 ORGEL, L. E. (1960). *An Introduction to Transition Metal Chemistry*. London: Methuen.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd Ed. Ithaca: Cornell Univ. Press.
 REILLY, C. A. (1963). Private communication.
 ROWE, J. M. (1962). *J. Chem. Soc.* p. 66.
 SMIDT, J. & HAFNER, W. (1959). *Angew. Chem.* **71**, 284.
 WELLS, A. F. (1938). *Z. Kristallogr.* **100** (A), 189.

Acta Cryst. (1965). **18**, 340

The Crystal Structure of Uranium Chloride π -Tricyclopentadienyl

BY CHI-HSIANG WONG, TUNG-MOU YEN*, AND TSENG-YUH LEE

Institute of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan, China

(Received 13 January 1964 and in revised form 7 May 1964)

The crystal structure of uranium chloride π -tricyclopentadienyl has been determined by analysis of X-ray diffraction data. The crystals are monoclinic, space group $P2_1/n$, with $a = 8.26$ Å, $b = 12.50$ Å, $c = 13.81$ Å, and $\beta = 90.6^\circ$. There are four molecules per unit cell. The coordinates for the uranium atom were determined from two Patterson projections. The structure was then deduced from a three-dimensional Fourier synthesis and, later, a difference synthesis. The positional and vibrational parameters for the uranium and chlorine atoms were refined by least-squares calculations, and the positional parameters for the carbon atoms were refined by another difference synthesis. The bond lengths are: U-Cl = 2.559 ± 0.016 Å, U-C = 2.74 Å. A regular planar pentagonal structure for the cyclopentadienyl rings with C-C $\simeq 1.4$ Å is compatible with the difference maps. These results indicate that the U-Cl bond is essentially ionic, and that there are approximately three pairs of electrons responsible for the bonding between the uranium atom and the three cyclopentadienyl groups. The cyclopentadienyl rings and the chlorine atom form a distorted tetrahedron about the uranium atoms.

Introduction

A number of structural studies of sandwich compounds and their derivatives have been reported during recent years, but no investigation of the structure of a metal

tricyclopentadienyl has yet been reported. We have chosen uranium chloride π -tricyclopentadienyl for it is the only metal tricyclopentadienyl compound that has been reported to have sandwich-type bonding* (Reynolds & Wilkinson, 1956). Because of the intrinsic difficulties involved in obtaining good intensity data (see Experimental), and because of the great difference

* Present address: Department of Physics, Harvard University, Cambridge, Massachusetts, U.S.A.

in scattering power between uranium and carbon, we fully realized that no precise determination of the carbon parameters could be obtained. However, in view of the large number of presumably identical bonds (15 for both U-C and C-C), we felt that some meaningful information could be deduced for the understanding of this type of bonding.

Experimental

The compound $(\pi\text{-C}_5\text{H}_5)_3\text{UCl}$ was synthesized in this Laboratory according to Reynolds & Wilkinson (1956); it is dark brown and very sensitive to air and moisture. Crystals were grown by sublimation in vacuum into thin-walled Pyrex capillaries. Several crops of crystals were prepared at various temperatures (from 190 to 220 °C), the lower temperatures giving better crystals. Most of the crystals were multiple-growth twins which appeared to be single under an ordinary microscope, but finally two single crystals of approximately optimum size for molybdenum radiation ($2/\mu \simeq 0.13$ mm) were chosen for X-ray photography. One was a plate with maximum dimension of about 0.1 mm and thickness of about 0.03 mm, and was oriented with the b axis approximately parallel to the capillary. The second was about the same size but more irregular in shape; its a axis was parallel to the capillary. In order to reduce absorption effects ($\mu r \simeq 2.5$ for $\text{Cu } K\alpha$), we decided to use $\text{Mo } K\alpha$ radiation ($\mu r \simeq 1.0$), in spite of the darker background caused by the closeness of $\text{Mo } K\alpha$ to one of the absorption edges of uranium. Equi-inclination multiple-film (interspersed with thin copper foils to give a film factor of about 3.6) Weissenberg photographs were taken with Zr-filtered $\text{Mo } K\alpha$ radiation. Data were collected for layer lines 0-5 around b and 0-1 around a . Intensities were estimated visually with the aid of an intensity strip prepared with the same crystals. For each observed plane, the average value of two sets of measurements from two separate quadrants on the same photograph was taken. After correction for Lorentz and polarization factors, the two sets of data (from the a and b axes) were correlated onto one arbitrary scale. The average discrepancy between these two sets of F 's was about 10%. Even with great care, the intensities were not of high quality, as indicated by the large discrepancies mentioned above and the narrow range of intensities (the largest value of F_o is only six times the smallest). The principal difficulties were: (1) the background was darker than ordinary because of scattering by the glass capillary and inelastic scattering by uranium; (2) because of the compound's sensitivity to air and moisture, crystals could not be made into spherical or cylindrical forms for suitable corrections of absorp-

tion, and consequently small crystals were necessary.

Unit-cell dimensions were obtained from two 15° oscillation photographs about a and b , taken with $\text{Cu } K\alpha$ radiation and superposed with the gold pattern as a standard. The values determined (based on $a_{\text{Au}} = 4.0702 \text{ \AA}$) are: $a = 8.26 \pm 0.03$, $b = 12.50 \pm 0.03$, $c = 13.81 \pm 0.03 \text{ \AA}$, and $\beta = 90.6 \pm 0.5^\circ$. The density determined by flotation is 2.19 g.cm^{-3} , in good agreement with the calculated value 2.184 g.cm^{-3} based on four molecules per unit cell.

Systematic absence of reflections $h0l$ for $h+l$ odd and $0k0$ for k odd indicated the space group $P2_1/n$. Out of a total of 1051 recorded reflections, 364 were too weak to be measured.

Patterson projections along 100 and 010 indicated the position of the uranium atom. Structure factors calculated for the uranium atom alone gave an R value of 0.25, and a three-dimensional Fourier synthesis was immediately calculated. This Fourier synthesis yielded the position of the chlorine atom and also gave faint images of three cyclopentadienyl rings located roughly at three vertices of a tetrahedron around the uranium atom, the chlorine atom occupying the fourth vertex.

Four cycles of structure-factor least-squares refinement of the positional and isotropic temperature parameters of the uranium and chlorine atoms reduced R to 0.17. For these and subsequent structure-factor calculations, the form factors used were those of Thomas-Fermi (*International Tables for X-ray Crystallography*, 1962) for uranium,* Tomiie & Stam (1958) for chlorine, and Hoerni & Ibers (1954) for carbon. Hydrogen contributions were not included. The quantity $\sum w(F_o - F_c)^2$ was minimized, and the weighting function was that suggested by Hughes (1941).

A difference synthesis was then calculated. Although background fluctuations were predominant, presumably because of the poor quality of the data, the three cyclopentadienyl rings appeared as positive regions with reasonable positions but rather distorted. On the basis of the map, tentative carbon positions were assigned consistent with plane regular pentagons approximately 1.4 \AA on an edge. An isotropic temperature factor with $B=10$ was arbitrarily assigned to each of the carbon atoms.

With the inclusion of the carbon atoms, R dropped to 0.15. Refinement was concluded with four cycles of structure-factor and block-diagonal least-squares calculations in which the three positional parameters and six anisotropic temperature parameters of the uranium and chlorine atoms were allowed to shift. R dropped to 0.12. The average shift in the positional parameters of the uranium atom during the last cycle was about 10% of its e.s.d. of 0.0015 \AA , and for chlorine about 70% of its e.s.d. of 0.015 \AA ; shifts in

* The rare earth tricyclopentadienide $\text{Sm}(\text{C}_5\text{H}_5)_3$ is at present under structural investigation in this laboratory. Our preliminary results show that it can not be a purely ionic bonding type compound. This result is not in concurrence with that reported by Birmingham & Wilkinson (1956).

* Correction for anomalous dispersion is significant (Dauben & Templeton, 1956). However, in view of the poor quality of the data, such corrections were deemed unwarranted.

Table 1. *The final parameters and their estimated standard deviations*

All values have been multiplied by 10^4 except in the case of carbon atoms, where they have been multiplied by 10^3 . The temperature factors are expressed in the form $T = \exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{23}kl - B_{31}lh)$. For carbon atoms, the assigned isotropic temperature factor is $B = 10.0$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
U	5379(2)	3442(1)	7189(1)	74(2)	55(1)	31(1)	00(5)	-4(3)	-12(2)
Cl	4476(17)	5365(14)	6859(9)	299(22)	107(13)	69(7)	-72(42)	39(19)	-80(23)
C(1)	368	179	638						
C(2)	275	274	616						
C(3)	368	334	549						
C(4)	509	272	526						
C(5)	510	178	583						
C(6)	303	276	842						
C(7)	315	380	860						
C(8)	472	408	900						
C(9)	550	304	910						
C(10)	440	224	870						
C(11)	822	370	615						
C(12)	845	278	673						
C(13)	854	294	772						
C(14)	837	408	783						
C(15)	817	455	688						

their anisotropic temperature parameters were also within the e.s.d. values listed in Table 1.

In hopes of obtaining more definitive information concerning the cyclopentadienyl rings, a second difference map was calculated based on the final parameters of the uranium and chlorine atoms. Disappointingly, the three cyclopentadienyl rings appeared no clearer than on the previous one, and hope for further refinement of the carbon-atom positions was abandoned. Sections of this difference map in the planes of the three cyclopentadienyls are shown in Fig. 1, with the final positions of the carbon atoms superposed on them. The section at $y=0.344$, which includes the uranium atom, is shown in Fig. 2; the peaks labelled I, II, and III are apparently spurious and are indicative of the over-all noise level.

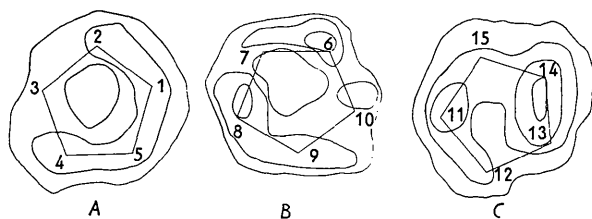


Fig. 1. The electron density in the planes of the three cyclopentadienyl rings. Contours are at intervals of $1.5 \text{ e.}\text{\AA}^{-3}$.

The final parameters, with e.s.d.'s derived in the usual way from the least-squares residuals, are listed in Table 1. The final calculated and observed structure factors are listed in Table 2.

Discussion

The three cyclopentadienyl rings and the chlorine atom are arranged approximately tetrahedrally about the uranium atom. If A , B , and C denote the centers

of the cyclopentadienyl rings, the angles $A-U-B$, $B-U-C$, and $C-U-A$ are 115° , 120° , and 115° and the angles $A-U-Cl$, $B-U-Cl$, and $C-U-Cl$ are 101° , 100° , and 101° .

The U-Cl bond length, $2.559 \pm 0.016 \text{ \AA}$, corresponds to a bond order of 0.75 if we take 2.41 \AA as the single-bond length and Zachariasen & Plettinger's (1959) curve for U-O bond order *versus* bond length. Since there is about 35% partial ionic character in the U-Cl single bond, this will lead to slightly over 50% ($0.25 + (0.35)(0.75)$) ionic character for the U-Cl bond,

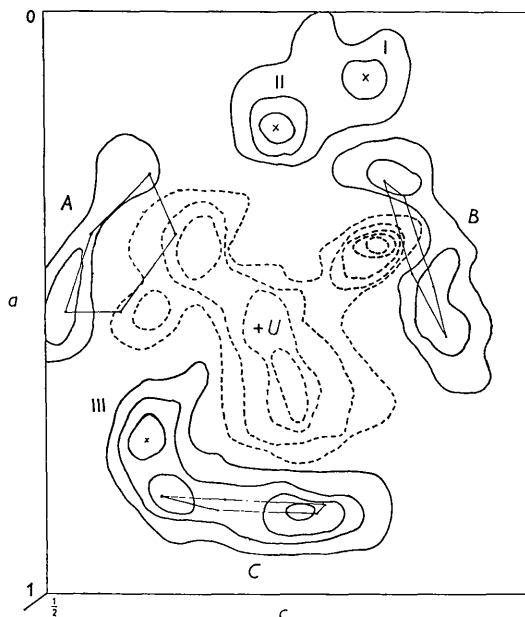
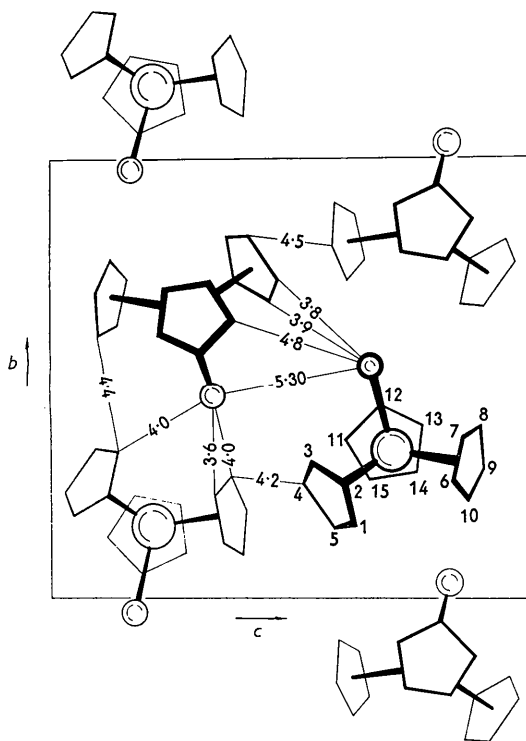


Fig. 2. A difference map in the plane $y=0.344$. Solid lines indicate positive regions, dashed lines negative regions. Contours are at intervals of $1.5 \text{ e.}\text{\AA}^{-3}$. I, II, and III are the three outstanding spurious peaks.

Table 2. Calculated and observed structure factors

The three columns in each group contains the values of l , $10|F_o|$ and $10F_c$.Reflections that have been cut off by the camera in MoK α data are asterisked; however, the calculated values are in approximate agreement with our CuK α data

h, k, l	l	$10 F_o $	$10F_c$	h, k, l	l	$10 F_o $	$10F_c$	h, k, l	l	$10 F_o $	$10F_c$	h, k, l	l	$10 F_o $	$10F_c$	
2 [*] 0 0 1	940	1 4117 672	2 356 417	6 258 376	0 398 315	0 1181 59	0 113 140	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
4 252 307	2 4117 672	1 408 638	7 4120 6	7 195 417	8 4185 240	1 591 571	1 591 571	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
8 142 129	3 212 176	1 408 638	8 212 377	8 1170 151	9 4110 174	0 4111 174	0 4111 174	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
10 245 250	4 142 129	3 158 171	10 287 294	5 474 540	5 4145 49	5 4145 49	5 4145 49	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
12 232 241	5 245 255	4 757 660	11 131 254	4 4123 102	4 4130 6	2 4141 111	2 4141 111	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
14 232 241	6 323 353	5 4117 156	12 131 254	2 4106 114	2 4106 114	2 4106 114	2 4106 114	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
16 199 158	7 257 267	6 4117 284	13 131 254	3 4121 140	3 4121 140	3 4121 140	3 4121 140	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
18 199 158	8 157 177	7 4104 84	14 131 254	4 4127 17	4 4127 17	4 4127 17	4 4127 17	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
20 199 158	9 109 211	8 1113 254	15 131 254	5 4133 22	5 4133 22	5 4133 22	5 4133 22	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
22 199 158	10 167 140	9 1012 51	16 131 254	6 4139 27	6 4139 27	6 4139 27	6 4139 27	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
24 199 158	11 174 148	10 1124 51	17 131 254	7 4145 32	7 4145 32	7 4145 32	7 4145 32	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
26 199 158	12 224 177	11 1131 254	18 131 254	8 4151 37	8 4151 37	8 4151 37	8 4151 37	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
28 199 158	13 274 216	12 1138 254	19 131 254	9 4157 42	9 4157 42	9 4157 42	9 4157 42	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
30 199 158	14 324 255	13 1145 254	20 131 254	10 4163 47	10 4163 47	10 4163 47	10 4163 47	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
32 199 158	15 374 294	14 1152 254	21 131 254	11 4169 52	11 4169 52	11 4169 52	11 4169 52	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
34 199 158	16 424 333	15 1159 254	22 131 254	12 4175 57	12 4175 57	12 4175 57	12 4175 57	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
36 199 158	17 474 372	16 1166 254	23 131 254	13 4181 62	13 4181 62	13 4181 62	13 4181 62	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
38 199 158	18 524 411	17 1173 254	24 131 254	14 4187 67	14 4187 67	14 4187 67	14 4187 67	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
40 199 158	19 574 450	18 1180 254	25 131 254	15 4193 72	15 4193 72	15 4193 72	15 4193 72	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
42 199 158	20 624 489	19 1187 254	26 131 254	16 4199 77	16 4199 77	16 4199 77	16 4199 77	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
44 199 158	21 674 528	20 1194 254	27 131 254	17 4205 82	17 4205 82	17 4205 82	17 4205 82	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
46 199 158	22 724 567	21 1201 254	28 131 254	18 4211 87	18 4211 87	18 4211 87	18 4211 87	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
48 199 158	23 774 606	22 1208 254	29 131 254	19 4217 92	19 4217 92	19 4217 92	19 4217 92	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
50 199 158	24 824 645	23 1215 254	30 131 254	20 4223 97	20 4223 97	20 4223 97	20 4223 97	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
52 199 158	25 874 684	24 1222 254	31 131 254	21 4229 102	21 4229 102	21 4229 102	21 4229 102	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
54 199 158	26 924 723	25 1229 254	32 131 254	22 4235 107	22 4235 107	22 4235 107	22 4235 107	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
56 199 158	27 974 762	26 1236 254	33 131 254	23 4241 112	23 4241 112	23 4241 112	23 4241 112	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
58 199 158	28 1024 801	27 1243 254	34 131 254	24 4247 117	24 4247 117	24 4247 117	24 4247 117	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
60 199 158	29 1074 840	28 1250 254	35 131 254	25 4253 122	25 4253 122	25 4253 122	25 4253 122	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
62 199 158	30 1124 879	29 1257 254	36 131 254	26 4259 127	26 4259 127	26 4259 127	26 4259 127	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
64 199 158	31 1174 918	30 1264 254	37 131 254	27 4265 132	27 4265 132	27 4265 132	27 4265 132	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
66 199 158	32 1224 957	31 1271 254	38 131 254	28 4271 137	28 4271 137	28 4271 137	28 4271 137	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
68 199 158	33 1274 996	32 1278 254	39 131 254	29 4277 142	29 4277 142	29 4277 142	29 4277 142	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
70 199 158	34 1324 1035	33 1285 254	40 131 254	30 4283 147	30 4283 147	30 4283 147	30 4283 147	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
72 199 158	35 1374 1074	34 1292 254	41 131 254	31 4289 152	31 4289 152	31 4289 152	31 4289 152	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
74 199 158	36 1424 1113	35 1299 254	42 131 254	32 4295 157	32 4295 157	32 4295 157	32 4295 157	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
76 199 158	37 1474 1152	36 1306 254	43 131 254	33 4301 162	33 4301 162	33 4301 162	33 4301 162	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
78 199 158	38 1524 1191	37 1313 254	44 131 254	34 4307 167	34 4307 167	34 4307 167	34 4307 167	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
80 199 158	39 1574 1230	38 1320 254	45 131 254	35 4313 172	35 4313 172	35 4313 172	35 4313 172	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
82 199 158	40 1624 1269	39 1327 254	46 131 254	36 4319 177	36 4319 177	36 4319 177	36 4319 177	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
84 199 158	41 1674 1308	40 1334 254	47 131 254	37 4325 182	37 4325 182	37 4325 182	37 4325 182	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
86 199 158	42 1724 1347	41 1341 254	48 131 254	38 4331 187	38 4331 187	38 4331 187	38 4331 187	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217	10 210 217
88 199 158	43 1774 1386	42 1348 254														

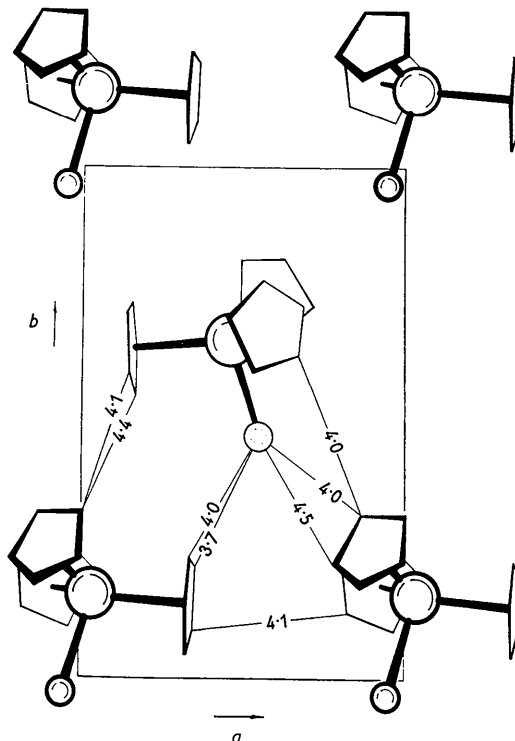
Fig. 3. The structure viewed down the a axis.

in agreement with reported chemical properties of this compound (Reynolds & Wilkinson, 1956).

The positions of the carbon atoms are very poorly determined, and about all that can be claimed is that they are consistent with the difference maps and with the expected geometry of the cyclopentadienyl rings. Nevertheless, a few comments may be in order. The average U-C bond length is 2.74 Å, individual values ranging from 2.82 to 2.68 Å. This corresponds to a bond order of 0.17, if we take 2.19 Å for U-C single bond distance, and again assume Zachariassen & Plettinger's (1959) curve for U-O bond order *versus* bond length. 2.55 pairs of electrons would then take part in the bonding between the uranium atom and the cyclopentadienyl rings in satisfactory agreement with Moffitt (Reynolds & Wilkinson, 1956) and Shirmazan & Diatkina's (1957) prediction that three pairs of electrons are responsible for the U-C bonding.

Packing drawings of the structure viewed along a and c are shown in Figs. 3 and 4.

The packing of the molecules is very loose, all the pertinent intermolecular distances being equal to or greater than normal van der Waals distances within the accuracy of this determination. In line with the looseness of packing, the temperature factors are large. The magnitudes, B , and the direction cosines, relative to the cell axes, of the principal axes of the thermal ellipsoids for the uranium and chlorine atoms are listed in Table 3.

Fig. 4. The structure viewed down the c axis (from 0 to $\frac{1}{2}c$).Table 3. Magnitudes B and direction cosines relative to the cell edges of the principal axes of the thermal ellipsoids

Atom	Axis i	B_i	q_{ia}	q_{ib}	q_{ic}
U	1	1.84	0.842	0.045	0.538
	2	3.47	0.032	0.991	-0.131
	3	2.53	0.537	-0.129	-0.834
Cl	1	3.35	0.435	0.493	-0.753
	2	9.36	0.891	-0.358	0.279
	3	7.46	0.132	0.793	0.595

Thanks are due to Messrs Yuan-tseh Lee, Li-chen Wang, and Cheung-chao Chou for their assistance in the synthesis of this compound, and to Prof. Lynne Merritt for the Fourier program he has kindly given to us. We also express our appreciation of the use of the fine computing facilities provided by the Computer Center of National Chiao Tung University. Finally, we are very grateful for the generous financial support given to us by the authority of this University.

References

- BIRMINGHAM, J. M. & WILKINSON, G. (1956). *J. Amer. Chem. Soc.* **78**, 42.
 DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 341.
 HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-ray Crystallography (1962). Vol. III. p. 212. Birmingham: Kynoch Press.

REYNOLDS, L. T. & WILKINSON, G. (1956). *J. Inorg. Nucl. Chem.* **2**, 246.
 SHIRMAZAN, M. G. & DYATKINA, M. E. (1957). *Zhur. Neorg. Khim. SSSR*, **2**, 1761.

TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
 ZACHARIASEN, W. H. & PLETTINGER, H. A. (1959). *Acta Cryst.* **12**, 526.

Acta Cryst. (1965). **18**, 345

The Structure of C_8F_{12} , a Saturated Dimer of Hexafluorobutadiene

BY I. L. KARLE AND J. KARLE

U.S. Naval Research Laboratory, Washington, D.C., U.S.A.

AND T. B. OWEN* AND J. L. HOARD

Cornell University, Ithaca, N.Y., U.S.A.

(Received 19 March 1964)

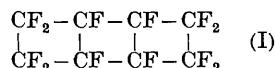
The molecular formula and configuration of the saturated C_8F_{12} molecule has been elucidated. The carbon skeleton contains two bridge bonds which make four-membered and five-membered rings (tricyclo[3,3,0,0^{2,6}]octane). The symmetry of the molecule is D_{2d} .

The material crystallizes in the triclinic system with one molecule in a unit cell having the dimensions $a = 6.02$, $b = 6.29$, $c = 7.27$, $\alpha = 103.6^\circ$, $\beta = 107.9^\circ$, $\gamma = 106.4^\circ$. The statistical averages of normalized structure factors strongly indicate that the space group is $P\bar{1}$, and since the molecule does not have a center of symmetry, this implies that the crystal structure is disordered. Attempts to refine an ordered structure in $P1$ failed. Satisfactory refinement was obtained with a disordered structure (utilizing space group $P1$) in which successive molecules may be subject to reversal of direction.

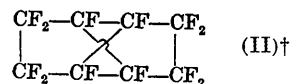
The structure was solved by obtaining the phases directly from the magnitudes of the structure factors by the application of the symbolic addition method for phase determination.

Introduction

Some years ago, the thermal reactions of hexafluorobutadiene were investigated by Prober & Miller (1949). The first step resulted in a mixture of dimers which were dienes. Further heating of the dimers in a bomb yielded a large fraction of a material which boiled at 80°C and melted at 40°C . The material was found to have the molecular formula C_8F_{12} and was shown to be fully saturated. Prober & Miller (1949) suggested that the structural formula of C_8F_{12} may be



The structure has been elucidated by the application of the symbolic addition method of phase determination (Karle & Karle, 1963) to three-dimensional X-ray intensity data. The X-ray analysis shows that the compound is not in the form of three fused butane rings, but assumes the following configuration:



Experimental measurements

Single crystals of the compound were grown under vacuum by sublimation in thin-walled glass capillaries. The capillaries were 1 mm in diameter and had an average wall thickness of 0.01 mm. The crystals were mounted on the goniometer head so that the face of growth in the capillary was perpendicular to the rotation axis. Multiple-film, equi-inclination Weissenberg photographs were taken along the 100, 010 and $\bar{1}10$ directions with $\text{Cu } K\alpha$ radiation. Zero-layer NaCl reflections were superimposed on zero-layer photographs of C_8F_{12} for lattice constant measurements.

The diffraction results show a triclinic cell with the following parameters:

[†] Note added in proof:—The configuration of a similar compound, C_8H_{12} , was inferred to be of type (II) on the basis of a nuclear magnetic resonance spectrum (Srinivasan, 1963).

* Present address: U.S. Naval Research Laboratory, Washington, D.C., U.S.A.