distances are listed in Table 5. These distances indicate that the molecules are all held together in the crystalline state mainly by van der Waals forces.

Table 5. *Intermolecular contacts less than* 4·0 Å

Contact	Position*	Distance
C(1)—Br(2)	4/000	3·97
C(2)—C(23)	4/000	3·63
C(4)—C(23)	4/001	3·84
C(4)—C(24)	4/001	3·67
C(16)–C(25)	2/$\bar{1}$00	3·81
C(16)–Br(1)	2/000	3·95
C(18)–Br(1)	2/000	3·98
C(22)–C(25)	2/$\bar{1}$00	3·98
C(23)–C(2)	4/$\bar{1}$00	3·63
C(23)–C(4)	4/$\bar{1}$01	3·84
C(24)–C(4)	4/$\bar{1}$01	3·67
C(25)–C(16)	2/$\bar{1}$0$\bar{1}$	3·81
C(25)–C(22)	2/$\bar{1}$0$\bar{1}$	3·98
O(2)—C(16)	2/$\bar{1}$0$\bar{1}$	3·80
O(2)—C(23)	2/$\bar{1}$00	3·54
O(2)—C(24)	2/$\bar{1}$00	3·66
O(2)—O(3)	2/$\bar{1}$00	3·99
O(2)—C(2)	3/0$\bar{1}$0	3·68
O(2)—C(3)	3/0$\bar{1}$0	3·87
O(3)—C(2)	4/$\bar{1}$00	3·34
O(3)—3C()	4/$\bar{1}$00	3·95
O(3)—C(4)	4/$\bar{1}$01	3·49

* Equivalent position nomenclature: C(23)–C(4) 4/$\bar{1}$01 is taken to mean that C(4) is at equivalent position 4, translated −1, 0 and +1 unit cells in the **a, b** and **c** directions, respectively. The equivalent positions are: $1 = (x,y,z)$; $2 = (\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$; $3 = (\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$; $4 = (\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$.

References

BONHAM, R. A. & BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3491.

BRUTCHER, F. V. & LEOPOLD, E. J. (1966). *J. Amer. Chem. Soc.* **88**, 3156.

GOPALAKRISHNA, E. M., COOPER, A. & NORTON, D. A. (1968). To be published.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521.

MATTOX, V. R., TURNER, R. B., ENGEL, L. L., McKENZIE, B. F., McGUCKIN, W. F. & KENDALL, E. C. (1946a). *J. Biol. Chem.* **164**, 582, 590, 599.

MATTOX, V. R., TURNER, R. B., ENGEL, L. L. McKENZIE, B. F., McGUCKIN, W. F. & KENDALL, E. C. (1946b). *J. Biol. Chem.* **166**, 345, 357.

MATTOX, V. R., TURNER, R. B., ENGEL, L. L., McKENZIE, B. F., McGUCKIN, W. F. & KENDALL, E. C. (1948). *J. Biol. Chem.* **173**, 283, 286, 290, 291.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

The Identification and Crystal Structure of a Hydropericardium-Producing Factor: 1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin

BY J. S. CANTRELL,* N. C. WEBB AND A. J. MABIS†

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239, *U.S.A.*

A crystalline material, isolated from a contaminated animal feed fat, and capable of producing hydropericardium in chicks, was shown by solution of its crystal structure to be 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin ($C_{12}O_2H_2Cl_6$). The triclinic unit cell has the dimensions $a = 7·952 \pm 0·005$, $b = 9·379 \pm 0·01$, $c = 9·433 \pm 0·01$ Å, $\alpha = 92·35° \pm 0·20°$, $\beta = 92·39° \pm 0·20°$, $\gamma = 109·92° \pm 0·30°$. The calculated density is 1·958 g.cm^{-3} for $Z = 2$, compared with 2·01 g.cm^{-3} measured for the bulk material. A statistical treatment of the 1158 measured reflections indicated a center of symmetry; the space group was therefore assumed to be P$\bar{1}$. The structure was solved by the symbolic addition method of Karle & Karle. The nearly planar molecules are almost parallel to the (0$\bar{1}$1) crystallographic planes. No unusual bond lengths or angles were found. The structure was refined to $R = 10·5\%$.

Introduction

The isolation, chemical analyses, and spectroscopic data on the hydropericardium toxic factor (HPTF) material have been described by Wootton, Artman & Alexander (1962), and by Wootton & Courchene

---

* Present address: Miami University, Department of Chemistry, Oxford, Ohio, U.S.A.

† Reprint requests should be addressed to this author at the Procter & Gamble address.

(1964). One of the active fractions of material isolated was that called α-3·17, where this nomenclature refers to the vapor phase chromatographic behavior as described by Wootton *et al.* (1962). Wootton and his colleagues proposed that HPTF was a chlorinated hexahydrophenanthrene with the empirical formula $C_{14}H_{10}Cl_6$. Following the molecular identification herein reported, Wootton (1966) showed that a synthetic hexachlorinated dibenzo-*p*-dioxin, whose physical properties are remarkably similar to the isolated

α-3·17 material, does indeed produce the hydropericardium condition in chickens.*

Experimental

Two types of crystals were isolated from a warm benzene–hexane solution of the α-3·17 material. The bulk of the crystalline material appeared to differ in phase from the material used for this study. No crystals of the bulk phase were found to be satisfactory for single-crystal studies, and only two crystals of the studied phase were isolated. Measured d-spacings of X-ray powder patterns taken of the bulk phase material did not match d-spacings calculated from the unit cell of 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin. However, when the bulk phase was heated to just below the melting point (230°C) a phase change occurred. Measured d-spacings from X-ray powder patterns of the transformed bulk phase match the calculated d-spacings of 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin reasonably well. Therefore, it was assumed that the material used for this crystal structure determination was a high temperature phase of the bulk crystalline material known as α-3·17 HPTF.

The single crystals used were diamond shaped and had the approximate dimensions $0.18 \times 0.10 \times 0.08$ mm ($a \times b \times c$).

The unit-cell parameters were determined from single-crystal data using a General Electric single-crystal orienter and Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The parameters of the triclinic cell chosen according to Dirichlet (Balashov & Ursell, 1957) are as follows:

$a = 7.952 \pm 0.005$ Å $\alpha = 92.35 \pm 0.20°$ $\varrho_c = 1.958$ g.cm^{-3}
$b = 9.379 \pm 0.01$ $\beta = 92.39 \pm 0.20$ $\varrho_o = 2.01$ g.cm^{-3}
$c = 9.433 \pm 0.01$ $\gamma = 109.92 \pm 0.30$ $Z = 2$
$V = 662.8$ Å^3

where ϱ_o was measured for the bulk phase by flotation.

Two-dimensionally integrated equi-inclination Weissenberg data were collected for the a-axis zones, $0kl$–$4kl$, and for the b-axis zones $h0l$–$h5l$ using the multiple-film technique (one pack each of four films, Eastman

---

* The composition for the structure reported here, namely $C_{12}O_2H_2Cl_6$, agrees well with unpublished microchemical analyses performed by Professor Wolfgang J. Kirsten, University of Uppsala, Uppsala, Sweden, at a very early stage of this structure work.

Kodak No-Screen). Intensity data were recorded for both crystals, reduced separately, then compared, edited, and averaged. Absorption corrections were made separately for each crystal using Busing & Levy's general absorption correction program as modified by Jeffrey (1964).

Owing to the very tiny crystals, and in part to the integration, very long exposures of approximately 150 hours were required to obtain satisfactory multiple-film data. The entire Weissenberg camera was placed inside a plastic bag and a helium atmosphere was provided to reduce background due to air scattering. Of the 3030 possible reflections, 1158 (38%) were recorded; 397 of these reflections had intensities less than a minimum threshold value and were classified as 'less-thans'. The intensities of most of the reflections were measured by a Joyce Loebl microdensitometer scanning at right angles to the longer integration direction. The weakest reflections were estimated visually. A standard intensity strip was prepared and used for the visually estimated intensities. To ensure that both types of intensity data were on the same scale, a sufficient number of medium intensities were measured both visually and by the densitometer. Radiation damage effects were found to be negligible by retaking data for earlier crystal settings.

Statistical treatment of the intensity data by Ramachandran & Srinivasan's (1959) modification of the method of Howells, Phillip & Rogers (1950) indicated a center of symmetry. The space group was assumed, therefore, to be $P\bar{1}$ (C_i^1) and this assumption was confirmed during the direct method calculations.

Solution and refinement of the structure

Initially we knew the weight of the molecule and the number of chlorine atoms per molecule, and we knew that the molecule possessed some aromatic character. Attempts to solve the structure from the three-dimensional Patterson map were not successful. The symbolic addition method of Karle & Karle (1963, 1966) was then employed.

The phases were determined for the 251 most intense reflections in terms of four algebraic quantities, a, b, c, g. A summary of the calculation of the unitary structure factors or E-values used for this determination is compared with theoretical values and is as follows:

Quantity	Non-centrosymmetric	Centrosymmetric	$C_{12}H_2O_2Cl_6$	Karle *et al.* (1964) 3-Indolyl-acetic acid
$\langle |E| \rangle$	0·886	0·798	0·772	0·769
$\langle |E^2 - 1| \rangle$	0·736	0·968	0·970	0·934
$\langle |E|^2 \rangle$	1·000	1·000	1·000	1·031
$|E| > 3·0$		0·3%	0·4%	0·2%
$|E| > 2·0$		5·0%	4·5%	3·3%
$|E| > 1·0$		32·0%	30·8%	36·1%

1·158 reflections   1·289 reflections
761 non-zero   865 non-zero
397 unobserved   424 zero
('less-than')

The overall temperature factor was 2·24.

A summary of the sixteen cases that resulted from the sign permutation of the four algebraic assignments is as follows:

some changes made in carbon and chlorine assignments resulting in, ideally, a planar 1,2,3,7,8,9-hexachloroanthracene with mm symmetry. This change in the structure dropped the R value to 35%. The plane

Case	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
a	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
b	+	+	+	−	−	−	−	+	+	+	+	−	−	−	−	+
c	−	+	−	+	−	−	+	+	−	+	−	+	−	−	+	+
g	−	−	+	+	+	−	−	+	−	−	+	+	+	−	−	+
No. refl. generated +	119	183	114	153	142	116	118	251	121	121	115	125	121	122	128	122
−	132	68	137	98	109	135	133	0	130	130	136	126	130	129	123	129
No. incorrect signs	117	132	125	132	133	129	130	129	121	128	104	130	35	61	120	117
% wrong sign	46·6	52·6	49·8	52·6	53·0	51·4	51·7	51·4	48·3	51·0	41·5	51·7	13·9	24·3	47·8	46·6
Objections to choice	√	√	√	√	√	√	√	√ †					*			

√ Electron density peaks were found at centers of symmetry when the special sections $x=0$ and $x=\frac{1}{2}$ were computed.

† It is very unlikely that all 251 most intense reflections would be positive.

* This correct case was selected after examining three-dimensional electron density maps for cases 9 to 16.

Case 13 was chosen over the other seven acceptable choices because of the appearance of a chemically reasonable structure in the electron density plot in an (044) plane. It had already been determined that the molecule had to be oriented approximately in alternate (044) planes, based on (a) the early analysis of the Patterson map, (b) the very high intensity of 022, (c) electron densities calculated from models based on the Patterson vectors, and (d) packing considerations. A nearly planar hexachlorinated phenanthrene structure was initially fitted to the E-map peaks located near an (044) plane. An R value of 50% was obtained for the initial trial coordinates and a three-dimensional electron density map suggested that the phenanthrene skeleton should be changed to an anthracene one with

of the molecule was originally in alternate (044) planes but required some tilting and when these changes were made the R value dropped to 24%. One cycle of least squares reduced the residual to 19%. At this point the two bridging atoms were recognized as oxygens, since their relative electron densities were 30% higher than those for the carbon atoms and the individual temperature factors for these atoms had gone negative. Substituting oxygen atoms for these carbon atoms in the proposed model resulted in an R value of 16%. There was a careful editing of the data, especially of those reflections classified as 'less-thans', at the R = 16% stage of refinement. This editing consisted of deleting a few doubtful reflections recorded near the edge of a film, correcting transcription errors, and reclas-

Table 1. *Final parameters and their standard deviations*

The fractional coordinates have been multiplied by 10^4 and the temperature factors by 10^2; the standard deviations are in parentheses. The anisotropic temperature factors of the chlorine atoms are in the form

$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+2B_{12}ha^*kb^*+B_{22}k^2b^{*2}\ldots)\right]$$

	X	Y	Z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	−0099 (6)	3158 (6)	5185 (6)	287 (20)	376 (29)	487 (26)	149 (21)	−035 (17)	−088 (22)
Cl(2)	−0145 (6)	0579 (6)	2931 (5)	362 (23)	378 (30)	417 (27)	025 (22)	−162 (19)	−043 (22)
Cl(3)	3314 (7)	−0257 (6)	2621 (5)	487 (26)	411 (30)	376 (26)	163 (24)	−056 (21)	−084 (24)
Cl(4)	9493 (6)	7375 (6)	10547 (5)	372 (23)	457 (30)	347 (24)	174 (23)	−018 (18)	−105 (22)
Cl(5)	6188 (6)	8434 (6)	10752 (5)	395 (24)	375 (29)	309 (23)	076 (22)	034 (18)	−024 (21)
Cl(6)	2919 (6)	6936 (6)	8629 (5)	282 (21)	421 (29)	473 (27)	148 (21)	028 (18)	−102 (23)
C(1)	1762 (24)	2601 (22)	4879 (20)	354 (41)					
C(2)	1718 (21)	1502 (20)	3979 (18)	262 (35)					
C(3)	3286 (25)	1118 (22)	3853 (20)	386 (43)					
C(4)	4753 (24)	1920 (23)	4673 (21)	370 (42)					
C(6)	7712 (23)	5516 (21)	8394 (19)	321 (39)					
C(7)	7706 (20)	6572 (19)	9388 (16)	219 (34)					
C(8)	6219 (27)	7051 (24)	9503 (22)	427 (45)					
C(9)	4754 (21)	6238 (19)	8539 (17)	249 (35)					
C(11)	3292 (23)	3471 (21)	5778 (19)	325 (39)					
C(12)	4776 (24)	2994 (22)	5629 (19)	360 (42)					
C(13)	6226 (21)	4811 (19)	7461 (18)	240 (34)					
C(14)	4752 (20)	5271 (19)	7591 (17)	213 (32)					
O(5)	6312 (15)	3742 (14)	6496 (13)	355 (27)					
O(10)	3266 (15)	4591 (14)	6713 (13)	334 (27)					

Table 2. *Observed and calculated structure factors*

Within each group are listed values of *h*, $10F_o$ and $10F_c$. Asterisks denote 'less than' reflections.

sifying some of the 'less-thans' to observed reflections on the basis of visual estimations of the weakest reflections.

The R value dropped to 13% during the next least-squares refinement. Fixing the chlorine atoms and refining only the carbon skeleton resulted in an R value of 11·8% at which time the anisotropic temperature refinement on the chlorine atoms was undertaken and gave the final R of 10·5%. Of the 397 'less-than' reflections only 42 calculated were larger than their threshold values and none by more than 36%. A weighting function similar to that given by Hughes (1941) was chosen so as to have little dependence on F_o; it was taken as $\sqrt{w} = K/(F_o + 53\cdot4)$ for $F_o > F_m$ and $\sqrt{w} = K/(F_m + 53\cdot4)$ for $F_o \le F_m$, where $F_m = 21\cdot4$, and the quantity minimized was $\Sigma\, w(F_o - F_c)^2$. 'Less-than' reflections having $F_c > F_o$ (threshold) contributed like an ordinary reflection, but those having $F_c < F_o$ did not influence the refinement at all. A full-matrix least-squares procedure was used throughout the refinement, and in the last cycle all parameter shifts were less than $\frac{1}{4}\sigma$. In a difference map calculated at the $R = 11\cdot8\%$ stage, the residual electron density ranged from $-0\cdot8$ to $+0\cdot6$ e.Å^{-3}, and the maxima and minima did not show any chemically or structurally significant features.

The final position and thermal parameters are given in Table 1. The observed and calculated structure factors are listed in Table 2. In this work, the scattering factors are taken from *International Tables for X-ray Crystallography* (1962); those for carbon are by Free-man (1959); those for oxygen by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); and those for chlorine by Dawson (1960).

Discussion

The molecule is nearly planar and the molecular plane is tilted 8° to the (0$\bar{1}$1) plane. Deviations of atoms from the (0$\bar{4}$4) plane essentially containing the molecule and
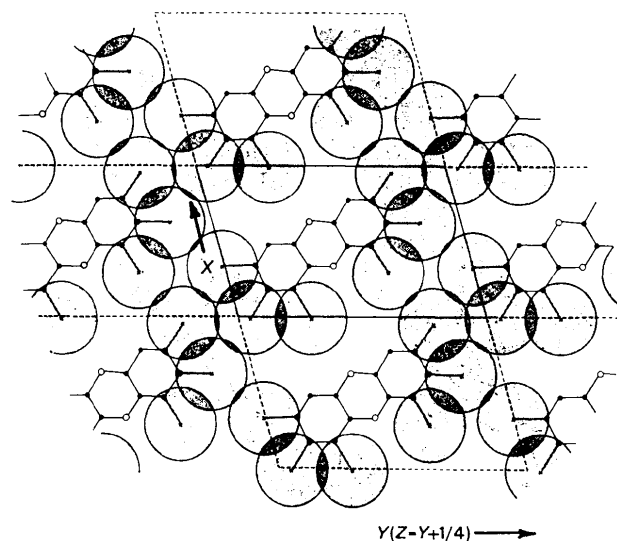

Fig. 1. Molecular packing in the (0$\bar{4}$4) plane containing the molecule. Large shaded circles are Cl, solid circles are C, and open circles are O.

Table 3. *Distances of atoms from least-squares planes*

Distances for atoms not defining the plane are marked with an asterisk; s.d. is the standard deviation of the atoms defining the plane. Under the (0$\bar{4}$4) heading are listed the deviations from the (0$\bar{4}$4) plane containing the molecule. The planes are defined in direct space by equations $Px + Qy + Rz = S$.

|	All	C+O	(0$\bar{4}$4)
Cl(1)	−0·10	−0·10*	0·33*
Cl(2)	−0·11	−0·12*	0·10*
Cl(3)	0·00	−0·03*	−0·25*
Cl(4)	−0·16	−0·18*	−0·45*
Cl(5)	−0·05	−0·06*	0·12*
Cl(6)	0·13	0·13*	0·54*
C(1)	−0·02	−0·03	0·15*
C(2)	−0·06	−0·08	0·02*
C(3)	−0·02	−0·05	−0·16*
C(4)	0·06	0·03	−0·17*
C(6)	0·00	−0·03	−0·25*
C(7)	−0·05	−0·07	−0·21*
C(8)	−0·01	−0·03	0·03*
C(9)	−0·01	−0·02	0·13*
C(11)	0·06	0·05	0·13*
C(12)	0·05	0·03	−0·09*
C(13)	0·05	0·02	−0·10*
C(14)	0·06	0·05	0·12*
O(5)	0·08	0·05	−0·17*
O(10)	0·09	0·08	0·25*
Origin	1·57*	1·55*	1·67*
s.d.	0·07	0·05	0·00
P	−1·1589	−1·1086	0·0000
Q	−5·9655	−6·0031	−6·6618
R	6·8500	6·8404	6·6618
S	1·5675	1·5497	1·6655
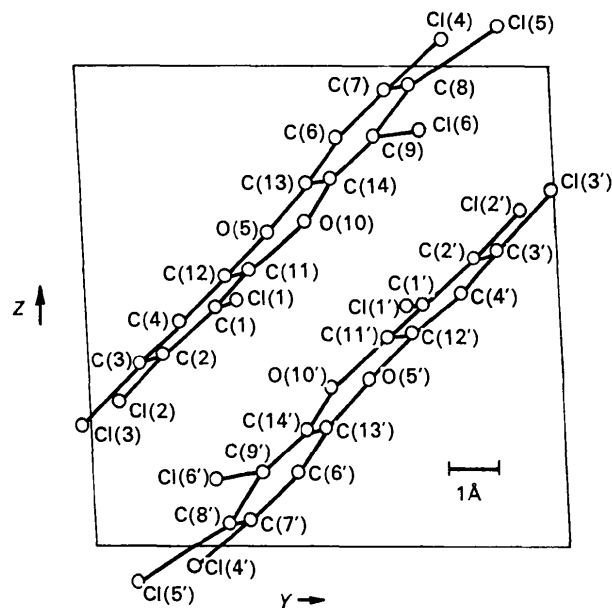
Fig. 2. Projection onto YZ plane.

from the least-squares planes of the entire molecule and of the carbon–oxygen skeleton are given in Table 3. The molecule appears to be slightly bowed in the middle and slightly twisted about a line from Cl(3) to Cl(5). The packing arrangement of chlorines 4, 5, and 6 appears to be more crowded than that for chlorines 1, 2, and 3. This packing difference could account for the slight twist of the molecule.

Fig. 1 pictures the molecular packing in the (0$\bar{4}$4) plane containing the molecule, and Fig. 2 gives a projected view of two adjacent molecules related by the center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Intermolecular distances in this (0$\bar{4}$4) plane of less than 4·0 Å are shown in Fig. 3. Between centrosymmetrically related molecules there are a number of Cl(n)–Cl(m') and equivalent Cl(m)–Cl(n') distances of 4·0 Å or less. From the parent molecule to the one related by the center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ the distances are Cl(2)–Cl(4') = 3·85 Å, Cl(3)–Cl(5') = 3·66 Å, and Cl(3)–Cl(6') = 3·83 Å; by the center at (0,0,$\frac{1}{2}$)–Cl(1)–Cl(3') = 3·84 Å; by the center at (0,$\frac{1}{2}$,$\frac{1}{2}$)–Cl(1)–Cl(1') = 3·39 Å and Cl(2)–Cl(6') = 3·98 Å; and by the center at

$(\frac{1}{2},\frac{1}{2},1)$–Cl(4)–Cl(6') = 4·00 Å. The least-squares planes of the two adjacent molecules related by the center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are 3·13 Å apart; between these two molecules the shortest interatomic distance is 3·30 Å from a C(12) to an O(10).

Fig. 3 indicates the bond distances and angles. The mean standard deviations are as follows: σ_{C-C} = 0·025 Å, σ_{C-Cl} = 0·019 Å, σ_{C-O} = 0·022 Å; for angles σ = 2·0°. The bond distances are not significantly different from those found by Davydova & Struchkov (1962) and Gafner & Herbstein (1962) for 1,4,5,8-tetrachloronaphthalene where molecular over-crowding results from the presence of many chlorine atoms substituted on adjacent aromatic positions. This compound belongs in group (I) according to the classification due to Harnik, Herbstein, Schmidt & Hirshfeld (1954) for compounds that are affected by molecular over-crowding.

An electron density map plotted in the (0$\bar{4}$4) plane containing the molecule is shown in Fig. 4.

The authors wish to acknowledge their appreciation to Dr J. M. Stewart of the University of Maryland, who furnished the X-ray 63 computer program and provided much information on its use. In addition, we wish to thank Dr Lyle Jensen for a number of helpful discussions on the use of the X-ray 63 computing system and on approaches to the solution of the structure in general.

We wish to express our appreciation to Drs Jerome and Isabella Karle who provided assistance in applying the direct method for determining the phases of a number of the most intense reflections.

Thanks are due to Mr Robert Gloss who obtained part of the data and provided the computer programs used in generating the relations between reflections necessary for applying the direct method.

(a)

(b)

Fig. 3. (a) Interatomic distances. Primed atoms are on neighboring molecules in the same plane. σ_{C-C} = 0·025 Å; σ_{C-Cl} = 0·019 Å; σ_{C-O} = 0·022 Å. View corresponds to Fig. 1. (b) Bond angles. σ = 2·0°.

References

BALASHOV, V. & URSELL, H. D. (1957). Acta Cryst. 10, 582.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). Acta Cryst. 8, 478.

DAVYDOVA, M. A. & STRUCHKOV, YU. T. (1962). Zh. Strukt. Khimii, 3, 184.

DAWSON, B. (1960). Acta Cryst. 13, 403.

FREEMAN, A. J. (1959). Acta Cryst. 12, 261.

GAFNER, G. & HERBSTEIN, F. H. (1962). Acta Cryst. 15, 1081.

GAFNER, G. & HERBSTEIN, F. H. (1963). Nature, Lond. 200, 130.

HARNIK, E., HERBSTEIN, F. H., SCHMIDT, G. M. J. & HIRSHFELD, F. L. (1954). J. Chem. Soc. p. 3288.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). Acta Cryst. 3, 210.

HUGHES E. W. (1941). J. Amer. Chem. Soc., 63, 1737.

International Tables for X-ray Crystallography, (1962). Vol. III. Birmingham: Kynoch Press.
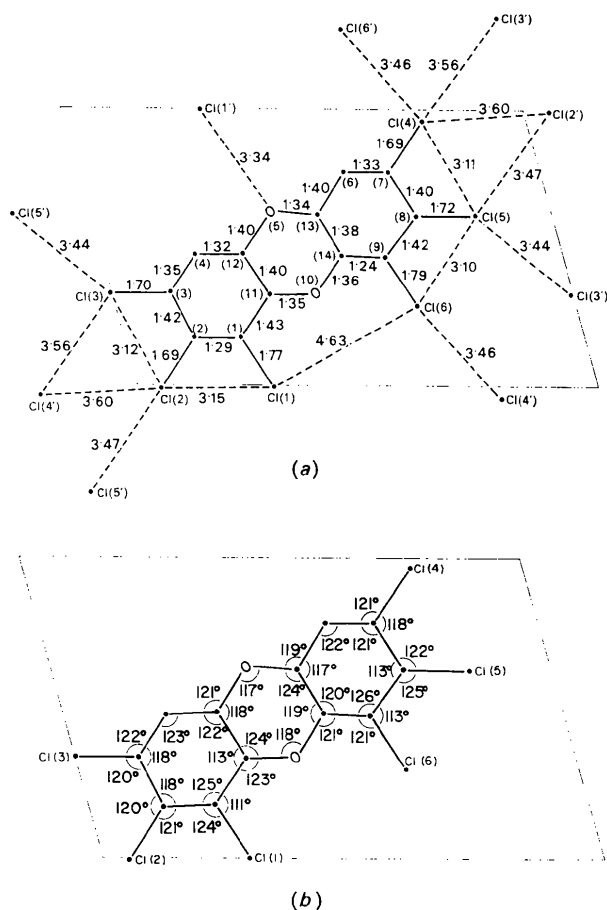
JEFFREY, G. A. (1964). Private communication.
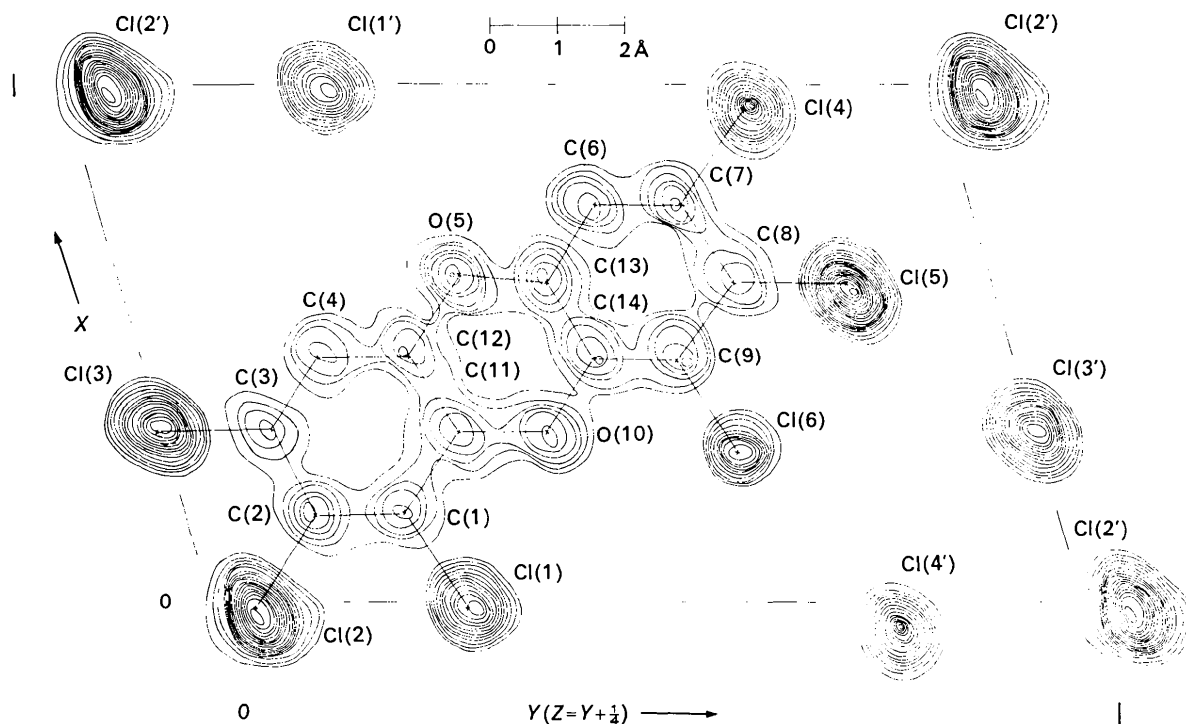
Fig. 4. Electron density in the (0$\bar{4}$4) plane containing the molecule. Contours are at 1 e.Å^{-3} starting at 2 e.Å^{-3}. The × marks are projections onto (0$\bar{4}$4) from the electron density maxima, which in most cases are a short distance from (0$\bar{4}$4).

KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* 17, 496.
KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* 16, 969.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849.
RAMACHANDRAN, G. N. & SRINIVASAN, R. (1959). *Acta Cryst.* 12, 410.

WOOTTON, J. C., ARTMAN, N. & ALEXANDER, J. C. (1962). *J. Assoc. Offic. Agr. Chemists*, 45, 739.
WOOTTON, J. C. & COURCHENE, W. L. (1964). *J. Agric. Food Chem.* 12, 94.
WOOTTON, J. C. (1966). Unpublished results.

The Crystal and Molecular Structure of Tetrafluorobispyridinesilicon(IV)

BY VALERIE A. BAIN*, R.C.G. KILLEAN* AND M. WEBSTER†

The University, St. Andrews, Scotland

The crystal and molecular structure of tetrafluorobispyridinesilicon(IV), SiF$_4$.2(NC$_5$H$_5$), has been determined by a three-dimensional X-ray analysis and is shown to have a centrosymmetric *trans* configuration. The crystals are triclinic with $a = 7.23 \pm 0.01$, $b = 6.42 \pm 0.01$ and $c = 6.99 \pm 0.01$ Å, $\alpha = 109°43' \pm 10'$, $\beta = 114°35' \pm 10'$, $\gamma = 95°42' \pm 10'$; space group $P\bar{1}$ with $Z = 1$. The silicon-nitrogen distance is 1.93 Å and the pyridine-silicon-pyridine part of the molecule is planar.

Introduction

Long wavelength infrared spectroscopy is now widely used to investigate the structure of coordination com-

---

* Department of Physics.
† Department of Chemistry. Present address: Department of Chemistry, The University, Southampton, England.

pounds, and it is important that in some selected cases other physical techniques should be used to confirm the spectroscopic conclusions. No adducts of silicon tetrahalides – of the type Si(halogen)$_4$.2(ligand) – have been examined in detail by single-crystal X-ray techniques, although the infrared spectra have been reported and interpreted usually in terms of six-coordinate *cis* or *trans* geometrical isomers. The infrared