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/T00	3.81
C(16) - Br(1)	2/000	3.95
C(18) - Br(1)	2/000	3.98
C(22)–C(25)	2/100	3.98
C(23)–C(2)	4/100	3.63
C(23) - C(4)	4/T01	3.84
C(24) - C(4)	4/T01	3.67
C(25)-C(16)	2/TOT	3.81
C(25)-C(22)	2/TOT	3.98
O(2)C(16)	2/TOT	3.80
O(2)C(23)	2/T00	3.54
O(2) - C(24)	2/T00	3.66
O(2)O(3)	2/100	3.99
O(2) - C(2)	3/0T0	3.68
O(2) - C(3)	3/010	3.87
O(3) - C(2)	4/T00	3.34
O(3) - 3C()	4/100	3.95
O(3)C(4)	4/101	3.49

\* Equivalent position nomenclature: C(23)-C(4)  $4/\overline{101}$  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);  $2 = (\frac{1}{2} - x, \overline{y}, \frac{1}{2} + z)$ ;  $3 = (\overline{x}, \frac{1}{2} + y, \frac{1}{2} - z)$ ;  $4 = (\frac{1}{2} + x, \frac{1}{2} - y, \overline{z})$ . The authors are grateful to Mr C. T. Lu and Mrs C. DeVine who were responsible for the collection and initial preparation of the intensity data. We also wish to thank Dr K. Johnson who supplied his program *ORTEP* with which various illustrations were prepared.

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

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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<sub>12</sub>O<sub>2</sub>H<sub>2</sub>Cl<sub>6</sub>). The triclinic unit cell has the dimensions  $a=7.952\pm0.005$ , b=9.379 $\pm0.01$ ,  $c=9.433\pm0.01$  Å,  $\alpha=92.35^{\circ}\pm0.20^{\circ}$ ,  $\beta=92.39^{\circ}\pm0.20^{\circ}$ ,  $\gamma=109.92^{\circ}\pm0.30^{\circ}$ . The calculated density is 1.958 g.cm<sup>-3</sup> for Z=2, compared with 2.01 g.cm<sup>-3</sup> 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*T. The structure was solved by the symbolic addition method of Karle & Karle. The nearly planar molecules are almost parallel to the (0T1) 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

(1964). One of the active fractions of material isolated was that called  $\alpha$ -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 hexa-hydrophenanthrene with the empirical formula C<sub>14</sub>H<sub>10</sub>Cl<sub>6</sub>. 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

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 $\alpha$ -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  $\alpha$ -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 dspacings 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  $\alpha$ -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 singlecrystal 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:

where  $\rho_o$  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 multiplefilm 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  $P\overline{1}(C_i^1)$  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 <i>et al.</i> (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 \cdot 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-t	han')

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
	а	+	+	+	+	+	+	+	+	_	_	_	_	_	_		_
	b	+	+	+	_	_		-	+	+	+	-+-	_			_	+
	С		+	—	+	-	-	+	+	—	+		+	-	-	+	+
	g		-	+	+	+	-	—	+	-		+	+	+	-	-	+
No. refl.	<b>∫</b> +	119	183	114	153	142	116	118	251	121	121	115	125	121	122	128	122
gencrated	1	132	68	137	98	109	135	133	0	130	130	136	126	130	129	123	129
No. incor- rect signs	{	117	132	125	132	133	129	130	129	121	128	104	130	35	61	120	117
% wrong sign	{	46.6	52.6	<b>49</b> ∙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	Ì	$\checkmark$	√ †					*									

 $\checkmark$  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  $(0\overline{4}4)$  plane. It had already been determined that the molecule had to be oriented approximately in alternate  $(0\overline{4}4)$  planes, based on (a) the early analysis of the Fatterson map, (b) the very high intensity of  $0\overline{2}2$ , (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  $(0\overline{4}4)$  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

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

	Х	Y	Ζ	$B$ or $B_{11}$	<b>B</b> <sub>22</sub>	<b>B</b> <sub>33</sub>	$B_{12}$	B <sub>13</sub>	B <sub>23</sub>
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)
<b>C</b> (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.

*.0		M.2.1	H4.1	+,7,2	H. 3?	H53	H.2.4	H0.4	н5	H.J.=0	H.J.1	H.JR
2 33	-271 297 985	1 630 -703 2 338 358	0 281 292 1 192 192 2 482 469	C 117+ 13 1 V++ 56 2 394 322	1 158 152 2 272 277 3 73• 30	1 262 243 2 89 .24 3 89 61	0 128 143	2 1544 -58	1 /10 /4/ 2 /67 -354 3 /17 1/3	1 327 293 2 108 -46 3 123 -176	1 364 -337	2 105 -157
* 255 5 152	198	3 435 -388 4 109 -99 5 734 69	3 577 595 4 125 80 5 192 201	H.8.2	5 510 -40	H3	3 70+ -17	Hili-4	5 -20 -414	- 105 L48 5 13083	3 R3	5 139 -10
7 84	• • • •	6 77 65 7 64 57	6 49 127 7 186 221	0 121 108	7 aC+ -97	1 107 -152	6 77	2 117• - 17 1 38• 40	H51	H10	6 5A+ 17 H,4,7	H1F
0 130	) -144	H,3.1	H5.1	H+0,-2	H, 4, -2	3 174 -171	H.3.4	4 175 182 5 134 -122 6 125 127	1 .17 .6*	1 214 -143 2 357 395	0 970 57	1 95• -90 2 R0 -95
1 110	-77	0 206 -231	C 76+ 29	2 579 543 3 347 -344	2 167 -158 3 830 - 33	1 101+ -79	0 109 61 1 215 -174		3 . 47 . 53	÷ د، د، د • •••	1 1.10 95 2 9.0 -18 3 770 57	3 142 -132 4 A34 -A7 5 2.3 -218
· · · ·	-56	2 342 -317 3 124 -99 4 924 -59	3 104 91 He-6.1	217 200	• 142 -155 5 96• -127	2 142 170 3 301 -247	2 111 14	P	H,-5,-5	5 7C+ -77 6 115 -127	4 157 145 5 55 113	H2
7 13	-113	5 163 -130 6 854 -84 7 774 18	0 107 -89	7 HL+ -35	H, 5, -2	н,-н3	5 22 78	1 144 157	1 123+ Po 2 121+ -21 1 1514+	H20	H. S. 7	1 1.5 5. 2 11.0 5n
H.,	•••	H.+.1	H,-7,1	1 370 39	2 222 -233	5 1	P	124 118 5 151 -202	H75	1 110 54	C 113+ -+.	j 4.0 - 40
0 259 1 394 2 130	-334	0 124 -104 1 155 150	0 107 121	2 176 184 3 158 -155 4 351 -291	H,6,-3	M1.3	1 4 - 25	H.J4	2 173+ -7, 3 65+ -~	3 930 73 6 146 130 8 313 477	1 11.00 -102	1 210 -200
3 6	-76	2 83• 11 3 17• -159	H8.1	5 276 252 6 123 -135	1 100+ -102 2 237 197	1 364 395	101	1 1115 110.	ar 1 + 5	H,-3,-t	2 13406 3 430 -67 4 430 10	3 167 14-
5 71 6 71 7 64	-1	5 01 - 56	U 45+ 7	7 93 -102 71. **	3 42 37 H. 7 2	3 135 -12.	5 9:0 -65	3 134 185 4 163 124 5 544 5	C 529 -44. 1 129 -10.	1 170 159	5 101+ -9+	H 4 *
н, 1		H,5,1	н.1,-1	H22	1 930 -74	6 7.0 P4 7 102 101	0 +0+ 3L	6 *3* 7.	2 211 -210 3 430 -300	3 90	1 111+ 2	2 314 -27-
0 557 L 344	335	1 131 -122 2 14194	2 255 -249	3 40+ -32	H.0.3	H2.3	1 92 44	1 640 -3.0	·· - 2.4	6 9:• -29	2 222 222	• 252 -244
2 176	631 207	, 780 29 H.6.1	• 1•2 103 5 175 -176 6 •16 -•32	5 62+ -19 6 74+ -8 7 182 183	1 364 384 2 359 -368	0 285 338	H.o.4	2 13: 5.	1 1.1.1 51	H	5 844 4	0 114 114
5 AC	209	0 850 6	7 243 282	H32	910 17 5 1070 1	2 134 -153 3 87 58 4 71+ -48	1 146 -102	н. 54	3 411 -375	2 230 -222	×27	: 189 -231 Maria
H.4		2 -20 -383	H,2,-1	1 160 173	6 110+ 19 7 12+ -110	5 471 -505 6 319 349	2 1350 -20	1 117 -107	6 -10 -15	5 16c -150 6 854 -45	1 73• -2, 2 365 317	y ;27 .ev
0 1+1	138	H.7.1 0 53 133	2 305 208	107 47 5 510 -55	H,1,3	8 134 -10.	C 111+ -12.	3 71 51 N.C.25	2 3CJ 2eC 3 152 137	4	• 101 -121 • 244 - 345	3 195 .36
2 101	-95 29	1 10+ -120 2 135+ -45	4 222 186 5 128 142	6 200 188 7 44 87	0 535 574	H1-313 0 142 -94	ו•5•••	1 +7+ 123	H	1 334 322	H 17	H,1,-8
• 232	217	H.8.1	H,3,-1	H42 1 771 797	2 421 405 3 240 330	1 644 14	1 101 107	Heve5	C 251 -2** 1 13** -75	3 55 ×	1 174 -210	2 313 -274 3 175 174
0 29	3 -324	0 141 135	1 218 257	3 272 -255	5 740 30	• 223 -155 5 100 -140	5 113 95	6 422 -440 1 427 -324	3 53 -50	1 290 254	* 101+ -67 5 146 -141	H+2+-*
2 20	-78 7 -242 7 -105	1 93 -60	3 108 -81 4 410 365	5 116 -94 6 824 -84	7 66+ -24	6 409 -44h 7 504 -26 8 172 -265	· ····	3 115 -115 • 197 -185		3 78+ -23	H4,-7	2 192
	6.0	2 367 -359 3 374 -43 4 299 -260	6 51 - 52 7 ec. 23	H,-5,-2 1 130 158	4 446 473	H	3 123 -111	5 /1+ -6. 6 103+ 37 7 91+ -10#	3 7. 59	H0	1 228 -204	0 220 -13-
U 27. 1 10	2 273	5 339 -296 5 220 -199 7 192 -18,	H,4,-1	3 107 -139	2 94 -163 3 163 165	0 77• 30 1 73• 48	3 56+ 20	8 67• -61	H.15 1 133 -113	1 80+ -63 2 121+ 27	• 215 -192 5 92• 32	2 117+ 61
2 13	-154	H+-1+-1	1 387 414 2 232 -192	M+-02	* 177 1** 5 67* 30 6 79* 21	2 135 -75 3 66* 37 4 45 108	5 134 -151 6 187 -174 7 954 -34	C 235 262	2 204 -220 3 214 -214	3 458 -396 H2.6	H57	5 85H3
н.	7.0	1 125 104	3 316 278 4 40+ 61 3 45+ -42	2 89 114 3 60+ 75	7 130 157	5 80• -15 6 91• -3•	8 65+ -A+	1 66 6. 2 1414 -43	• .55 -164	0 90+ -76	1 10** 23 2 15** 79	H+1+9 C 175 -178
1 13	0 11. 0 10	3 578 568 4 100 -68 5 182 18:	H.S1	H72 1 910 -27	0 203 -271	H5.3	1 715 -730	72• -54 5 151 -123	H+21-3	2 357 -313 3 267 -265	3 80+ -+7	1 208 202 2 117 126
н,	8.6	6 174 139 7 714 -43	1 344 368	2 80 105 3 790 -69	1 102 85 2 95 55 3 211 -180	0 109 118	3 366 354	6 724 4L H.2.5	2 121+ -91 3 #7+ 83	43.6	0 88+ -12	H.3.9
v 9 	9 -94	8 71 36 H,-2,-1	H,6,-1	Ha2	4 109 107 5 211 176	2 359 -376 3 368 388	5 67• 59 6 150 144	0 #2+ 26 1 235 -207	H.35	0 230 151 1 100+ -+7 2 130+ 111	2 1474 40	1 101• -25 2 116 -12• 3 63• -55
1 60	. 687	1 135 137	1 100+ -95	2 123+ -110	7 102 124	H0,3	H34	2 203 -172 3 105 -101	1 92* oC 2 8C -9*	3 53 9	0 237 276	• 155 -1•0 H.e.9
3 57	-277	3 535 -544	3 71 81	40-1.2	0 74+ -19	3 267 -273	2 312 -398 3 185 '61	5 80 101 6 135 -182	5 AP+ -32	0 864 -49	2 177 149 3 131 102	0 101- 5-
, jo	3 5) 1 296	6 730 -60 7 750 -4	1 123- 41	1 490 -21	2 480 401 3 129 104	H7.3 2 206 -192	4 321 -240 5 61+ 85 6 17+ 185	H. 3.5	n5	2 123 -116	H3.T	2 12: 77
н,-	2.0	H31	H,8,-1	3 183 -149	* 33, 290 	H+13	7 143 -127	0 277 -296	1 45• 25 2 177• -72	H5.6	0 21h 217 1 890 -44	Pr-1+7
1 3-	8• -59 3 -562	1 330 -359 2 1035 -110.	1 101 187	5 338 -325 6 63+ 7	0 138 129	1 234 -258	1 91	2 123+ -109	H,5,-5	0 79 -117 2 357 -314	2 1770 70 H4.7	H.G7
3 29	5 30C 8 -20u	• •17 -40+ • •9• -•3•	H.O.2	H,-2,2 0 2320 -2344	1 406 401 2 135+ 78 3 85+ -17	3 127 -137 4 624 42 5 684 -83	2 245 -351 3 146 -145 4 322 -311	79• -49 6 105 -98	1 9** -16	H0.0	2 217 -250	1 117+ -25 2 137 -142
6 8	6,	6 108 -113 7 101 -108	1 803 74.	1 444 -23	H.A.3	is •1 <sup>7</sup> •	5 301 -287	7 125 -140	H.65	0 158 -197	H.17	3 79+ 23
H,- 1 34	3,0 2 379	H,-4,-1	3 37. 44	4 267 -259 5 298 -299	0 202 -208	1 70+ 05	H,-54	0 133 121	1 10" 107	1 89 116	1 11:- 87	H19
3 12	7 102	2 136 121 3 52• 27	6 100+ -80 7 95+ 19	6 292 -302 H3.2	2 420 -480 3 97+ -38	2 189 171 3 200 182 4 247 287	1 126 -100	2 379 427	H, J, 6	3 125 -100	3 860 65	1 133 139 2 7512
5 19	3 -189 5• 20	5 100 -66	8 107 91 H.1.2	0 142 103	H,7,3	5 133 130 6 147 164	3 172 138	950 - 30 5 R70 - 8	1 113 A9 2 114 95	H+2,-6	1	3 130 -91 4 79• 84 5 118 100
н	4.0	7 44 -74	0 308 -+01	2 60 32	1 844 -45	H.33	1 162 -138	H.5.5	+ 18+ 176 5 L01+ 38	2 1410 -41 3 124 94	2 223 221 3 332 285	H29
1 18	2 -145	1 128 145	2 176 139	4 406 372 5 53 A6	H.P.J	1 720	2 292 251	1 250 274	6 102* 91 7 113 112	H,3,-0	H.37	1 169 147
3 20	9 178	3 00 -03	4 382 -352 5 694 -48	7 55 -53	5 107 127	4 130 -78 5 804 44	H74	3 35+ -11	H.1.0	1 10: 11	1 770 - #2 2 970 9 3 179 121	3 143 -104 - 136 147
5 14 5 7	6 -109 3• 40 3 -115	H61	7 178 -203	0 74+ 33	1 312 -316	7 223 -267	2 44 -72	0 144 -177	1 335 339	3 03+ 28 4 135 -142	H,4,-7	H9
8 17 H	8 -225 5.0	2 446 -479 3 120 -115	0 157 -210	2 227 224 3 342 -320	2 425 417 3 133 88 4 547 -578	H,4,-3 1 390 -432	HAL	H.7.5	3 A1+ -22 4 170 159 5 A7 -A7	r.a0	2 186 + -0	1 1104 -11 2 1.04 99
1 30	-318	H,-7,-1	1 647 -743 2 388 -351 3 228 -211	5 30° 63 • 30° -98	5 167 157 6 1000 -58	2 149 -162 3 176 172 4 185 -187	2 251 -175	a 55 73	o 674 -61	1 107+ -129 2 121+ -83 3 150 -130	0 95+ -72 1 108 -135	3 102+ -23 Helpilo
\$ 50	-255	2 136 10	4 346 -321 5 156 -137	H,-5.2	H,-1,-3	5 138 -148	0 020 -57	76*	H+2+6	H.50	2 9731	0 142 -138
H,-	6.C 9 -447	HL	7 755	0 168 -198 1 440 -364	2 731 778	1 197 -174	2 279 -235	3 511 -534 95* -15	0 90% -2%	1 598 -551 2 198 197	5 78. 77	Heielu
2 12	1• 11 9• -12	2 121+ 50 3 187 162	0 690 5	3 801	• • • • • • • • • • • • • • • • • • •	2 165+ -57 3 171 151	4 174 132	6 178 -213	2 123+ 25 3 99 -91	H1247	F.i.e 6 :67 -177	2 95 45
н,-	7.0	H1.1	1 274 256	H5.2	7 115 92 8 178 202	H.63 1 160 -154	6 1.• 52	H+-1+-5	• 94• -41 5 75• 4 6 135 -110	0 BH+7	1 113- 64 2 .50 -118	4 99 112
3 7 H	1 42 8.0	0 129 82 1 281 -292 2 234 208	4 364 298 5 197 176	H,-7,2	H,-2,-3	2 168+ 31 3 162 -165	1 735 -283 2 1030 -15 3 470 4	2 11 10	H. J. 6	3 1.1. 59	• •8• •	
	2• •0	3 647 548	110 119	0 211 240 3 176 161	1 104 -114 2 186 135 3 474 479	H,7,-3	6 810 -73 5 167 -156	5 75+ -56	0 114 71 1 142 -124	5 160 -164 6 94 127 7 113 155	0 157 140	H.2.10
н,	0.1	6 615 6C5 7 137 -116	H.4.2	M8.2	5 157 159	. 100 -177 Prove	H,-3,4	7 153 143 8 93 -+9	3 Rd+ 50 + 96+ -23		1 252 -254	H+3+10
2 19	6* -47 7 -319 2 -156	H2.1	1 172 167	0 107 -124	7 40 1.73	0 146 145	1 78+ -7 2 6L7 637		5 142 130 6 44 77	No.1.47	4 147 -124 5 121 -136	1 167 .67
10	9 116 • -24 • 150	C 145 -181 1 107 -83	3 165 122	M. 1 2	H,-3,-3	2 535 560	3 304 330 5 371 366 6 49 123	H2,-5	P.4.6	U 104 173 1 509 547 2 119 114	*****	H+++10 0 123 -100
, ,,	-393	3 107 -77	↑ 71 -62	1 1361 -1489 2 124 -105 3 341 -145	1050 -40 3 96 -83	5 247 270	H	2 .28+ -73 3 102 144	1 206 236	224 213	0 99 -13	421.
	-100	6 182 154 Humbrid	9 139 -120	5 143 -126	80. 537	117 165	0 714 748 1 824 -40	5 65• 46 6 90• •1	4 193 113 5 141 141	0 130 145 7 113 172	3 147 67	1 113 136 2 157 141
н, 0 12	1.1 9 -134	0 107 -67	1 1150 -3 2 1540 -18 3 900 -41	H, 2, -2	/ 240 -269 H43	H.1.4	2 247 231 3 162 138 5 290 392	H35	4,5,0	1.2.7	· .47 -127	H+-3+-10
1 19	7 -364	2 310 253	4.0.2	1 416 492 2 152 -153	1 322 348 2 470 419 3 110 -79	0 408 487 1 153 -144 2 199 -164	6 200 204 H5.6	i 139 -146 2 267 -256 3 255 -261	C 107 63 1 44 71 2 178 /44	C 121 115 1 30- 312 2 205 -210	0 130+	1 72• 22 2 12• 12e
5 1	8 -574 3 144	5 474 -59	0 123 112	3 305 -025	5 105 140	3 410 391 4 235 -107 5 146 -135	1 207 -230	• 235 -233 5 90• 7	H,015		1 166 -172	H,-4,-10
6 12 7 L1	1 -107	7 70* -68 8 76* -15	2 121* 10 ) 172 149	252 -271	7 90+ -59	6 102 132	1 10 12	7 90 -78	0 113* -53	· · · · · · · · · · · · · · · · · · ·	* 118 -171	1 117 -76 2 141+ 25

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

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The R value dropped to 13% during the next leastsquares 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  $\sqrt{w} = K/(F_o + 53.4)$  for  $F_o > F_m$  and  $\sqrt{w} = K/(F_m + 53.4)$ for  $F_o \leq F_m$ , where  $F_m = 21.4$ , 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 = 11.8% stage, the residual electron density ranged from -0.8 to +0.6 e.Å<sup>-3</sup>, 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-

### 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 (04) heading are listed the deviations from the (04) plane containing the molecule. The planes are defined in direct space by equations Px + Qy + Rz = S.

	All	C+O	(044)
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)	-0.02	- 0.06*	0.12*
Cl(6)	0.13	0.13*	0.54*
C(1)	-0.05	~0.03	0.15*
C(2)	- 0.06	-0.08	0.02*
C(3)	-0.05	-0.05	-0.16*
C(4)	0.06	0.03	-0.17*
C(6)	0.00	-0.03	-0.25*
C(7)	-0.02	-0.01	-0.21*
C(8)	-0.01	-0.03	0.03*
C(9)	-0.01	-0.05	0.13*
C(11)	0.06	0.02	0.13*
C(12)	0.02	0.03	-0.09*
C(13)	0.02	0.02	-0.10*
C(14)	0.06	0.02	0.12*
O(5)	0.08	0.02	-0.17*
O(10)	0.09	0.08	0.25*
Origin	1.57*	1.55*	1.67*
s.d.	0.02	0.02	0.00
Р	-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

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  $8^{\circ}$  to the (011) plane. Deviations of atoms from the (044) plane essentially containing the molecule and



Fig.1. Molecular packing in the (044) plane containing the molecule. Large shaded circles are Cl, solid circles are C, and open circles are O.



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  $(0\overline{4}4)$ 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  $(0\overline{4}4)$ 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  $(0, 0, \frac{1}{2})-Cl(1)-Cl(3')=$ 3.39 Å and Cl(2)-Cl(6')=3.98 Å; and by the center at







Fig. 3. (a) Interatomic distances. Primed atoms are on neighboring molecules in the same plane.  $\sigma_{C-C} = 0.025 \text{ Å}$ ;  $\sigma_{C-C1} = 0.019 \text{ Å}$ ;  $\sigma_{C-C1} = 0.022 \text{ Å}$ . View corresponds to Fig. 1. (b) Bond angles.  $\sigma = 2.0^{\circ}$ .

 $(\frac{1}{2}, \frac{1}{2}, 1)$ -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:  $\sigma_{C-C} = 0.025 \text{ Å}$ ,  $\sigma_{C-C1} = 0.019 \text{ Å}$ ,  $\sigma_{C-O} = 0.022 \text{ Å}$ ; for angles  $\sigma = 2.0^{\circ}$ . 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  $(0\overline{4}4)$  plane containing the molecule is shown in Fig. 4.

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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.

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Fig.4. Electron density in the (044) plane containing the molecule. Contours are at 1 e.Å<sup>-3</sup> starting at 2 e.Å<sup>-3</sup>. The × marks are projections onto (044) from the electron density maxima, which in most cases are a short distance from (044).

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## The Crystal and Molecular Structure of Tetrafluorobispyridinesilicon(IV)

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The crystal and molecular structure of tetrafluorobispyridinesilicon(IV), SiF<sub>4</sub>.2(NC<sub>5</sub>H<sub>5</sub>), has been determined by a three-dimensional X-ray analysis and is shown to have a centrosymmetric *trans* configuration. The crystals are triclinic with  $a=7\cdot23\pm0\cdot01$ ,  $b=6\cdot42\pm0\cdot01$  and  $c=6\cdot99\pm0\cdot01$  Å,  $\alpha=109^{\circ}43'\pm10'$ ,  $\beta=114^{\circ}35'\pm10'$ ,  $\gamma=95^{\circ}42'\pm10'$ ; space group PT 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 compounds, 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)<sub>4</sub>.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

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