crystal structure consists of layers of purines alternating with layers of hydrogen-bonded ribose moieties. These layers run parallel to the ab plane. The H atoms of the three hydroxyl groups are all involved in hydrogen bonding. O(2') hydrogen-bonds to O(5') and apparently also forms a weak hydrogen bond with O(2') of a symmetry-related ribose moiety.

In the layers of purine residues, the bases are essentially parallel to each other, and are perpendicular (within 2–3°) to the ab plane. The purine planes intersect the a axis at approximately $x = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$. Thus the average interplanar spacing between adjacent stacked bases is about $a/4 = 3\cdot4$ Å. Fig. 2 shows the base-stacking pattern. The N(7) regions of imidazole rings overlap, and the C(6)–Cl bonds are sandwiched between the C(8)–C(9) bond of an imidazole moiety and the N(1)–C(6) bond of a pyrimidine ring. None of the stacking contacts is shorter than a normal van der Waals distance. Similar stacking interactions involving the halogen substituents have been noted in the majority of crystal structures that contain halogenated pyrimidines or purines. These interactions may contribute to the enhanced stacking of halogenated bases in aqueous solution and within polynucleotides [reviews: Bugg, Thomas, Sundaralingam & Rao (1971), Bugg (1972), Bugg & Sternglanz (1974)].

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1,3,6,8-Tetrafluoro-2,4,5,7,9,10-hexachloropyrene, C16F4Cl6: an Overcrowded Molecule

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Abstract. $C_{16}F_4Cl_6$, M.W. 480·92, monoclinic, space group $P2_1/a$; $a = 15\cdot418$ (10), $b = 4\cdot864$ (5), $c = 11\cdot022$ (10) Å, $\beta = 113\cdot85$ (10)°, $V = 756\cdot0$ Å^3, $Z = 2$, $D_x = 2\cdot11$, $D_c = 2\cdot11$ g cm^{-3}, μ(Mo $K\alpha$) = 11·6 cm^{-1}, $F(000) = 468$, packing coefficient 0·76. Full-matrix least-squares refinement gave $R = 0\cdot058$ and $R_w = 0\cdot067$ for 118 parameters and 1359 significant reflexions. The molecule, which lies on a centre of symmetry, is almost planar, the overcrowding of the halogen atoms being accommodated by in-plane distortions of the angles. The mean value for C–Cl is 1·715 (2) Å, and for C–F 1·337 (3) Å.

give $C_{16}F_4Cl_6$, and their ^{19}F n.m.r. measurements indicated that the F atoms are chemically equivalent. Our structure determination shows the reaction product to be 1,3,6,8-tetrafluoro-2,4,5,7,9,10-hexachloropyrene.

Introduction. Berg & Hornbæk (1975) showed that decachloropyrene reacts with potassium fluoride to

Yellow prismatic crystals, elongated along [010], were obtained from a dimethylformamide solution by controlled cooling. Intensities were collected on a computer-controlled Supper diffractometer with graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter and a pulse-height analyser. 2170 independent reflexions were measured to sin $\theta_{max} = 0\cdot5$ by the background-peak-background method. The crystal used was 4 mm long and $0\cdot13 \times 0\cdot13$ mm in cross section and was mounted about **b**.

The orientation of the pyrene skeleton was determined from the weighted reciprocal lattice and the positions of the halogen atoms by trial and error. Coordinates, anisotropic thermal parameters and a scale factor were refined by full-matrix least-squares calculations (LINUS: Coppens & Hamilton, 1970) to $R = 0.059$ and $R_w = 0.067$ for 118 parameters and 1359 significant reflexions [$I > 3\sigma(I)$]. The weighting scheme was $w = 1/\sigma(F)^2$ where $\sigma(F) = [\sigma_c(F^2) + (1 + A)F^2]^{1/2} - |F|$, $\sigma_c(F^2)$ is the standard deviation of F^2 from counter statistics and A ($= 0.04$) a parameter chosen to make $\langle w\Delta F^2 \rangle$ independent of $|F|$. The scattering factors were those of Cromer & Mann (1968).

Final coordinates and thermal parameters are shown in Table 1.* The thermal parameters were analysed (Cruickshank, 1956) and the atomic coordinates corrected for libration. T and L (S is zero as the molecule is on a centre of symmetry) are shown in Table 1, the r.m.s. value of Δ, where $\Delta = U_{ij}(\text{obs}) - U_{ij}(\text{calc})$ was 0.0055 and $\sigma(\Delta) = 0.0060$. Bond distances and angles are given in Tables 2 and 3, the labelling of the atoms in Fig. 1.

Discussion. The molecule is almost planar (Table 1). The maximum deviations are for Cl(4) -0.038 Å and Cl(5) $+0.049$ Å which are less than the greatest deviations found for pyrene itself (Hazell, Larsen & Lehmann, 1972). Strain arising from the close contacts between F(2) and Cl(4) and between F(7) and Cl(5) is reduced by the opening of angles bd, bh, and di which are 1.5°, 2.7°, and 2.1° larger than the corresponding angles for pyrene. The C–C distances are similar to those found in the X-ray studies of pyrene (Allmann, 1970), 2,7-di-t-butylpyrene (Hazell & Lomborg, 1972)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31275 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and pyrene/TCNE (Larsen, Little & Coppens, 1975). The C–F distance is similar to that in C_6F_6 (Boden, Davis, Stam & Weiselink, 1973), the C–Cl distance to that in C_6Cl_6 (Brown & Strydom, 1974), and in $C_{16}Cl_{10}$ (Hazell & Jagner, 1975). The Cl···Cl distance, 2.968 (2) Å, is shorter than in C_6Cl_6, 3.11 Å. The packing (Fig. 2) is similar to that for coronene (Fawcett & Trotter, 1966).

That substitution takes place most readily at positions 1, 3, 6, and 8 can be explained by the fact that such a substitution converts the highly strained decachloropyrene molecule to a planar molecule.
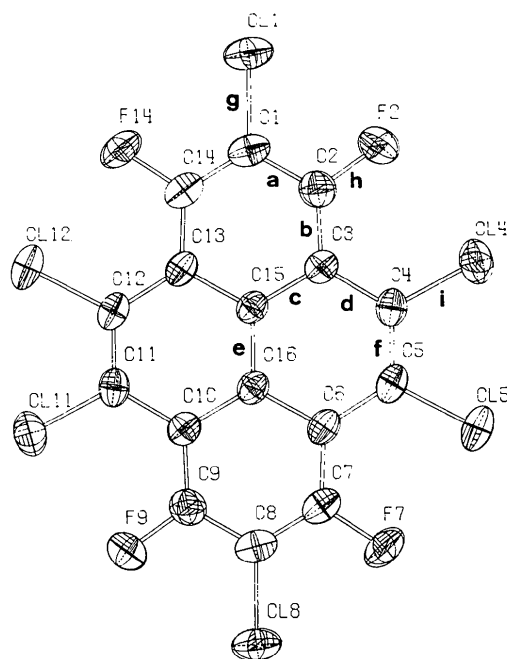

Fig. 1. The $C_{16}F_4Cl_6$ molecule viewed at right angles to the best plane; there is a centre of symmetry half way between C(15) and C(16).

Table 1. Fractional atomic coordinates ($\times 10^4$), thermal parameters ($\text{Å}^2 \times 10^{-4}$), the deviation of atoms from the best plane ($\text{Å} \times 10^{-3}$), and T ($\text{Å} \times 10^{-4}$) and L ($\deg^2$) relative to an orthogonal axial system with A parallel to **a** and C parallel to **c***

T' and L' are referred to molecular axes along the molecule and perpendicular to the molecule.

|	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Δ
C(1)	683 (3)	3503 (9)	−2250 (4)	482 (21)	525 (21)	411 (20)	97 (18)	250 (17)	110 (17)	0
C(2)	1127 (3)	4070 (8)	−901 (4)	351 (18)	488 (19)	463 (21)	13 (16)	160 (16)	36 (17)	−1
C(3)	879 (2)	2735 (7)	21 (3)	323 (16)	413 (18)	326 (16)	52 (14)	127 (13)	12 (14)	3
C(4)	1329 (2)	3288 (8)	1425 (4)	318 (17)	433 (19)	365 (18)	15 (15)	74 (14)	−42 (15)	5
C(5)	1067 (3)	1899 (8)	2284 (4)	387 (19)	481 (19)	292 (16)	52 (16)	70 (14)	−29 (15)	8
C(6)	319 (3)	−107 (7)	1845 (3)	369 (17)	399 (17)	280 (16)	70 (14)	88 (13)	5 (13)	−9
C(7)	19 (3)	−1589 (8)	2688 (4)	488 (21)	504 (21)	325 (17)	88 (18)	164 (16)	51 (16)	2
C(15)	145 (2)	711 (7)	−454 (3)	298 (16)	396 (17)	290 (15)	51 (13)	103 (13)	11 (13)	3
Cl(1)	1009 (1)	5276 (3)	−3333 (1)	696 (8)	732 (7)	541 (7)	41 (6)	354 (6)	215 (5)	−28
Cl(4)	2200 (1)	5724 (2)	2045 (1)	422 (5)	598 (6)	566 (6)	−125 (5)	140 (5)	−139 (5)	−38
Cl(5)	1658 (1)	2618 (3)	3943 (1)	685 (7)	829 (8)	308 (5)	−153 (6)	60 (4)	−119 (5)	49
F(2)	1804 (2)	5991 (6)	−560 (3)	586 (15)	764 (17)	588 (16)	−254 (14)	218 (13)	53 (14)	−3
F(7)	414 (2)	−1173 (6)	3993 (2)	929 (20)	737 (16)	293 (11)	−100 (15)	227 (12)	6 (12)	3
T				275 (25)	358 (25)	270 (20)	90 (24)	−32 (18)	11 (18)	
T'				362	319	222	63	−17	−48	
L				8.0 (9)	9.7 (9)	7.9 (1.1)	2.5 (7)	−1.1 (6)	−1.2 (6)	
L'				11.5	7.8	6.4	1.4	−0.9	−0.5	
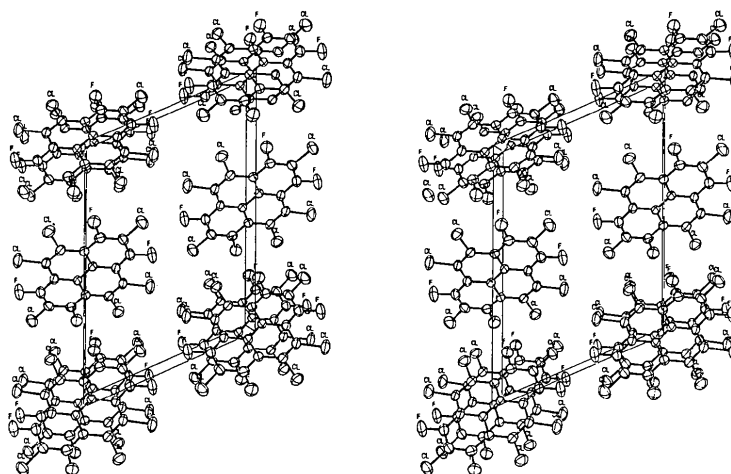
Fig. 2. A stereo view of the unit cell contents as seen along **b**; **a** is down the page.

Table 2. *Bond distances, l, and their standard deviations, together with the values, l_{corr}, corrected for thermal motion* (Å)

Halogen–halogen distances are also given. Standard deviations are in parentheses.

		l	l_{corr}				l	l_{corr}
a	C(1)—C(2)	1·390 (6)	1·394	g	C(1)–Cl(1)	1·704 (4)	1·708
a	C(7)—C(8)	1·360 (6)	1·363	h	C(2)–F(2)	1·337 (5)	1·340
b	C(2)—C(3)	1·383 (5)	1·386	h	C(7)–F(7)	1·332 (4)	1·335
b	C(6)—C(7)	1·395 (5)	1·398	i	C(4)–Cl(4)	1·712 (4)	1·716
c	C(3)—C(15)	1·431 (5)	1·434	i	C(5)–Cl(5)	1·717 (4)	1·722
c	C(6)—C(16)	1·435 (5)	1·439		Cl(1)–F(2)	2·816 (3)	2·834
d	C(3)—C(4)	1·443 (5)	1·447		Cl(4)–F(2)	2·687 (3)	2·694
d	C(5)—C(6)	1·436 (5)	1·439		Cl(5)–F(7)	2·678 (3)	2·684
e	C(15)-C(16)	1·428 (7)	1·431		Cl(8)–F(7)	2·834 (3)	2·840
f	C(4)—C(5)	1·352 (6)	1·355		Cl(4)–Cl(5)	2·961 (2)	2·968

Table 3. *Angles and their standard deviations* (°)

aa	C(14)-C(1)—C(2)	119·5 (3)	df	C(3)—C(4)-C(5)	120·6 (3)
ab	C(1)—C(2)—C(3)	122·0 (4)	df	C(4)—C(5)-C(6)	121·9 (3)
ab	C(6)—C(7)—C(8)	123·2 (3)	ag	C(2)—C(1)-Cl(1)	119·5 (3)
bc	C(2)—C(3)—C(15)	117·8 (3)	ag	C(14)-C(1)-Cl(1)	121·0 (3)
bc	C(7)—C(6)—C(16)	116·7 (3)	ah	C(1)—C(2)-F(2)	115·5 (4)
bd	C(2)—C(3)—C(4)	123·0 (3)	ah	C(8)—C(7)-F(7)	116·0 (3)
bd	C(5)—C(6)—C(7)	124·2 (3)	bh	C(3)—C(2)-F(2)	122·5 (3)
cc	C(3)—C(15)-C(13)	120·7 (3)	bh	C(6)—C(7)-F(7)	120·8 (4)
cd	C(4)—C(3)—C(15)	119·2 (3)	di	C(3)—C(4)-Cl(4)	121·1 (3)
cd	C(5)—C(6)—C(16)	119·0 (3)	di	C(6)—C(5)-Cl(5)	120·4 (3)
ce	C(3)—C(15)-C(16)	120·1 (4)	fi	C(5)—C(4)-Cl(4)	118·3 (3)
ce	C(13)-C(15)-C(6)	119·2 (4)	fi	C(4)—C(5)-Cl(5)	117·6 (3)

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