Discussion. A stereoscopic drawing of the molecule made with *ORTEP* (Johnson, 1965) is shown in Fig. 1. The bond distances and angles are respectively given in Fig. 2 and Table 3 with their estimated standard deviations. The mean value of the benzene ring bonds is 1·377 Å and is shorter than the expected value of 1·395 Å. One bond distance, C(2)–C(3), differs considerably: the difference between the observed value and the normal value (0·06 Å) is about nine standard deviations. There is, however, no obvious explanation for this discrepancy; the most plausible is the mediocre measurement of the weak and zero reflexions. The least-squares plane of the phenyl ring and the deviations of the atoms from this plane are shown in Table 4. The values of the C–H bond lengths are in a reasonable range of 0·81–1·06 Å (mean value: 0·92 Å). The four atoms C(7), C(8), C(9) and O(2) lie approximately in a plane (maximum deviation from the least-squares plane: 0·030 Å). The torsional angle between the two carbonyl groups C(7)–O(1) and C(8)–O(2) is 36·16° while that between the planes O(1)–C(7)–C(8) and C(7)–C(8)–C(9) is 30·63°.

The X-ray structure determination of this aziridine compound gives the nitrogen stereochemistry which enables the mechanism of formation and the physical and chemical properties of these heterocycles to be studied.

Table 4. *Deviations* (Å) *from least-squares plane of the phenyl ring* $0·8667X+0·4955Y-0·0571Z=9·9325$

C(1)	−0·0042	H(1)	−0·0487
C(2)	−0·0047	H(2)	0·1398
C(3)	0·0125	H(3)	−0·1142
C(4)	−0·0112	H(4)	0·0912
C(5)	0·0023	H(5)	−0·1096
C(6)	0·0052		

The authors thank Dr R. Grée and Dr R. Carrié for suggesting the problem and providing the compound.

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Acta Cryst. (1975). B**31**, 2888

Stacking Patterns of Halogenated Purines: Crystal Structure of 6-Chloropurine Riboside

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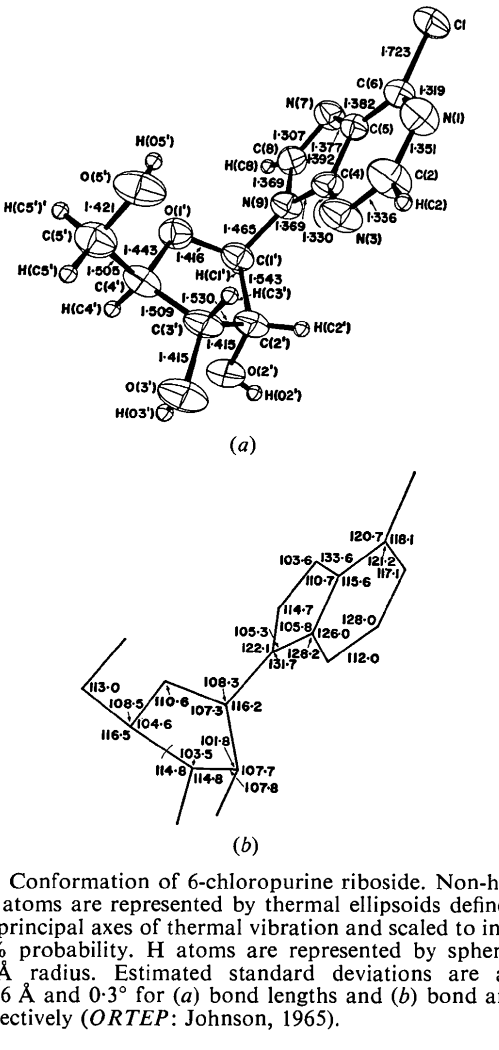
(*Received* 2 *June* 1975; *accepted* 16 *July* 1975)

Abstract. $C_{10}H_{11}N_4O_4Cl$, monoclinic, $C2$, $a=13·615$ (6), $b=8·067$ (2), $c=12·474$ (3) Å, $\beta=121·14$ (2)°, $Z=4$, M.W. 286·67, $D_c=1·605$, $D_m=1·61$ g cm^{-3}, $\mu=30·6$ cm^{-1}. The base stacking pattern involves Cl–purine contacts.

Introduction. Many investigators have suggested that halogen substituents affect purine and pyrimidine stacking interactions in aqueous solutions of nucleosides, in crystal structures of purine and pyrimidine derivatives, and within polynucleotides [*e.g.* review by Bugg & Sternglanz (1975) and references therein]. We determined the crystal structure of 6-chloropurine riboside to obtain additional information about the base-stacking patterns of halogenated purines. Prismatic crystals were obtained by slowly evaporating an acetonitrile–n-butyl ether solution of the nucleoside. Oscillation and Weissenberg photographs showed that the optically active crystals are monoclinic, and the space group $C2$ was indicated by the systematic absence of reflections hkl with $h+k$ odd. A crystal approximately $0·15\times0·18\times0·2$ mm was mounted on a Picker FACS-1 diffractometer with **b** slightly inclined to the φ axis of the goniostat. Approximate cell parameters for use in collection of intensity data were calculated by least-squares analysis of the angular settings for eight medium-angle reflections (Cu $K\bar{\alpha}$, $\lambda=1·5418$ Å). Intensity data were collected on the diffractometer with a scintillation counter, Ni-filtered Cu radiation, and a θ–2θ scan. The scan speed was 1° min^{-1}, and the background was counted for 20 s at each terminus of the scans. Measurements were made for each of the 1162 independent reflections with $2\theta\le128°$. Three reference reflections, which were monitored periodically,



(*a*)

(*b*)

Fig. 1. Conformation of 6-chloropurine riboside. Non-hydrogen atoms are represented by thermal ellipsoids defined by the principal axes of thermal vibration and scaled to include 50% probability. H atoms are represented by spheres of 0·1 Å radius. Estimated standard deviations are about 0·006 Å and 0·3° for (*a*) bond lengths and (*b*) bond angles, respectively (*ORTEP*: Johnson, 1965).

showed no significant intensity fluctuations during the collection of intensity data. More accurate values for the unit-cell parameters were determined immediately after data collection by a least-squares analysis of 2θ values for 10 high-angle reflections (Cu $K\alpha_1$, $\lambda = 1{\cdot}54051$ Å). These cell parameters were not significantly different from those obtained prior to collecting intensity data. Reflections that had scan counts below background level were assigned intensity values of 0·0 and were retained in all subsequent calculations. This manner of handling reflections with intensities less than background introduces a bias in our refinement on F^2, but probably has a negligible effect on the final results. The intensities were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts plus a correctional term $(0{\cdot}03S)^2$, S being the scan counts. Intensities and their variances were corrected for Lorentz and polarization factors and absorption corrections were applied by using the computer program *ORABS* (Wehe, Busing & Levy, 1962). The data were scaled by means of a Wilson (1942) plot.

A suitable trial structure was obtained by the heavy-atom method, using Cl as the heavy atom. The structure was refined by use of a modified version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962; Busing, 1971). The quantity minimized was $\sum w(F_o^2 - F_c^2/k^2)^2$, where k is a scale factor, and the weight w is equal to $1/\sigma^2(F_o^2)$. Scattering factors for the non-hydrogen atoms were from *International Tables for X-ray Crystallography* (1962); real and imaginary dispersion corrections for these atoms were from Cromer & Liberman (1970). All H atoms were located in difference Fourier maps that were computed during the later stages of refinement. Scattering factors for the H atoms were from Stewart, Davidson & Simpson (1965). Final cycles of refinement in-

Table 1. *Nonhydrogen atom parameters and their estimated standard deviations*

All values have been multiplied by 10^4. The y coordinate of the Cl atom was not refined. The temperature parameters are coefficients in the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The final value of the isotropic extinction parameter is $g = 0{\cdot}008$ (2).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	4532 (1)	2640 (0)	1498 (1)	618 (7)	566 (8)	409 (6)	−95 (7)	217 (5)	−176 (6)
N(1)	3185 (3)	2713 (6)	−940 (3)	650 (23)	417 (23)	409 (20)	37 (24)	212 (17)	35 (22)
C(2)	2591 (5)	1979 (7)	−2075 (4)	792 (36)	395 (31)	401 (26)	62 (26)	148 (24)	38 (23)
N(3)	2492 (3)	360 (5)	−2338 (3)	662 (27)	404 (23)	291 (18)	10 (20)	98 (17)	29 (19)
C(4)	3058 (3)	−561 (6)	−1309 (3)	336 (21)	336 (24)	259 (20)	25 (19)	68 (17)	35 (19)
C(5)	3688 (3)	28 (6)	−86 (4)	339 (22)	400 (29)	309 (22)	12 (20)	130 (18)	−56 (19)
C(6)	3735 (4)	1733 (6)	43 (4)	393 (22)	441 (28)	343 (22)	−19 (21)	162 (18)	−61 (21)
N(7)	4175 (3)	−1264 (5)	749 (3)	482 (21)	449 (23)	263 (16)	49 (19)	116 (15)	14 (17)
C(8)	3833 (3)	−2577 (6)	33 (3)	412 (22)	439 (30)	293 (20)	99 (23)	121 (17)	56 (20)
N(9)	3151 (3)	−2251 (5)	−1221 (3)	429 (18)	316 (19)	284 (16)	−1 (19)	124 (14)	27 (18)
C(1′)	2834 (4)	−3540 (6)	−2173 (4)	475 (24)	333 (25)	290 (20)	−3 (21)	142 (18)	10 (18)
O(1′)	3738 (2)	−3706 (4)	−2412 (2)	450 (16)	525 (20)	299 (14)	55 (15)	145 (12)	15 (13)
C(2′)	1721 (4)	−3238 (6)	−3443 (3)	468 (24)	391 (27)	257 (19)	−39 (21)	107 (17)	−27 (19)
O(2′)	1194 (3)	−4796 (5)	−3913 (3)	501 (17)	471 (19)	375 (15)	−136 (15)	156 (13)	−50 (15)
C(3′)	2191 (3)	−2634 (6)	−4254 (3)	494 (23)	339 (26)	197 (17)	−36 (20)	70 (15)	19 (17)
O(3′)	1428 (3)	−2819 (4)	−5559 (2)	707 (20)	511 (22)	251 (13)	−88 (17)	103 (13)	5 (13)
C(4′)	3309 (4)	−3561 (6)	−3736 (4)	582 (26)	338 (23)	282 (18)	−66 (21)	185 (18)	−41 (17)
C(5′)	4219 (4)	−2753 (7)	−3901 (4)	586 (27)	528 (33)	362 (22)	−85 (25)	223 (20)	−25 (22)
O(5′)	4488 (3)	−1117 (5)	−3409 (3)	695 (21)	541 (23)	305 (15)	−180 (18)	162 (14)	16 (15)

cluded the scale factor k, all positional parameters, anisotropic temperature parameters for the non-hydrogen atoms, isotropic temperature parameters for the H atoms and Zachariasen's (1963) isotropic extinction parameter g [as formulated by Coppens & Hamilton (1970)]. Since limited core storage prevented simultaneous variation of all parameters, the 19 non-hydrogen atoms were refined together, and the 11 H atoms were refined together in the alternate cycles. Both enantiomers were refined. The correct enantiomer (D-ribose) refined to an R ($\sum ||F_o|-|F_c||/\sum|F_o|$) of 0·040 and a goodness-of-fit $\{[\sum(F_o^2-F_c^2)^2/(m-s)]^{1/2}$, where m is the number of reflections used and s is the number of parameters refined$\}$ of 1·52. The incorrect enantiomer (L-ribose) refined only to $R=0{\cdot}044$ and a goodness-of-fit of 1·65. During the last cycle of refinement of the correct enantiomer the average parameter shift was less than one tenth of the estimated standard deviation, and no parameter shifted more than one third of its estimated standard deviation. A final difference Fourier map showed no peaks or troughs that exceeded 0·23 e Å^{-3} in magnitude. The final refined parameters are given in Tables 1 and 2.*

Discussion. The conformation of the molecule, together with bond lengths and angles involving only non-hydrogen atoms, is shown in Fig. 1. The C–H lengths range from 0·93 to 1·02 Å with an average value of 0·99 Å, and the O–H bond lengths range from 0·70 to 0·79 Å with an average value of 0·75 Å. The glycosyl torsion angle defined by the atoms O(1′)–C(1′)–N(9)–C(8) (Sundaralingam, 1969) is −83·3°, corresponding to a *syn* conformation (Donohue & Trueblood, 1960). The ribose moiety assumes the C(3′)-*endo* conformation, with O(1′), C(1′), C(2′) and C(4′) lying in a common plane, and C(3′) displaced by 0·53 Å from this plane. The torsion angles O(5′)–C(5′)–C(4′)–O(1′) and O(5′)–C(5′)–C(4′)–C(3′) are −62·5 and 55·1°, respectively, corresponding to a *gauche–gauche* conformation about the C(5′)–C(4′) bond (Shefter & Trueblood, 1965). The atoms of the purine ring are coplanar to within 0·01–0·02 Å. The Cl atom and C(1′) deviate by 0·065 and 0·220 Å, respectively, from the least-squares plane through the nine atoms of the purine ring.

The crystal-packing scheme, viewed perpendicular to the purine moieties, is depicted in Fig. 2. Hydrogen-bond distances and angles are listed in Table 3. The

Table 2. *Hydrogen atom parameters and their estimated standard deviations*

All values have been multiplied by 10^3. The isotropic temperature parameter is the coefficient in the expression $T=\exp[-8\pi^2U\sin^2\theta/\lambda^2]$.

	x	y	z	U
H–C(2)	217 (4)	270 (8)	−286 (4)	82 (14)
H–C(8)	403 (3)	−374 (5)	29 (3)	32 (9)
H–C(1′)	269 (2)	−452 (4)	−182 (3)	23 (8)
H–C(2′)	119 (3)	−239 (6)	−338 (3)	43 (9)
H–C(3′)	236 (3)	−140 (4)	−410 (3)	34 (9)
H–C(4′)	319 (3)	−465 (5)	−404 (3)	33 (9)
H(1)–C(5′)	395 (4)	−265 (7)	−477 (4)	74 (14)
H(2)–C(5′)	494 (3)	−341 (5)	−347 (3)	55 (12)
H–O(2′)	61 (5)	−481 (9)	−395 (5)	108 (20)
H–O(3′)	133 (3)	−367 (5)	−566 (3)	46 (11)
H–O(5′)	480 (4)	−128 (6)	−268 (4)	64 (13)

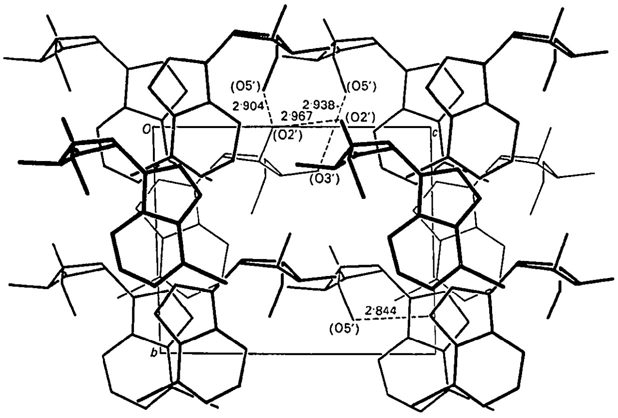


Fig. 2. Crystal packing viewed perpendicular to the planes of the purine moieties (approximately down **a**). The lightest lines correspond to purines whose planes intersect the a axis near $x=\frac{1}{8}$; the next heaviest near $x=\frac{3}{8}$; the next near $x=\frac{5}{8}$; and the heaviest near $x=\frac{7}{8}$. The trace of the bc plane is shown. Hydrogen bonds are represented by dashed lines and donor–acceptor distances (Å) are given.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

Estimated standard deviations are about 0·006 Å for donor–acceptor distances, 0·05 Å for hydrogen–acceptor distances and 3° for donor–hydrogen–acceptor angles.

Donor D		Acceptor A	Symmetry code	D–A	A–H	∠D–H–A
O(2′)	H(O2′)	O(5′)	*a*	2·904	2·24	145
O(2′)	H(O2′)	O(2′)	*b*	2·967	2·51	120
O(3′)	H(O3′)	O(5′)	*c*	2·938	2·27	161
O(5′)	H(O5′)	N(7)	*d*	2·844	2·07	167

(*a*) $x-\frac{1}{2},y-\frac{1}{2},z$. (*b*) $-x,y,-z-1$. (*c*) $\frac{1}{2}-x,y-\frac{1}{2},-z-1$. (*d*) $1-x,y,-z$.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31274 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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 $a/4=3{\cdot}4$ 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)].

We thank Miss Catherine Sims and Miss Mary Ann Comer for assistance with the preparation of this manuscript. This work was supported by N.I.H. grants CA-12159 and DE-02670, and by grant IN-66M of the American Cancer Society.

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1,3,6,8-Tetrafluoro-2,4,5,7,9,10-hexachloropyrene, $C_{16}F_4Cl_6$: an Overcrowded Molecule

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(*Received* 12 *July* 1975; *accepted* 16 *July* 1975)

Abstract. $C_{16}F_4Cl_6$, M.W. 480·92, monoclinic, space group $P2_1/a$; $a=15{\cdot}418$ (10), $b=4{\cdot}864$ (5), $c=11{\cdot}022$ (10) Å, $\beta=113{\cdot}85$ (10)°, $V=756{\cdot}0$ Å^3, $Z=2$, $D_x=2{\cdot}11$, $D_c=2{\cdot}11$ g cm^{-3}, μ(Mo $K\alpha$) = 11·6 cm^{-1}, $F(000)=468$, packing coefficient 0·76. Full-matrix least-squares refinement gave $R=0{\cdot}058$ and $R_w=0{\cdot}067$ 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.

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

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 $\sin\theta_{\max}=0{\cdot}5$ by the background-peak-background method. The crystal used was 4 mm long and 0·13 × 0·13 mm in cross section and was mounted about **b**.