

peripheral atoms assigned as O, since no bond-length difference was observed to distinguish S—F from S—O; this anion therefore exhibits O/F disorder: S(3) and S(4) anions, twofold disordered about the axis on which the S atoms lie; the O and F atoms could be distinguished by their bond lengths to S. In addition, the following distances were constrained to be equal within the given e.s.d.'s by the addition of extra observational equations to the least-squares matrix: all S—O (0.02 Å), both S—F (0.02 Å), all non-bonded O···F (0.04 Å), and all non-bonded O···O (0.04 Å). High resulting thermal parameters for O and F indicate, however, that the disorder may be more severe than that allowed for here.

In the final stages of refinement H atoms were included at calculated positions (C—H fixed at 1.08 Å) with an overall isotropic temperature factor. All refinement employed blocked full-matrix least squares with three blocks (cation 1, cation 2 and all anions respectively), interlayer scale factors being refined in each cycle. Convergence was achieved at  $R = 0.0831$  with a corresponding  $R' = \Sigma w^{1/2}\Delta / \Sigma w^{1/2}|F_o|$  of

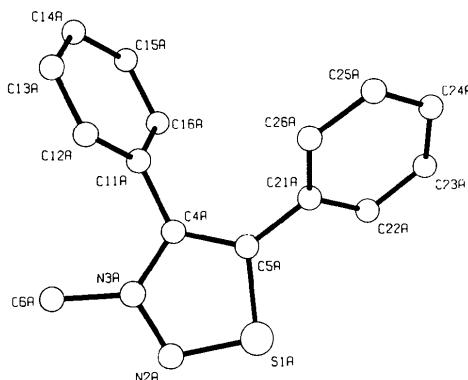


Fig. 1. Cation *A* showing the atomic numbering system. H atoms (omitted) are given the number of the C atom to which they are bonded. Cation *B* is numbered in the same way.

0.0893; the weighting scheme was  $w = 1/[\sigma^2(F) + 0.001F^2]$ . Final values of the constrained distances were: S—O, 1.405 (6); S—F, 1.541 (15); F···O, 2.29 (2); O···O, 2.293 (11) Å. A final difference map had no peaks  $> 0.42 \text{ e } \text{Å}^{-3}$ . Final positional parameters are given in Table 1, with derived bond lengths and angles in Tables 2 and 3.\* The atomic numbering system is shown in Fig. 1.

**Discussion.** The heterocyclic rings of the two independent cations show no significant differences in bond lengths and angles; the phenyl rings show some deviation from ideal geometry (bond lengths 1.339 to 1.397 Å). All rings are planar (maximum deviation from planarity 0.01 Å). Angles between mean ring planes are: heterocycle–phenyl 1: 118.5 and 104.3°; heterocycle–phenyl 2: 43.5 and 52.4° (cations *A* and *B* respectively). The substituent atoms on the heterocyclic rings are significantly out of the ring plane; deviations are C(6*A*) 0.02, C(11*A*) 0.10, C(21*A*) 0.06, C(6*B*) 0.02, C(11*B*) 0.05, C(21*B*) 0.05 Å. The angles C(6)–N(3)–C(4), C(11)–C(4)–C(5) and C(21)–C(5)–C(4) are considerably greater than 120° in both cations.

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33063 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

#### Reference

CROOK, S., JONES, P. G., KENNARD, O. & SYKES, P. (1977). *Chem. Ind. (London)*, p. 840.

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## 8-Iodoguanosine Monohydrate

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**Abstract.**  $\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_5\text{I}\cdot\text{H}_2\text{O}$ , monoclinic,  $P2_1$ ,  $a = 6.981$  (5),  $b = 11.139$  (7),  $c = 10.196$  (7) Å,  $\beta = 108.1$  (1)°,  $U = 753.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.886$  g cm<sup>-3</sup>.

Linear diffractometer data using Mo  $K\alpha$  radiation. The structure was refined to an  $R$  of 0.085 for 1296 unique reflexions. The molecule is in the *syn* confor-

mation and the C(5')—O(5') bond is *gauche* relative to C(4')—O(1') and *trans* relative to C(4')—C(3'). The sugar pucker is C(2')-*endo*-C(3')-*exo* relative to the mean plane of the ring. The degree of overlap between bases is small.

**Introduction.** Crystals were obtained by slow evaporation of an aqueous solution of 8-iodoguanosine (8-IG). The intensities of 1606 unique reflexions within a sphere corresponding to the limiting sphere for Cu  $K\alpha$  radiation were measured on a linear diffractometer with Mo  $K\alpha$  radiation and balanced filters. Reflexions were considered unobserved if the counts were less than the background count. Two crystals, mounted about **a** and **b**, were used for data collection. The crystals were small and uniform and no absorption corrections were applied.

The iodine position was determined from a Patterson synthesis. Rather than interpret the electron density map based on the iodine alone, which contains the true molecule and its mirror image, Patterson interpretation methods were used to determine most of the molecular structure. The plane of the purine ring was determined from an  $I(\theta, \phi)$  calculation (Tollin & Cochran, 1964) using the 200 largest  $|F|^2$  and a disc radius of 4.5 Å. The orientation of the purine base within this plane was determined from an  $I(\theta_1, \theta_2, \theta_3)$  rotation-function calculation (Munns, 1971; Tollin, 1976) using a model guanine base. Finally, two model sugar rings, one with a C(2')-*endo* pucker and the other with a C(3')-*endo* pucker, were attached in turn to the model base and rotation functions calculated for rotation about the glycosyl bonds (Walker & Tollin, to be published). The highest peak in the rotation function corresponded

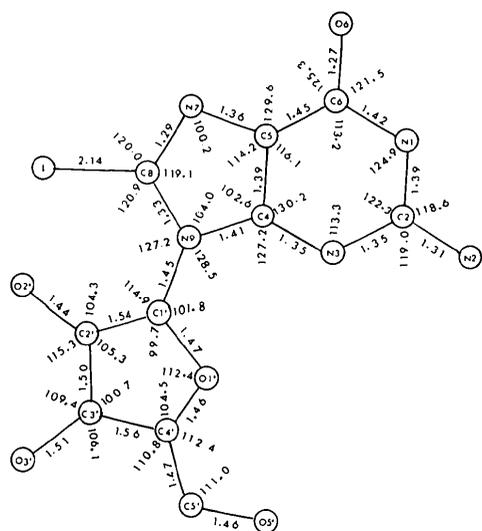


Fig. 1. Bond lengths (Å) and angles ( $^{\circ}$ ) in 8-iodoguanosine. The average e.s.d. in bond lengths is 0.03 Å, and in bond angles is 2.2 $^{\circ}$ .

Table 1. Positional parameters ( $\times 10^4$ ) and isotropic thermal parameters ( $\times 10^3$ ) of the non-hydrogen atoms with estimated standard deviations

|       | x          | y         | z          | $U$ (Å $^2$ ) |
|-------|------------|-----------|------------|---------------|
| I     | -2691 (2)  | 7512 (0)  | -1048 (2)  | *             |
| N(1)  | -1767 (25) | 2437 (34) | 2178 (18)  | 33 (4)        |
| C(2)  | -2354 (40) | 1959 (20) | 858 (21)   | 30 (6)        |
| N(2)  | -2530 (32) | 792 (23)  | 715 (25)   | 31 (5)        |
| N(3)  | -2823 (25) | 2654 (18) | -278 (16)  | 30 (4)        |
| C(4)  | -2603 (37) | 3838 (18) | 8 (25)     | 27 (5)        |
| C(5)  | -2004 (42) | 4431 (28) | 1271 (29)  | 34 (7)        |
| C(6)  | -1509 (36) | 3676 (24) | 2490 (24)  | 30 (5)        |
| O(6)  | -890 (28)  | 4048 (18) | 3723 (19)  | 38 (4)        |
| N(7)  | -1886 (31) | 5643 (21) | 1170 (17)  | 34 (5)        |
| C(8)  | -2501 (34) | 5766 (23) | 153 (17)   | 27 (5)        |
| N(9)  | -1957 (31) | 4791 (20) | -943 (16)  | 33 (5)        |
| C(1') | -3481 (23) | 4734 (20) | -2430 (16) | 22 (5)        |
| O(1') | -5554 (21) | 4277 (15) | -2817 (15) | 29 (4)        |
| C(2') | -2477 (32) | 3713 (21) | -2991 (21) | 21 (4)        |
| O(2') | -649 (25)  | 4233 (16) | -3094 (16) | 31 (4)        |
| C(3') | -3984 (36) | 3359 (25) | -4335 (24) | 31 (5)        |
| O(3') | -4138 (27) | 4340 (18) | -5384 (18) | 39 (4)        |
| C(4') | -5976 (39) | 3416 (21) | -3947 (22) | 32 (5)        |
| C(5') | -6508 (39) | 2221 (24) | -3545 (26) | 39 (7)        |
| O(5') | -8404 (23) | 2261 (15) | -3230 (16) | 33 (4)        |
| O(W)  | -1285 (31) | 1157 (23) | 4551 (22)  | 54 (6)        |

\* Anisotropic temperature factors for I ( $\times 10^4$ )

| $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$  | $U_{13}$ | $U_{12}$ |
|----------|----------|----------|-----------|----------|----------|
| 328 (7)  | 175 (6)  | 455 (7)  | -139 (11) | 147 (5)  | -51 (13) |

to a C(2')-*endo* sugar pucker. An electron-density map based on this model revealed atom O(5') of the sugar, which had not been included in the model, and indicated the presence of a water molecule. The value of  $R$  at this stage was 0.14.

Full-matrix least-squares refinement of the positional and isotropic thermal parameters was first made, for 1296 reflexions with  $F_o > 4\sigma(F_o)$ . This was followed by refinement with anisotropic thermal parameters for the iodine atom but isotropic for the other atoms. Hydrogen-atom positions were calculated on the basis of the chemical structure and hydrogen-bonding scheme suggested by interatomic distances and angles. With fixed hydrogen-atom coordinates and isotropic temperature factors, the positional parameters of the non-hydrogen atoms, the anisotropic thermal parameters of the iodine atom, and the isotropic thermal parameters of the other atoms were refined. After four cycles of refinement the  $R$  value was 0.085\* and there were no shifts in the parameters greater than 0.03 $\sigma$ . The data were not good enough to refine the thermal parameters of all the non-hydrogen atoms anisotropically.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33021 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

cally, possibly because absorption corrections were not applied, and attempts to do so resulted in some atoms having non-positive-definite values for the thermal parameters. Positional and thermal parameters are in Table 1. Bond lengths and angles are in Fig. 1.

**Discussion.** The nucleoside is in the *syn* conformation and is thus similar to 8-bromoguanosine (Bugg & Thewalt, 1969; Tavale & Sobell, 1970). The purine base is essentially planar (Table 2) and the sugar ring has a C(2')-*endo*-C(3')-*exo* pucker relative to the mean plane of the ring. The orientation of C(5')-O(5') is *gauche* relative to C(4')-O(1') and *trans* relative to C(4')-C(3'). In this respect 8-IG differs from 8-bromoguanosine and no intramolecular hydrogen bond is formed between O(5') and N(3). Bond lengths and angles are in reasonably good agreement with those found in other nucleosides and nucleotides. Nucleosides and water molecules are linked together by a network of hydrogen bonds (Table 3), but the hydrogen atoms attached to N(2) are not involved in hydrogen bonding.

Halogen substitution affects the base stacking in nucleic acid components. Thus there is a marked decrease in the degree of base overlap in 8-bromoguanosine as compared with guanosine (Bugg & Thewalt, 1969). In 8-IG the degree of base overlap (Fig. 2) is even less than in the bromo derivative. The shortest distance between the iodine atom and atoms in adjacent bases involves atom C(2), and is 3.60 Å. This is shorter than the expected sum of the van der Waals radii of 3.85 Å (Pauling, 1960). Iodine and

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

|                              |      |                   |     |
|------------------------------|------|-------------------|-----|
| O(5')-H...N(7) <sup>a</sup>  | 2.73 | C(5')-O(5')-N(7)  | 98  |
| O(2')-H...O(5') <sup>b</sup> | 2.73 | C(2')-O(2')-O(5') | 109 |
| N(1)-H...O(W)                | 2.70 | C(2)-N(1)-O(W)    | 112 |
| O(3')-H...O(6) <sup>c</sup>  | 2.71 | C(3')-O(3')-O(6)  | 123 |
| O(W)-H...O(5') <sup>d</sup>  | 2.80 |                   |     |
| O(W)-H...O(6) <sup>e</sup>   | 3.04 |                   |     |

Symmetry code

|     |                |     |                   |
|-----|----------------|-----|-------------------|
| (a) | -x, -½ + y, -z | (d) | 1 + x, y, 1 + z   |
| (b) | 1 + x, y, z    | (e) | -x, -½ + y, 1 - z |
| (c) | x, y, -1 + z   |     |                   |

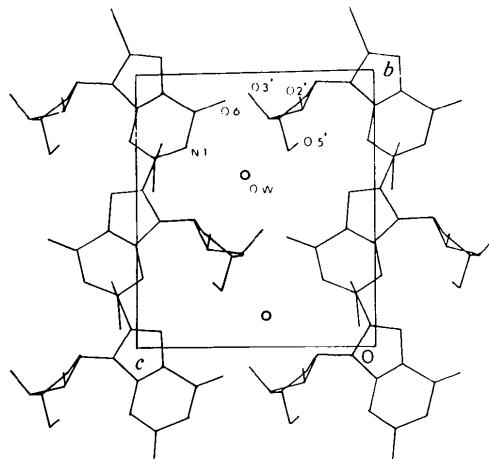


Fig. 2. A projection of the structure viewed along *a*, showing the base stacking in 8-iodoguanosine.

Table 2. *Deviations (Å) of atoms from the least-squares planes, and torsion angles (°)*

The atoms marked with an asterisk were used to calculate the mean planes. *X*, *Y* and *Z* are coordinates, in Å, relative to *a*, *b* and *c*\*

(1) Purine ring

$$6.9705X - 0.6078Y - 3.1151Z + 2.0460 = 0$$

|       |        |       |        |
|-------|--------|-------|--------|
| N(3)* | 0.004  | C(6)* | -0.004 |
| N(1)* | -0.011 | C(8)* | 0.001  |
| C(2)* | 0.019  | I     | 0.041  |
| C(5)* | -0.016 | O(6)  | 0.020  |
| N(9)* | -0.013 | N(2)  | 0.012  |
| N(7)* | 0.025  | C(1') | 0.089  |
| C(4)* | -0.004 |       |        |

(2) Sugar ring

$$0.5318X + 8.5317Y - 6.4283Z - 5.2228 = 0$$

|        |        |       |        |
|--------|--------|-------|--------|
| O(1')* | -0.059 | O(2') | 0.343  |
| C(1')* | 0.194  | O(3') | 1.721  |
| C(2')* | -0.264 | C(5') | -1.395 |
| C(3')* | 0.217  | O(5') | -1.665 |
| C(4')* | -0.089 |       |        |

Torsion angles

|                         |       |
|-------------------------|-------|
| O(1')-C(1')-N(9)-C(8)   | 243.0 |
| O(5')-C(5')-C(4')-C(3') | 182.0 |

carbon do not differ in electronegativity (Pauling, 1960), so the contribution to the stability of the stacking in 8-bromoguanosine attributed to the C(8)-Br bond (Bugg & Thewalt, 1969) does not apply in the case of 8-IG.

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### References

- BUGG, C. E. & THEWALT, U. (1969). *Biochem. Biophys. Res. Commun.* **37**, 623-629.
- MUNNS, A. R. I. (1971). PhD Thesis, Univ. of Dundee.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- TAVALE, S. S. & SOBELL, H. M. (1970). *J. Mol. Biol.* **48**, 109-123.
- TOLLIN, P. (1976). In *Crystallographic Computing Techniques*, edited by F. R. AHMED. Copenhagen: Munksgaard.
- TOLLIN, P. & COCHRAN, W. (1964). *Acta Cryst.* **17**, 1322-1324.