stacked in the column with alternate interplanar distances of 3·558 and 7·233 Å between adjacent anthracene ring systems. The *B* molecules related by symmetry centers at 0, 0, 0 and 0, $\frac{1}{2}$, 0 form the other column with these distances of 3·822 and 7·324 Å respectively. These alternating short and long separations in each column result from the shape of the molecules.

The Br atoms lie on puckered ribbons extending in the **c** direction and passing through the centers of unit cells. The closest contact between Br atoms (of *A* and *B* molecules) is 3·693 (1) Å, which is 0·207 Å shorter than the expected van der Waals contact of 3·90 Å using Pauling's (1960) radius of 1·95 Å for Br. However, it is nearly twice the van der Waals radius using Bondi's (1964) corrected value of 1·85 Å. The other intermolecular distances are in the normally expected range for nonbonding contacts.

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# Structure of 8-Methylguanosine Trihydrate

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**Abstract.** $C_{11}H_{15}N_5O_5.3H_2O$, $M_r = 351·3$, orthorhombic, $C222_1$, $a = 8·464$ (1), $b = 30·848$ (4), $c = 12·233$ (1) Å, $V = 3194·0$ (7) Å$^3$, $Z = 8$, $D_m = 1·459$ (3), $D_x = 1·462$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu = 1·09$ mm$^{-1}$, $F(000) = 1488$, $T = 295$ K, final $R = 0·053$ for 1448 unique reflections. The glycosidic torsion angle, $\chi = 52·7$ (5)°, is in the *syn* conformation. The ribose ring has a C(2′)-*endo* ($^2E$) pucker and the conformation around the C(5′)—C(4′) bond is *gauche–gauche* (g,g). An intramolecular hydrogen bond connects the O(5′) hydroxyl group with the N(3) atom of the guanine base. The crystal structure is stabilized by intermolecular face-to-face base stackings and extensive hydrogen-bond networks involving guanine–guanine base-pairing.

**Introduction.** The glycosidic torsion angle defines the orientation of the base plane relative to the sugar moiety and it is one of the most important parameters for determining the molecular conformation of a

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nucleoside. Although many naturally occurring purine nucleosides in the solid state take either *syn* or *anti* conformations, the latter is more frequently observed. However, an 8-substituted purine nucleoside is usually in the *syn* conformation because of its steric hindrance, and some physicochemical properties of purine nucleosides and nucleotides with a bulky substituent at the 8-position have been investigated in solution (Sarma, Lee, Evans, Yathindra & Sundaralingam, 1974; Uesugi & Ikehara, 1977). In this report, we describe the structure of 8-methylguanosine trihydrate as part of the structural studies on the stereochemical properties of nucleic acid constituents and analogues.

**Experimental.** 8-Methylguanosine was synthesized according to the published procedure (Maeda, Nushi & Kawazoe, 1974), and crystallized as colorless plates from an aqueous solution. Density by flotation in benzene and carbon tetrachloride mixture. Approximate crystal size 0·45 × 0·20 × 0·05 mm. Rigaku AFC-5 automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Cell parameters determined by least-squares refinement of 31 reflections with $30 < 2\theta < 47°$. Intensities of 1511 independent reflections within $\sin\theta/\lambda \leq 0{\cdot}583$ Å$^{-1}$ ($0 \leq h \leq 9$, $0 \leq k \leq 34$, $0 \leq l \leq 14$) measured by $\omega$–$2\theta$ scan technique, scan speed 0·5° ($\omega$) min$^{-1}$. Crystal deterioration checked by monitoring intensities of three standard reflections every 100 reflections: variation 0·01. 1448 reflections with $F_o > 1{\cdot}5\sigma(F_o)$ used for structure analysis. Corrections for Lorentz–polarization, but not for absorption or extinction. Structure solved by the direct method using the program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The $E$ map revealed the positions of all non-hydrogen atoms. After the positional and thermal parameters for non-hydrogen atoms had been refined (on $F$) by block-diagonal least-squares method, the positions of all H atoms were determined on a difference Fourier map. The final refinement including positional and isotropic thermal parameters for H atoms gave $R = 0{\cdot}053$, $wR = 0{\cdot}065$ and $S = 1{\cdot}280$; $w = [\sigma^2(F_o) - 0{\cdot}030F_o + 0{\cdot}002F_o{}^2]^{-1}$. In final cycle of refinement $(\Delta/\sigma)_{\max} = 0{\cdot}2$ for C(10). No peak higher than 0·28 e Å$^{-3}$ on final difference Fourier map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The computations were accomplished by an ACOS-900 computer with the *UNICS* (1979) system at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

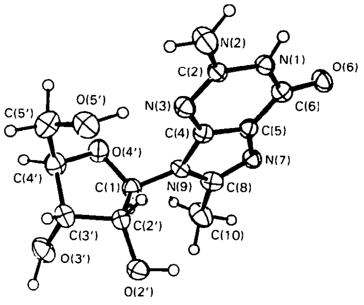

Fig. 1. The molecular geometry and atom numbering.

Table 1. *Atomic positional parameters* (×10$^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| N(1) | 3569 (4) | 203 (1) | 3576 (2) | 2·32 (7) |
| C(2) | 2933 (4) | 191 (1) | 2541 (3) | 2·28 (8) |
| N(2) | 2782 (5) | −203 (1) | 2078 (3) | 3·64 (9) |
| N(3) | 2524 (4) | 543 (1) | 1984 (3) | 2·56 (7) |
| C(4) | 2789 (5) | 915 (1) | 2552 (3) | 2·15 (7) |
| C(5) | 3445 (4) | 952 (1) | 3582 (3) | 2·13 (8) |
| C(6) | 3831 (5) | 575 (1) | 4174 (3) | 2·50 (8) |
| O(6) | 4357 (4) | 548 (1) | 5120 (2) | 2·85 (6) |
| N(7) | 3506 (4) | 1382 (1) | 3902 (3) | 2·40 (7) |
| C(8) | 2925 (5) | 1600 (1) | 3078 (3) | 2·71 (9) |
| N(9) | 2469 (4) | 1333 (1) | 2222 (2) | 2·24 (7) |
| C(10) | 2738 (7) | 2082 (1) | 3060 (4) | 3·85 (12) |
| C(1′) | 1782 (5) | 1482 (1) | 1196 (3) | 2·51 (9) |
| C(2′) | 2794 (4) | 1410 (1) | 175 (3) | 2·37 (8) |
| C(3′) | 1545 (5) | 1413 (1) | −719 (3) | 2·79 (9) |
| C(4′) | 112 (5) | 1207 (1) | −160 (4) | 3·07 (9) |
| C(5′) | −57 (6) | 727 (2) | −375 (4) | 3·87 (11) |
| O(4′) | 361 (3) | 1259 (1) | 1009 (2) | 2·99 (7) |
| O(2′) | 3953 (3) | 1739 (1) | 29 (2) | 3·17 (6) |
| O(3′) | 1177 (4) | 1845 (1) | −1040 (2) | 3·69 (8) |
| O(5′) | 1364 (4) | 500 (1) | −190 (2) | 3·63 (7) |
| O($W$1) | 3635 (5) | 1053 (1) | 6873 (2) | 4·14 (8) |
| O($W$2) | 8328 (5) | 6949 (1) | 7199 (3) | 4·83 (10) |
| O($W$3) | 3464 (5) | 2639 (1) | 601 (3) | 5·22 (10) |

Table 2. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| N(1)–C(2) | 1·377 (5) | N(1)–C(6) | 1·377 (5) |
| C(2)–N(2) | 1·348 (6) | C(2)–N(3) | 1·325 (5) |
| N(3)–C(4) | 1·360 (5) | C(4)–C(5) | 1·382 (6) |
| C(4)–N(9) | 1·379 (5) | C(5)–C(6) | 1·411 (5) |
| C(5)–N(7) | 1·382 (5) | C(6)–O(6) | 1·243 (5) |
| N(7)–C(8) | 1·309 (5) | C(8)–N(9) | 1·387 (5) |
| C(8)–C(10) | 1·493 (7) | N(9)–C(1′) | 1·458 (5) |
| C(1′)–O(4′) | 1·403 (5) | C(1′)–C(2′) | 1·530 (6) |
| C(2′)–C(3′) | 1·521 (6) | C(2′)–O(2′) | 1·422 (5) |
| C(3′)–C(4′) | 1·530 (6) | C(3′)–O(3′) | 1·426 (5) |
| C(4′)–C(5′) | 1·510 (7) | C(4′)–O(4′) | 1·455 (5) |
| C(5′)–O(5′) | 1·411 (6) | | |

| | | | |
|---|---|---|---|
| C(2)–N(1)–C(6) | 125·0 (3) | N(1)–C(2)–N(2) | 116·6 (4) |
| N(1)–C(2)–N(3) | 123·6 (4) | N(2)–C(2)–N(3) | 119·8 (4) |
| C(2)–N(3)–C(4) | 112·6 (4) | N(3)–C(4)–C(5) | 127·1 (4) |
| N(3)–C(4)–N(9) | 127·5 (4) | C(5)–C(4)–N(9) | 105·4 (3) |
| C(4)–C(5)–C(6) | 119·5 (4) | C(4)–C(5)–N(7) | 110·7 (3) |
| C(6)–C(5)–N(7) | 129·6 (3) | N(1)–C(6)–C(5) | 112·2 (3) |
| N(1)–C(6)–O(6) | 119·8 (4) | C(5)–C(6)–O(6) | 128·0 (4) |
| C(5)–N(7)–C(8) | 105·1 (3) | N(7)–C(8)–N(9) | 112·3 (4) |
| N(7)–C(8)–C(10) | 124·3 (4) | N(9)–C(8)–C(10) | 123·4 (4) |
| C(4)–N(9)–C(8) | 106·3 (3) | C(4)–C(9)–C(1′) | 128·6 (3) |
| C(8)–N(9)–C(1′) | 125·1 (3) | N(9)–C(1′)–O(4′) | 109·2 (3) |
| N(9)–C(1′)–C(2′) | 115·8 (3) | C(2′)–C(1′)–O(4′) | 106·1 (3) |
| C(1′)–C(2′)–C(3′) | 101·4 (3) | C(1′)–C(2′)–O(2′) | 112·7 (3) |
| C(3′)–C(2′)–O(2′) | 112·7 (3) | C(2′)–C(3′)–C(4′) | 103·2 (3) |
| C(2′)–C(3′)–O(3′) | 110·7 (3) | C(4′)–C(3′)–O(3′) | 109·7 (3) |
| C(3′)–C(4′)–C(5′) | 113·8 (4) | C(3′)–C(4′)–O(4′) | 106·2 (3) |
| C(5′)–C(4′)–O(4′) | 107·1 (4) | C(4′)–C(5′)–O(5′) | 112·3 (4) |
| C(1′)–O(4′)–C(4′) | 109·8 (3) | | |

**Discussion.** Final atomic parameters are listed in Table 1.* The molecular structure drawn by *ORTEP*II (Johnson, 1976) is shown in Fig. 1. Most of the bond distances and angles listed in Table 2 are in agreement with those of guanosine dihydrate (Thewalt, Bugg & Marsh, 1970). However, some are significantly different from those of 8-bromoguanosine (Tavale & Sobell, 1970): C(8)—N(9) is 1·387 (5) Å in 8-methylguanosine and 1·369 (9) Å in 8-bromoguanosine, while N(7)—C(8)—C(10) and N(9)—C(8)—C(10) are 124·3 (4) and 123·4 (4)° in this crystal, and 122·8 (5) and 121·7 (5)° in 8-bromoguanosine. These differences are probably due to the electronic structure of the substituent at the 8-position of the guanine base. Also, the C(6)—O(6) and C(1')—C(2') bond lengths, 1·243 (5) and 1·530 (6) Å, deviate from those in 8-bromoguanosine [1·270 (9) and 1·509 (10) Å].

The C(8)—C(10) bond length of 1·493 (7) Å is the same as that of 1·493 (11) Å in 8-methyladenosine 3'-monophosphate (Yasuniwa, Tokuoka, Ogawa, Yamagata, Fujii, Tomita, Lim & Ikehara, 1979). The torsion angle $\chi$ around the glycosidic bond is 52·7 (5)°, corresponding to the *syn* conformation, which is apparently favored to avoid the steric hindrance between the methyl group at the 8-position of the base and the ribose ring; this conformation is also favored for some other nucleosides and nucleotides having a bulky substituent at the 8-position of the purine base. The ribose ring has a C(2')-*endo* ($^2E$) pucker with C(2') displaced by 0·561 (6) Å from the least-squares plane through C(1'), C(3'), C(4') and O(4'), and has phase angle $P = 159{\cdot}5°$ and maximum amplitude of pseudorotation $\tau_m = 36{\cdot}0°$ (Altona & Sundaralingam, 1972). The conformation of the C(5')—C(4') bond is *gauche–gauche* (g,g), and the hydroxyl group O(5')—H forms an intramolecular hydrogen bond of 2·839 (5) Å with N(3) of the guanine base. Most nucleosides having the *syn* conformation (determined by X-rays) exhibit a C(2')-*endo* ($^2E$) sugar pucker and an O(5')—H···N(3) intramolecular hydrogen bond. The dihedral angle between the base plane and the plane formed by C(1'), C(3'), C(4') and O(4') in the sugar moiety is 112·4 (2)°.

The molecular packing projected along the *a* axis is illustrated in Fig. 2. It is interesting to note that an intermolecular face-to-face base stacking was found in the crystal structure, and the separation and dihedral angle between each base plane are about 3·4 Å and 6·7 (7)°, respectively. Because this stacking is quite different from that in guanosine dihydrate or in 8-bromoguanosine, the methyl group at the 8-position may affect the base-stacking mode in the crystalline state. N(1) and O(6) of the guanine moiety are respectively used as a donor and an acceptor for intermolecular hydrogen-bonding dimer formation, whereas the angle N(1)—H···O(6) is 160·5 (7)° and the dihedral angle between two base planes is 45·5 (7)°. N(7) and N(2) of the guanine moiety are also used as an acceptor and a donor for an intermolecular hydrogen bond with the neighboring molecule. The water molecules [O(*W*1), O(*W*2) and O(*W*3)] form hydrogen-bond networks and fill the space between the stacked columns of 8-methylguanosine. Therefore, the crystal structure is mainly stabilized by base stackings and hydrogen-bond networks.

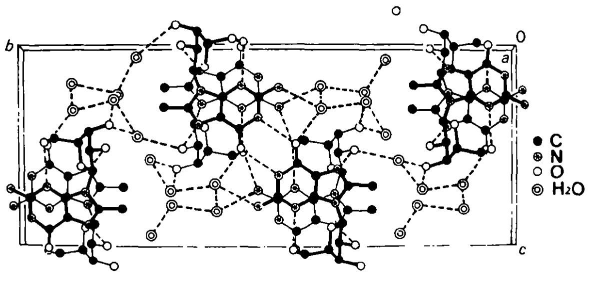

Fig. 2. Packing of the molecules in the unit cell. Broken lines show the hydrogen bonds.

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[*] Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for H atoms and hydrogen-bond distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42298 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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