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Structure of 9-(2-Hydroxyethyl)guanine

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Abstract. $C_7H_9N_5O_2$, $M_r = 195\cdot18$, triclinic, $P\bar{1}$, $a = 12\cdot060\,(1)$, $b = 13\cdot832\,(1)$, $c = 4\cdot993\,(1)$ Å, $\alpha = 89\cdot86\,(1)$, $\beta = 92\cdot66\,(1)$, $\gamma = 75\cdot11\,(1)°$, $V = 804\cdot0\,(2)$ Å^3, $Z = 4$, $D_m = 1\cdot610$, $D_x = 1\cdot612$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 10\cdot6$ cm^{-1}, $F(000) = 408$, room temperature, $R = 0\cdot092$ for 1633 reflexions. Two independent molecules are self-associated into base pairs through N(2)—H···N(3) hydrogen bonds around inversion centres. These base pairs are linked by N(1)—H···N(7) and N(2)—H···O(6) hydrogen bonds to form a ribbon along **b**. The hydroxyl groups interact with guanine moieties at N(7), O(6), N(1) and N(2). These hydrogen bonds join the molecular ribbons to form a sheet parallel to the (013) plane. There are no unusual bond distances or angles.

Introduction. As part of a series of studies on hydrogen bonds between hydroxyl groups and nucleic acid bases (Shibata, Takenaka, Sasada & Ohki, 1985*a*,*b*; Shibata, Takenaka & Sasada, 1985), the present paper deals with the structure of 9-(2-hydroxyethyl)guanine.

Experimental. The yield of 9-(2-hydroxyethyl)guanine was rather low in the reaction reported by Yamazaki (1969). We applied a simple reaction after Ueda, Kondo, Kono, Takemoto & Imoto (1968); reaction of 2-*N*-acetylguanine with ethylene carbonate in dimethyl sulfoxide at 403 K in the presence of a trace of sodium hydroxide yielded both 9-substituted and 7-substituted derivatives. When *N*,*N*-dimethyl-4-pyridylamine was used instead of sodium hydroxide, the deacetylated 9-substituted derivative was obtained by isolation and purification on porous resin column. Small thin plate crystals from dimethyl sulfoxide solution. D_m by flotation in a mixture of carbon tetrachloride and bromoform. Rigaku four-circle diffractometer; graphite-monochromated Cu $K\alpha$ radiation; crystal $0\cdot2 \times 0\cdot1 \times 0\cdot05$ mm;* unit-cell dimensions determined with 45 reflexions, $17 < 2\theta < 40°$; intensities measured for $3 < 2\theta < 125°$; h −13–13, k −15–15, l 0–5; ω-scan mode; scan rate 4° (ω) min^{-1}; scan width 1·2° (ω); five reference reflexions showed intensity deterioration; corrections for intensity decay, Lorentz and polarization factors, but not for absorption or extinction; 2559 independent reflexions; 869 zero-reflexions; standard deviations $\sigma^2(F_o) = \sigma_p^2(F_o) + qF_o^2$, where $\sigma_p(F_o)$ was evaluated by counting statistics and q was estimated to be $7\cdot15 \times 10^{-5}$. Since the E distribution suggested the structure was centrosymmetric, the space group was assumed to be $P\bar{1}$; structure solved by the direct method; in calculating E's, the molecular scattering factor of guanine was used; full-matrix least-squares refinement; all H-atom parameters calculated geometrically; $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/\sigma^2(F_o)$; zero reflexions with $|F_c| > F_{\rm lim}$ ($F_{\rm lim} = 2\cdot227$) included in the refinement by assuming $F_o = F_{\rm lim}$ and $w = w(F_{\rm lim})$; final $R = 0\cdot092$ for 1633 reflexions with $F_o > 3\sigma$ ($wR = 0\cdot051$, $S = 1\cdot840$); $(\Delta/\sigma)_{\rm max} = 0\cdot02$ for non-H atoms; $\Delta\rho$ peak $0\cdot52$ e Å^{-3}; the R factor converged at rather a high value, probably owing to the small size of the specimen; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *LSAP*80 (Takenaka & Sasada, 1980), *DCMS*82 (Takenaka & Sasada, 1982) and *LISTUP* (Takenaka & Sasada, 1983).

Discussion. Final atomic parameters are given in Table 1.* Fig. 1 shows the bond distances and angles. There are no significant differences in the molecular dimensions of guanine moieties between the two independent molecules *A* and *B*. The averaged dimensions of the guanine moieties are in good agreement with those of the related compounds guanine (Thewalt, Bugg & Marsh, 1971), 9-ethylguanine (Destro, Kistenmacher & Marsh, 1974), 9-(2-carboxyethyl)guanine (Fujita, Takenaka & Sasada, 1984), 9-(2-carbamoylethyl)-

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* The crystal size was too small to give good intensity data; however, this size was the largest available. All efforts to obtain larger crystals failed.

* Lists of structure factors, anisotropic thermal parameters and atomic parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42305 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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guanine (Fujita, Takenaka & Sasada, 1985) and guanosine (Thewalt, Bugg & Marsh, 1970). The purine ring is planar within 0·034 Å for *A* and 0·024 Å for *B*. The torsion angles in the two molecules are 236·8 (8) and 272 (1)° for C(4)—N(9)—C(10)—C(11), and 59·1 (8) and −47·2 (9)° for N(9)—C(10)—C(11)—O(12), respectively.

The crystal structure is shown in Fig. 2. The guanine moieties of *A* form a pair around the inversion centre at $(\frac{1}{2},0,\frac{1}{2})$ through N(2)—H···N(3) hydrogen bonds. A similar hydrogen-bonded pair of *B* is observed around the inversion centre at $(\frac{1}{2},\frac{1}{2},-1)$. The N(1)—H···N(7) and N(2)—H···O(6) hydrogen bonds link these two base pairs to form a molecular ribbon along **b**. The hydroxyl group of *A* is a donor of the hydrogen bond to N(7) of another *A* at $(-x,-y,1-z)$, and at the same time is an acceptor from N(1) of *B* at $(1-x,-y,-z)$. On the other hand, the hydroxyl group of *B* is a donor to O(6) of *A* at $(-x,1-y,-z)$ and an acceptor from N(2) of *B* at $(1-x,1-y,-1-z)$. These hydrogen bonds constitute a molecular sheet parallel to the (013) plane.

In crystals of the guanine derivatives, the ribbon structures are commonly found (Thewalt, Bugg & Marsh, 1971; Destro, Kistenmacher & Marsh, 1974), even if the hydroxyl group is present (Thewalt, Bugg & Marsh, 1970). The hydrogen bonds between the hydroxyl group and the guanine moiety are not so strong as to disturb the base–base interactions.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors*

$B_{eq} = 8\pi^2(U_1 + U_2 + U_3)/3$, where U_1, U_2 and U_3 are the principal components of the mean-square displacement matrix **U**. Values in parentheses are e.s.d.'s and those in angle brackets give the anisotropicity defined by $[\sum(B_{eq}-8\pi^2U_i)^2/3]^{1/2}$; they refer to the last decimal places.

	x	y	z	B_{eq}(Å^2)
N(1)*A*	0·2617 (5)	0·1868 (5)	0·178 (1)	2·2 ⟨10⟩
C(2)*A*	0·3476 (6)	0·1131 (6)	0·301 (2)	2·4 ⟨8⟩
N(2)*A*	0·4534 (5)	0·1037 (6)	0·216 (2)	3·1 ⟨18⟩
N(3)*A*	0·3323 (5)	0·0533 (4)	0·503 (1)	2·2 ⟨10⟩
C(4)*A*	0·2202 (6)	0·0718 (5)	0·550 (1)	1·7 ⟨3⟩
C(5)*A*	0·1275 (6)	0·1437 (6)	0·443 (2)	2·3 ⟨2⟩
C(6)*A*	0·1462 (6)	0·2090 (5)	0·242 (2)	2·3 ⟨9⟩
O(6)*A*	0·0748 (4)	0·2796 (4)	0·128 (1)	3·0 ⟨15⟩
N(7)*A*	0·0253 (5)	0·1368 (5)	0·551 (1)	2·8 ⟨17⟩
C(8)*A*	0·0597 (6)	0·0613 (6)	0·726 (2)	2·8 ⟨14⟩
N(9)*A*	0·1754 (5)	0·0203 (4)	0·737 (1)	2·4 ⟨9⟩
C(10)*A*	0·2415 (7)	−0·0660 (6)	0·908 (2)	2·8 ⟨14⟩
C(11)*A*	0·1973 (7)	−0·1576 (6)	0·874 (2)	2·7 ⟨8⟩
O(12)*A*	0·2023 (5)	−0·1894 (5)	0·599 (1)	3·7 ⟨18⟩
N(1)*B*	0·5783 (5)	0·3063 (5)	−0·512 (1)	2·1 ⟨11⟩
C(2)*B*	0·5384 (6)	0·3831 (5)	−0·699 (2)	2·2 ⟨8⟩
N(2)*B*	0·6210 (6)	0·4048 (5)	−0·838 (1)	2·9 ⟨12⟩
N(3)*B*	0·4291 (5)	0·4298 (5)	−0·743 (1)	2·4 ⟨9⟩
C(4)*B*	0·3592 (6)	0·3957 (5)	−0·577 (1)	2·0 ⟨6⟩
C(5)*B*	0·3907 (6)	0·3231 (5)	−0·377 (1)	2·1 ⟨7⟩
C(6)*B*	0·5077 (6)	0·2723 (5)	−0·337 (1)	1·8 ⟨8⟩
O(6)*B*	0·5522 (4)	0·2035 (4)	−0·171 (1)	2·9 ⟨15⟩
N(7)*B*	0·2959 (5)	0·3105 (4)	−0·250 (1)	2·2 ⟨10⟩
C(8)*B*	0·2104 (6)	0·3733 (5)	−0·373 (2)	2·0 ⟨7⟩
N(9)*B*	0·2410 (5)	0·4277 (4)	−0·577 (1)	2·1 ⟨9⟩
C(10)*B*	0·1627 (7)	0·5031 (6)	−0·747 (2)	2·6 ⟨9⟩
C(11)*B*	0·1436 (8)	0·6072 (6)	−0·632 (2)	3·3 ⟨20⟩
O(12)*B*	0·1207 (6)	0·6046 (5)	−0·357 (1)	5·1 ⟨38⟩

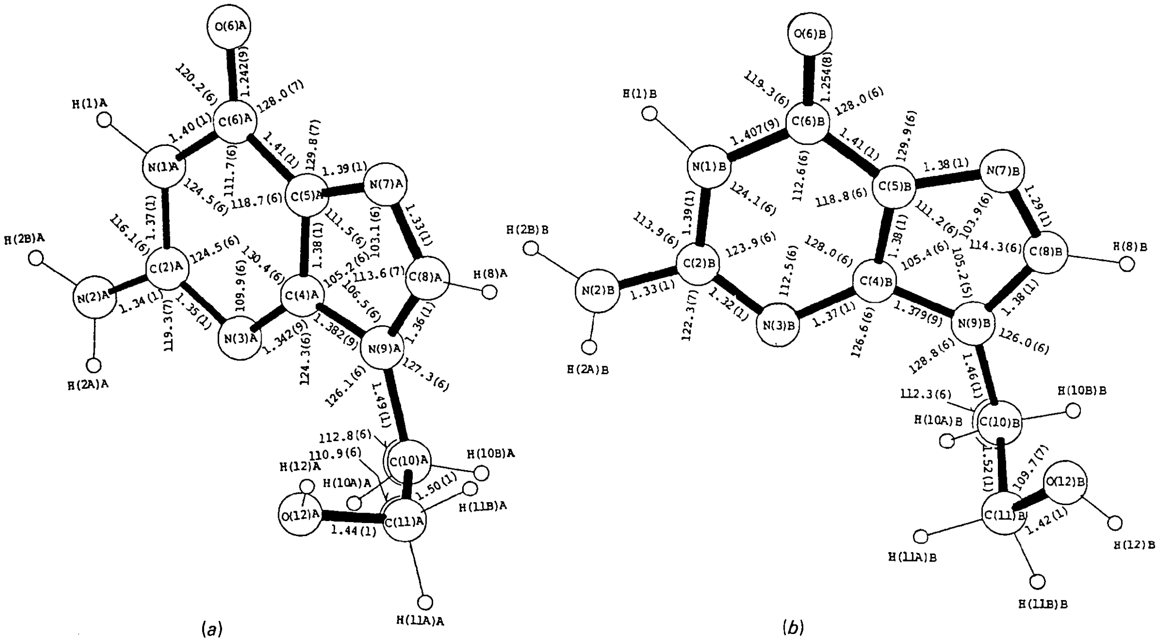

Fig. 1. Bond distances (Å) and angles (°) for (*a*) molecule *A*, and (*b*) molecule *B*. E.s.d.'s are shown in parentheses.

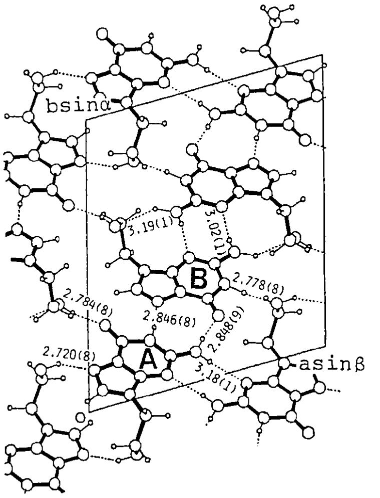

Fig. 2. The crystal structure projected along **c**. Broken lines indicate the hydrogen bonds. Distances (Å) for N···N, N···O, O···N or O···O are given with e.s.d.'s in parentheses.

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Structure of Tetramethylammonium Hydrogen Maleate

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Abstract. $N(CH_3)_4^+.C_4H_3O_4^-$, $M_r = 189{\cdot}2$, monoclinic, $P2_1/c$, $a = 5{\cdot}789\,(1)$, $b = 9{\cdot}718\,(1)$, $c = 18{\cdot}362\,(2)$ Å, $\beta = 90{\cdot}83\,(1)°$, $V = 1032{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}20\,(5)$, $D_x = 1{\cdot}217$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}091$ mm^{-1}, $F(000) = 408$, $T = 293\,(1)$ K, final $R = 0{\cdot}047$ for 1109 unique observed reflexions. There is an intramolecular hydrogen bond O···H···O of 2·403 (4) Å in the hydrogen maleate residue. The skeletal C atoms are planar, but the carboxyl groups are twisted out of the plane by 6·0 (4) and 5·4 (4)°. The tetramethylammonium ion has the usual tetrahedral shape.

Introduction. The structural investigation reported here is a part of the research programme dealing with the acid salts of carboxylic acids. The main purpose of this work is to obtain additional data about the intramolecular hydrogen bond in the hydrogen maleate residue and to make a comparison with known structures which contain this structural unit [see Olovsson, Olovsson & Lehmann (1984) for a concise list].

Experimental. Single crystals grown from the equimolar aqueous solutions of tetramethylammonium hydroxide and maleic acid; density measurement by flotation in chlorobenzene/CCl_4; colourless prisms, 0·34 × 0·38 ×

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