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Structure of 3-Methylxanthine

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Abstract. $C_6H_6N_4O_2$, $M_r = 166 \cdot 1$, monoclinic, $P2_1/c$, $a = 3 \cdot 742 (5)$, $b = 14 \cdot 710 (8)$, $c = 12 \cdot 159 (8)$ Å, $\beta = 96 \cdot 8 (1)°$, $U = 666 \cdot 5$ Å^3, $Z = 4$, $D_x = 1 \cdot 66$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 84$ cm^{-1}, $F(000) = 344$, $T = 293$ K, $R = 0 \cdot 058$ for 957 unique reflections. The molecules form base-paired hydrogen-bonded dimers, with each molecule involved in four H bonds. The base ring is planar within experimental error. Propeller twist is absent.

Introduction. The structure of 3-methylxanthine was studied as part of an investigation into the self base-pairing of nucleic acid constituents. Of especial interest is the propeller twist of the base pair (Dickerson, 1983), this being the angle between the base planes about an axis joining them. Wilson (1985) has investigated the propeller twist for a number of such compounds.

Experimental. Crystals of a suitable size were produced by forming a saturated solution of 3-methylxanthine in water at 353 K. This solution was then allowed to stand in a water bath at 303 K for several days. The resulting crystals had a prismatic habit elongated along **a**. Space group and initial cell dimensions were obtained from Weissenberg photographs. These Weissenberg photographs also showed evidence of very strong thermal diffuse scattering. Refined cell dimensions measured on a Stoe Stadi 2 two-circle diffractometer using crystals mounted along **a** and **b**.

Intensities measured on the diffractometer using an *a*-axis-mounted crystal of dimensions $0 \cdot 6 \times 0 \cdot 3 \times 0 \cdot 3$ mm. Range of indices $0 < h < 3$, $-18 < k < 18$, $-15 < l < 15$; $\theta_{max} = 27°$. Standard reflections, which showed less than 5% variation, measured every 100 measurements. No absorption corrections applied.

3421 reflections measured, 957 unique with $I > 3\sigma I$ regarded as observed, $R_{int} = 0 \cdot 018$, the $\bar{1}12$ reflection was not used in the refinement on grounds of extinction. Structure solved by Patterson methods using *PATMET* (Wilson & Tollin, 1985). Refinement (on F) by full-matrix least squares with *SHELX76* (Sheldrick, 1976). H-atom positions obtained from difference Fourier map. Non-H atoms refined anisotropically. H atoms included as fixed atoms with isotropic temperature factor of $0 \cdot 08$ Å^2. 109 parameters refined, $R = 0 \cdot 058$, $wR = 0 \cdot 080$, $w = 1 \cdot 8044[\sigma(F)^2 + 0 \cdot 002362F^2]$. Max. $\Delta/\sigma = 0 \cdot 013$, max. difference map peak $0 \cdot 4$, min. $-0 \cdot 39$ e Å^{-3}. The largest of these peaks is close to the methyl C atom and suggests that there may be a degree of rotational disorder in the methyl H-atom positions. Other programs used: *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.
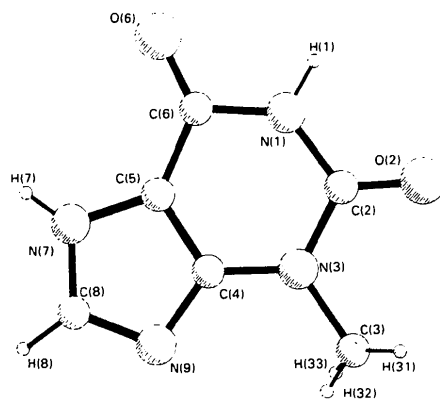

Fig. 1. View of the molecule showing the atom numbering.

Table 1. *Coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for non-*H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	4982 (7)	2533 (2)	998 (2)	30 (1)
C(2)	3673 (8)	1742 (2)	471 (3)	28 (1)
O(2)	4235 (6)	995 (1)	889 (2)	41 (1)
N(3)	1788 (6)	1853 (2)	−551 (2)	28 (1)
C(3)	490 (9)	1041 (2)	−1177 (3)	39 (1)
C(4)	1323 (7)	2719 (2)	−982 (2)	25 (1)
C(5)	2714 (7)	3472 (2)	−423 (2)	26 (1)
C(6)	4652 (8)	3421 (2)	630 (2)	28 (1)
O(6)	6033 (6)	4041 (1)	1204 (2)	42 (1)
N(7)	1732 (7)	4194 (2)	−1107 (2)	33 (1)
C(8)	−143 (8)	3843 (2)	−1997 (2)	34 (1)
N(9)	−488 (7)	2947 (2)	−1961 (2)	31 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°)

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C(6)—N(1)	1·382 (4)	C(4)—C(5)	1·371 (4)
N(1)—C(2)	1·391 (3)	N(7)—C(5)	1·374 (4)
N(3)—C(2)	1·367 (4)	C(5)—C(6)	1·400 (4)
O(2)—C(2)	1·220 (3)	O(6)—C(6)	1·227 (3)
C(3)—N(3)	1·468 (4)	N(7)—C(8)	1·326 (4)
N(3)—C(4)	1·381 (3)	C(8)—N(9)	1·325 (4)
N(9)—C(4)	1·344 (3)		
C(6)—N(1)—C(2)	128·8 (2)	C(4)—C(5)—C(6)	122·6 (3)
N(3)—C(2)—N(1)	116·0 (2)	N(7)—C(5)—C(6)	132·1 (3)
O(2)—C(2)—N(1)	121·8 (3)	N(7)—C(5)—C(4)	105·4 (2)
O(2)—C(2)—N(3)	122·2 (3)	C(5)—C(6)—N(1)	111·4 (2)
C(4)—N(3)—C(2)	119·0 (2)	O(6)—C(6)—N(1)	120·1 (3)
C(3)—N(3)—C(2)	118·8 (2)	O(6)—C(6)—C(5)	128·4 (3)
C(3)—N(3)—C(4)	122·2 (2)	C(8)—N(7)—C(5)	105·9 (2)
N(3)—C(4)—C(5)	122·2 (2)	N(7)—C(8)—N(9)	113·9 (2)
N(9)—C(4)—C(5)	111·2 (3)	C(8)—N(9)—C(4)	103·7 (2)
N(9)—C(4)—N(3)	126·6 (3)		
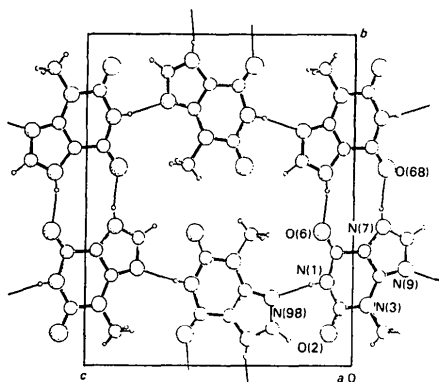
Fig. 2. View along **a** of the unit-cell contents showing hydrogen bonding.

Discussion. The atomic numbering is shown in Fig. 1. Atomic coordinates of the non-H atoms are given in Table 1.* The bond lengths and angles (Table 2) are similar to those obtained for 7-methylxanthine hydrochloride monohydrate (Kistenmacher & Sorrell, 1975), the most significant differences being accounted for by the different exocyclic substituents on N(3), N(7) and N(9). Each molecule is involved in four hydrogen bonds, two of which are to molecules related by the inversion centre. These latter use the bonding sites which are used in Hoogsteen-type base-pairing. The hydrogen bonds are N(1)—(0·892 Å)H(1)$\cdots$ (2·046 Å)N(9) $(1+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z)$ 2·927 (4) Å and N(7)—(0·838 Å)H(7)$\cdots$(1·910 Å)O(6) $(1-x, 1-y, -z)$ 2·734 (4) Å and the symmetry-related ones; the angles subtended at the H atoms are 169·2 and 167·5°, respectively. The hydrogen bonding is shown in Fig. 2.

The base ring is planar within experimental error, with a maximum deviation of 0·013 (6) Å from the ring mean plane for N(9). The absence of propeller twist [value of this parameter is 0(1)°] is in keeping with the expected result for this type of self-paired base (Wilson, 1985).

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43140 (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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