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6-Amino-2-thiouracil Monohydrate

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Abstract. $C_4H_5N_3OS.H_2O$, M_r = 161·3, monoclinic, $C2/c$, a = 14·913 (24), b = 7·601 (12), c = 13·004 (18) Å, β = 113·50 (5)°; Z = 8, D_m = 1·59, D_x = 1·586 g cm^{-3}, μ(Cu $K\alpha$) = 35·22 cm^{-1}. The structure of this modified nucleic acid base has been solved by the heavy-atom method with 1074 diffractometer-measured reflections and refined to an R of 0·082. All the hydrogens [except H at C(5)] take part in hydrogen bonding. S makes a weak O—H···S interaction with the water O atom. There is an unusually short S···S contact across the diad axis of 3·27 Å.

Introduction. Crystal structure investigation of biological antagonists is part of the research scheme undertaken in this laboratory. These compounds are structurally similar to normal metabolites and so they can easily be mistaken for normal metabolites by biological systems. In this context the crystal structure of a modified pyrimidine base 6-amino-2-thiouracil (6-amino-2-thiopyrimidin-4-one) has been analysed. This study is interesting as there are numerous hydrogen bonding possibilities, unlike in the structure of 1,3-dimethyluracil, a crystal structure without hydrogen bonds (Banerjee, Dattagupta, Saenger & Rabczenko, 1977). Structural studies of nucleobases and nucleosides have been shown to have certain characteristic patterns (Voet & Rich, 1970; Bugg, Thomas, Sundaralingam & Rao, 1971) and it is also of interest to study this modified base and compare it with generally observed patterns.

6-Amino-2-thiouracil monohydrate, in the form of pale yellow needles (needle axis along b), was obtained from the Sigma Chemical Company, USA. X-ray data were obtained from a crystal of cross-section 0·15 × 0·25 × 0·35 mm. Preliminary study was by Weissenberg and precession photography and unit-cell parameters were determined by least-squares refinement of the 2θ angles of 20 reflections measured on a Picker four-circle diffractometer. Intensities above 2$\sigma(I)$ were collected by a θ–2θ scan with Ni-filtered Cu $K\alpha$ radiation to a maximum value of 2θ = 130°, at a scan speed in 2θ of 2° min^{-1}. Background counts were taken for 10 s on either side of the peak. The data for 1074 reflections were corrected for Lorentz and polarization effects. Small asymmetry due to absorption was corrected by taking a φ plot for the 020 reflection and the data were initially scaled by the Wilson method.

The position of S was located from a Patterson map and gave an initial R of 0·55. A heavy-atom-phased Fourier synthesis revealed all non-hydrogen atoms. The structure was refined by a full-matrix least-squares method (Gantzel, Sparks & Trueblood, 1961) with isotropic temperature factors to an R of 0·13. A difference Fourier synthesis at this stage revealed all H atoms, which were included in the structure-factor calculations for later anisotropic refinement. Convergence was obtained at an R of 0·082. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). An anomalous dispersion correction, f' (0·32), for S was made. The weighting scheme employed for the final cycles was that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), given by $w = 1/(A + |F_o| + C|F_o|^2)$, where the constants A and C were given values of 10·0 and 0·016 respectively. The final positional parameters are listed in Table 1, Table 2 gives the hydrogen coordinates.* The bond lengths and angles are given in Fig. 1.

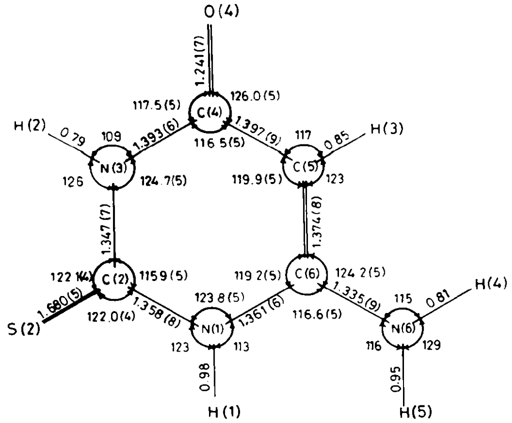

Fig. 1. Bond lengths (Å) and angles (°).

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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 33645 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *The final positional parameters* (× 10⁴) *of non-hydrogen atoms*

	x	y	z
N(1)	7812 (3)	4729 (6)	4083 (4)
C(2)	7119 (4)	5375 (7)	4411 (4)
N(3)	7287 (3)	5139 (5)	5499 (4)
C(4)	8115 (4)	4333 (7)	6287 (4)
C(5)	8792 (4)	3674 (7)	5891 (4)
C(6)	8632 (4)	3878 (7)	4781 (4)
S(2)	6095 (1)	6339 (2)	3505 (1)
O(4)	8177 (3)	4238 (6)	7265 (3)
N(6)	9225 (4)	3257 (7)	4321 (4)
O(*W*)	5906 (3)	3521 (5)	1308 (3)

Table 2. *Positional parameters of* H *atoms* ($\times 10^3$) *together with isotropic thermal parameters*

	Bonded to	x	y	z	B (Å^2)
H(1)	N(1)	781	495	334	2·00
H(2)	N(3)	695	545	580	2·20
H(3)	C(5)	933	329	638	1·62
H(4)	N(6)	975	288	476	2·98
H(5)	N(6)	901	343	353	2·98
H(6)	O(*W*)	623	262	189	2·01
H(7)	O(*W*)	592	409	187	2·01

Discussion. The C(2)–S(2) distance of 1·680 Å is normal for a thiopyrimidine in the thione (rather than the mercapto) form [see *e.g.* the reviews in Saenger & Suck (1971) and Lin, Sundaralingam & Arora (1971)]. The bond distances C(2)–N(3) (1·347 Å) and C(4)–C(5) (1·397 Å) appear to be shorter while C(5)–C(6) (1·374 Å) is longer than normal values (Voet & Rich, 1970). The exocyclic angles about C(2) are very nearly the same unlike the cases generally observed by Lin *et al.* (1971) for other thiopyrimidines. The valence angles at N(3) and N(1) are larger than 120° and these N atoms have extra-annular H atoms in accordance with the observations of Singh (1965). The least-squares-plane calculation for the pyrimidine ring (Table 3) shows that S(2) and N(6) are on the same side of the ring (by 0·047 and 0·053 Å respectively) while O(4) is on the opposite side (0·021 Å).

The molecular packing viewed down *b* is given in Fig. 2. Introduction of the S atom at C(2) and the amino group at C(6) have not changed the tendency of this type of molecule to form stacks. The molecules related by a centre of symmetry are stacked in infinite columns parallel to *b*; the interplanar spacing between these (nearly overlapping) molecules is 3·3 Å. Fig. 3 shows an overlapping pair of molecules projected perpendicular to the mean plane. The general packing features of this structure are similar to those of 6-mercaptopurine monohydrate (Sletten, Sletten & Jensen, 1969).

Table 3. *The equation and deviations* (Å) *of atoms from the least-squares plane through atoms* N(1), C(2), N(3), C(4), C(5) *and* C(6)

$$0\cdot432x + 0\cdot876y + 0\cdot215z = 8\cdot31$$

N(1)	−0·008	C(4)	−0·012	S(2)	0·047
C(2)	−0·002	C(5)	0·003	O(4)	−0·021
N(3)	0·012	C(6)	0·007	N(6)	0·053

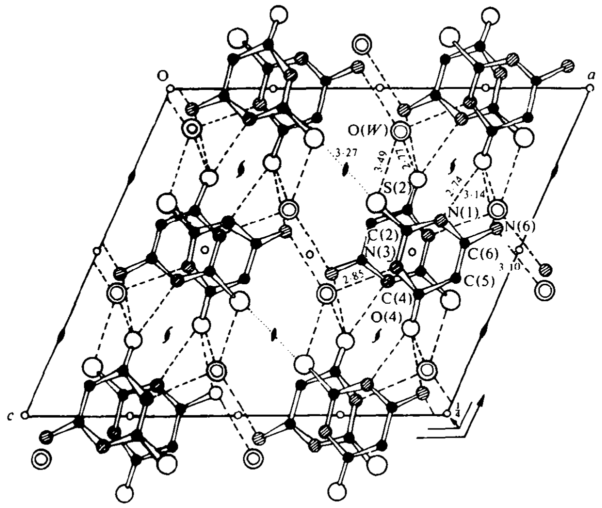

Fig. 2. The molecular packing viewed down *b*.

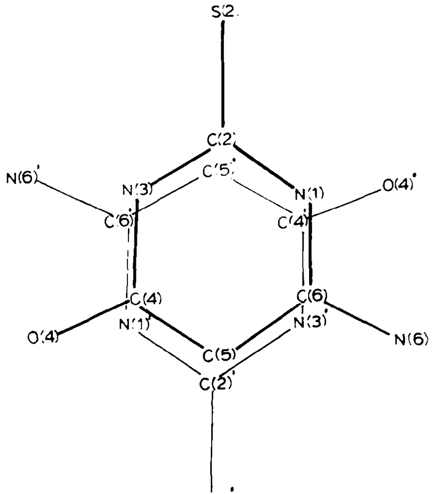

Fig. 3. Overlapping molecules projected perpendicular to the mean ring plane.

Voet & Rich (1970) have reviewed the crystal structures of nucleic acid bases and found that uracil derivatives, whether they are substituted at C(5), C(6) or N(1) or whether they have keto, thioketo or selenoketo groups, form essentially three paired hydrogen-bonded structures with N(3)···O(4),

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···A	D···A	H···A	∠D–H···A
N(1)–H(1)···O(4)^{ii}	2·74	1·80	159·6
N(3)–H(2)···O(W)^{i}	2·85	2·07	169·9
N(6)–H(4)···O(W)^{iv}	3·10	2·32	161·1
N(6)–H(5)···O(4)^{ii}	3·14	2·40	134·5
O(W)–H(6)···O(4)^{iii}	2·77	1·79	169·4
O(W)–H(7)···S(2)	3·49	2·66	170·3

Symmetry code
(i) $x,\ 1-y,\ \frac{1}{2}+z$
(ii) $x,\ 1-y,\ \frac{1}{2}+z-1$
(iii) $\frac{3}{2}-x,\ \frac{1}{2}-y,\ 1-z$
(iv) $\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

N(1)···O(2) or N(3)···O(2) interactions, and that they occur in dimeric form (see also Banerjee *et al.*, 1977). However, in this structure as expected we have a different type of hydrogen-bonding pattern (Table 4), mainly attributable to the amino substitution at C(6). H atoms at N(6), N(1) and N(3) enter into strong hydrogen-bonded interactions with symmetry-related O(W) and O(4) atoms. O(W) has a nearly tetrahedral coordination: while it acts as an acceptor for two strong hydrogen bonds from symmetry-related N(3) and N(6) atoms, it also acts as a donor to O(4) and S(2) atoms. The O(W)···S(2) interaction is 3·49 Å, with an H···S distance of 2·66 Å and O(W)–H···S angle of 170·3°, which shows that it is a linear but weak hydrogen bond. This is according to the general observation that in crystal structures of thio-analogues of nucleic acid constituents, S is expected to form weaker hydrogen bonds than the corresponding O analogues (Lin *et al.*, 1971). There is an unusually short intermolecular S···S distance of 3·27 Å between molecules related by the diad axis. This suggests that the van der Waals radius of S should be assumed to be near 1·65 Å, instead of a value of 1·85 Å (Pauling, 1960). Evidence from several S-containing compounds suggests that S should have a lower value; however, 1·65 Å is probably an extreme limit. In the structure of 6-mercaptopurine monohydrate (Sletten *et al.*, 1969) there is an S···S contact of 3·365 Å.

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DL-Diethyl α-Anilinobenzylphosphonate

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Abstract. $C_{17}H_{22}NO_3P$, FW 319·34, triclinic, $P\bar{1}$, a = 8·824 (4), b = 10·053 (5), c = 9·959 (4) Å, α = 94·13 (2), β = 92·10 (3), γ = 94·97 (3)°, Z = 2, U = 877·01 Å^3, D_c = 1·205, D_m = 1·204 g cm^{-3}, Mo $K\alpha$ radiation (λ = 0·7107 Å, μ = 1·43 cm^{-1}). The structure was solved by *MULTAN* and refined to R = 0·066. Both D and L forms appear in the structure and form centrosymmetric hydrogen-bonded dimers, with N–H···O(phosphoryl) = 2·990 Å. The mean value for P–O is 1·566 (4) Å and that for O–Et is 1·455 (9) Å. The phosphoryl P=O bond length is 1·465 (4) Å; C–P is 1·821 (6) Å.