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Sodium 5,6-Dihydro-2-thiouracil-6-sulfonate Monohydrate

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Abstract. $C_4H_7N_2O_5S_2Na$, monoclinic, $P2_1/c$, $Z = 4$, $a = 13{\cdot}101$ (4), $b = 7{\cdot}043$ (3), $c = 9{\cdot}654$ (5) Å, $\beta = 101{\cdot}98$ (4)°, $D_m = 1{\cdot}90$ (1), $D_c = 1{\cdot}90$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $R = 0{\cdot}033$ for 2045 observed reflections. This is the product of a bisulfite addition reaction of 2-thiouracil at pH 8. The sulfonate group is found attached axially at the 6-position of the thiouracil.

Introduction. The title compound was prepared by addition of bisulfite ion to 2-thiouracil. Preliminary precession photographs of the crystals obtained from aqueous solution showed monoclinic symmetry and extinction patterns ($0k0$ reflections absent when k odd, $h0l$ reflections absent when l odd) consistent with the space group $P2_1/c$. The calculated density for $Z = 4$ agreed with the experimental density obtained by flotation in a monobromoethane–chloroform mixture. A small crystal (0·4 × 0·2 × 0·2 mm) was then mounted on a Syntex $P2_1$ diffractometer. Accurate cell dimensions were determined from a least-squares fit of 2θ, ω, φ and χ for 15 reflections with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). Data were collected with a θ–2θ scan technique, the details of which have been reported (Seccombe, Lee & Henry, 1975). 2642 reflections were measured with $2\theta \leq 60°$ of which 2045 had $I \geq 3\sigma(I)$ and were used for data analysis. The data were then corrected for the 1·8% decay that was observed, and reduced to the structure factor amplitudes by the application of the Lorentz–polarization correction. Because of the small linear absorption coefficient, 3·39 cm^{-1}, and the small size of the crystal, no absorption or extinction correction was made.

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The positions of the S and Na atoms were found from a Patterson map. All other atoms, including H, were found in subsequent electron density and difference electron density maps. For the refinement, all non-hydrogen atoms were treated with anisotropic thermal parameters and all H atoms with fixed isotropic thermal parameters. The final discrepancy indices were $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}033$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0{\cdot}042$.

The positional and isotropic thermal parameters are given in Table 1 with their estimated standard

Table 1. *Positional* (× 10^5; *for* H × 10^3) *and isotropic thermal* (Å^2) *parameters with e.s.d.'s in parentheses*

	x	y	z	B
S(1)	15760 (4)	73961 (8)	11856 (6)	1·24 (6)
S(2)	35651 (4)	23543 (7)	−4964 (5)	1·93 (5)
Na	49649 (7)	1112 (11)	25919 (9)	1·94 (9)
O(1)	36431 (12)	5781 (22)	−12501 (16)	1·72 (17)
O(2)	43941 (11)	25652 (21)	7689 (14)	2·13 (15)
O(3)	34528 (12)	39906 (23)	−14219 (16)	2·35 (17)
O(4)	4164 (12)	32891 (25)	−29360 (15)	2·24 (18)
O(w)	40357 (13)	76443 (25)	12326 (17)	1·50 (18)
N(1)	22447 (13)	39237 (26)	9063 (17)	1·84 (18)
N(3)	10175 (14)	50569 (27)	−9873 (18)	1·34 (19)
C(2)	16249 (15)	53378 (29)	3377 (21)	1·47 (20)
C(4)	9205 (15)	33624 (31)	−17239 (20)	1·57 (21)
C(5)	14085 (16)	16806 (30)	−9085 (22)	1·58 (21)
C(6)	23815 (16)	21612 (29)	1978 (20)	2·08 (19)
H(w,1)	341 (3)	763 (5)	115 (4)	3·29
H(w,2)	408 (3)	774 (5)	48 (4)	3·29
H(1)	258 (3)	414 (5)	163 (3)	2·12
H(2)	63 (3)	609 (5)	−136 (3)	2·85
H(5,1)	87 (3)	137 (5)	−43 (3)	2·34
H(5,2)	154 (3)	72 (4)	−154 (3)	2·34
H(6)	251 (2)	112 (5)	89 (3)	2·06

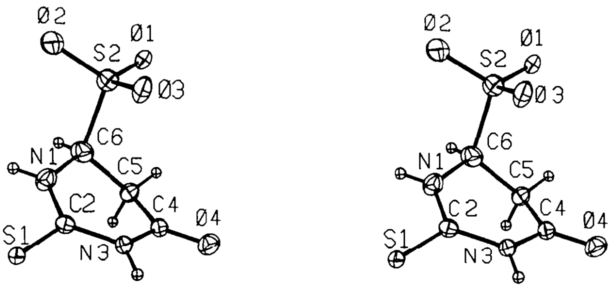


Fig. 1. Stereoview of DHTUS anion. The 50% probability thermal ellipsoids are shown for non-hydrogen atoms.

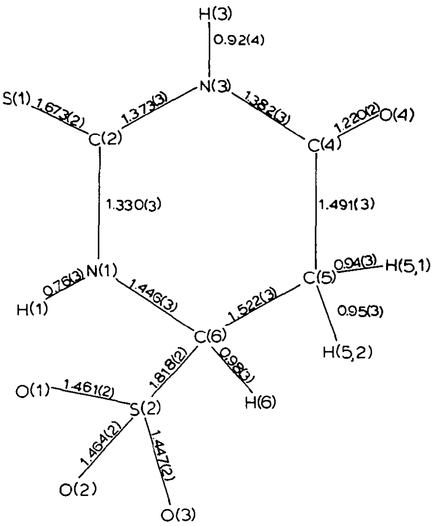


Fig. 2. Bond lengths (Å) with e.s.d.'s in parentheses; not shown on the figure: O(w)–H(w,1) 0·81 (4), O(w)–H(w,2) 0·74 (4).

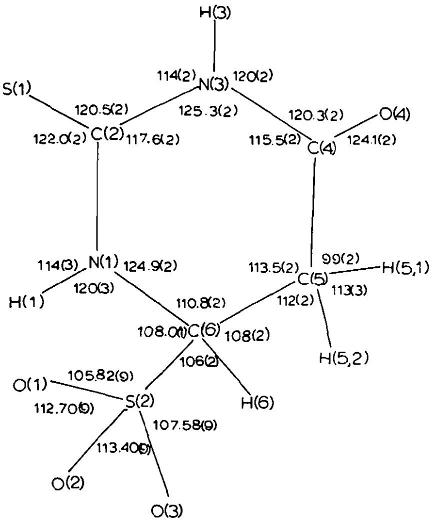
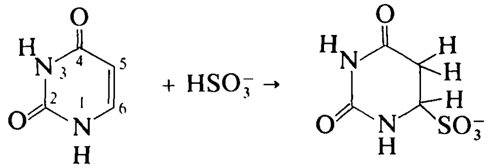


Fig. 3. Bond angles (°) with e.s.d.'s in parentheses; not shown on the figure: O(1)–S(2)–O(3) 112·5 (1), O(2)–S(2)–C(6) 104·0 (1), C(5)–C(6)–S(2) 114·4 (1), H(6)–C(6)–N(1) 110 (2), H(5,1)–C(5)–C(6) 108 (2), H(5,2)–C(5)–C(4) 110 (2), H(w,1)–O(w)–H(w,2) 101 (4).

deviations.* A stereodrawing of the molecule and its atom numbering scheme are shown in Fig. 1 and the bond lengths and angles are given in Figs. 2 and 3.

Discussion. The common bisulfite ion modifies nucleic acid bases such as uracil under mild conditions (room temperature and neutral pH):



(I) (II)

The product of this reaction has been identified and characterized by means of various spectroscopic techniques (Shapiro, Servis & Welcher, 1970). The title compound was obtained by a similar reaction of 2-thiouracil. The elemental analysis and its IR and NMR spectra are consistent with the expected structure but its UV spectrum shows a large absorbance (log ε = 4·14) at λ = 274 nm. This was unexpected since (II) shows only end absorption at this wavelength. The structure shown in Fig. 1, however, clearly shows that the reaction went as expected. Apparently, the shift in the UV absorption spectrum is caused by the substitution of S for O at position 2.

The structure of the anion (DHTUS) is in general similar to that of the 5,6-dihydro-2-thiouracil molecule (DHTU) (Kojić-Prodić, Ružić-Toroš & Coffou, 1976) except, of course, that one H at the 6-position is replaced by a sulfonate group. The differences in bond lengths and angles in these two structures are mostly minor with one notable exception: the C(5)–C(6) bond length of 1·522 (3) Å in DHTUS is much closer to the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33138 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Dihedral angles* (°)

The positive sense of rotation is clockwise while looking along the BC bond.

A–B–C–D	DHTUS	DHTU
C(6)–N(1)–C(2)–N(3)	−4·5 (3)	−7·4 (4)
N(1)–C(2)–N(3)–C(4)	−6·6 (3)	−5·2 (4)
C(2)–N(3)–C(4)–C(5)	−8·6 (3)	−5·6 (4)
N(3)–C(4)–C(5)–C(6)	32·3 (2)	27·4 (4)
C(4)–C(5)–C(6)–N(1)	−40·1 (2)	−36·9 (4)
C(5)–C(6)–N(1)–C(2)	27·9 (2)	28·6 (4)

normal C—C single bond length than the corresponding bond length of 1·474 (5) Å in DHTU. A less remarkable difference that may be noted is a slight opening of about 1° of each of the ring bond angles at C(5) and C(6).

The six-membered ring is puckered in both structures. The ring in DHTUS is, however, somewhat more puckered than that in DHTU. The following may be listed as evidence for this conclusion. (1) The sum of the dihedral angles within the ring is greater for DHTUS (120°) than for DHTU (111°) (Table 2). (2) The sum of the ring bond angles is less for DHTUS (707·6°) as compared with DHTU (709·7°). (3) The r.m.s. displacement of the atoms N(1), C(2), N(3), and C(4) from their mean plane is greater for DHTUS than for DHTU as discussed below.

In both structures the six-membered ring is puckered in such a manner that the four atoms N(1), C(2), N(3), and C(4) lie closely on one plane but the atoms C(5) and C(6) are substantially displaced from this plane on either side (the 'pseudo-chair' form). The r.m.s. deviation of N(1), C(2), N(3), and C(4) from their least-square-displacement plane is 0·021 Å in DHTUS as compared with 0·016 Å in DHTU. The two structures are substantially different in the manner in which the atoms C(5) and C(6) are displaced from this plane. In DHTU these two atoms are about equally displaced from the plane, with out-of-plane displacements of 0·226 and 0·238 Å respectively for C(5) and C(6). In DHTUS, however, C(5) is much more displaced than C(6) since the corresponding distances are 0·323 and 0·198 Å, respectively. This trend is also reflected in the values of the dihedral angles N(3)—C(4)—C(5)—C(6) and C(2)—N(1)—C(6)—C(5). Since N(1), C(2), N(3) and C(4) lie nearly on one plane, these two dihedral angles essentially define the conformation of the ring. They are nearly equal in DHTU, but in DHTUS the former is substantially larger than the latter (Table 2).

Table 3. Na *ion interactions*

Distances are in Å, angles in degrees.

Na—O(w)^{i}	2·358 (2)	O(w)^{i}—Na—O(3)^{iii}	92·34 (6)
Na—O(w)^{ii}	2·360 (2)	O(w)^{ii}—Na—O(2)^{ii}	99·38 (6)
Na—O(2)^{ii}	2·423 (2)	O(w)^{ii}—Na—O(2)	82·49 (6)
Na—O(3)^{iii}	2·452 (2)	O(w)^{ii}—Na—O(1)^{iv}	90·25 (6)
Na—O(2)	2·469 (2)	O(w)^{ii}—Na—O(3)^{iii}	91·75 (6)
Na—O(1)^{iv}	2·494 (2)	O(2)^{ii}—Na—O(1)^{iv}	90·20 (6)
O(w)^{i}—Na—O(2)^{ii}	83·52 (6)	O(2)^{ii}—Na—O(3)^{iii}	97·80 (6)
O(w)^{i}—Na—O(2)	94·25 (6)	O(2)—Na—O(3)^{iii}	86·94 (6)
O(w)^{i}—Na—O(1)^{iv}	85·19 (6)	O(2)—Na—O(1)^{iv}	84·95 (6)

Symmetry code for superscripts

None	x,y,z	(iii)	$x,\frac{1}{2}-y,\frac{1}{2}+z$
(i)	$x,y-1,z$	(iv)	$1-x,-y,-z$
(ii)	$1-x,(\frac{1}{2}+y)-1,\frac{1}{2}-z$		

The sulfonate group is attached to the ring *axially*. The dihedral angle around the C(6)—S(2) bond is such that the three sulfonate O atoms are nearly staggered with respect to the substituents around C(6). The O atoms are arranged tetrahedrally around S but the average S—O distance of 1·46 Å indicates the existence of significant π-bond character in these bonds (Cruickshank, 1961). Consistent with this interpretation are the observations that all O—S—O bond angles are somewhat larger and all C—S—O angles are somewhat smaller than the tetrahedral angle of 109·5°. A similar phenomenon occurs in 2-amino-1-methylpyrimidinium 6-sulfonate (Pitman, Shefter & Ziser, 1970) and other sulfonate structures (Hall & Maslen, 1967).

The crystal may be considered to consist of sheets which are two anions thick and stacked parallel to the bc plane. Each sheet occupies the space between $x=-\frac{1}{2}$ and $+\frac{1}{2}$. The two surfaces of these sheets are lined with sulfonate groups. The interface between these sheets,

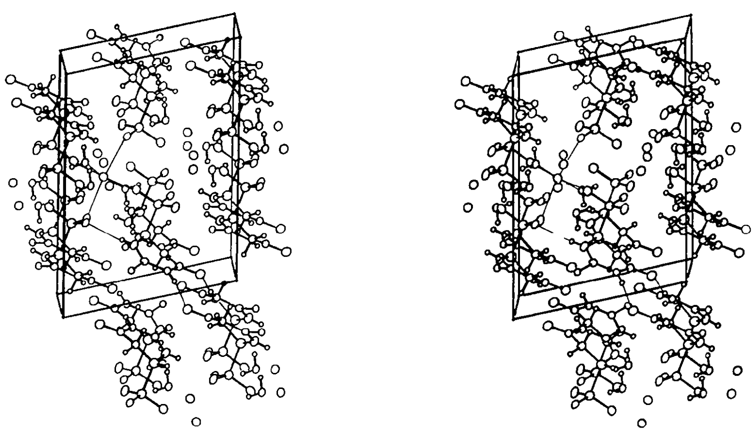


Fig. 4. Packing diagram. The a axis runs nearly vertically up, the b axis runs into the page, and the c axis runs horizontally across.

Table 4. *Hydrogen-bond parameters*

X–H$\cdots Y$	$X\cdots Y$ (Å)	H$\cdots Y$ (Å)	$\angle X$–H$\cdots Y$(°)
N(1)–H(1)$\cdots$O(1)^{i}	2·988 (2)	2·23 (3)	173 (3)
N(3)–H(3)$\cdots$O(4)^{ii}	2·997 (2)	2·09 (4)	172 (3)
O(w)–H(w,1)$\cdots$S(1)	3·218 (2)	2·41 (4)	172 (4)
O(w)–H(w,2)$\cdots$O(1)^{iii}	3·125 (2)	2·59 (4)	130 (4)
O(w)–H(w,2)$\cdots$O(2)^{iv}	3·104 (2)	2·54 (4)	134 (3)

Symmetry code for superscripts

None	x,y,z	(iii)	$x, 1 + y, z$
(i)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	(iv)	$1 - x, 1 - y, -z$
(ii)	$-x, \frac{1}{2} + y, (\frac{1}{2} - z) - 1$		

occurring at $x = \frac{1}{2}$, is largely hydrophilic and is where the Na ion and the water molecule are found. The Na atom is nearly on the crystallographic 2_1 screw axis and is surrounded by six O atoms in an octahedral array, with O—Na—O angles ranging from 82·5 to 99·4° (Table 3). The equatorial plane of this octahedron is made by four sulfonate O atoms. The axial positions are occupied by water O atoms. One H of this water molecule is involved in a hydrogen bond with S(1) (Table 4). The other appears to be involved in a bifurcated hydrogen bond, being close to both O(1) of one DHTUS and O(2) of another (Table 4).

Each sheet, in turn, may be considered to be made of long chains. These chains run parallel to **b** and possess crystallographic 2_1 symmetry at $x = 0$, $z = \frac{3}{4}$. The DHTUS anions in a given chain are connected to one another by a strong hydrogen bond between N(3) of one anion and O(4) of its neighbor (Table 4). Neighboring chains in each sheet are related to one another by crystallographic c-glide symmetry (or, equivalently, by crystallographic center of inversion symmetry). There are numerous van der Waals interactions between chains, but also there is one strong hydrogen bond per anion connecting these chains. This hydrogen bond occurs near the surface of the sheet between N(1) of one DHTUS and O(1) of another.

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Calcium Di(hydrogen maleate) Pentahydrate

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Abstract. $Ca(C_4H_3O_4)_2.5H_2O$, orthorhombic, *Pnam*, $a = 11{\cdot}737$ (2), $b = 6{\cdot}477$ (1), $c = 19{\cdot}593$ (2) Å, $Z = 4$, $D_m = 1{\cdot}590$, $D_c = 1{\cdot}586$ g cm^{-3}, $\mu = 1{\cdot}40$ cm^{-1}, final $R(F^2)$ of 0·060. Ca is seven coordinate with distorted monocapped trigonal prismatic geometry (Ca—O ranges from 2·359 to 2·469 Å). The hydrogen maleate ion is coordinated to Ca through one O and possesses a short intramolecular O$\cdots$O hydrogen bond [O$\cdots$O 2·426 (1), O—H 1·13 (3) and 1·31 (3) Å].

Introduction. The title compound was prepared by titrating a saturated aqueous solution of maleic acid with calcium hydroxide to pH = 3·95. Solvent was then removed by slow evaporation at room temperature to produce crystals suitable for diffraction studies. Precession photographs gave the systematic absences $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$, which indicated that the space group was either *Pnam* or $Pna2_1$. The former was indicated by statistical examination of the distribution of E values and was confirmed by the structure refinement. Any deviation from *Pnam* would be necessarily small because of the very successful refinement in *Pnam*. A crystal (0·7 × 0·6 × 0·3 mm) was mounted on a programmed Picker four-circle