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Crystal structure of 2-thiouracil

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Crystal structure / 2-Thiouracil / $C_4H_4N_2OS$

Abstract. The crystal structure of the title compound has been examined at room temperature. Crystals are triclinic, space group $P\bar{1}$ with a = 4.2859(7), b = 6.036(1), c = 10.6563(5) Å, α = 73.35(1), β = 83.81(1), γ = 89.11(2)°, V = 262.5(2) Å^3, Z = 2, D_x = 1.621 g cm^{-3}. The structure was refined by a full-matrix least-squares procedure to final R = 0.063 for 1003 reflections with $I \geqslant 3.0\,\sigma(I)$ measured on a CAD4 diffractometer. The molecule is essentially planar and exists in the lactam-thione form with the C(2)–S(2) and C(4)–O(4) distances being 1.683(3) and 1.227(4) Å respectively. Intermolecular hydrogen bonding, involving the sulphur and oxygen atoms, leads to infinite ribbons which stack in a layer structure; the vertical distance between successive layers is approximately 3.48 Å.

Introduction

The heterocyclic base 2-thiouracil is a sulphur-containing analogue of the pyrimidine uracil, a component of certain nucleic acids. 2-Thiouracil [systematic name: 4(1H)-2,3-dihydro-2-thioxo-pyrimidinone] is known to be a minor component of transfer ribonucleic acid; for example 2-thiouracil has been characterized in *t*RNA$^{\mathrm{Glu}}$ isolated from *Escherichia coli* (Yaniv and Folk, 1975). A short report of a structure analysis of 2-thiouracil (and the 2-seleno derivative) exists in the literature (Tsernoglou, 1967) however, except for unit-cell data and some key parameters, few details of the structure were listed. This communication reports a full structure determi-

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nation of 2-thiouracil and an analysis of its hydrogen bonding scheme as determined by contemporary X-ray diffraction methods.

Experimental

Suitable crystals for X-ray diffraction studies were obtained by the slow evaporation of an aqueous methanol solution of the compound (Sigma). The metric crystal data are given in the Abstract.

Intensity data for a crystal with dimensions 0.05 × 0.25 × 0.65 mm were measured at room-temperature, 295 K, on an Enraf-Nonius CAD4 diffractometer fitted with graphite monochromatised Mo$K\alpha$ radiation, λ = 0.7107 Å. The $\omega/2\theta$ scan technique was employed to measure the intensities for 1413 reflections up to a maximum Bragg angle of 27.5°. Cell parameters were refined by a least-squares procedure on the setting angles of 25 reflections ($6 \leqslant \theta \leqslant 13°$). No decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects but not for absorption (μ = 0.435 mm^{-1}). Of the reflections measured 1217 were unique and of these 1003 satisfied the $I \geqslant 3.0\,\sigma(I)$ criterion of observability and were used in the subsequent analysis.

The structure was solved by direct-methods with the aid of MULTAN (Main et al., 1978) and refined by a full-matrix least-squares procedure based on F (Sheldrick, 1976). Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were refined isotropically. A weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$ was introduced and the refinement proceeded smoothly to convergence when R = 0.063, R_w = 0.062 for k = 15.3 and $g = 2.5 \times 10^{-4}$. No correction was made for extinction. The analysis of variance showed no special features and the maximum and minimum residual electron density peaks in the final difference map were + 0.82 and − 0.66 e Å^{-3} respectively. The relatively high value for R promted an examination of a model in the space group $P1$, however, this model was discarded owing to the presence of non-sensible interatomic parameters. The $P\bar{1}$ space group was further supported by the distribution of E-statistics i.e. $\langle|e^2 - 1|\rangle$ was computed to be 0.92 which compares well with the theoretical expectation of 0.968 for centro symmetric space groups (Stout and Jensen, 1968). It is noted that the application of the transformation matrix ($0\bar{1}2$, 010, $\bar{1}00$) to the primative cell leads to an approximate C-centred monoclinic cell with angles α = 90.89(2), β = 96.19(1) and γ = 89.80(1)°. Given these results it was concluded that the transformed cell was not metrically monoclinic.

Table 1. Fractional atomic coordinates and B_{eq} values (Å). $B_{eq} = 8\pi^2\,(U_{11} + U_{22} + U_{33})/3$.

Atom	x	y	z	B_{eq}
S(2)	0.4583(2)	0.7196(2)	0.1294(1)	2.77
O(4)	−0.2419(7)	0.2693(5)	0.5093(2)	3.49
N(1)	0.1443(7)	0.3367(5)	0.1441(3)	2.36
N(3)	0.0830(6)	0.4565(5)	0.3302(3)	2.34
C(2)	0.2175(7)	0.4919(5)	0.2046(3)	2.02
C(4)	−0.1318(8)	0.2809(6)	0.3964(3)	2.36
C(5)	−0.2061(9)	0.1263(6)	0.3236(3)	2.56
C(6)	−0.0636(8)	0.1564(6)	0.2017(3)	2.53
H(1)	0.2411(99)	0.3512(65)	0.0628(46)	3.14
H(3)	0.1267(84)	0.5504(62)	0.3787(40)	2.37
H(5)	−0.3404(91)	0.0183(67)	0.3515(41)	2.88
H(6)	−0.0871(85)	0.0588(62)	0.1482(40)	2.71

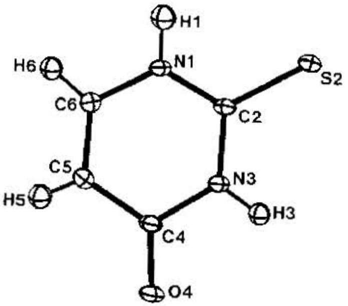

Fig. 1. An ORTEP (Johnson, 1976) diagram of 2-thiouracil showing 25% probability ellipsoids and the numbering scheme employed.

Scattering factors for all atoms were those incorporated in the SHELX-76 (Sheldrick, 1976) program. Fractional atomic coordinates are listed in Table 1 and the numbering scheme used is shown in Figure 1. Listings of thermal parameters, mean-plane data and structure factor tables have been deposited.[1]

Results and discussion

A molecule of 2-thiouracil is shown in Figure 1 and interatomic bond distances and angles are listed in Table 2. The twelve atoms comprising the molecule are essentially coplanar with the maximum deviation out of the plane being 0.13(4) Å for H(5).

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[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 52542, the name of the author and the title of the paper.

Table 2. Bond distances (Å) and angles (°).

N(1)−C(2)	1.338(4)	N(1)−C(6)	1.373(4)
N(1)−H(1)	0.90(5)	C(2)−S(2)	1.683(3)
C(2)−N(3)	1.357(4)	N(3)−C(4)	1.389(4)
N(3)−H(3)	0.90(4)	C(4)−O(4)	1.227(4)
C(4)−C(5)	1.432(5)	C(5)−C(6)	1.338(5)
C(5)−H(5)	0.84(4)	C(6)−H(6)	0.94(4)
C(2)−N(1)−C(6)	122.9(3)	C(2)−N(1)−H(1)	118(3)
C(6)−N(1)−H(1)	120(3)	N(1)−C(2)−S(2)	122.2(2)
N(1)−C(2)−N(3)	116.0(3)	S(2)−C(2)−N(3)	121.8(2)
C(2)−N(3)−C(4)	125.2(3)	C(2)−N(3)−H(3)	121(2)
C(4)−N(3)−H(3)	113(2)	N(3)−C(4)−O(4)	119.2(3)
N(3)−C(4)−C(5)	115.4(3)	O(4)−C(4)−C(5)	125.4(3)
C(4)−C(5)−C(6)	119.2(3)	C(4)−C(5)−H(5)	124(3)
C(6)−C(5)−H(5)	117(3)	C(5)−C(6)−N(1)	121.2(3)
C(5)−C(6)−H(6)	126(2)	N(1)−C(6)−H(6)	113(2)

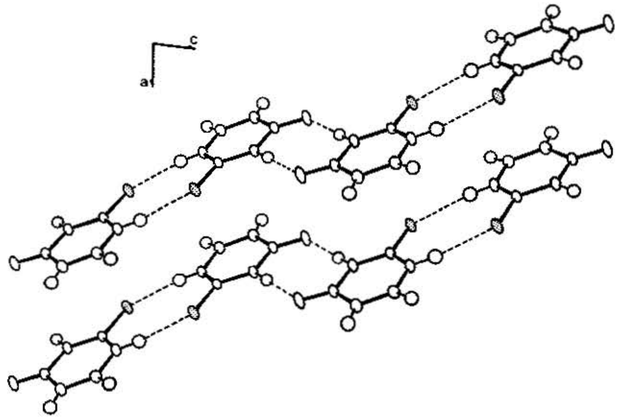

Fig. 2. Unit-cell contents for 2-thiouracil projected down the *b* axis direction.

The C(2)−S(2) bond distance of 1.683(3) Å is longer than 1.61 Å, the distance expected for a C−S double bond (Pauling, 1960) and similarly the C(4)−O(4) bond distance of 1.227(4) Å is slightly longer than the expected C−O double bond distance of 1.20 Å. The lengthening of these bonds probably reflects the effect of the substantial hydrogen bonding involving these atoms in the crystal lattice (see below). Nevertheless the observed bond distances are entirely consistent with the molecule existing in the lactam-thione form in accord with spectroscopic studies on the molecule (Igarashi-Yamamoto et al., 1981; Tajiri et al., 1984). Further support for this conclusion is found in the C(5)−C(6) bond distance of 1.338(5) Å which along with the remaining interatomic parameters suggest there is only limited delocalization of π-electron density throughout the molecule.

In keeping with the assignment of the lactam-thione model for the molecule the exocyclic C−S and C−O bond parameters lie in the ranges found for related systems: thus C−S and C−O bond lengths of 1.680(5) and 1.241(7) Å are found in 6-amino-2-thiouracil · H_2O (Swaminathan and Chacko, 1978); 1.676(3) and 1.216(4) Å in 5,6-dihydro-2-thiouracil (Kojić-Prodić, Ruzić-Toros and Coffou, 1976); 1.669(3) and 1.213(3) Å for 1-methyl-4-thiouracil (Hawkinson, 1975).

A view of the unit cell contents for 2-thiouracil is shown in Figure 2 from which can be seen the substantial lateral hydrogen bonding between the centrosymmetrically related molecules. Intermolecular hydrogen