octahedra which are thought to be Fe$^{IV}$O$_6$ is however longer than expected and may be a result of an overall expansion due to the presence of the large Ba$^{2+}$ ions. The O–O distance in the hexagonal layer is short, 2·448 Å. This appears to be a general feature of ABO$_{3-x}$ systems and is found in $4H$ Ba$_{0.5}$Sr$_{0.5}$MnO$_{2.83}$ (2·471 Å) and $8H$ BaMnO$_3$ (2·507 Å). The shortest distance corresponds to the highest vacancy concentration.

A further experiment concerning the vacancy distribution in the ABO$_{3-x}$ systems is at present in progress for BaCoO$_{3-x}$.

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# The Molecular and Crystal Structure of 5,6-Dihydro-2,4-dithiouridine, C$_9$H$_{14}$N$_2$O$_4$S$_2$

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5,6-Dihydro-2,4-dithiouridine crystallizes in the space group $P2_1$ with $a = 15·393$, $b = 7·7509$, $c = 4·9850$ Å, $\beta = 92·814°$, $Z = 2$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R = 0·035$. The heterocyclic ring displays a twist half-chair conformation with C(5) and C(6) displaced by 0·158 and 0·504 Å on either side of the nucleobase plane. The heterocycle exists in the diketo form. The ribose moiety has C(3')-*endo* conformation. The glycosidic torsional angle, 23·5°, is *anti*. The conformation about C(4')–C(5') is *gauche–trans*. Both S atoms are involved in intermolecular hydrogen bonding; S(2) to O(5') (3·342 Å) and S(4) to N(3) (3·310 Å). Sugar–sugar interaction is realized through the O(2')–H···O(3') (2·724 Å) and O(3')–H···O(5') (2·811 Å) hydrogen bonds. There is no base stacking.

## Introduction

The occurrence of some S-containing minor nucleosides in t-RNA's has been established. The synthesis of thio-analogues of 5,6-dihydrouridine forms part of a study of possible unusual constituents of t-RNA. These investigations have been undertaken at the 'Ruđer Bošković' Institute by Dr V. Škarić and his coworkers (references in Kojić-Prodić, Liminga, Šljukić & Ružić-Toroš, 1974). Crystals of 5,6-dihydro-2,4-dithiouridine were provided by Dr V. Škarić.

## Experimental

Weissenberg photographs recorded with Cu $K\alpha$ radiation indicated $P2_1$ or $P2_1/m$. Since the molecule is optically active, the space group is necessarily $P2_1$.

Table 1. *Crystallographic and physical data*

| | |
|---|---|
| 5,6-Dihydro-2,4-dithiouridine | $C_9H_{14}N_2O_4S_2$ |
| F.W. | 278·35 |
| Space group | $P2_1$ |
| $a$ | 15·393 (2) Å* |
| $b$ | 7·7509 (5) |
| $c$ | 4·9850 (3) |
| $\beta$ | 92·814 (6)° |
| $U$ | 594·03 Å$^3$ |
| $Z$ | 2 |
| $D_x$ | 1·556 g cm$^{-3}$ |
| $\mu$(Mo $K\alpha$) | 4·29 cm$^{-1}$ |

* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digit.
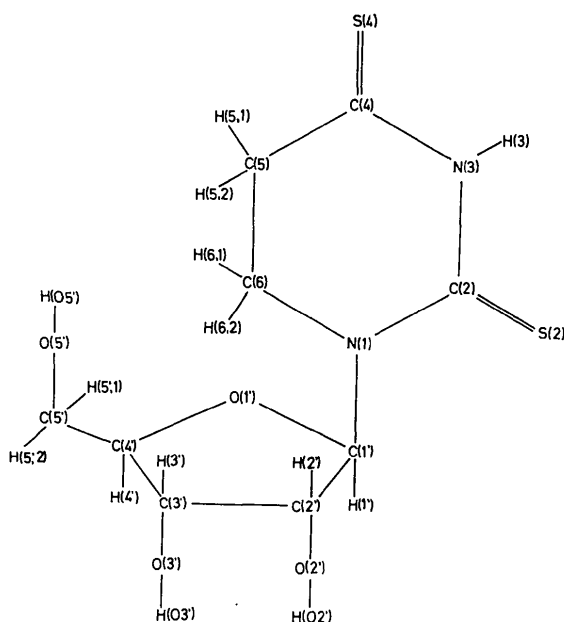


Fig. 1. The structural formula and the numbering of the atoms.

The cell dimensions were determined from powder photographs taken with a Guinier–Hägg powder camera at 24 °C with monochromated Cr $K\alpha$ radiation ($\lambda = 2\cdot28962$ Å). CoP$_3$ ($a = 7\cdot7073$ Å) was used as an internal standard. 25 reflexions were used in a least-squares procedure to obtain the cell constants (Table 1).

A crystal, bounded by eight faces with the forms {100}, {101} and {110}, was used for data collection which was carried out at 24 °C on a PDP8/I controlled four-circle Stoe X-ray diffractometer with graphite-monochromated Mo radiation ($\lambda = 0\cdot7107$ Å). An $\omega$–2$\theta$ scan technique was used. Automatic filter selection made it possible to reduce the count rate in the detector by a ratio of up to 8:1. This, in combination with automatic scan-speed selection ($\times 1$, $\times 2$ or $\times 4$), resulted in a maximum absolute interval scale factor of 32. Three standard reflexions measured at regular intervals showed only those variations expected from counting statistics.

2788 reflexions were measured with sin $\theta/\lambda < 0\cdot756$ Å$^{-1}$. This set included some equivalent reflexions which were averaged after absorption correction. Removal of reflexions of zero intensity due to space group extinction left 2288 reflexions; 1894 of these had $F_o^2 > 3\sigma(F_o^2)$.

The data were corrected for background, Lorentz, polarization and absorption effects with *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965). A correction for monochromator polarization was also included according to

$$p = \frac{1 + \cos^2 2\theta_M \cos^2 2\theta}{1 + \cos^2 2\theta_M}$$

with $\theta_M = 6\cdot1°$ and $\theta$ the scattering angle for the measured reflexion.

### Structure determination and refinement

An overall temperature factor ($B = 2\cdot73$ Å$^2$) and scale factor were determined (Wilson, 1942) and used to

Table 2. *Final positional parameters* ($\times 10^4$) *and anisotropic thermal parameters* ($\times 10^5$) *for the non-hydrogen atoms*

The anisotropic thermal parameters refer to the expression: exp $(-\beta_{11}h^2 \ldots -2\beta_{12}hk \ldots)$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 7909 (1) | 5790 (3) | 4333 (4) | 237 (6) | 936 (28) | 2715 (72) | −66 (11) | −25 (17) | −44 (38) |
| C(2) | 8241 (1) | 4441 (3) | 5701 (5) | 227 (8) | 995 (35) | 3274 (96) | −34 (14) | −51 (22) | −1 (49) |
| S(2) | 7893 (1) | 2397 (1) | 5454 (2) | 360 (2) | 906 (8) | 5248 (35) | −69 (4) | −242 (7) | −89 (14) |
| N(3) | 8944 (1) | 4776 (3) | 7502 (5) | 279 (8) | 1120 (33) | 4081 (100) | −55 (13) | −248 (23) | 248 (51) |
| C(4) | 9463 (1) | 6188 (4) | 7527 (5) | 260 (8) | 1235 (38) | 3208 (95) | −47 (16) | −49 (22) | −259 (55) |
| S(4) | 10381 (1) | 6210(−) | 9358 (2) | 364 (3) | 1571 (14) | 5469 (39) | −36 (5) | −488 (8) | −596 (19) |
| C(5) | 9173 (2) | 7584 (4) | 5645 (6) | 333 (9) | 1411 (46) | 3314 (100) | −220 (18) | −44 (25) | 85 (60) |
| C(6) | 8194 (2) | 7551 (4) | 5083 (6) | 319 (9) | 877 (34) | 3534 (102) | −106 (16) | −132 (25) | 61 (53) |
| O(1') | 7029 (1) | 6957 (3) | 754 (3) | 274 (6) | 1269 (29) | 2286 (57) | 4 (11) | 137 (15) | 415 (35) |
| C(1') | 7157 (1) | 5484 (3) | 2408 (4) | 245 (7) | 969 (31) | 2193 (73) | −57 (13) | 30 (19) | 11 (43) |
| C(2') | 6305 (1) | 5189 (3) | 3816 (4) | 237 (8) | 1013 (33) | 2008 (70) | −70 (13) | 6 (18) | 249 (41) |
| O(2') | 5758 (1) | 4143 (3) | 2131 (4) | 324 (7) | 1082 (28) | 2909 (74) | −187 (13) | −105 (19) | 147 (37) |
| C(3') | 5936 (1) | 7017 (3) | 3878 (4) | 262 (8) | 1130 (36) | 1773 (66) | −27 (13) | 73 (18) | −134 (41) |
| O(3') | 5034 (1) | 7094 (3) | 4323 (4) | 262 (6) | 1543 (37) | 2777 (70) | −8 (13) | 132 (17) | −544 (42) |
| C(4') | 6184 (1) | 7725 (3) | 1167 (4) | 268 (8) | 963 (33) | 1766 (66) | −27 (13) | −25 (19) | −85 (38) |
| C(5') | 6229 (2) | 9669 (4) | 1099 (5) | 421 (12) | 961 (35) | 2743 (93) | −53 (17) | −78 (26) | −79 (47) |
| O(5') | 6330 (1) | 10266 (3) | −1581 (4) | 429 (9) | 1160 (31) | 3366 (78) | −173 (14) | −21 (21) | 474 (40) |

compute normalized structure factors. The statistical distribution of the $|E|$ values suggested a non-centrosymmetric space group. The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). The solution was based on 300 reflexions with $|E| > 1.4$. The $E$ map corresponding to the solution with the best figure of merit revealed the positions of all non-hydrogen atoms.

Atomic coordinates for the heavy atoms and a scale factor were refined with *FLINUS*. The function minimized was $\sum w(F_o^2 - |F_c|^2)^2$. Each reflexion was assigned a weight $w$, inversely proportional to the estimated variance of the observation:

$$w^{-1} = \sigma_c^2(F_o^2) + (kF_o^2)^2 = \sigma^2(F_o^2)$$

where $\sigma_c(F_o^2)$ is based on counting statistics and $k = 0.04$ in the final cycles. The heavy atoms were refined initially with isotropic temperature factors. Anisotropic refinement and a subsequent difference synthesis using data with $\sin\theta/\lambda < 0.5$ Å$^{-1}$ then revealed all H atoms as peaks varying between 0.31 and 0.55 e Å$^{-3}$. In the final cycles one scale factor, the atomic coordinates
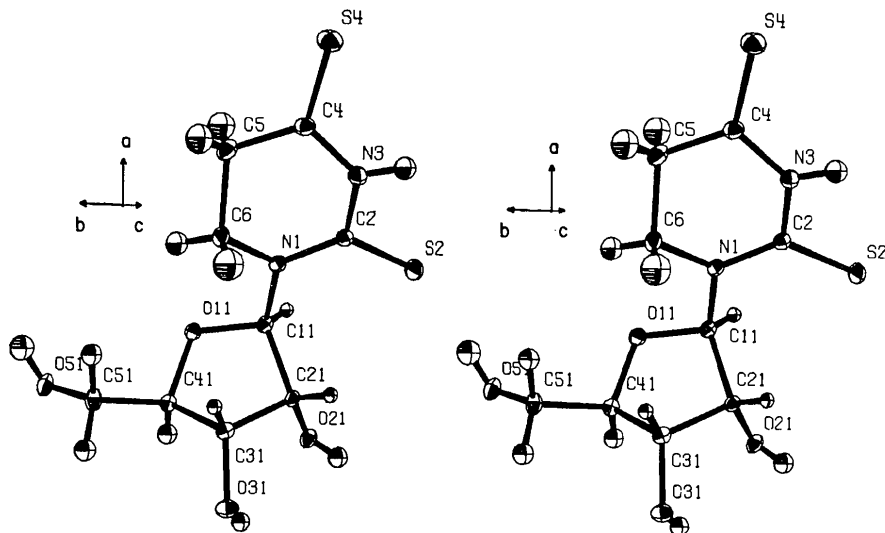


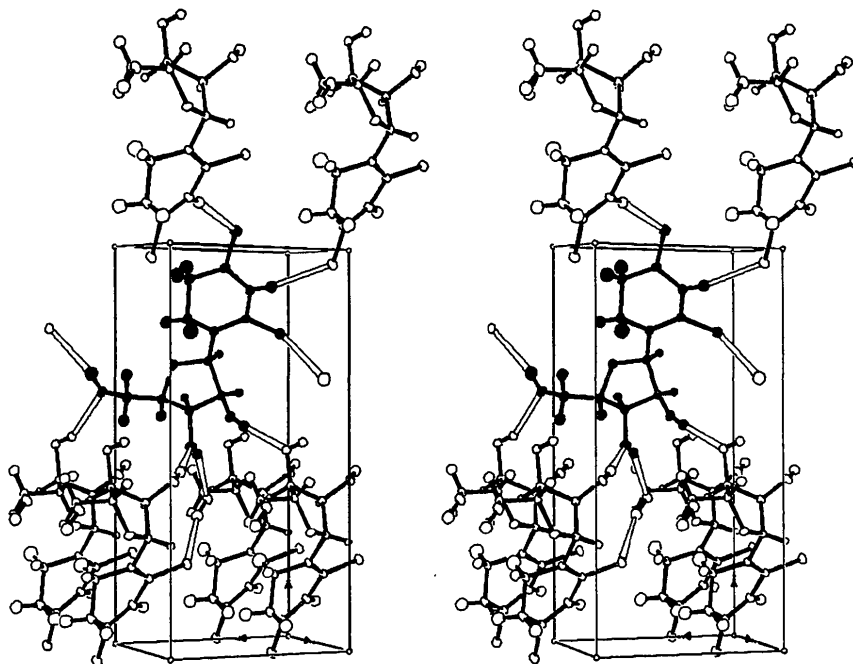Fig. 2. Stereoscopic drawing. Thermal ellipsoids are scaled to enclose 20 % probability.



Fig. 3. Molecular packing and hydrogen bonds.

for all atoms, anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the H atoms (209 parameters in all) were varied. The $y$ coordinate of S(4) was kept fixed to define the origin. The final shifts were all smaller than $0.3\sigma$. No evidence of secondary extinction was observed. All reflexions, even those with $F_o^2 < 0$, were included in the calculations. The final agreement indices were $R = \sum |F_o^2 - |F_c|^2|/\sum |F_o|^2 = 0.051$; $R_w = [\sum w |F_o^2 - |F_c|^2|^2/\sum w F_o^4]^{1/2} = 0.097$. The corresponding $R$ was 0.035 if the 384 reflexions with $F_o^2 < 0$ were excluded. The standard deviation of an observation of unit weight $S = [\sum w (F_o^2 - |F_c|^2)^2/(m-n)]^{1/2} = 1.56$, where $m$ is the total number of observations and $n$ the number of parameters varied.

Scattering factors for the heavy atoms were those of Cromer & Mann (1968) and for H, Stewart, Davidson & Simpson (1965). The anomalous scattering factors for S, O, N and C were from Cromer & Liberman (1970).

The calculations were performed on the IBM 370/155 computer in Uppsala, the CDC 7600 and CDC 6600 computers at Brookhaven National Laboratory and the UNIVAC 1110 computer in Zagreb. The final positional and thermal parameters are listed in Tables 2 and 3.*
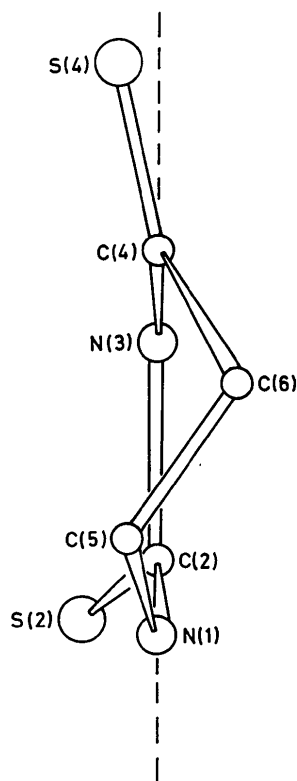


Fig. 4. Schematic view of the base parallel to the plane defined by N(1), C(2), N(3), C(4) illustrating the displacements of C(5) and C(6).
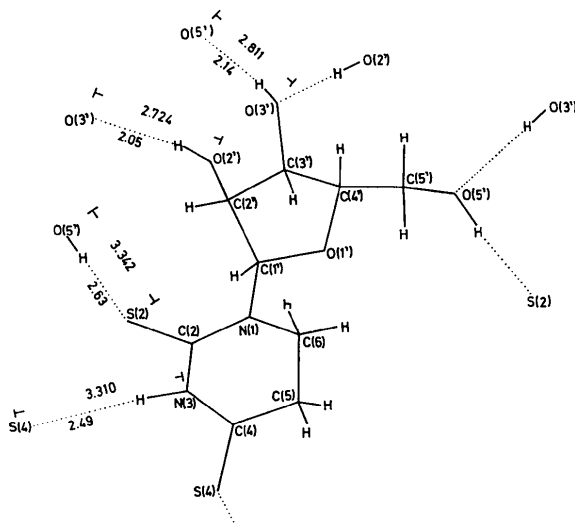
Table 3. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters of the* H *atoms*

|  | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(5)1 | 925 (3) | 863 (7) | 676 (9) | 5.7 (1.0) |
| H(5)2 | 947 (3) | 725 (7) | 405 (10) | 5.9 (1.0) |
| H(6)1 | 810 (2) | 831 (6) | 384 (7) | 3.8 (0.7) |
| H(6)2 | 788 (3) | 784 (8) | 666 (10) | 7.0 (1.2) |
| H(1') | 732 (2) | 454 (4) | 138 (5) | 1.8 (0.5) |
| H(2') | 639 (2) | 475 (4) | 550 (6) | 1.7 (0.5) |
| H(3') | 626 (2) | 775 (4) | 529 (5) | 1.7 (0.5) |
| H(4') | 576 (2) | 736 (5) | −18 (7) | 3.4 (0.7) |
| H(5')1 | 566 (2) | 1005 (5) | 179 (7) | 3.7 (0.8) |
| H(5')2 | 677 (2) | 999 (5) | 212 (7) | 3.5 (0.7) |
| H(O2') | 554 (2) | 356 (6) | 286 (8) | 3.5 (0.8) |
| H(O3') | 482 (2) | 644 (5) | 341 (7) | 2.8 (0.7) |
| H(O5') | 677 (2) | 1088 (7) | −158 (8) | 5.0 (0.9) |

## Description and discussion of the structure

The structural formula and the numbering of the atoms are shown in Fig. 1. A stereoscopic drawing of the molecule is given in Fig. 2 and the hydrogen-bonding scheme in Figs. 3 and 5. Interatomic distances and angles are listed in Table 4, displacements of the atoms from the least-squares planes through the heterocycle and ribose in Table 5. Dihedral angles defining the conformation are in Table 6.

### Base

The 5,6-dihydro-2,4-dithiouracil residue is not planar owing to the saturation of C(5)–C(6). The puckering of the base is illustrated in Fig. 4 and can be numerically described by the dihedral angles N(3)–C(4)–C(5)–C(6), 27.1°, and C(2)–N(1)–C(6)–C(5), 43.3°. These values are very similar to the corresponding angles found in

Fig. 5. Schematic drawing of the hydrogen bonding.

Table 4. *Bond distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| C(2) –N(1) | 1·331 (3) | C(2)——N(3)–H(3) | 109 (3) |
| C(2) –S(2) | 1·674 (2) | C(4)——N(3)–H(3) | 124 (2) |
| C(2) –N(3) | 1·384 (3) | C(4)——C(5) –H(5)1 | 103 (3) |
| C(4) –S(4) | 1·630 (2) | C(4)——C(5) –H(5)2 | 100 (3) |
| C(4) –N(3) | 1·354 (3) | C(6)——C(5) –H(5)1 | 102 (3) |
| C(4) –C(5) | 1·482 (4) | C(6)——C(5) –H(5)2 | 111 (2) |
| C(5) –C(6) | 1·515 (4) | H(5)1 –C(5)——H(5)2 | 129 (4) |
| C(6) –N(1) | 1·474 (3) | N(1)——C(6) –H(6)1 | 115 (3) |
| C(1')–N(1) | 1·474 (3) | N(1)——C(6) –H(6)2 | 106 (3) |
| C(1')–C(2') | 1·545 (3) | C(5)——C(6) –H(6)1 | 104 (2) |
| C(2')–C(3') | 1·527 (3) | C(5)——C(6) –H(6)2 | 112 (3) |
| C(3')–C(4') | 1·530 (3) | H(6)1 –C(6) –H(6)2 | 110 (4) |
| C(4')–C(5') | 1·509 (4) | N(1)——C(1')–H(1') | 105 (2) |
| O(1')–C(1') | 1·414 (3) | C(2')——C(1')–H(1') | 113 (2) |
| O(1')–C(4') | 1·458 (3) | O(1')——C(1')–H(1') | 110 (2) |
| O(2')–C(2') | 1·406 (3) | C(1')——C(2')–H(2') | 113 (2) |
| O(3')–C(3') | 1·422 (3) | C(3')——C(2')–H(2') | 111 (2) |
| O(5')–C(5') | 1·432 (3) | O(2')——C(2')–H(2') | 112 (2) |
| | | | |
| C(5) –H(5)1 | 0·99 (5) | C(2')——C(3')–H(3') | 111 (2) |
| C(5) –H(5)2 | 0·98 (5) | C(4')——C(3')–H(3') | 106 (1) |
| C(6) –H(6)1 | 0·86 (4) | O(3')——C(3')–H(3') | 108 (1) |
| C(6) –H(6)2 | 0·97 (5) | C(3')——C(4')–H(4') | 108 (2) |
| N(3) –H(3) | 0·84 (4) | C(5')——C(4')–H(4') | 108 (2) |
| C(1')–H(1') | 0·94 (3) | O(1')——C(4')–H(4') | 111 (2) |
| C(2')–H(2') | 0·91 (3) | C(4')——C(5')–H(5')1 | 104 (2) |
| C(3')–H(3') | 1·01 (3) | C(4')——C(5')–H(5')2 | 106 (2) |
| C(4')–H(4') | 0·95 (3) | O(5')——C(5')–H(5')1 | 112 (2) |
| C(5')–H(5')1 | 1·01 (4) | O(5')——C(5')–H(5')2 | 105 (2) |
| C(5')–H(5')2 | 0·98 (3) | H(5')1 –C(5')–H(5')2 | 119 (3) |
| O(2')–H(O2') | 0·68 (4) | C(2')——O(2')–H(O2') | 111 (3) |
| O(3')–H(O3') | 0·74 (4) | C(3')——O(3')–H(O3') | 105 (2) |
| O(5')–H(O5') | 0·83 (4) | C(5')——O(5')–H(O5') | 109 (3) |

| | |
|---|---|
| C(2) –N(1)–C(6) | 120·0 (2) |
| N(1)–C(2) –N(3) | 116·2 (2) |
| S(2)——C(2) –N(1) | 126·5 (2) |
| S(2)——C(2) –N(3) | 117·3 (2) |
| C(2) –N(3)–C(4) | 126·4 (2) |
| S(4)——C(4) –N(3) | 120·2 (2) |
| S(4)——C(4) –C(5) | 124·1 (2) |
| N(3)–C(4) –C(5) | 115·5 (2) |
| C(4) –C(5) –C(6) | 111·1 (2) |
| C(5) –C(6) –N(1) | 109·7 (2) |
| C(2) –N(1)–C(1') | 117·7 (2) |
| C(6) –N(1)–C(1') | 121·4 (2) |
| N(1)–C(1')–C(2') | 112·5 (2) |
| N(1)–C(1')–O(1') | 108·8 (2) |
| C(2')–C(1')–O(1') | 107·1 (2) |
| C(1')–C(2')–C(3') | 101·5 (2) |
| C(1')–C(2')–O(2') | 107·8 (2) |
| C(3')–C(2')–O(2') | 109·8 (2) |
| C(2')–C(3')–O(3') | 114·2 (2) |
| C(2')–C(3')–C(4') | 101·5 (2) |
| C(4')–C(3')–O(3') | 115·2 (2) |
| C(3')–C(4')–C(5') | 113·1 (2) |
| C(3')–C(4')–O(1') | 104·8 (2) |
| C(4')–O(1')–C(1') | 109·8 (2) |
| O(1')–C(4')–C(5') | 111·2 (2) |
| C(4')–C(5')–O(5') | 110·6 (2) |

5,6-dihydrouridine (Suck, Saenger & Zechmeister, 1972) and in dihydrouracil (Rohrer & Sundaralingam, 1970). The displacements of C(5) and C(6) from the

Table 5. *Displacements from least-squares planes through the base and sugar* (Å)

Atoms included in calculations of least-squares planes are denoted by an asterisk.

| Heterocycle | | Ribose | |
|---|---|---|---|
| N(1)* | -0·034 | C(1')* | 0·026 |
| C(2)* | 0·071 | C(2')* | -0·015 |
| N(3)* | -0·074 | C(4')* | 0·017 |
| C(4)* | 0·037 | O(1')* | -0·027 |
| S(2) | 0·356 | C(3') | 0·594 |
| S(4) | 0·153 | C(5') | 0·839 |
| C(5) | 0·158 | O(2') | -1·365 |
| C(6) | -0·504 | O(3') | 0·327 |
| C(1') | 0·107 | O(5') | 0·151 |
| H(3) | -0·165 | | |
| H(5)1 | -0·463 | | |
| H(5)2 | 1·135 | | |
| H(6)1 | -0·298 | | |
| H(6)2 | -1·467 | | |

Table 6. *Dihedral angles describing the conformation of the molecule*

The positive sense of the rotation is clockwise while looking along the *BC* bond. Greek letters correspond to Sundaralingam's (1969) notation. Estimated standard deviations are 0·2° for all listed angles.

| | *A    B    C    D* | Angles (°) |
|---|---|---|
| $\chi$ | O(1')—C(1')–N(1)–C(6) | 23·5 |
| $\tau_0$ | C(4')—O(1')–C(1')–C(2') | 4·9 |
| $\tau_1$ | O(1')—C(1')–C(2')–C(3') | -27·1 |
| $\tau_2$ | C(1')—C(2')–C(3')–C(4') | 37·4 |
| $\tau_3$ | C(2')—C(3')–C(4')–O(1') | -35·7 |
| $\tau_4$ | C(3')—C(4')–O(1')–C(1') | 19·5 |
| | O(1')—C(1')–N(1)–C(2) | -166·9 |
| | C(2)——N(1)–C(6) –C(5) | 43·3 |
| | N(3)——C(4)–C(5) –C(6) | 27·1 |
| | C(4)——C(5) –C(6) –N(1) | -49·9 |
| | C(2')—C(1')–N(1)–C(2) | 74·5 |
| | C(2')—C(1')–N(1)–C(6) | -95·0 |
| | O(2')—C(2')–C(3')–O(3') | 48·1 |
| | O(5')—C(5')–C(4')–O(1') | 71·3 |
| | O(5')—C(5')–C(4')–C(3') | -171·1 |
| | N(1)——C(1')–C(2')–O(2') | -152·2 |
| | N(1)——C(1')–C(2')–C(3') | 92·4 |
| | N(1)——C(1')–O(1')–C(4') | -116·9 |
| | C(5')—C(4')–C(3')–O(3') | 79·0 |
| | C(5')—C(4')–C(3')–C(2') | -157·0 |
| | C(5')—C(4')–O(1')–C(1') | 142·1 |
| | H(2')—C(2')–O(2')–H(O2') | 15·6 |
| | H(3')—C(3')–O(3')–H(O3') | -171·0 |
| | H(5')1–C(5')–O(5')–H(O5') | 120·4 |
| | H(5')2–C(5')–O(5')–H(O5') | -9·6 |

Table 7. *Hydrogen-bond distances and angles*

| X-H···Y | X···Y | X-H | H···Y | ∠X-H···Y | Symmetry operation | | |
|---|---|---|---|---|---|---|---|
| N(3)-H(3)······S(4) | 3·310 (3) Å | 0·84 (4) Å | 2·49 (4) Å | 165 (3)° | -x, | ½+y, | -z;    x, y, z |
| O(5')-H(O5')···S(2) | 3·342 (2) | 0·83 (4) | 2·63 (4) | 146 (4) | 1-x, | 1-y, | z;    x, y, z |
| O(3')-H(O3')···O(5') | 2·811 (3) | 0·74 (4) | 2·14 (3) | 150 (3) | x, y, z; | 1-x, | -½+y, -z |
| O(2')-H(O2')···O(3') | 2·724 (3) | 0·68 (4) | 2·05 (4) | 169 (4) | x, y, z; | -x, | -½+y, -z |

least-squares plane defined by N(1), C(2), N(3), C(4) are 0·158 and −0·504 Å. Thus the nucleobase exhibits a half-chair conformation. S(2) and S(4) are displaced from the best least-squares plane by 0·356 and 0·153 Å, respectively (Table 5). The heterocycle exists in the diketo form; the C–S distances, 1·674 (3) and 1·636 (2) Å, indicate some double-bond character for both. C(2)–S(2) is significantly longer than C(4)–S(4) owing to the hydrogenation at the 5 and 6 positions. The relationship between the C–S distances is reversed in 2,4-dithiouracil (Shefter & Mautner, 1967) and 2,4-dithiouridine monohydrate (Saenger & Suck, 1971).

*Ribose moiety*

Bond lengths and angles (Table 4) are comparable to the values found in compounds containing C(3')-*endo* ribose (Sundaralingam & Jensen, 1965).

Among calculated least-squares planes, the best is defined by C(1'), O(1'), C(2') and C(4') (Table 5); deviations range from 0·015 to 0·027 Å. C(3') is displaced by 0·594 Å from this plane on the same side as C(5'). The conformation of the sugar is the envelope C(3')-*endo*. The dihedral angle O(2')–C(2')–C(3')–O(3') of 48·1° is comparable to the values found in similar structures. The conformation of the ribose part is described by means of dihedral angles listed in Table 6. The values of $\tau_0$, $\tau_1$, $\tau_2$, $\tau_3$ and $\tau_4$ agree with those in 2-thiocytidine dihydrate (Lin, Sundaralingam & Arora, 1971) and in 5,6-dihydro-2-thiouridine (Kojić-Prodić *et al.*, 1974; for this comparison the dihedral angles are recalculated with the other enantiomorph to avoid a sign change). Shefter & Trueblood (1965) have defined the angles $\varphi_{OO}$ and $\varphi_{OC}$ as the dihedral angles O(5')–C(5')–C(4')–O(1') and O(5')–C(5')–C(4')–C(3'), respectively. In the present compound these angles are $\varphi_{OO} = 71·3°$ and $\varphi_{OC} = −171·2°$ so that the hydroxymethyl group O(5')–C(5') is *gauche* to C(4')–O(1') and *trans* to C(4')–C(3'). Other examples of this rather unusual *gauche–trans* conformation can be found in inosine (Munns & Tollin, 1970) and in 5,6-dihydro-2-thiouridine (Kojić-Prodić *et al.*, 1974).

*Conformation of the molecule*

The orientation of the base relative to the sugar ring, described in terms of rotation about C(1')–N(1) for the sequence of atoms O(1')–C(1')–N(1)–C(6) is 23·5° (Sundaralingam, 1969; Altona & Sundaralingam, 1972) and the nucleoside molecule is *anti*.

*Hydrogen bonding and molecular packing*

The molecules are connected by hydrogen bonds between sugar–sugar, base–base and base–sugar resi-

dues to form a three-dimensional network. Base stacking does not occur. The shortest base–base distance of 4·985 Å is given by a period of translation along [001].

Each molecule is involved in four independent hydrogen bonds with surrounding molecules (Table 7, Figs. 3 and 5). The hydroxyl groups in the ribose moiety are engaged in hydrogen bonds O(2')–H···O(3'), 2·724, O(3')–H···O(5'), 2·811, and O(5')–H···S(2), 3·342 Å. S(4) is included in an interbase hydrogen bond N(3)–H···S(4), 3·310 Å. The participation of S atoms in hydrogen bonding was observed in other crystal structures of thio-analogues of nucleic acid constituents, *e.g.* N(3)–H···S(4), 3·331, and O(5')–H···S(2), 3·227 Å, in 2,4-dithiouridine monohydrate (Saenger & Suck, 1971) and N(3)–H···S(4), 3·315 Å, in 2,4-dithiouracil (Shefter & Mautner, 1967).

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