the PTC, yielded the title compound. The mechanism of this reaction is not known, as yet. However, it is believed that this X-ray structural investigation will help resolve the problem.

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Structure of Tetrahydrothiamin Hemihydrate

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Abstract. 3-[(4-Amino-2-methyl-5-pyrimidinyl)methyl]-4-methyl-5-thiazolidineethanol hemihydrate, $C_{12}H_{20}N_4OS.\frac{1}{2}H_2O$, $M_r = 277.38$, monoclinic, $P2_1/c$, $a = 9.533$ (2), $b = 23.568$ (5), $c = 13.666$ (3) Å, $\beta = 103.47$ (3)°, $V = 2986$ (1) Å^3, $Z = 8$, $D_x = 1.234$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 18.9$ cm^{-1}, $F(000) = 1192$, $T = 295$ K, $R = 0.048$ for 2071 reflections with $I \geq 2\sigma(I)$. Two independent molecules, both of which are in the *syn* diastereoisomeric form, assume a similar overall conformation. However, only one molecule has an intramolecular hydrogen bond between the thiazolidine N and 4'-amino N atoms. The thiazolidine rings with the sp^3-N atoms assume a half-chair conformation. There are two kinds of hydrogen-bonded molecular dimer which are interconnected by water molecules to form a three-dimensional hydrogen-bonding network.

Experimental. The title compound was prepared by reduction of thiamin with NaBH$_4$ in water (Clark & Sykes, 1967). Colourless tabular crystals were obtained from an ethanol solution by slow evaporation. A crystal *ca* 0.2 × 0.2 × 0.4 mm was used for data collection on a Rigaku AFC diffractometer with graphite-monochromated Cu $K\alpha$ radiation and ω–2θ scans of speed 2° min^{-1} in 2θ, and ω-scan width $(1.7 + 0.1\tan\theta)°$ for $2\theta \leq 110°$. Background was

measured for 10 s on either side of the peak. Cell parameters were determined by least-squares fit to observed 2θ values for 25 centred reflections with $23 \leq 2\theta \leq 48°$. Intensity checks for three standard reflections showed little ($\pm 3\%$) variation. 3627 independent reflections were collected (h 0 to 9, k 0 to 25, l −14 to 14), of which 2071 (57%) were observed with $I \geq 2\sigma(I)$ and used in refinement. Lp corrections, but no absorption or extinction correction were made. The structure was solved by direct methods and refined by full-matrix least squares on F with anisotropic thermal parameters, using *SHELX*76 (Sheldrick, 1976). H atoms were identified in the difference map and refined isotropically.
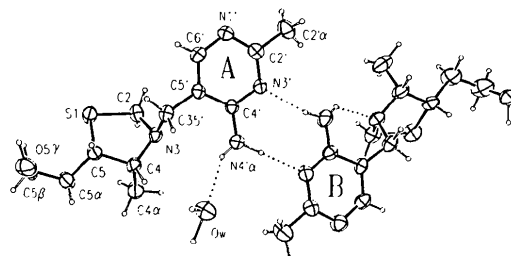

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the asymmetric unit of tetrahydrothiamin hemihydrate with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The dotted line denotes the hydrogen bond. The view is tilted from the pseudo-twofold axis to avoid the overlap of the atoms.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Molecule A				
S(1)	9710 (1)	4200 (1)	12270 (1)	0.067
C(2)	9585 (6)	4500 (3)	10992 (4)	0.059
N(3)	8488 (4)	4186 (2)	10303 (3)	0.050
C(4)	8594 (5)	3595 (2)	10615 (3)	0.057
C(5)	8686 (6)	3570 (2)	11771 (3)	0.058
C(4α)	9891 (8)	3322 (3)	10319 (5)	0.089
C(5α)	9278 (8)	3030 (3)	12276 (5)	0.077
C(5β)	9075 (8)	2971 (3)	13331 (5)	0.087
O(5γ)	7614 (5)	2907 (2)	13354 (3)	0.093
C(35')	7053 (5)	4429 (2)	10236 (4)	0.052
N(1')	6352 (4)	5942 (2)	9365 (3)	0.057
C(2')	6346 (5)	5874 (2)	8388 (4)	0.057
N(3')	6538 (4)	5383 (2)	7956 (3)	0.051
C(4')	6783 (4)	4913 (2)	8535 (3)	0.047
C(5')	6805 (4)	4942 (2)	9580 (3)	0.046
C(6')	6586 (5)	5468 (2)	9917 (4)	0.055
C(2'α)	6105 (10)	6385 (3)	7740 (6)	0.083
N(4'α)	6962 (5)	4431 (2)	8077 (4)	0.067
Molecule B				
S(1)	8933 (2)	6020 (1)	2486 (1)	0.087
C(2)	9053 (7)	5718 (3)	3747 (5)	0.076
N(3)	7696 (4)	5818 (2)	4019 (3)	0.062
C(4)	7189 (7)	6378 (2)	3627 (4)	0.074
C(5)	7286 (6)	6419 (2)	2529 (4)	0.067
C(4α)	8063 (14)	6840 (4)	4269 (7)	0.144
C(5α)	7236 (10)	7014 (3)	2127 (6)	0.099
C(5β)	7078 (11)	7049 (3)	1022 (7)	0.113
O(5γ)	5733 (5)	6840 (2)	484 (3)	0.091
C(35')	6655 (6)	5369 (2)	3620 (4)	0.064
N(1')	7100 (4)	3835 (2)	4403 (3)	0.072
C(2')	7036 (5)	3896 (2)	5373 (4)	0.062
N(3')	6947 (4)	4384 (2)	5838 (3)	0.061
C(4')	6889 (5)	4858 (2)	5303 (4)	0.058
C(5')	6902 (5)	4853 (2)	4264 (3)	0.054
C(6')	7016 (5)	4324 (3)	3888 (4)	0.067
C(2'α)	7113 (12)	3363 (3)	5971 (7)	0.096
N(4'α)	6811 (6)	5352 (2)	5768 (4)	0.073
O(W)	6435 (5)	3177 (2)	8405 (3)	0.093

$\Sigma w(|F_o| - |F_c|)^2$ was minimized, with $w = k/[\sigma^2(F_o) + gF_o^2]$ [$\sigma(F)$ from counting statistics; k and g optimized in the least-squares procedure; $k = 0.902$; $g = 0.00126$]. $R = 0.048$ and $wR = 0.051$ for 2071 observed reflections and 502 variables; $R = 0.143$ and $wR = 0.176$ for all data; $S = 1.187$; $(\Delta/\sigma)_{max} = 0.828$ [z of H(4'αbB)] in the final refinement cycle. Maximum and minimum heights in final difference map were 0.25 and -0.20 e $\mathring{A}^{-3}$, respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 99). Final atomic parameters are listed in Table 1.* An *ORTEP*II (Johnson, 1976) view of the asymmetric unit with the atomic numbering scheme is presented in Fig. 1. Bond distances and angles are listed in Table 2.

Related literature. The structure of tetrahydrothiamin (THT) has been published with the atomic

Table 2. *Bond distances* ($\mathring{A}$) *and angles* (°)

|	Molecule A	Molecule B
S(1)—C(2)	1.862 (6)	1.843 (7)
S(1)—C(5)	1.820 (5)	1.843 (6)
C(2)—N(3)	1.438 (7)	1.446 (8)
N(3)—C(4)	1.453 (7)	1.464 (7)
N(3)—C(35')	1.466 (6)	1.466 (7)
C(4)—C(5)	1.563 (6)	1.528 (8)
C(4)—C(4α)	1.530 (9)	1.520 (12)
C(5)—C(5α)	1.494 (8)	1.503 (9)
C(5α)—C(5β)	1.505 (10)	1.485 (12)
C(5β)—O(5γ)	1.409 (9)	1.410 (11)
C(35')—C(5')	1.491 (7)	1.487 (7)
N(1')—C(2')	1.343 (7)	1.349 (7)
N(1')—C(6')	1.337 (7)	1.343 (8)
C(2')—N(3')	1.331 (7)	1.326 (7)
C(2')—C(2'α)	1.481 (9)	1.491 (9)
N(3')—C(4')	1.350 (6)	1.329 (7)
C(4')—C(5')	1.425 (6)	1.423 (7)
C(4')—N(4'α)	1.327 (7)	1.337 (7)
C(5')—C(6')	1.355 (7)	1.362 (8)
N(3)—C(2)—S(1)	107.3 (4)	108.2 (4)
C(4)—N(3)—C(2)	108.1 (4)	107.0 (5)
C(4)—C(5)—S(1)	104.3 (3)	104.2 (4)
C(5)—S(1)—C(2)	92.7 (2)	92.0 (3)
C(5)—C(4)—N(3)	108.4 (4)	109.0 (4)
C(4α)—C(4)—N(3)	109.3 (4)	110.2 (5)
C(4α)—C(4)—C(5)	113.1 (4)	111.8 (6)
C(5α)—C(5)—S(1)	114.2 (4)	114.8 (5)
C(5α)—C(5)—C(4)	115.2 (4)	114.5 (5)
C(5β)—C(5α)—C(5)	113.7 (6)	114.2 (6)
O(5γ)—C(5β)—C(5α)	112.3 (6)	112.0 (7)
C(35')—N(3)—C(2)	111.4 (4)	110.8 (4)
C(35')—N(3)—C(4)	113.1 (4)	112.2 (4)
N(3')—C(2')—N(1')	125.1 (5)	125.9 (5)
C(4')—N(3')—C(2')	118.4 (4)	117.7 (4)
C(4')—C(5')—C(35')	121.8 (4)	123.1 (4)
C(5')—C(35')—N(3)	111.7 (4)	111.7 (4)
C(5')—C(4')—N(3')	120.5 (4)	122.2 (4)
C(5')—C(6')—N(1')	126.3 (5)	126.0 (5)
C(6')—N(1')—C(2')	115.0 (4)	114.4 (5)
C(6')—C(5')—C(35')	123.6 (4)	122.7 (4)
C(6')—C(5')—C(4')	114.6 (4)	113.8 (4)
C(2'α)—C(2')—N(1')	117.5 (5)	116.2 (5)
C(2'α)—C(2')—N(3')	117.4 (5)	117.9 (5)
N(4'α)—C(4')—N(3')	116.7 (4)	118.1 (5)
N(4'α)—C(4')—C(5')	122.7 (4)	119.7 (5)
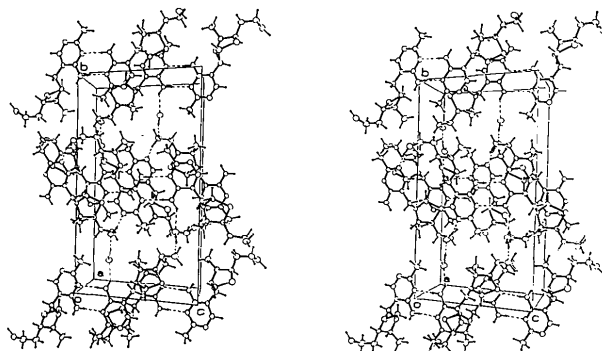
Fig. 2. Stereoscopic *ORTEP*II (Johnson, 1976) packing drawing. The dotted line denotes the hydrogen bond.

coordinates incorrectly truncated (Bau, Hyun, Lim, Choi, Yannopoulos, & Hadjiliadis, 1988). The structure of its Co^II complex has also been published in the same paper. THT is the first example that has an sp^3-N(3) atom among the thiamin-related compounds whose crystal structures have been determined. Two independent molecules, related by pseudo-twofold-axis symmetry, assume a similar

Table 3. *Hydrogen-bond and close contact geometry* (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O(5γA)—H⋯N(1′B′)	0.91 (5)	1.82 (5)	2.721 (6)	176 (5)
O(5γB)—H⋯N(1′A″)	1.03 (7)	1.86 (7)	2.754 (6)	143 (6)
N(4′αA)—H(a)⋯N(3′B)	1.05 (7)	2.01 (7)	3.059 (7)	178 (3)
N(4′αB)—H(a)⋯N(3′A)	0.88 (4)	2.19 (4)	3.062 (7)	168 (4)
N(4′αA)—H(b)⋯O(W)	0.81 (5)	2.33 (5)	3.048 (7)	149 (5)
N(4′αB)—H(b)⋯N(3B)	0.81 (2)	2.30 (5)	2.928 (7)	135 (5)
O(W)—H(a)⋯O(5γA‴)	1.22 (7)	1.59 (7)	2.798 (7)	171 (5)
O(W)—H(b)⋯O(5γBⁱᵛ)	0.92 (8)	1.96 (8)	2.896 (6)	159 (8)
N(4′αA)—H(b)⋯N(3A)	0.81 (2)	2.69 (5)	3.105 (7)	114 (4)

Symmetry code: (none) x, y, z; (i) x, y, $1 + z$; (ii) x, y, $-1 + z$; (iii) x, $0.5 - y$, $-0.5 + z$; (iv) $1 - x$, $1 - y$, $1 - z$.

overall conformation but there is a small but significant difference in the relative orientations of the two rings, the N(3)—C(35′)—C(5′)—C(6′) torsion angles showing the largest difference of 12.6°. This difference is related to the asymmetric hydrogen-bonding pattern involving the 4′α-amino groups as shown in Fig. 1 and Table 3. Molecule *B* has a weak

N(4′α)—H⋯H(3) hydrogen-bonding interaction [H⋯N(3) 2.30 (5), N⋯N 2.928 (7) Å, N—H⋯N 135 (5)°] which has never been observed in any crystal structures of thiamin and its analogues with an intact thiazolium ring. There is no comparable interaction for moleucle *A* [H⋯N 2.69 (5) Å]. The packing is shown in Fig. 2.

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Structure of 1,5-Dihydroxyanthraquinone: a Redetermination

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Abstract. $C_{14}H_8O_4$, $M_r = 240.21$, monoclinic, $P2_1/c$, $a = 6.0092$ (5), $b = 5.3074$ (2), $c = 15.7538$ (6) Å, $\beta = 93.672$ (5)°, $V = 501.41$ (5) Å³, $Z = 2$, $D_x = 1.591$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 9.39$ cm⁻¹, $F(000) = 248$, $T = 300$ K, $R = 0.035$, $wR = 0.054$ for 638 reflections $[I \geq 3\sigma(I)]$. The H atom involved in the intramolecular hydrogen bond is found to be asymmetrically placed, with O(1)—H(1) = 0.94 Å, and for the intramolecular hydrogen bond O(1)⋯O(7′) = 2.607 (1) Å.

Experimental. The compound was crystallized by the slow diffusion of deionized water into a solution of 1,5-dihydroxyanthraquinone in chromatographically pure acetone at room temperature. An orange parallelpiped crystal of $C_{14}H_8O_4$ having approximate dimensions $0.4 \times 0.4 \times 0.5$ mm was used for data collection on a Rigaku AFC-6R diffractometer using Cu $K\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range $40.37 < 2\theta < 49.80°$. The data were collected at a temperature

of 300 K using the ω–2θ-scan technique to a maximum 2θ value of 118.10° ($h\ 0 \to 6$, $k\ 0 \to 5$, $l\ -17 \to 16$). ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.280° with a take-off angle of 6.00°. Scans of $(1.26 + 0.30\tan\theta)°$ were made at a speed of 16.00° min⁻¹ (in ω).

Of the 880 reflections which were collected, 798 were unique ($R_{int} = 0.015$) and equivalent reflections were merged. The intensities of three representative reflections, measured after every 150 reflections, declined by 0.93% and a linear correction factor was applied. The linear absorption coefficient of Cu $K\alpha$ is 9.4 cm⁻¹. An empirical absorption correction was also applied (transmission factors 0.95–1.00) and the data were corrected for Lorentz and polarization effects ($p = 0.03$).

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). The non-H atoms were refined with anisotropic thermal parameters. H atoms were located by difference Fourier synthesis and refined with isotropic thermal parameters. Based on 638 observed