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Thiaminium dipicrate

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In the title molecular structure, $C_{12}H_{18}N_4OS^{2+}\cdot 2C_6H_2N_3O_7^-$, the thiazolium ring bearing the hydroxyethyl side chain is disordered over two sites about the methylene bridge. In the minor occupancy component, the dihedral angles are quite different from the range observed in related structures. In the crystal structure, the thiaminium cation and one of the picrate anions form a centrosymmetric hydrogen-bonded cluster. Both anions form 'anionic holes' with the thiaminium cation.

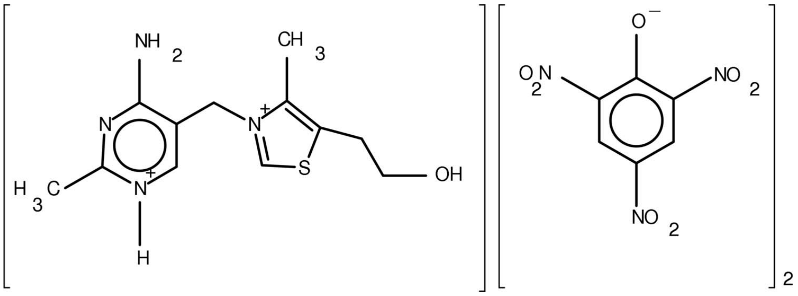
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.067
wR factor = 0.240
Data-to-parameter ratio = 10.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In thiamine, the thiazole ring is responsible for the coenzyme's activity in pyruvate metabolism where it helps to perform a nonoxidative decarboxylation (Breslow, 1958). Thiamine deficiency disease, known as beriberi, is manifested by numerous neurological and metabolic disorders. Thiamine disulfide is one of the open-ring derivatives which is frequently used as a starting material for syntheses of other thiamine derivatives (Shin & Chun, 1987). We have recently reported the crystal structures of thiamine with bisulfate and perclorate anions (Athimoolam & Rajaram, 2006*a*; Athimoolam & Rajaram, 2006*b*). As a part of our ongoing work on biologically important compounds, thiamine was complexed with picric acid and the crystal structure of the resulting compound, (I), is reported here.



(I)

In (I), the effective protonation site, as found in other related thiamine structures, is the N atom (N1) *para* to the amino group. The thiazolium ring bearing the hydroxyethyl side chain is disordered over two sites about the methylene bridge. The dihedral angles between the planes of the pyrimidine and thiazolium rings are 83.41 (2)° for the major occupancy and 89.5 (5)° for the minor occupancy component. Three types of conformers have been found in thiamine-based molecules (Shin *et al.*, 1977): $F(\varphi_T = 0°, \varphi_P = \pm 90°)$, $S(\varphi_T = \pm 100°, \varphi_P = \pm 150°)$ and $V(\varphi_T = \pm 90°, \varphi_P = \pm 90°)$. In (I), the thiamine molecule adopts the unusual *S* conformation with respect to the C7 methylene bridge atom.

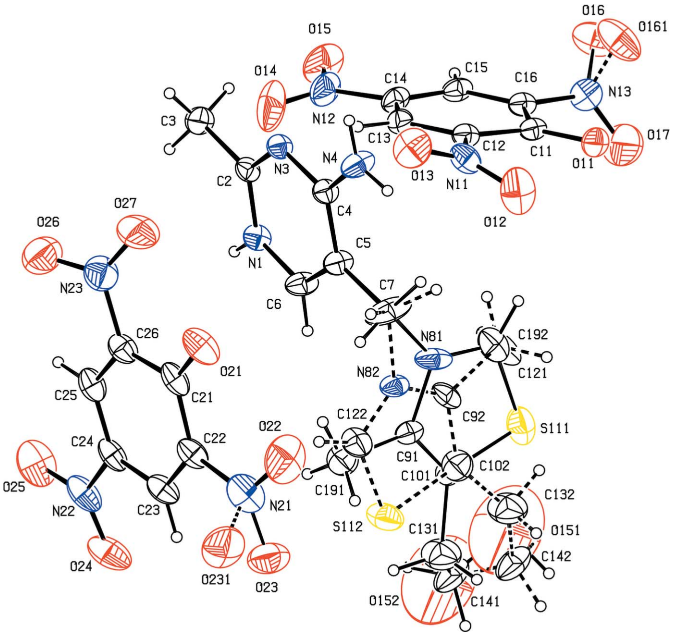


Figure 1

The asymmetric unit of (I), showing displacement ellipsoids drawn at the 30% probability level and H atoms as small spheres. The minor component of disorder is shown with dashed bonds.

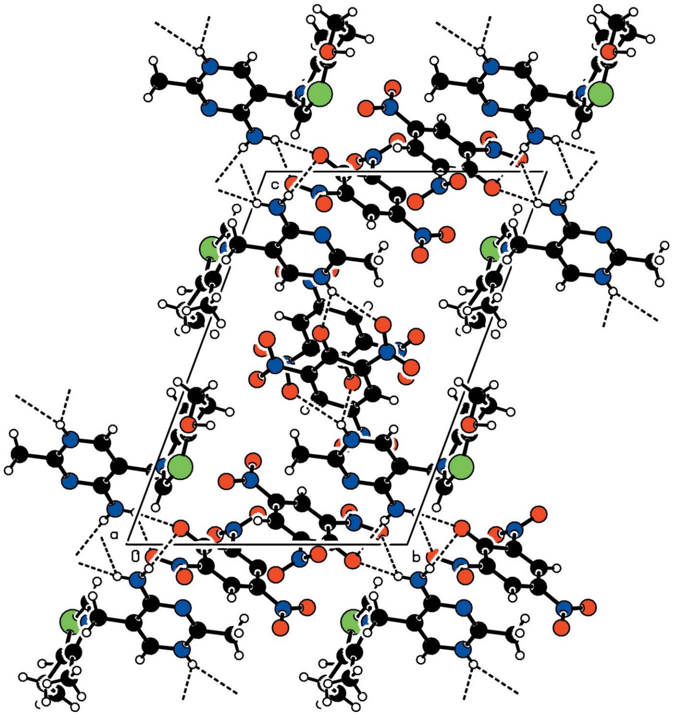


Figure 2

Crystal structure of (I), viewed along the *a* axis. Hydrogen bonds are drawn as dashed lines.

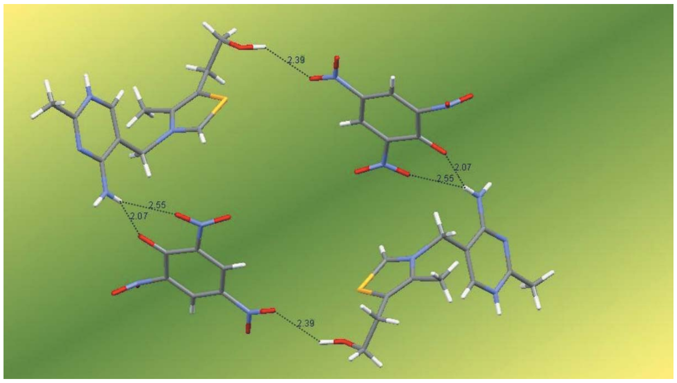


Figure 3

Centrosymmetric cluster involving the cation and one type of anion. Hydrogen bonds are drawn as dashed lines.

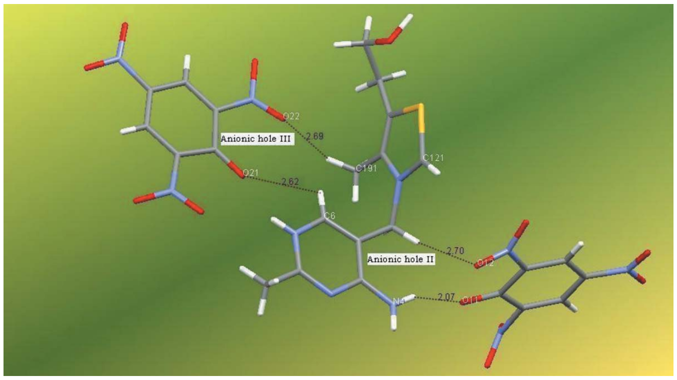


Figure 4

Anionic holes formed by the cation with picrate anions. Hydrogen bonds are shown as dashed lines.

The 5-(β-hydroxyethyl) side chain can be described by the two torsion angles $\varphi_{5\alpha}$ and $\varphi_{5\beta}$. For major occupancy $\varphi_{5\alpha}$ and $\varphi_{5\beta}$ are −48.1 (19) and 38 (2)°. This type of conformation results in a close contact between electronegative O151 and electropositive S111 atoms with a distance of 2.4032 (8) Å. A common structural feature of thiamine is that the hydroxyethyl side chain is folded back towards the thiazolium ring. For the minor occupancy component the conformation angles are 52 (4) and −6 (4)°. A similar variation in conformation is also found in thiamine naphthalene-1,5-disulfonate monohydrate (Shin & Lah, 1987).

The picrate anions play an important role in forming hydrogen bonds with the cation and stabilizing the structure. One of the two noteworthy features in this structure is the hydrogen bond from the acidic C121/C122 position of the thiazolium ring and the other is the presence of hydrogen bonding involving atom N1 (see Table 2). The amino group of the pyrimidine ring forms one two-centered and one three-centered hydrogen bond, thus forming a centrosymmetric cluster. These clusters are, in turn, linked by hydrogen bonds to form extended chains along [110] (Table 2).

As described by Hu *et al.* (2000), the thiamine cation forms well defined 'anionic holes' between the thiazolinium and pyrimidine rings. Normally, because of the electrostatic interaction, the anions are located close to these 'anionic holes' and this leads to host–guest-like thiamine–anion complexation. There are three anion holes around the cation occupied by an anion. Anionic hole type (I) does not exist when thiaminium has an *S* conformation, but in (I) one of the picrate anions is located close to anionic hole (II), which is in the area of the N4—H4*A*···O11$^{\rm ii}$ (Table 2) hydrogen bond and anion/thiazolium ring electrostatic interaction. Anionic

Acta Cryst. (2006). E**62**, o2324–o2326 Anitha *et al.* • $C_{12}H_{18}N_4OS^{2+}\cdot 2C_6H_2N_3O_7^-$ **o2325**

hole (III) involving the other anion is characterized by the weak C6—H6$\cdots$O21^{iii} hydrogen bond (Table 2 and Fig. 3).

Experimental

The title compound was crystallized from an aqueous solution of thiamine hydrochloride and picric acid in a stoichiometric ratio of 1:2 at room temperature, using the slow evaporation method.

Crystal data

$C_{12}H_{18}N_4OS^{2+}\cdot 2C_6H_2N_3O_7^-$
$M_r = 722.58$
Triclinic, $P\overline{1}$
$a = 8.269\ (3)$ Å
$b = 12.252\ (4)$ Å
$c = 16.641\ (3)$ Å
$\alpha = 69.35\ (4)^\circ$
$\beta = 86.35\ (5)^\circ$
$\gamma = 72.82\ (3)^\circ$
$V = 1505.6\ (9)$ Å^3
$Z = 2$
$D_x = 1.594$ Mg m^{-3}
$D_m = 1.59$ Mg m^{-3}
D_m measured by flotation using a liquid mixture of bromoform and xylene
Mo $K\alpha$ radiation
$\mu = 0.20$ mm^{-1}
$T = 293\ (2)$ K
Block, yellow
0.20 × 0.17 × 0.15 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.946$, $T_{max} = 0.960$
6473 measured reflections
5276 independent reflections
2399 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 25^\circ$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.240$
$S = 1.02$
5276 reflections
518 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1133P)^2 + 0.9209P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C11—O11	1.263 (5)	N1—C2	1.340 (5)
C21—O21	1.242 (6)	N1—C6	1.345 (5)
O11—C11—C12	126.5 (4)	O21—C21—C22	123.8 (5)
O11—C11—C16	121.9 (4)	C26—C21—C22	111.8 (4)
C12—C11—C16	111.6 (4)	C2—N1—C6	121.2 (4)
O21—C21—C26	124.4 (6)		
C13—C12—N11—O13	17.4 (7)	C21—C26—N23—O27	−18.9 (9)
C11—C12—N11—O12	20.4 (7)	C25—C26—N23—O26	−23.7 (8)
C13—C14—N12—O14	6.6 (8)	C4—C5—C7—N82	177.8 (8)
C15—C14—N12—O15	7.7 (7)	C4—C5—C7—N81	−142.7 (8)
C11—C16—N13—O17	−63.3 (7)	C5—C7—N81—C121	85.3 (2)
C15—C16—N13—O16	−47.7 (9)	S111—C101—C131—C141	−48.1 (2)
C21—C22—N21—O22	16.1 (9)	C101—C131—C141—O151	38 (2)
C23—C22—N21—O23	−7.7 (1)	C5—C7—N82—C122	−93.8 (2)
C23—C24—N22—O24	5.1 (7)	S112—C102—C132—C142	52 (4)
C25—C24—N22—O25	7.4 (8)	C102—C132—C142—O152	−6 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4*B*$\cdots$O12^{i}	0.86	2.55	3.062 (7)	119
N4—H4*B*$\cdots$O11^{i}	0.86	2.07	2.885 (5)	159
N4—H4*A*$\cdots$O11^{ii}	0.86	2.28	3.102 (5)	161
N1—H1$\cdots$O27^{iii}	0.86	2.57	3.348 (7)	151
N1—H1$\cdots$O21^{iii}	0.86	1.99	2.667 (5)	135
O151—H151$\cdots$O14^{iv}	1.12	2.39	3.33 (4)	140
O152—H152$\cdots$O26	1.11	2.37	3.40 (5)	154
C6—H6$\cdots$O21^{iii}	0.93	2.62	2.993 (6)	104
C3—H3*A*$\cdots$O27^{iii}	0.96	2.29	3.205 (7)	159
C3—H3*C*$\cdots$O16^{v}	0.96	2.37	3.307 (10)	167
C121—H12*A*$\cdots$O12^{iii}	0.93	2.65	3.33 (3)	131
C122—H12*B*$\cdots$O151^{vi}	0.93	2.58	3.39 (3)	146

Symmetry codes: (i) $x-1, y+1, z-1$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$; (v) $x, y, z-1$; (vi) $x-1, y, z$.

All H atoms, except the hydroxy H atom in the thiaminium cation, were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). The hydroxy H atoms were located in a difference map and fixed in position. The thiazolium ring and carboxyethyl side chain in the thiaminium cation show positional disorder with site occupation factors of 0.536 (1) and 0.464 (1) for N81/C91$\cdots$/O151 and N82/C92$\cdots$/O152, respectively. One of the O atoms in each of the picrate anions is disordered over two sites with assigned occupancies 0.65/0.35 for O16/O161 and 0.55/0.45 for O23/O231.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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o2326 Anitha *et al.* • $C_{12}H_{18}N_4OS^{2+}\cdot 2C_6H_2N_3O_7^-$ *Acta Cryst.* (2006). E**62**, o2324–o2326