Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen bonding in 2-(2-oxothiazolidin-3-yl)-4,5-dihydrothiazolium hydrogen sulfate monohydrate

Rodrigo S. Corrêa,[a,b]* Felipe T. Martins,[b] Javier Ellena,[b] Marcelo H. dos Santos[c] and Antonio C. Doriguetto[a]

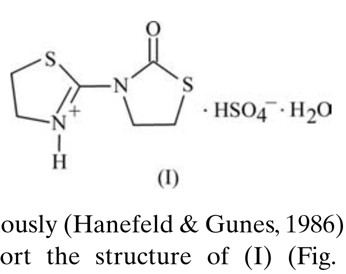
[a]Laboratório de Cristalografia, Departamento de Ciências Exatas, Universidade Federal de Alfenas–Unifal–MG, Rua Gabriel Monteiro da Silva 714, CEP 37130-000 Alfenas MG, Brazil, [b]Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970 São Carlos SP, Brazil, and [c]Laboratório de Fitoquímica e Química Medicinal, Departamento de Farmácia, Universidade Federal de Alfenas–Unifal–MG, Rua Gabriel Monteiro da Silva 714, CEP 37130-000 Alfenas MG, Brazil
Correspondence e-mail: rodrigocorrea@ursa.ifsc.usp.br

Received 16 May 2008
Accepted 10 June 2008
Online 14 June 2008

The asymmetric unit of the title compound, $C_6H_9N_2OS_2^{+}\cdot HSO_4^{-}\cdot H_2O$, contains a heterocyclic cation, a hydrogen sulfate anion and a water molecule. There are strong hydrogen bonds between the hydrogen sulfate anions and water molecules, forming an infinite chain along the [010] direction, from which the cations are pendent. The steric, electronic and geometric features are compared with those of similar compounds. In this way, structural relationships are stated in terms of the influence of the sulfate group on the protonation of the heterocycle and on the tautomeric equilibrium in the solid state.

Comment

Thiazolidinone derivatives are attractive targets for drug synthesis (Lesyk & Zimenkovsky, 2004) because these pharmacologically active compounds present various biological properties. For instance, antitumour (Lesyk *et al.*, 2006), antimicrobial (Vicini *et al.*, 2006), antidiarrhoeal (Mazzoni *et al.*, 2006), anti-inflammatory (Ottanà *et al.*, 2005) and antioxidant activities (Shimizu *et al.*, 2002) have been attributed to them. In addition, they are potentially useful for neuropathic pain treatment (Shimizu *et al.*, 2002). The synthesis and spectroscopic analysis of the title compound, (I), have been described previously (Hanefeld & Gunes, 1986). In the present paper, we report the structure of (I) (Fig. 1). A related compound, the monohydrated hydrogen sulfate salt of bis(pyrimethamine) (Devi *et al.*, 2006), crystallizes in the same space group ($P2_12_12_1$) as (I). Therefore, the presence of the hydrogen sulfate anion and the water molecule may play an important role in the assembly of these compounds.



(I)

The intramolecular geometric parameters of (I) were compared with those of similar structures deposited in the Cambridge Structural Database (CSD, Version 5.29 of January 2008; Allen, 2002) using *Mogul* (Bruno *et al.*, 2004). The lengths of the C1—N1 [1.408 (3) Å] and C1=O1 [1.218 (3) Å] bonds are typical of their types [average values = 1.40 (1) and 1.21 (2) Å, respectively]. The length of the N1—C4 bond which links the two rings [1.357 (3) Å] is very similar to that of the corresponding bond [1.350 (5) Å] in the analogous compound 1-(5-nitro-1,3-thiazol-2-yl)imidazolidin-2-one (Peeters *et al.*, 1984), and these values are both typical for bonds of this type [average value = 1.35 (1) Å].

Each of the rings adopts an envelope conformation, with atoms C2 and C6 in the flap positions of the thiazolidin-2-one and dihydrothiazole groups, respectively. The largest deviation from the least-squares plane through the five atoms of the thiazolidin-2-one ring occurs for atom C2 [displacement = 0.094 (2) Å], with an r.m.s. deviation of 0.0682 Å for the ring atoms. In the dihydrothiazole ring, the largest displacement is for atom C6 [0.78 (22) Å], with an r.m.s. deviation of 0.0547 Å. The nonplanarity of the rings arises from the adjacent CH_2 groups within each ring (Raper *et al.*, 1983; Corrêa *et al.*, 2006). The dihedral angle between the mean planes of the two rings in the cation is only 2.1 (2)°, so that overall the cation is close to being planar.

Within the anion, the S—OH distance of 1.539 (2) Å is clearly distinct from the other three S—O distances, which are in the range 1.422 (2)–1.437 (2) Å, indicating that the H-atom site is static, rather than mobile between the O atoms. The O—S—O angles [103.9 (2)–114.2 (2)°] are typical of those found in hydrogen sulfate anions in crystalline salts.

The crystal packing of (I) is strongly stabilized by a network of hydrogen bonds (Table 1). Moreover, the presence of the water molecule and the hydrogen sulfate anion play a key role

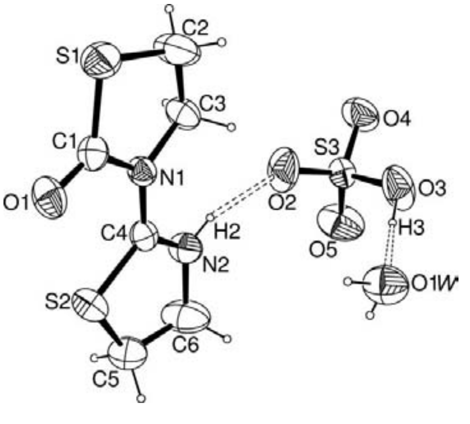


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

doi:10.1107/S0108270108017502

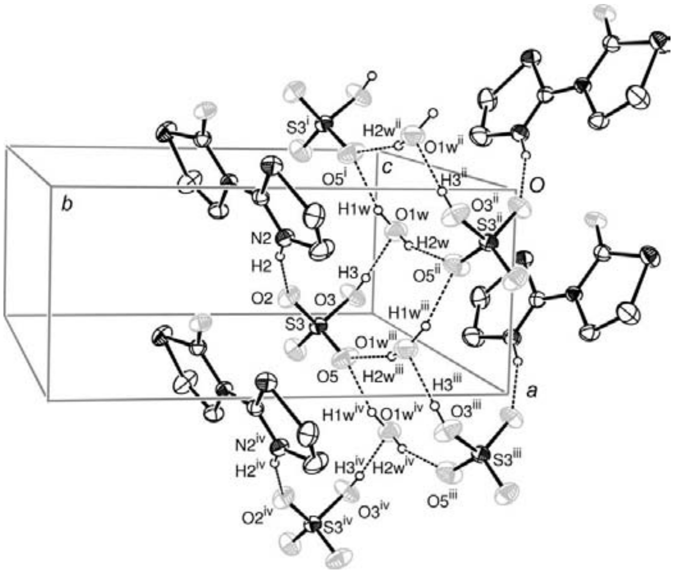


Figure 2
The hydrogen bonds linking the water molecules and hydrogen sulfate anions of (I). [Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$; (iii); $x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iv) $x+1, y, z$.]

in the molecular aggregation, where the anions and water molecules form a helical chain of edge-fused hydrogen-bonded rings running along along the [100] direction (Fig. 2). Atom O5 acts as an acceptor from two neighbouring water molecules, while atom O1*W* acts as acceptor from the anion. The cation is linked to the anion *via* a strong N—H$\cdots$O hydrogen bond (Table 1), so that the cations are all pendent from the water/anion chains.

Other hydrated sulfate and hydrogen sulfate salts containing organic cations have been described, in which the inorganic components form dimers (Lu *et al.*, 2004), chains (Gomes *et al.*, 1996), or networks in two and three dimensions (Warden *et al.*, 2004; Białońska & Ciunik, 2005). In 4-carboxyphenylammonium perchlorate monohydrate (Athimoolam & Natarajan, 2006), the water molecules and the anions form chains of edge-fused hydrogen-bonded rings which resemble those reported here for (I).

Experimental

The title compound was synthesized according a minor modification of the reported procedure of Hanefeld & Gunes (1986), in which hydrogen peroxide was used as the oxidant instead of nitric acid. Colourless needle-shaped single crystals of (I) were obtained by slow evaporation of a solution in diethyl ether. The hydrogen sulfate and water components are by-products of the synthetic procedure.

Crystal data

$C_6H_9N_2OS_2^{+}\cdot HSO_4^{-}\cdot H_2O$
$M_r = 304.36$
Orthorhombic, $P2_12_12_1$
$a = 5.8508$ (2) Å
$b = 13.0999$ (4) Å
$c = 15.4187$ (5) Å
$V = 1181.84$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.65$ mm^{-1}
$T = 294$ K
$0.14 \times 0.05 \times 0.03$ mm

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O1W—H1$W\cdots$O5^{i}	0.85	1.92	2.755 (4)	166
N2—H2$\cdots$O2	0.86	1.98	2.816 (4)	164
O1W—H2$W\cdots$O5^{ii}	0.85	1.95	2.766 (4)	161
O3—H3$\cdots$O1W	0.82	1.75	2.550 (4)	164

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$.

Data collection

Nonius KappaCCD diffractometer
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.878$, $T_{\max} = 0.966$
14972 measured reflections
2712 independent reflections
2266 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.106$
$S = 1.03$
2712 reflections
158 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Absolute structure: Flack (1983), with 1126 Friedel pairs
Flack parameter: −0.04 (10)

Methylene, amine and hydroxyl H atoms were placed in idealized locations and refined using a riding model, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N) or $1.5U_{\rm eq}$(O), and with C—H = 0.97 Å, N—H = 0.86 Å and O—H = 0.82 Å. Water H atoms were permitted to ride at the positions derived from difference maps, with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O), giving O—H distances of 0.85 Å.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the Brazilian agencies CNPq, FAPEMIG, FAPESP and CAPES. RSC thanks the CNPq for a fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3216). Services for accessing these data are described at the back of the journal.

References

Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 271. Copenhagen: Munksgaard.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Athimoolam, S. & Natarajan, S. (2006). *Acta Cryst.* C**62**, o612–o617.
Białońska, A. & Ciunik, Z. (2005). *Acta Cryst.* C**61**, o161–o164.
Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.
Corrêa, R. S., Santana, S. A., Salloum, R., Silva, R. M. & Doriguetto, A. C. (2006). *Acta Cryst.* C**62**, o115–o117.
Devi, P., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2006). *J. Chem. Crystallogr.* **12**, 857–861.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gomes, A. C., Biswas, G., Pain (Biswas), S., Ghosh, S., Ghosh, D., Iitaka, Y. & Banerjee, A. (1996). *Acta Cryst.* C**52**, 2020–2022.
Hanefeld, W. & Gunes, Z. E. (1986). *Arch. Pharm.* **6**, 521–527.

Lesyk, R. B. & Zimenkovsky, B. S. (2004). *Curr. Org. Chem.* **16**, 1547–1577.

Lesyk, R., Zimenkovsky, B., Atamanyuk, D., Jensen, F., Kiec'-Kononowiczc, K. & Gzella, A. (2006). *Bioorg. Med. Chem.* **14**, 5230–5240.

Lu, L.-P., Zhang, H.-M., Feng, S.-S. & Zhu, M.-L. (2004). *Acta Cryst.* C**60**, o740–o743.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Mazzoni, O., Di Bosco, A. M., Grieco, P., Novellino, E., Bertamino, A., Borrelli, F., Capasso, R. & Diurno, M. V. (2006). *Chem. Biol. Drug Des.* **67**, 432–436.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Ottanà, R., Maccari, R., Barreca, M. L., Bruno, G., Rotondo, A., Rossi, A., Chiricosta, G., Di Paola, R., Sautebin, L., Cuzzocrea, S. & Vigorita, M. G. (2005). *Bioorg. Med. Chem.* **13**, 4243–4252.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Peeters, O. M., Blaton, N. M. & De Ranter, C. J. (1984). *Acta Cryst.* C**40**, 1748–1750.

Raper, E. S., Oughtred, R. E. & Nowell, I. W. (1983). *Inorg. Chim. Acta*, **77**(3), L89–L93.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shimizu, S., Shiratori, K., Hisada, S., Takayama, Y., Kobayashi, M. & Takeuchi, T. (2002). *Pancreatology*, **2**, 217–361.

Vicini, P., Geronikaki, A., Anastásia, K., Incertia, M. & Zani, F. (2006). *Bioorg. Med. Chem.* **14**, 3859–3864.

Warden, A. C., Warren, M., Hearn, M. T. W. & Spiccia, L. (2004). *New J. Chem.* **28**, 1301–1308.