

## 2,3-Dihydro-1,3-benzothiazol-2-iminium hydrogen oxydiacetate: a combined structural and theoretical study

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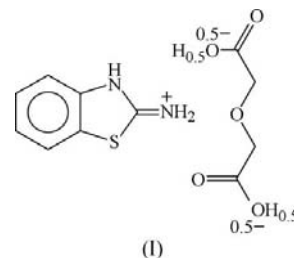
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In the title compound,  $C_7H_7N_2S^+ \cdot C_4H_5O_5^-$ , the ions are connected by  $N-H \cdots O$  hydrogen bonds. The hydrogen oxydiacetate residues are linked together by  $O-H \cdots O$  hydrogen bonds disordered about centres of inversion into hydrogen-bonded ribbon layers crosslinked by weak  $C-H \cdots O$  and stacking interactions. The cation exists mainly in the 2,3-dihydro-1,3-benzothiazol-2-iminium form, with a small participation of the 2-aminobenzothiazolium form, based on the structural data and quantum mechanical calculations. This study provides structural insights relevant to the biochemical activity of benzothiazole molecules.

### Comment

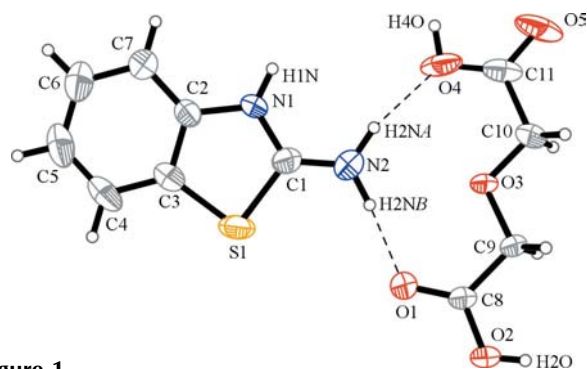
Benzothiazole derivatives possess antitumour properties (Jin *et al.*, 2006; Mortimer *et al.*, 2006; Akhtar *et al.*, 2008). The precise mechanism of action for these selectively acting compounds has not yet been identified (O'Brien *et al.*, 2003; Choi *et al.*, 2006). It has been postulated that benzothiazoles are metabolized to as-yet unidentified reactive species, which then form DNA adducts provoking cancer cell death. Knowledge of geometric parameters, the primary sites available for noncovalent interactions, charge distribution, stereoelectronic properties and conformational flexibility is helpful in determining the mechanism of drug molecular interactions. Since 2-aminobenzothiazole is often used as a model for complex biologically active molecules (Padilla-Martínez *et al.*, 2003), the crystal structure of its adduct with oxydiacetic acid, *viz.* the title compound, (I), as well as the results of quantum mechanical calculations, are reported here. This dicarboxylic acid was chosen because it contains different hydrogen-bond donor/acceptor groups (two carboxyl groups and one ether O atom), which may serve for the better understanding of macromolecules containing these functional groups.

One of the oxydiacetic acid H atoms is transferred to the 2-aminobenzothiazole molecule, so that the asymmetric unit of (I) consists of a 2-aminobenzothiazolium ion and oxydiacetic acid in the monoionized state, *i.e.* as hydrogen oxydiacetate (Fig. 1). The oxygen-bonded H atoms (H2O and H4O) of the hydrogen oxydiacetate anion are disordered (by symmetry centres) over two positions. The cation is slightly distorted from planarity, with the largest deviation being for atom N2 [0.0205 (11) Å] from the weighted least-squares plane calculated through all non-H atoms of the cation. Each of the five- and six-membered rings of the cation is planar and

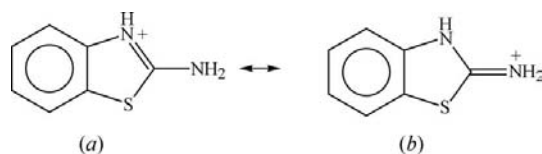


they are inclined at  $0.92 (8)^\circ$  to each other. The anion is also close to planarity, but the distortion is larger than in the cation, with a maximum deviation of  $0.0742 (12) \text{ \AA}$  for atom O5. The 2-aminobenzothiazolium and hydrogen oxydiacetate ions are almost coplanar, with an interplanar angle of  $6.69 (5)^\circ$ .

The bond distances and angles within the anion show no unusual values (Table 1). The bond lengths and angles of the 2,3-dihydro-1,3-benzothiazol-2-iminium cation are within the ranges reported for its adducts with organic anions (Lynch *et al.*, 1998, 1999; Smith *et al.*, 1999), and are close to these of pure 2-aminobenzothiazole (ABT) (Goubitz *et al.*, 2001). In comparison with ABT, the C2–N1, S1–C3 and C1–N2 bonds of (I) are shortened insignificantly [by  $0.012 (11)$ ,  $0.017 (9)$  and  $0.035 (12) \text{ \AA}$ , respectively], while the C1–N1 bond is elongated by  $0.049 (8) \text{ \AA}$  (the C1–S1 bond has the same length in both compounds). For similar 2-amino heterocyclic compounds, shortening of the C–NH<sub>2</sub> bond has been explained by the attraction of a more electron-accepting heterocyclic ring (Lynch & Jones, 2004). The C1–N2 distance



**Figure 1**  
A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The H2O and H4O atoms have site occupancies of 0.5. Hydrogen bonds are indicated by dashed lines.



**Figure 2**  
(a) The endocyclic and (b) the exocyclic iminium resonance forms of the cation of (I).

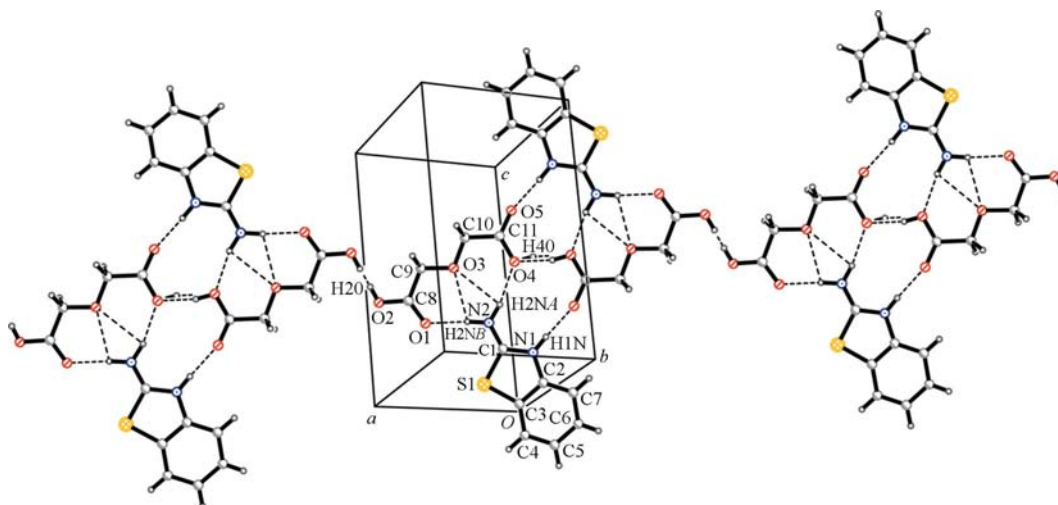
(Table 1) is close to that of exocyclic C=N double bonds found in iminobenzothiazole derivatives (Garcia-Hernandez *et al.*, 2006; Shi *et al.*, 2003; Tellez *et al.*, 2004). These observations point to a significant contribution of the exocyclic iminium resonance form, *i.e.* the 2,3-dihydro-1,3-benzothiazol-2-iminium ion (Fig. 2*b*), to the overall molecular electronic structure, with a lesser contribution from the 2-amino-benzothiazolium form (Fig. 2*a*). Thus, (I) is the first reported example of a compound containing the 2,3-dihydro-1,3-benzothiazol-2-iminium ion. Exocyclic imines or iminium ions in equilibrium with endocyclic ones have previously been found and discussed for other compounds containing the  $N_{\text{exo}}CN_{\text{endo}}$  group (Lynch & Jones, 2004; Lynch *et al.*, 2000; Low *et al.*, 2003; Donga *et al.*, 2002).

The 2,3-dihydro-1,3-benzothiazol-2-iminium cations and hydrogen oxydiacetate anions of (I) are linked by imine-carboxylate N—H...O hydrogen bonds (Table 2), forming  $N_2R_2^2(10)$ ,  $N_2R_4^4(16)$  and  $N_2R_4^4(24)$  rings (Bernstein *et al.*, 1995). The small N2—H2NA...O3 and N2—H2NB...O3 angles, the existence of imine-carboxylate N2—H...O hydrogen bonds and the weak (in comparison with carboxylate O atoms) electron-donating properties of the ether O atoms indicate that the N2—H...O3 interactions are forced by the relative arrangement of the ions. Additionally, between the hydrogen oxydiacetate anions there are O—H...O hydrogen bonds disordered about centres of inversion, which generate the (averaged)  $N_2C_4^4(16)$  chain structure (Fig. 3). Hydrogen oxydiacetate anions linked end-to-end by hydrogen bonds have been observed in two structures to date, namely

ammonium hydrogen oxydiacetate (Herbertsson & Hedman, 1982) and pentane-1,5-diammonium bis(oxydiacetate) monohydrate (Urbanczyk-Lipkowska, 2000). The above-mentioned interactions link the molecules into hydrogen-bonded ribbons parallel to the  $(12\bar{1})$  plane and these ribbons extend along the  $[2\bar{1}0]$  axis.

An interesting feature of the structure of (I) is the presence of weak  $\pi$ – $\pi$  stacking interactions (along the  $[010]$  axis) between the almost parallel [inclined at  $0.92(8)^\circ$ ] five-membered heterocyclic and benzene rings of adjacent 2,3-dihydro-1,3-benzothiazol-2-iminium ions oriented in opposite directions [symmetry codes:  $(-x, -y, -z)$  and  $(-x, -y + 1, -z)$ ]. The perpendicular distances between the first ring centroid and that of the second ring are 3.964 (3) and 3.805 (3) Å, and the angles between the vector linking the ring centroids and the normal to the five-membered ring plane are  $26.7(2)$  and  $24.5(2)^\circ$ , respectively. The molar enthalpy of the  $\pi$ – $\pi$  stacking interaction, as calculated by the total self-consistent field energy method (for two interacting cations) is  $1.4 \text{ kcal mol}^{-1}$  ( $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$ ), including a basis set superposition error calculated by the counterpoise method of Boys & Bernardi (1970). Moreover, there are two short C—H...O contacts in the structure which, according to Desiraju & Steiner (1999), can be classified as weak hydrogen bonds (Table 2). These weak C—H...O hydrogen-bond and  $\pi$ – $\pi$  stacking interactions thus provide some linkage between the hydrogen-bonded ribbons.

The molecular electronic properties of (I) have been calculated at a single point for both diffraction-derived coordinates and the optimized structure. Sets containing from one to four cation–anion pairs were used for the calculations. The cation and anion of each pair were arranged as in the asymmetric unit and then the second and following pairs were added one by one to the first pair along the crystallographic  $[2\bar{1}0]$  axis (*i.e.* along the chain created by anions linked by O—H...O hydrogen bonds). The B3LYP functional (Becke, 1993; Lee *et al.*, 1988) in the triple- $\zeta$  6-31++G(d,p) basis set was used, as implemented in GAUSSIAN03 (Frisch *et al.*, 2004).



**Figure 3**  
Part of the packing of molecules in (I). Dashed lines indicate close interactions (see *Comment*).

The differences in electronic properties and energies originating from the different numbers of molecules used in the calculations are given in parentheses (as standard deviations) in Table 2. For example, the N2—H2NB···O1 hydrogen-bond energy calculated for one cation–anion pair was slightly different than the two energies calculated for the set containing two pairs (with three energies calculated for the set containing three pairs, and so on). Thus, for all calculations, ten values were obtained. The arithmetic mean and standard deviation of this ten-element discrete data set were then calculated. Where no deviation is given, the values were the same within the range of reported precision.

The atomic charges were calculated according to natural population analysis (NPA) (Foster & Weinhold, 1980; Reed & Weinhold, 1985; Reed *et al.*, 1988), Merz–Kollman–Singh (MKS) (Singh & Kollman, 1984; Besler *et al.*, 1990) and Breneman (Breneman & Wiberg, 1990) schemes. Although the calculation of effective atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems, the unambiguous dividing up of the overall molecular charge density in atomic contributions is still an unresolved problem, and none of the known procedures give fully reliable values of atomic charges. Thus, a discussion of atomic charges should cover more than one algorithm used for charge density division (Table 3). Generally, it can be stated that less reliable values are given by the Mulliken population analysis and more reliable results are provided by the Breneman method [for a detailed discussion of the methodology and reliability of the methods used, see Martin & Zipse (2005), and references therein]. The results show that, in general, the atomic charges do not depend on the method used for calculation (Table 3). Both N atoms are negatively charged, but the NH group of the thiazole ring has a negative group charge, whereas the NH<sub>2</sub> group has a positive group charge. Such distribution of charges can be observed only in the 2,3-dihydro-1,3-benzothiazol-2-iminium ion (Fig. 2*b*), so these calculated values confirm the postulate about the dominance of the exocyclic iminium resonance form.

To determine the multiplicity of the C—N bonds in (I), the bond orders were calculated by means of the bond-valence method (BVM) (Brown, 2002; Mohri, 2000) using the Brown–Altermatt equation (Brown & Altermatt, 1985)  $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ . The bond-valence parameters  $R_{ij}$  taken as mean single-bond lengths are 1.47, 1.35 and 1.75 Å for exocyclic C—N, endocyclic C—N and endocyclic C—S bonds, respectively. The BVM bond orders are then 1.06, 1.58 and 1.04 v.u. (valence units), respectively, for the C1—N1, C1—N2 and C1—S1 bonds, which suggests a considerable degree of double-bond character between atoms C1 and N2. The natural localized molecular orbital bond order (Reed & Schleyer, 1988, 1990) is 0.952 for the C1—N1 bond, 0.968 for S1—C1 and 1.262 for C1—N2. The Wiberg bond indexes (Wiberg, 1968) are higher (1.217, 1.179 and 1.438, respectively) but exhibit similar dependence. Moreover, natural bond orbital (NBO) analysis shows that there are two C1—N2 bonding orbitals ( $\sigma$  and  $\pi$ ) occupied by 1.991 and 1.993 electrons, respectively, and only one C1—N1 bonding orbital occupied

by 1.986 electrons. These observations clearly indicate that  $\pi$ -electron density is localized in the exocyclic rather than heterocyclic C—N bond, and again confirms that the resonance equilibrium is largely shifted towards the exocyclic iminium resonance form. It is worth mentioning that during the geometry optimization process, one H atom of the imine group migrated to the hydrogen oxydiacetate anion, forming the adduct of 2-imino-2,3-dihydro-1*H*-benzothiazole and oxydiacetic acid.

The energies of the hydrogen bonds calculated in terms of an NBO energetic analysis (Foster & Weinhold, 1980; Reed & Weinhold, 1985; Reed *et al.*, 1988) are presented in Table 2. In general, the values obtained lie in ranges typical for similar hydrogen bonds (Desiraju & Steiner, 1999). The small energy values of both the N2—H2NA···O3 and N2—H2NB···O3 hydrogen bonds (entries 4 and 5, Table 2) confirm that these are fortuitous interactions forced by the relative arrangement of the ions. It is noteworthy that the energy of the two seemingly similar O—H···O hydrogen bonds differs by about 19 kcal mol<sup>-1</sup>. This originates from the arrangement of the H atoms towards the anion backbone (*cis* for H<sub>2</sub>O and *trans* for H<sub>4</sub>O). Thus, in both cases, the distance between donor and acceptor is short enough to allow interaction, but the unfavorable arrangement of orbitals (electron lone pairs of the O atom) leads to a decrease in the O<sub>4</sub>—H<sub>4</sub>O···O<sub>4</sub><sup>i</sup> bond strength (entry 7, Table 2).

## Experimental

An ethanolic solution (2 ml) of 2-aminobenzothiazole (0.150 g, 1 mmol) was mixed with a hot aqueous solution (5 ml) of oxydiacetic acid (0.270 g, 2 mmol). The resulting solution was allowed to cool to room temperature and, after several days, colourless crystals of (I) suitable for X-ray diffraction were separated (yield 76%).

### Crystal data

C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> <sup>+</sup> ·C <sub>7</sub> H <sub>7</sub> N <sub>2</sub> S <sup>-</sup>	$\gamma = 85.364 (3)^\circ$
$M_r = 284.29$	$V = 618.16 (5) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.0414 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.6933 (3) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$c = 11.4621 (6) \text{ \AA}$	$T = 291.0 (3) \text{ K}$
$\alpha = 87.216 (3)^\circ$	$0.38 \times 0.08 \times 0.08 \text{ mm}$
$\beta = 89.845 (3)^\circ$	

### Data collection

Kuma KM-4-CCD diffractometer	6112 measured reflections
Absorption correction: numerical ( <i>X-RED</i> ; Stoe & Cie, 1999)	2182 independent reflections
$T_{\min} = 0.967$ , $T_{\max} = 0.979$	1662 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

**Table 1**  
Selected bond lengths (Å).

N1—C1	1.327 (2)	O1—C8	1.2267 (19)
N1—C2	1.393 (2)	C8—O2	1.283 (2)
C1—N2	1.299 (2)	O4—C11	1.283 (2)
C1—S1	1.7360 (18)	C11—O5	1.222 (3)
S1—C3	1.7544 (18)		

**Table 2**

Hydrogen-bond geometry (Å, °) and molar enthalpy  $E$  (kcal mol<sup>-1</sup>) calculated on the NBO basis.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$	$E^\ddagger$
N1—H1N $\cdots$ O5 <sup>i</sup>	0.87	1.82	2.691 (2)	174	14.2 (1)
N2—H2NA $\cdots$ O4	0.94	1.97	2.872 (2)	161	9.4 (3)
N2—H2NB $\cdots$ O1	0.94	1.82	2.753 (2)	171	21.7 (9)
N2—H2NA $\cdots$ O3	0.94	2.56	2.833 (2)	97	0.2
N2—H2NB $\cdots$ O3	0.94	2.41	2.833 (2)	107	0.8
O2—H2O $\cdots$ O2 <sup>ii</sup>	0.80	1.68	2.467 (2)	168	34.6 (6)
O4—H4O $\cdots$ O4 <sup>i</sup>	0.84	1.65	2.474 (2)	167	15.9 (4)
C10—H10B $\cdots$ O1 <sup>iii</sup>	0.97	2.66	3.446 (2)	138	0.03
C4—H4 $\cdots$ O1 <sup>iv</sup>	0.93	2.63	3.534 (2)	164	0.03

† For numbers in brackets (and a discussion of the N—H $\cdots$ O3 interactions) see *Comment*. Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + 2, -y, -z + 1$ ; (iii)  $-x + 1, -y, -z + 1$ ; (iv)  $-x + 1, -y, -z$ .

**Table 3**

Calculated atomic charges for an isolated molecule of (I) (atomic units).

1 Atomic unit = 1.60217653 (14)  $\times 10^{-19}$  Coulombs. See *Comment* for a detailed description of the abbreviations and methods used.

Atom/group	NPA charge	NPA group charge	Breneman charge	Breneman group charge	MKS charge	MKS group charge
N1/NH	-0.526	-0.124	-0.623	-0.158	-0.518	-0.075
H1N	0.402		0.465		0.443	
N2/NH2	-0.695	0.196	-0.661	0.044	-0.570	0.056
H2NA	0.425		0.360		0.335	
H2NB	0.466		0.345		0.291	

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.091$   
 $S = 1.02$   
 2182 reflections

172 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.15 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$

The carbon-bonded H atoms were placed in calculated positions, while the other H atoms were found from difference Fourier syntheses after eight cycles of anisotropic refinement. The isotropic displacement parameters of these latter H atoms were then refined to check the correctness of their positions. After eight cycles, the refinement reached stable convergence with isotropic displacement parameters of 0.061, 0.053, 0.079, 0.133 and 0.128 Å<sup>2</sup>, respectively, for H1N, H2NA, H2NB, H2O and H4O. The relatively large values of the isotropic displacement parameters of the oxygen-bonded H atoms suggested that these atoms, placed on symmetry centres on the basis of difference Fourier synthesis, might be in the wrong positions (the O2—H2O and O4—H4O distances were 1.23 and 1.24 Å, respectively). Atoms H2O and H4O were therefore manually shifted off the special positions (with sites occupancies set to 0.5). Refinement of this model converged with isotropic displacement parameters adopting more reasonable values (0.057 and 0.058 Å<sup>2</sup> for H2O and H4O, respectively) and with acceptable though short O—H bonds distances (Table 2). So in the final model, atoms H2O and H4O atoms were set as equally disordered (by symmetry) over two positions. We note that difference Fourier maps show maxima at symmetry centres with slightly elongated shoulders along the O $\cdots$ O lines. Because elongation can be caused by polarization of the electron density by the O atoms, there is a distinct possibility that oxygen-bonded H

atoms are ordered and reside at symmetry centres inside or outside the crystalline state. Thus, the existence of symmetric hydrogen bonds cannot be categorically excluded without supporting neutron diffraction data. Additionally we note the presence of windows (Albert, 1961) in the IR spectrum of (I) (at 821 and 849 cm<sup>-1</sup>) which also suggests symmetric O—H $\cdots$ O hydrogen bonds. All H atoms were refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$ . The 001 reflection, affected by the beam stop ( $F_o^2 = 0.00$  and  $F_c^2 = 65.91$ ), was excluded from the refinement.

Data collection: *CrysAlis CCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 2008) and *ORTEP-3* (Version 1.062; Farrugia 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3105). Services for accessing these data are described at the back of the journal.

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