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A new sulfate acid polymorph of 1,3-dihydrobenzotriazole

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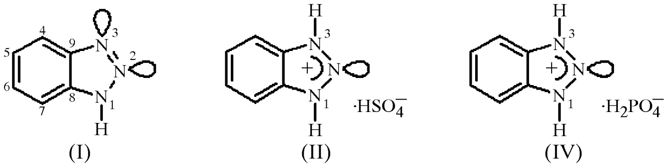
A new sulfate acid polymorph of 1,3-dihydrobenzotriazole, *viz*. 1,3-dihydrobenzotriazolium hydrogensulfate, $C_6H_6N_3^+\cdot HSO_4^-$, differs from an existing polymorph in that the polymeric interaction between the HSO_4^- anions, together with different classical (D—H$\cdots$$A$) and nonclassical (C—H$\cdots$$A$) interactions, changes the space group.

Comment

Heterocyclic compound (I) (see scheme) contains acidic H atoms and N atoms with lone electron pairs. The presence of both acidic and basic characteristics gives the molecule the ability to participate in a wide variety of interactions. Moreover, tautomerism in (I) can change the reactivity depending on the starting material (Jagerovic *et al.*, 2002; Katritzky *et al.*, 1998; Gallinek, 1897; Elderfiel, 1957). This diversity gives rise to the possibility of different structural arrangements or polymorphs. For aliphatic amines this outcome is expected, but in this case the molecule is planar and polymorphs are not common (Blagden & Davey, 2003; Davey, 2003; Mak & Zhou, 1992; Dunitz, 1979).



The title compound, (II), crystallized in the monoclinic space group $P2_1/c$ from a mixture of tetrahydrofuran (THF) and hexane. The structure (Fig. 1) shows the presence of acidic H atoms on atom N3 and on the HSO_4^- counter-ion. The crystal packing (Fig. 2) is structured by classical and nonclassical hydrogen bonds, the most important of which are listed in Table 1. Three of these are classical hydrogen bonds (N—H$\cdots$O), while the others are nonclassical (C—H$\cdots$O). Two particularly strong interactions are H3$\cdots$O4 and H1$\cdots$O3. Some of the hydrogen bonds are complex. For example, the N1—H1 group is considered a bifurcated donor because it interacts with atoms N2 and O3. Atom O2 is considered as a trifurcated acceptor because it interacts with the C6—H6, C4—H4 and C7—H7 bonds. All such interactions are important because they contribute to the geometry of the lattice. The HSO_4^- ions are joined together by strong O—H$\cdots$O═S hydrogen bonds that are nearly ideal in geometry (Steiner, 1998, 2002; Jeffrey, 1997).

As a result of these interactions, the 1,3-dihydrobenzotriazolium cations pack in a herring-bone pattern in the *ab* plane with the hydrogensulfate anions interspersed (Fig. 3). A polymorphic structure of (II) was reported by Giordano (1980), which crystallizes in the orthorhombic space group *Pbcn*. The phosphoric acid salt of 1,3-dihydrobenzotriazole, (IV), is also known (Emsley *et al.*, 1988) and crystallizes in the triclinic space group $P\overline{1}$ with similar packing to (II).

In Table 2, the bond distances for polymorphs (II) and (III) (Giordano, 1980) and compound (IV) (Emsley *et al.*, 1988) are compared. Polymorphs (II) and (III) show similar bond distances, while in (IV) they are slightly longer. It can also be

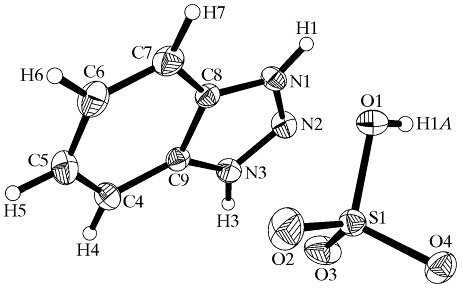


Figure 1
A view of the molecule of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

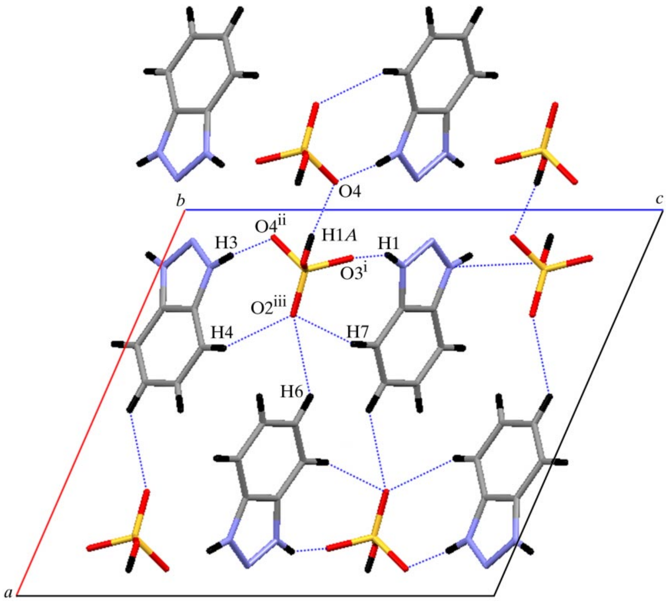


Figure 2
The polymeric arrangements in (II), formed by classical and nonclassical hydrogen bonds (dotted lines). The view is along the *b* axis. [Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.]

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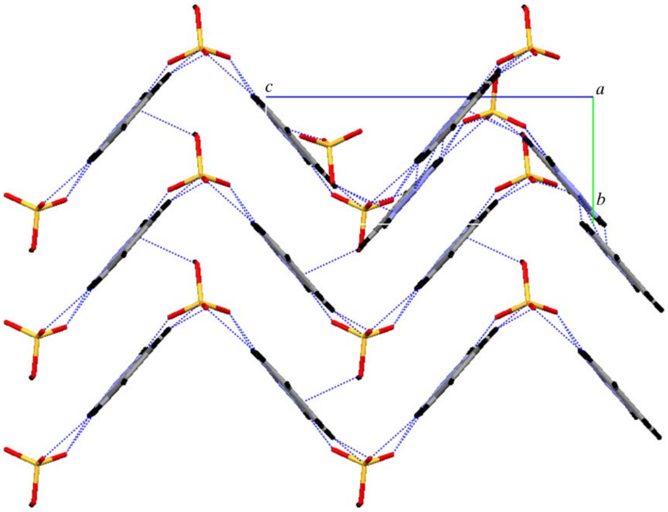


Figure 3
The herring-bone arrangement formed by classical and nonclassical hydrogen bonds (dotted lines) in the crystalline network of (II). The view is along the *a* axis.

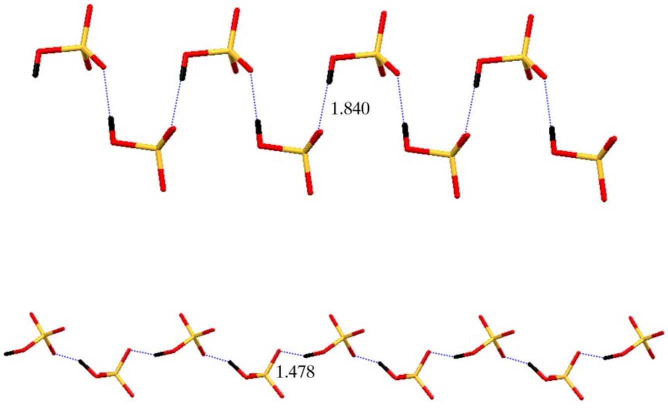
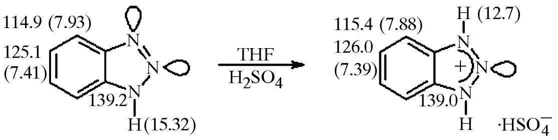


Figure 4
Hydrogen bonds (in Å) between HSO_4^- anions in (II) (upper figure; this work) and (III) (lower figure; Giordano, 1980).

observed that the distances decrease in the crystal system order *triclinic* → *monoclinic* → *orthorhombic*. This reflects better packing as the symmetry increases. Fig. 4 shows the rearrangement of the HSO_4^- anion corresponding to polymorphs (II) and (III). The $S-O-H\cdots O{=}S$ hydrogen bond [1.84 (4) and 1.478 Å] is in fact the reason that the HSO_4^- ions stay together in the supramolecular polymeric structure. We can conclude that these interactions are stronger in (III) than in (II). Consequently, the chains in (III) have an almost linear shape, while those in (II) have a zigzag shape, and the distances are shorter, stronger and more efficient in the orthorhombic lattice in (III) compared with the monoclinic lattice in (II).

Experimental

A mixture of (I) (400 mg, 3.36 mmol) and dry THF (10 ml) was cooled to 223 K; H_2SO_4 (0.18 ml, 329 mg, 3.36 mmol) was added and the mixture was stirred for half an hour. The mixture was then filtered and the white powdered product (II) (98% yield, m.p. 437–439 K) was partially dissolved for crystallization in a THF/hexane mixture. *m*/*z* (intensity, %): 207 (1), 133.35 (100), 105 (100). IR (KBr), $\nu_{\max}$: 2100–3600 (OH), 3300 (NH), 1723 (N=N), 1612 (C=C). Analysis calculated: C 33.18, H 3.25, N 19.35, S 14.76%; observed: C 33.53, H 3.30, N 19.02, S 13.24%. The structure of (I) (see scheme below) was analyzed by ^1H and ^{13}C NMR spectroscopy, which showed a symmetrical molecule, three signals for ^1H and four for ^{13}C. The N—H chemical shift in (II) was shifted to lower frequency (2.62 p.p.m.) compared with N—H for (I). Double protonation was not observed for (I); in fact, atom N2 is not a basic position, because no different –NH signal was observed in the ^1H NMR spectrum. No significant changes were observed in the ^{13}C NMR spectrum because there were no changes in the aromatic ring.



(I) (II)

Crystal data

$C_6H_6N_3^+\cdot HSO_4^-$
$M_r = 217.21$
Monoclinic, $P2_1/c$
$a = 12.715$ (3) Å
$b = 5.133$ (1) Å
$c = 14.406$ (4) Å
$\beta = 113.63$ (1)°

$V = 861.4$ (4) Å^3
$Z = 4$
Mo *K*α radiation
$\mu = 0.37$ mm^{-1}
$T = 273$ (2) K
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.913$, $T_{\max} = 0.930$

9336 measured reflections
1969 independent reflections
1637 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.095$
$S = 1.07$
1969 reflections

156 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3$^{\rm i}$	0.83 (2)	1.93 (3)	2.695 (2)	153 (2)
O1—H1*A*···O4$^{\rm ii}$	0.82 (4)	1.84 (4)	2.659 (2)	173 (3)
N3—H3···O4	0.87 (3)	1.93 (3)	2.792 (2)	173 (3)
C4—H4···O2	0.90 (2)	2.48 (3)	3.269 (3)	146 (2)
C6—H6···O2$^{\rm iii}$	0.96 (3)	2.57 (3)	3.306 (3)	133.7 (19)

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

All H atoms were refined freely [C—H = 0.90 (2)–0.97 (3) Å].

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

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Table 2

Comparison of selected of bond distances (Å) of (II), (III) and (IV).

	(II)[a]	(III)[b]	(IV)[c]
N1—N2	1.315 (2)	1.310	1.317 (3)
N2—N3	1.311 (2)	1.312	1.314 (3)
C4—C5	1.364 (3)	1.365	1.368 (4)
C5—C6	1.406 (3)	1.416	1.414 (4)
C6—C7	1.369 (3)	1.356	1.370 (4)
C7—C8	1.397 (3)	1.391	1.402 (4)
C8—C9	1.389 (2)	1.391	1.390 (3)
C4—C9	1.404 (3)	1.392	1.400 (4)
C9—N3	1.363 (3)	1.367	1.364 (3)
C8—N1	1.358 (3)	1.362	1.365 (3)
O1—S1	1.5576 (17)	1.539	–
O2—S1	1.4179 (18)	1.431	–
O3—S1	1.4453 (17)	1.435	–
O4—S1	1.4696 (14)	1.449	–

Notes: (*a*) this work, monoclinic; (*b*) Giordano (1980), orthorhombic; (*c*) Emsley *et al.* (1988), triclinic.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3078). Services for accessing these data are described at the back of the journal.

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