Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.065$
$S = 0.989$
3112 reflections
239 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.077$

$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.0039 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C14	1.356 (4)	C4—C7	1.460 (4)
N—C6	1.331 (4)	C7—C8	1.325 (4)
N—C2	1.341 (4)	C8—C9	1.462 (4)
N—C1	1.477 (4)		
C5—C4—C3	116.0 (3)	C14—C9—C10	116.9 (3)
C3—C4—C7	124.0 (3)	C14—C9—C8	125.5 (3)
C8—C7—C4	124.6 (3)	O1—C14—C13	120.9 (3)
C7—C8—C9	129.6 (3)	O1—C14—C9	118.2 (3)
C5—C4—C7—C8	−178.9 (3)	C7—C8—C9—C10	−179.3 (3)
C4—C7—C8—C9	179.5 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O2	2.677 (3)	172.5 (6)
O2—H2O···I^{i}	3.425 (5)	160.8 (3)
O1—H1O···O2^{ii}	3.520 (6)	100.9 (5)

Symmetry codes: (i) $-1 - x, 1 - y, -z$; (ii) $-1 - x, 1 - y, -1 - z$.

The title structure was solved by direct methods. Except for the H atoms on C1 and C15, which were placed in calculated positions and not refined, all other H atoms were located from difference maps and their displacement parameters refined isotropically. During refinement, the C—H distances and H—C—H angles were restrained to be 0.96 Å and 109.5°, respectively. $U_{\rm iso}$ values were in the range 0.049 (8)–0.17 (3) Å^2.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1059). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. XCVIII.[†] 1,2-Benzenedisulfonylamine Acetonitrile Solvate (1/1)

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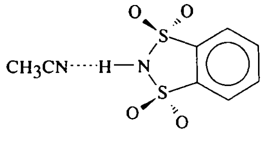
Abstract

In the 1:1 acetonitrile solvate of 1,3,2-benzodithiazole-1,1,3,3-tetrone, $C_6H_5NO_4S_2.C_2H_3N$, the nitrile molecule is linked to the NH function by a slightly bent N—H···N hydrogen bond of medium strength [H···N 1.99 (3) and N···N 2.834 (3) Å]. One methyl H atom forms a three-centre C—H···O bond to different symmetry-related formula units. The five-membered heterocycle possesses an envelope conformation, the N atom deviating by 0.358 (2) Å from the mean plane of the C_6S_2 moiety.

Comment

Molecules containing the $(SO_2)_2NH$ moiety are strong NH acids (*e.g.* Dauphin & Kergomard, 1961; Ali *et al.*, 1980; Foropoulos & DesMarteau, 1984). With appropriate bases *B*, they either form onium salts $B\mathrm{H}^+.(X\mathrm{SO}_2)_2\mathrm{N}^-$ (Henschel, 1996, and references therein) or uncharged hydrogen-bonded complexes $(X\mathrm{SO}_2)_2\mathrm{N}$—H···*B*. Among the latter class of compounds, crystal structures presently known involve a variety of O-atom acceptors; see, for example, $B = H_2O$ (Attig & Mootz, 1975), Ph_3PO (Blaschette *et al.*, 1990), Me_2SO (Schomburg, Blaschette & Schulte-Körne, 1990; Blaschette *et al.*, 1993) and 18-crown-6 (Blaschette *et al.*, 1994; Henschel *et al.*, 1995). We now report the first structure of such a complex, (1), in which the N atom of a nitrile function acts as the hydrogen-bond acceptor.

[†] Part XCVII: Henschel, Wijaya, Moers, Blaschette & Jones (1997).



(1)

A single crystal of the markedly unstable title adduct was accidentally formed (see *Experimental*) and characterized by low-temperature X-ray diffraction. The asymmetric unit is shown in Fig. 1 (selected intramolecular geometric data in Table 1 and hydrogen-bonding geometry in Table 2). The donor molecule (HZ) is connected to the N atom of the nitrile *via* an asymmetric and slightly bent N—H···N hydrogen bond of medium strength [*cf.* van der Waals distances H···N 2.74 and N···N 3.08 Å (Emsley, 1991)]. The orientation of the nitrile with respect to the S1, N1, S2 plane is described by the angles C98—N99···N1, S1—N1···N99 and S2—N1···N99 of 156.53 (19), 110.36 (10) and 118.98 (10)°, respectively. One H atom of the nitrile forms a nearly symmetric three-centre C—H···O bond to two adjacent HZ units.

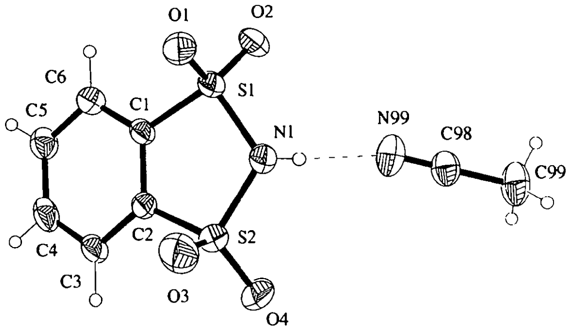


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

The geometry of HZ in (1) does not differ significantly from that of the uncomplexed compound (Blaschette *et al.*, 1997; this publication will discuss an extensive series of related structures with no complicating features such as solvent of crystallization). In both structures, the molecule approximates to C_s symmetry with σ_v perpendicular to the NS_2 triangle. The C—C distances range from 1.379 (3) to 1.390 (3) Å and the C—C—C angles from 117.5 (2)° at C3 to 121.5 (2)° at C4. The C atoms are coplanar within ±0.007 (1) Å. In contrast to the related structures of *o*-sulfobenzoic imide (saccharin) (Bart, 1968; Okaya, 1969) and phthalimide (Matzat, 1972; Ng, 1992), where the six- and five-membered fused rings are essentially coplanar, the five-membered ring in (1) adopts an envelope conformation. The hetero atoms S1, S2 and N lie 0.004 (1), −0.049 (1) and 0.358 (2) Å, respectively, out of the least-squares plane of the C_6S_2 moiety, and the acidic H atom deviates by 1.18 (3) Å from the same reference plane.

It is of interest that the conjugate anions Z^-, as observed in $[Ca(H_2O)_7]^{2+}.2Z^-$ (Moers, Blaschette & Jones, 1997), are nearer to planarity than HZ in the present structure. Moreover, the anions display markedly shorter N—S bonds (*ca* 1.59 Å), longer S—O bonds (*ca* 1.44 Å) and smaller O—S—O angles (*ca* 114°). Similar effects occurring on deprotonation have frequently been observed for acyclic disulfonylamines (Bombicz *et al.*, 1996).

Experimental

A crystal of (1) originated *via* an unspecified protolysis process in the course of a silver salt metathesis using equimolar amounts of AgZ and 2-bromo-1,3,2-benzodioxaborole in 'dry' acetonitrile (20 h, 225 → 300 K). The stoichiometric amount of AgBr was removed by filtration, the solution reduced to a small volume and kept at 253 K for 24 h, when colourless crystals separated. A suitable crystal was selected from the mother liquor and without delay subjected to the structure determination. All attempts to isolate (1) in bulk quantities failed; recrystallizing HZ from MeCN and drying the crystals for a few minutes *in vacuo* at ambient temperature resulted in pure uncomplexed HZ (^{1}H NMR evidence).

Crystal data

$C_6H_5NO_4S_2.C_2H_3N$
$M_r = 260.28$
Triclinic
$P\bar{1}$
$a = 7.372\ (5)$ Å
$b = 7.688\ (5)$ Å
$c = 10.760\ (8)$ Å
$\alpha = 83.56\ (5)°$
$\beta = 81.60\ (4)°$
$\gamma = 67.46\ (4)°$
$V = 556.2\ (7)$ Å^3
$Z = 2$
$D_x = 1.554$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 52 reflections
$\theta = 10.0–11.5°$
$\mu = 0.478$ mm^{-1}
$T = 143\ (2)$ K
Block
0.5 × 0.4 × 0.4 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
3740 measured reflections
2543 independent reflections
2153 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$

$\theta_{max} = 27.50°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.090$
$S = 1.071$
2543 reflections
151 parameters
H atoms: see below

$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 0.309$ e Å^{-3}
$\Delta\rho_{min} = -0.320$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.012 (3)

$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.3251P]$ where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—S2	1.661 (2)	S1—C1	1.761 (2)
N1—S1	1.664 (2)	S2—O4	1.421 (2)
S1—O1	1.422 (2)	S2—O3	1.424 (2)
S1—O2	1.424 (2)	S2—C2	1.760 (2)
S2—N1—S1	113.26 (11)	O4—S2—C2	112.69 (11)
O1—S1—O2	119.19 (10)	O3—S2—C2	107.71 (11)
O1—S1—N1	109.37 (10)	N1—S2—C2	96.73 (10)
O2—S1—N1	107.07 (10)	C2—C1—S1	113.15 (16)
O1—S1—C1	109.07 (10)	C6—C1—S1	125.62 (15)
O2—S1—C1	112.70 (10)	C1—C2—S2	113.49 (15)
N1—S1—C1	97.10 (10)	C3—C2—S2	125.09 (17)
O4—S2—O3	120.04 (12)	H01—N1—S1	108 (2)
O4—S2—N1	108.06 (11)	H01—N1—S2	114 (2)
O3—S2—N1	109.05 (11)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···N99	0.86 (3)	1.99 (3)	2.834 (3)	169 (3)
C99—H99C···O3^{i}	0.98	2.70	3.488 (4)	138
C99—H99C···O4^{ii}	0.98	2.65	3.418 (3)	136

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

The methyl group was refined as a rigid group allowed to rotate but not tip, the NH H atom was refined freely, and other H atoms were treated as riding.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1377). Services for accessing these data are described at the back of the journal.

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A π-Stacked Complex Between 4,4′-Dimethyl-4,4′-bipyridinium Bis(hexafluorophosphate) and 1,5-Bis[(hydroxyethoxy)ethoxy]naphthalene

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Abstract

The title π-electron-rich naphthalene-containing polyether {alternative name: 2,2′-[1,5-naphthylenebis(oxyethoxy)]diethanol} forms a 1:1 crystalline complex with the π-electron acceptor 4,4′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate), $C_{12}H_{14}N_2^{2+}.2PF_6^{-}.C_{18}H_{24}O_6$. The molecular packing exhibits extensive intermolecular hydrogen bonding and infinite π-stacking of the complex along the direction of the *b* axis.

Comment

The π-electron-rich molecule 1,5-bis[(hydroxyethoxy)ethoxy]naphthalene, (I), is well known for its propensity to enter into aromatic π–π stacking interactions with π-electron-acceptor bipyridinium-containing compounds (Asakawa *et al.*, 1997). However, the 1:1 complex of