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Polysulfonylamines. CIX.† 1,2,4-Triazolium di(methanesulfonyl)amidate

Oliver Moers, Karna Wijaya, Peter G. Jones* and Armand Blaschette*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

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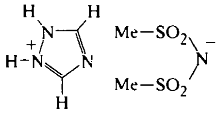
Abstract

The first accurate crystal structure involving the discrete unsubstituted 1,2,4-triazolium cation is reported. In the title salt, $C_2H_4N_3^+\cdot C_2H_6NO_4S_2^-$, the cation is linked to five adjacent anions by a set of N—H···N/O hydrogen bonds and C—H···O interactions, one of the latter being remarkably short and acceptably linear [H···O 2.26 (2), C···O 3.046 (2) Å, C—H···O 161 (2)°]. We suggest on the basis of bond lengths, hydrogen bonding and *U* values that the X-ray structure of $C_2H_4N_3^+\cdot Sb_2F_7^-$ [Udovenko, Gorbunova, Zemnukhova, Mikhailov & Davidovich (1998). *Koord. Khim.* **24**, 655–657; *Russ. J. Coord. Chem.* **24**, 611–613] contains an incorrectly refined cation in which both C atoms have been assigned as N and two N atoms as C.

Comment

The title compound, (I), was investigated as part of a systematic study of hydrogen-bond patterns in crystalline onium di(methanesulfonyl)amidates (Henschel, 1996; Wijaya, 1999). Surprisingly, a search of the October 1998 version of the Cambridge Structural Database (Allen & Kennard, 1993) failed to reveal any crystal structure containing the unsubstituted 1,2,4-triazolium (T^+) cation as a discrete species. Recently we became aware of the X-ray structure of $T^+Sb_2F_7^-$, (II), which mainly focused on the constitution of the fluoroantimonate(III) anion (Udovenko *et al.*, 1998). In this case, published details strongly suggest that the positions of the NH and CH groups in the heterocyclic cation have been erroneously assigned (see below). Thus, in all likelihood, the present result is the first reliable crystal structure of a T^+ salt.



(I)

The formula unit of (I) is shown in Fig. 1. The bond lengths, bond angles and torsion angles of the approximately C_2 symmetric anion are closely similar to those found for the corresponding 1-aza-4-azoniabicyclo[2.2.2]octane salt (Henschel *et al.*, 1997) and will not be rediscussed. Table 1 contains the bond lengths and bond angles of the T^+ heterocyclic ring, which is

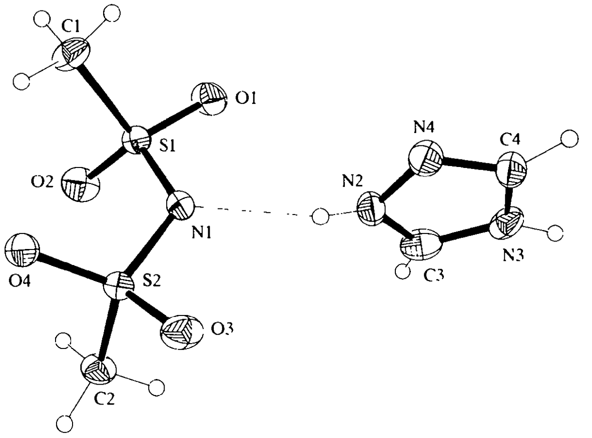


Fig. 1. Structure of the title salt in the crystal. Ellipsoids represent 50% probability levels and H atoms are shown as spheres of an arbitrary radius.

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† Part CVIII: Wirth *et al.* (1998).

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essentially planar (all absolute torsion angles $< 1°$; all deviations from best plane ≤ 0.035 Å). These data do not differ by more than 0.03 Å and 1.5°, respectively, from the corresponding average values calculated for five 3-amino-1,2,4-triazolium structures extracted from the Cambridge Structural Database (refcodes and references: KUFCAP, Byriel *et al.*, 1992; LEJRUN, Lynch *et al.*, 1994; VOYPAA, Li *et al.*, 1992; ZIVROL and ZIVRUR, Smith *et al.*, 1996).

As shown in Fig. 2 and quantified in Table 2, the cation is linked to five adjacent anions by a set of traditional hydrogen bonds and acceptably short C—H···O interactions (for cutoff criteria used in the detection of C—H···O bonds, see Desiraju, 1996; Steiner, 1997; Steiner & Desiraju, 1998). The interionic bonding consists of one N—H···N two-centre bond (N···N 2.76 Å), one N—H···$(O)_2$ three-centre bond (N···O 2.84 and 3.00 Å), one strikingly short and fairly linear C—H···O contact (H···O 2.26, C···O 3.05 Å, C—H···O 161°), and a less pronounced C—H···$(O)_2$ three-centre interaction. Moreover, there exist two longer C—H···N contacts (H···N 2.80 Å) between the unprotonated ring atom N4 and two anions not shown in Fig. 2.

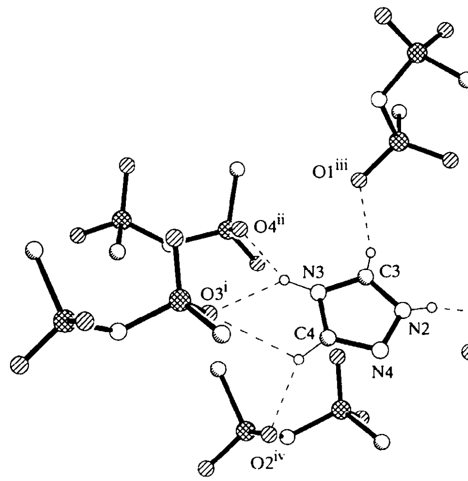

Fig. 2. The environment of the cation in the title salt. Hydrogen bonds are indicated by dashed lines and the symmetry operators are given in Table 2.

Our suspicion that the structure determination of (II) might not be error-free is based on the following facts. First, the bond lengths for the ring sequence (H)N—N—C(H) are given as N—N 1.26 (2) and C—N 1.34 (1) Å, whereas we find N—N 1.362 (2) and C—N 1.294 (2) Å, in good agreement with the aforementioned mean values for 3-amino-1,2,4-triazolium [calculated: N—N 1.381 (4), C—N 1.290 (5) Å]. Secondly, the N—H···F and C—H···F hydrogen-bond geometries reported for (II) are not credible, since the latter are alleged to be much shorter than the former [(C)H···F 1.75–2.00 and C···F 2.72 (1)–2.86 (1) Å *versus* (N)H···F 2.18–2.69 and N···F 3.05 (1)–3.36 (1) Å]. In contrast, all N—H···N/O and C—H···O distances found for (I) lie in plausible ranges (Table 2). Thirdly, the *U* values for the cation C atoms in (II) are low, and those of the relevant N atoms high.

Experimental

To a solution of 1,2,4-triazole (0.21 g, 3.0 mmol) in methanol (5 ml) was added a solution of di(methanesulfonyl)amine (0.52 g, 3.0 mmol) in the same solvent (5 ml). The resulting clear solution was evaporated under reduced pressure at room temperature. After redissolving the colourless solid residue in a minimum amount of acetone, petroleum ether was added to produce a permanent turbidity and the mixture then cooled to 275 K for several days. The crystals, which separated in a yield of 89% (0.65 g), were suitable for X-ray analysis; m.p. 378–383 K. ^{1}H NMR (CD_3CN, 200 MHz): δ 3.90 (*s*, 6H, Me), 9.89 (*s*, 2H, CH), 10.47 p.p.m. (*bs*, 2H, NH). A satisfactory elemental analysis was obtained.

Crystal data

$C_2H_4N_3^+\cdot C_2H_6NO_4S_2^-$
$M_r = 242.28$
Orthorhombic
$Pna2_1$
$a = 7.3239\,(14)$ Å
$b = 9.8199\,(14)$ Å
$c = 13.738\,(3)$ Å
$V = 988.0\,(3)$ Å^3
$Z = 4$
$D_x = 1.629$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 54 reflections
$\theta = 10$–$11.5°$
$\mu = 0.536$ 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
3800 measured reflections
1176 independent reflections (plus 1072 Friedel-related reflections)
2209 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\rm max} = 27.52°$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 7$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.055$
$S = 1.068$
2248 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.0744P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0107 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.05 (5)

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

N2—C3	1.306 (2)	C4—N3	1.349 (2)
N2—N4	1.362 (2)	N3—C3	1.321 (3)
C4—N4	1.294 (2)		
C3—N2—N4	110.99 (15)	N2—C3—N3	107.22 (17)
N4—C4—N3	111.53 (17)	C4—N4—N2	103.76 (14)
C3—N3—C4	106.50 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H01···N1	0.74 (3)	2.04 (3)	2.7576 (19)	166 (3)
N3—H02···O3^{i}	0.91 (3)	2.47 (2)	2.997 (2)	117 (2)
N3—H02···O4^{ii}	0.91 (3)	2.04 (3)	2.8415 (19)	146 (2)
C3—H3···O1^{iii}	0.81 (2)	2.26 (2)	3.046 (2)	161 (2)
C4—H4···O3^{i}	0.95 (2)	2.42 (2)	2.974 (2)	117 (2)
C4—H4···O2^{iv}	0.95 (2)	2.58 (2)	3.076 (2)	113 (2)
C1—H1*C*···N4^{v}	0.98	2.81	3.777 (2)	168
C2—H2*C*···N4^{vi}	0.98	2.80	3.503 (2)	130

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

Methyl groups were identified from difference syntheses and refined as rigid groups allowed to rotate but not tip. Other H atoms were refined freely. The origin was fixed by the method of Flack & Schwarzenbach (1988). The absolute structure was determined from 1072 Friedel pairs.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1307). Services for accessing these data are described at the back of the journal.

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Heterocycle-substituted [2.2]paracyclophanes

INA DIX,[a] HENNING HOPF[a] AND PETER G. JONES[b]

[a] *Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany, and* [b] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

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Abstract

The observed geometries of the cyclophane groups of 4-(2′-furyl)[2.2]paracyclophane [systematic name: 5-(2-furyl)tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene], $C_{20}H_{18}O$, and 5-(2′-thienyl)[2.2]paracyclophane [systematic name: 5-(2-thienyl)tricyclo[8.2.2.2^{4,7}]-hexadeca-4,6,10,12,13,15-hexaene], $C_{20}H_{18}S$, are very similar both to the skeleton of the parent compound and to [2.2]paracyclophane fragments in other structures; the bridgehead C atoms are characteristically bent out of the plane of the other four coplanar atoms building the typical boat conformation of the aromatic rings in [2.2]-paracyclophanes. These rings are twisted with respect to each other. The thiophene ring of (2) is disordered over two positions, which could however be well resolved. The heterocyclic substituents are rotated out of the plane of the four coplanar C atoms C4, C5, C7 and C8 by 25.1 (1)° in (1), and 34.7 (6) and 32.9 (6)° in (2) for both positions of disorder.