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

N1—S1	1.590 (2)	S2—O9	1.441 (2)
N1—S2	1.590 (2)	S2—O10	1.441 (2)
S1—O7	1.435 (2)	S1—C21	1.787 (3)
S1—O8	1.438 (2)	S2—C31	1.772 (3)
S2—N1—S1	123.18 (11)	O7—S1—C21	105.43 (12)
O7—S1—N1	107.30 (12)	O8—S1—C21	106.77 (11)
O8—S1—N1	113.96 (10)	O9—S2—C31	106.50 (12)
O9—S2—N1	105.63 (11)	O10—S2—C31	106.20 (11)
O10—S2—N1	114.32 (11)	O7—S1—O8	116.32 (12)
N1—S1—C21	106.26 (12)	O9—S2—O10	116.12 (12)
N1—S2—C31	107.55 (12)		
S2—N1—S1—O7	−149.3 (2)	S1—N1—S2—O9	−175.2 (2)
S2—N1—S1—O8	−19.0 (2)	S1—N1—S2—O10	−46.3 (2)
S2—N1—S1—C21	98.3 (2)	S1—N1—S2—C31	71.4 (2)
N1—S1—C21—C22	126.0 (2)	N1—S2—C31—C36	80.1 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N40—H40*A*···O1	0.91	2.05	2.920 (3)	159
N40—H40*B*···O3	0.91	1.96	2.861 (3)	170
N40—H40*C*···O5	0.91	1.95	2.860 (3)	174

Considering Friedel opposites as equivalent, the data are complete to $2\theta = 50°$; additionally, some data between 50 and 55° were collected. The absolute structure was based on 1466 Friedel pairs. Further Friedel opposites were inaccessible because of geometric limitations imposed by the low-temperature apparatus. The origin was fixed according to the method of Flack & Schwarzenbach (1988). Methyl and ammonium moieties were refined as rigid groups allowed to rotate but not tip; other H atoms were refined as riding. The cation C—C bond is unexpectedly short, which may be attributed to libration effects.

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: LN1011). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. XCII.† 1-Aza-4-azoniabicyclo[2.2.2]octane Di(methanesulfonyl)amidate

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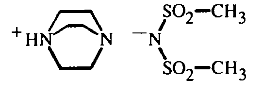
Abstract

In the title onium salt, $C_6H_{13}N_2^+.C_2H_6NO_4S_2^-$, the anion adopts an extended conformation closely approximating to C_2 symmetry. The cations are connected by an N—H···N hydrogen bond to form chains parallel to the *x* axis, whereas the anions are assembled into chains parallel to the *z* axis by two C—H···O interactions. Further C—H···O hydrogen bonds occur between cations and anions.

Comment

The structure of the title compound, $(DabcoH)^+.(CH_3SO_2)_2N^-$, (1), where Dabco is 1,4-diazabicyclo[2.2.2]octane, was examined as part of an extensive study of interionic hydrogen-bond patterns in onium salts, $BH^+.(CH_3SO_2)_2N^-$, derived from the strong acid $(CH_3SO_2)_2NH$ and organic nitrogen or oxygen bases *B* (Henschel, 1996). The anion in question displays five potential hydrogen-bond acceptors; (1) proves to be a rare example of an onium salt in which this species is not connected to BH^+ by at least one strong *D*—H···*A* hydrogen bond (*D* = N or O; *A* = N or O).



(1)

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† Part XCI: Henschel, Blaschette & Jones (1997).

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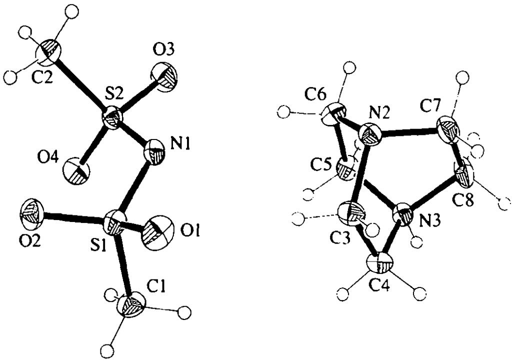

Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

Both ions occurring in the structure of (1) are shown in Fig. 1 (geometrical data in Table 1). The anion adopts an extended conformation approximating closely to C_2 symmetry (*cf.* torsion angles in Table 1). The methyl groups lie on opposite sides of the S—N—S plane. Two S—N—S—O*n* torsion angles are *gauche* (n = 2, 4), while the others are *transoid* (n = 1, 3). Thus, the sequence O1—S1—N1—S2—O3 forms a nearly planar zigzag chain that is pre-organized for the hydrogen-bond-mediated recognition of onium cations possessing a complementary or partially complementary set of NH and/or OH donors (Henschel, 1996, and unpublished results from this laboratory). The prototypical conformation observed in the present structure appears to be persistent for the non-coordinating anion; apart from numerous onium salts, it was also shown to have pseudo-C_2 symmetry in a series of ionic organotin di(methanesulfonyl)amides, and exact crystallographic C_2 symmetry in its $[(C_6H_5)_3AsO]_2H^+$ salt (Weitze *et al.*, 1995, and references therein).

In the cation, the N—C bond lengths involving the protonated N atom [mean 1.494 (3) Å] are, as expected, longer than those at the unprotonated N atom [mean 1.474 (3) Å]. The mean 'twist' N—C—C—N torsion angle is −11.5 (7)°.

In the crystal packing of (1), (DabcoH)$^+$ cations related by translation are connected through an N—H···N hydrogen bond to form infinite chains in the **x** direction (Fig. 2; hydrogen-bond geometry in Table 2). Similar chains have occasionally been found in other $[(\text{DabcoH})^+]_n.X^{n-}$ salts, *e.g.* X^- = ClO_4^- (Głowiak, Sobczyk & Grech, 1975) or polyiodide (Bandrauk, Truong, Carlone & Hanson, 1987), and X^{2-} = $[Zn(NCS)_4]^{2-}$ (Petrusenko, Kokosay & Fritzky, 1997), whereas for X^- = $(C_6H_5)_4B^-$ (Bakshi *et al.*, 1994) or $[(L)Co(CO)_3]^-$ (L = CO, Ph_3P) (Zhao *et al.*, 1996), the chain-building N—H···N hydrogen bond is surprisingly replaced by unusual N—H···π(phenyl) or N—H···Co interactions.

In addition to the N—H···N bond, (1) features a number of C—H···O sequences that may be viewed as hydrogen bonds (Desiraju, 1996); those with H···O < 2.5 Å and C—H···O > 150° are included in Table 2. As shown in Fig. 2, glide-plane-related anions are connected into chains parallel to the z axis by two C—H···O bonds using the *gauche* oriented O atoms as acceptors. The *transoid*-oriented O atoms, on the other hand, act as acceptors for fairly strong C—H···O bonds originating from the adjacent cations. The N atom of the anion is not involved in C—H···A bonding.

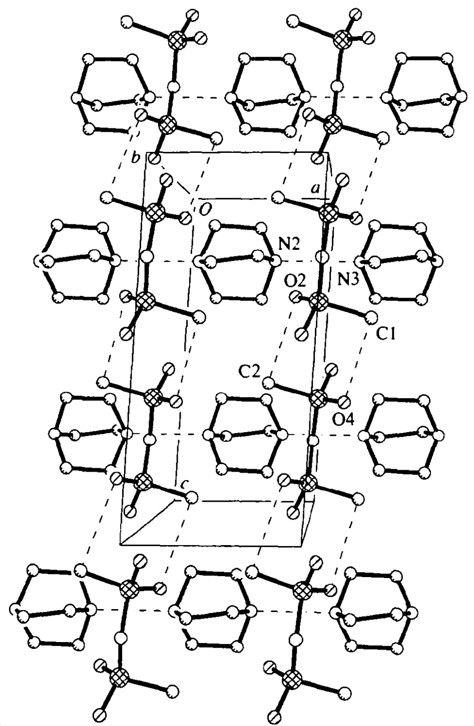

Fig. 2. Packing diagram viewed (approximately) parallel to the y axis. H atoms have been omitted and selected hydrogen bonds (see text) are indicated by broken lines.

Experimental

Salt (1) was prepared from equimolar amounts of Dabco and $HN(SO_2CH_3)_2$ in water (Blaschette *et al.*, 1983) and crystallized from the same solvent. Physical data: m.p. 435–438 K; ^{1}H NMR (CD_3CN, 200 MHz): 2.89 (*s*, 6H, CH_3), 3.08 (*s*, 12H, CH_2), 4.48 (*sbr*, 1H, NH).

Crystal data

$C_6H_{13}N_2^+.C_2H_6NO_4S_2^-$
M_r = 285.38
Monoclinic
$P2_1/c$
a = 5.3498 (11) Å
b = 19.754 (3) Å
c = 11.665 (2) Å
β = 93.97 (2)°
V = 1229.8 (4) Å^3
Z = 4
D_x = 1.541 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10.0–11.5°
μ = 0.441 mm^{-1}
T = 143 (2) K
Needle
0.60 × 0.15 × 0.10 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
2876 measured reflections
2795 independent reflections
2129 reflections with
  $I > 2\sigma(I)$
$R_{\rm int} = 0.064$

$\theta_{\rm max} = 27.50°$
$h = -6 \rightarrow 0$
$k = 0 \rightarrow 25$
$l = -14 \rightarrow 15$
3 standard reflections
  frequency: 60 min
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.117$
$S = 1.033$
2795 reflections
160 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.8982P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.335$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.389$ e Å^{-3}
Extinction correction:
  *SHELXL*93
Extinction coefficient:
  0.0073 (11)
Scattering factors from
  International Tables for Crystallography (Vol. C)

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

N1—S1	1.595 (2)	S1—C1	1.755 (3)
N1—S2	1.600 (2)	S2—O4	1.4459 (19)
S1—O2	1.4445 (18)	S2—O3	1.4480 (19)
S1—O1	1.4486 (18)	S2—C2	1.751 (3)
S1—N1—S2	118.87 (13)	O4—S2—O3	115.95 (12)
O2—S1—O1	115.68 (11)	O4—S2—N1	113.11 (11)
O2—S1—N1	113.38 (11)	O3—S2—N1	106.28 (11)
O1—S1—N1	106.21 (11)	O4—S2—C2	107.11 (12)
O2—S1—C1	106.92 (12)	O3—S2—C2	106.75 (13)
O1—S1—C1	107.10 (12)	N1—S2—C2	107.15 (12)
N1—S1—C1	107.09 (13)		
S2—N1—S1—O2	−36.88 (19)	S1—N1—S2—O4	−37.39 (19)
S2—N1—S1—O1	−165.01 (14)	S1—N1—S2—O3	−165.72 (14)
S2—N1—S1—C1	80.80 (17)	S1—N1—S2—C2	80.42 (17)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N2$^{\rm i}$	0.95 (3)	1.87 (3)	2.817 (3)	177 (3)
C1—H1*C*···O4$^{\rm ii}$	0.98	2.43	3.374 (3)	162
C2—H2*C*···O2$^{\rm iii}$	0.98	2.41	3.360 (3)	163
C4—H4*A*···O1$^{\rm iv}$	0.99	2.43	3.342 (3)	152
C4—H4*B*···O1$^{\rm i}$	0.99	2.41	3.344 (3)	157
C5—H5*B*···O3$^{\rm v}$	0.99	2.29	3.256 (3)	164
C6—H6*B*···O3	0.99	2.43	3.393 (3)	165

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

Many pairs of atoms are related by a translation of *ca* $0,\frac{1}{2},0$; reflections with k odd are thus weak. H-atom treatment: NH coordinates free, U fixed; rigid methyl groups (allowed to rotate but not tip); others riding.

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*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP*5 (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Tricyclohexylphosphoniodithioformate

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Abstract

The two molecules in the asymmetric unit of the title compound, $C_{19}H_{33}PS_2$, have similar conformations. The PCS_2 fragments are planar and the C—S distances are 1.669 (2) and 1.640 (2) Å in molecule *A*, and 1.672 (3) and 1.637 (3) Å in molecule *B*. The S—C—S angles are 130.2 (1) and 130.5 (1)° in molecules *A* and *B*, respectively.

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