Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.107$
$S = 1.083$
2312 reflections
190 parameters
H atoms were located from ΔF synthesis and refined using a riding model

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.1659P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4*S*—H4*S*···N5	1.05	1.816 (3)	2.844 (3)	163.77 (8)
N10—H10···N13^{i}	0.98	2.067 (3)	2.953 (3)	149.56 (7)
C14—H14···N8^{i}	1.04	2.520 (3)	3.301 (3)	131.57 (7)
C2—H2···N9^{ii}	1.14	2.852 (3)	3.931 (3)	156.94 (6)
C16—H16···O4*S*^{iii}	1.18	2.646 (3)	3.379 (3)	118.80 (7)
C3—H3···O4*S*^{iv}	1.11	2.535 (3)	3.521 (3)	147.69 (7)
C15—H15···C1*S*^{v}	1.06	2.836 (3)	3.769 (3)	146.99 (7)
C15—H15···C2*S*^{v}	1.06	2.704 (3)	3.759 (3)	173.83 (7)
C15—H15···C3*S*^{v}	1.06	2.841 (3)	3.788 (3)	148.82 (7)

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

Data collection: *XSCANS* (Fait, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1161). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. XCI.† Ethylammonium Di(benzenesulfonyl)amide 1,4,7,10,13,16-Hexaoxacyclooctadecane (1/1/1)

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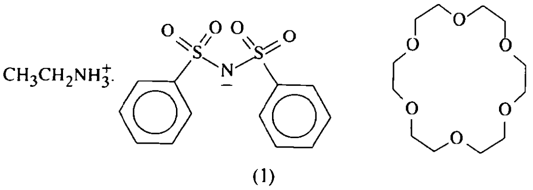
Abstract

In the structure of the title compound, $C_2H_8N^+.C_{12}H_{10}NO_4S_2^-.C_{12}H_{24}O_6$, the non-coordinating $(C_6H_5SO_2)_2N^-$ anion adopts an extended conformation with the phenyl groups lying on opposite sides of the S—N—S plane. The conformation of the macrocycle and the hydrogen-bond geometry in the complex cation closely resemble those in related adducts between 18-crown-6 and primary alkylammonium salts.

Comment

We are interested in the structures of polysulfonylamines in general and in the conformation of di(benzenesulfonyl)amine in particular. Di(benzenesulfonyl)amine, $HN(SO_2C_6H_5)_2$, adopts an extended conformation in the solid state, the $N(SO_2C)_2$ moiety approximating to C_2 symmetry, whereas in the corresponding sodium salt the conjugate anion has a folded pseudo-C_s symmetry that favours close contacts between Na^+ and the electronegative N and O atoms (Cotton & Stokely, 1970).



(1)

In contrast to the Na salt, the title compound, (1), consists of a large organic cation, with effectively shielded charge, and a non-coordinating $(C_6H_5SO_2)_2N^-$ anion (Fig. 1). The closest cation–anion contact is observed between a methylene H and a sulfonyl O atom [H40*D*···O9 2.80, C40···O9 3.314 (4) Å and C40—H40*D*···O9 113°]. In this environment, the anion adopts an extended conformation resembling that of its parent acid; however, the deviation of the $N(SO_2C)_2$ group

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† Part XC: Wijaya, Moers, Blaschette & Jones (1997).

from ideal C_2 symmetry is appreciably more pronounced (*cf.* torsion angles in Table 1). The phenyl groups lie on opposite sides of the S—N—S plane. This geometry was shown to alleviate the overall steric congestion in the molecule (Cotton & Stokely, 1970). In general, the bond lengths and angles of the anion (Table 1) are in good agreement with the parameters of the Na salt; a noteworthy discrepancy occurs in the NS_2 group and is probably induced by strong electrostatic interactions in the metal salt [in (1): N—S 1.590 (2) Å (× 2), S—N—S 123.18 (11)°; Na salt: N—S 1.571 (5), 1.598 (5) Å, S—N—S 127.5 (3)°].

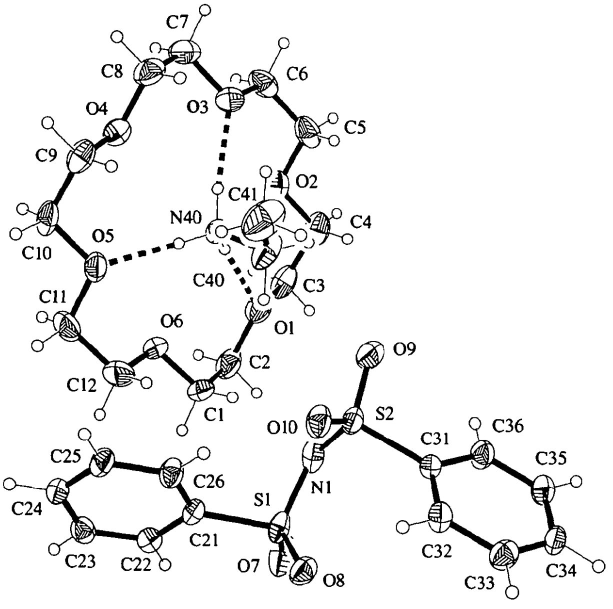

Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

The structure of the cation (Fig. 1) is essentially similar to those observed for other 1:1 complexes between 18-crown-6 and primary alkylammonium salts, *e.g.* methylammonium perchlorate (Trueblood, Knobler, Lawrence & Stevens, 1982), methylammonium trifluoromethanesulfonate (Spek, Roelofsen, Noltes & Alberts, 1982), benzylammonium thiocyanate (Bovill, Chadwick, Sutherland & Watkin, 1980) or (benzoylmethyl)ammonium hexafluorophosphate (Maud, Stoddart & Williams, 1985). The symmetry of the macrocycle approximates to D_{3d}, with all C—C torsion angles *gauche* and alternating in sign, and all C—O and O—C torsion angles *trans*. The observed bond lengths (average C—O 1.424 and C—C 1.488 Å), bond angles (average C—O—C 112.1 and C—C—O 109.1°) and torsion angles (average absolute values C—O—C—C 177.7 and O—C—C—O 65.0°) lie in the commonly found ranges (Goldberg, 1989).

A triangle of alternating crown O atoms forms $N^+—H\cdots O$ hydrogen bonds (Table 2). The $N^+\cdots O$ distances to the other three O atoms are also short and are indicative of strong dipolar attractions [2.995 (3), 3.018 (3) and 2.936 (3) Å from N40 to O2, O4 and O6, respectively]. The N atom is displaced by 0.684 (2) Å from the former O_3 plane, 1.085 (2) Å from the latter and 0.885 (2) Å from the best plane of all six crown O atoms. The angle between N40—C40 and the normal to the latter plane is 9°.

Experimental

Compound (1) was prepared by dissolving 0.25 g (0.84 mmol) di(benzenesulfonyl)amine and 0.38 g (1.4 mmol) 18-crown-6 in 2 ml 70% aqueous ethylamine at room temperature. After stirring for a few minutes, a colourless solid separated and was isolated by filtration. Recrystallization from 70% aqueous ethylamine gave a final yield of 0.21 g (41%) and crystals suitable for X-ray study (m.p. 375–378 K). ^{1}H NMR (CD_3CN, 200 MHz): 1.61 (*t*, 3H, J = 7.3 Hz, CH_3), 2.81 (*q*, 2H, J = 7.3 Hz, cation CH_2), 3.60 (*s*, 24H, 18-crown-6), 4.28 (*sbr*, 3H, NH_3), 7.30–7.45 and 7.73–7.79 (6H and 4H, aromatic H).

Crystal data

$C_2H_8N^+.C_{12}H_{10}NO_4S_2^-.$-$C_{12}H_{24}O_6$
M_r = 606.74
Monoclinic
$P2_1$
a = 13.237 (3) Å
b = 8.309 (2) Å
c = 13.954 (4) Å
β = 104.17 (3)°
V = 1488.0 (6) Å^3
Z = 2
D_x = 1.354 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 48 reflections
θ = 10.0–11.5°
μ = 0.236 mm^{-1}
T = 143 (2) K
Tablet
0.70 × 0.40 × 0.15 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω scans
Absorption correction: none
4643 measured reflections
4373 independent reflections
4135 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.014

$\theta_{\rm max}$ = 27.51°
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 5$
$l = -16 \rightarrow 6$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.080
S = 1.042
4368 reflections
364 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.4511P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.372 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.245 e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.0087 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (6)

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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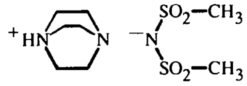
(*Received 27 May 1997; accepted 1 September 1997*)

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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