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Polysulfonylamines. CXXXII.[1] A robust eight-membered ring motif in the hydrogen-bonded structure of 2-aminopyridinium di(benzenesulfonyl)amidate

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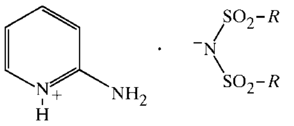
The crystal structure of the title compound, $C_5H_7N_2^+\cdot C_{12}H_{10}NO_4S_2^-$, consists of two independent cation–anion pairs, *A* and *B*. Within each pair, the H—N—C—N*—H grouping (N*—H is the pyridinium function) and one N—S—O moiety of the anion are linked by N*—H···N and N—H···O hydrogen bonds to form an antidromic ring motif of type $R^2_2(8)$. The remaining amino donors give rise to N—H···O hydrogen bonds, connecting the ion pairs into *A–B–A–B–* chains. The structure testifies to the persistence of the $R^2_2(8)$ motif in question, which was previously detected as a highly robust supramolecular synthon in a series of onium di(methanesulfonyl)amidates. The structure is pseudosymmetric; the anion positions correspond to space group $P2_1/n$, but those of the cations do not.

Comment

The design process in crystal engineering depends crucially on the 'robustness', or high probability of formation, of a limited number of supramolecular synthons (Desiraju, 1995; Aakeröy, 1997). Among these non-covalent interactions, bimolecular hydrogen-bonded ring motifs (Allen *et al.*, 1999) are prominently utilized for controlling the assembly of complementary molecular building blocks into finite or infinite architectures (Subramanian & Zaworotko, 1994). Since the hydrogen bond is primarily electrostatic in nature, the strengths of such interactions involving charged species is enhanced and, as a result, acyclic or preferentially cyclic hydrogen-bonded motifs become a powerful tool for linking ions together in a predictable manner (Aakeröy, 1997; Aakeröy & Seddon, 1993; Mascal *et al.*, 1995; Braga & Grepioni, 1998).

This laboratory has synthesized and characterized a series of onium di(methanesulfonyl)amidates, $BH^+\cdot(MeSO_2)_2N^-$, in which a novel and remarkably robust antidromic ring synthon of second-level graph set $R^2_2(8)$ (Bernstein *et al.*, 1995) is systematically formed from a V-shaped O—S—N fragment of the conformationally rigid anion and *syn,syn*-[H—N—C*sp*^{2}—N—H] sequences drawn from a variety of organic cations. In order to demonstrate its high probability of formation, the motif in question was successfully integrated into hydrogen-bonded assemblies of increasing complexity, *i.e.* prototypical ion pairs (Wijaya *et al.*, 1999), cyclodimers and catemers of ion pairs (Moers, Wijaya *et al.*, 2000), and three-dimensional networks (Wijaya *et al.*, 2000). The 2-aminopyridinium salt (I) represents an example for a catemeric structure composed of $R^2_2(8)$ bonded ion pairs, and the structure determination of the analogous title compound, (II), was carried out in order to evaluate the influence of a sterically more demanding disulfonylamidate anion on the robustness of the target motif.



(I) $R = \mathrm{Me}$
(II) $R = \mathrm{Ph}$

The asymmetric unit of (II) consists of two crystallographically independent ion pairs, *A* (unprimed labels) and *B* (primed labels), as shown in Fig. 1. Important bond lengths, bond angles, torsion angles and intra-ionic non-bonded distances are summarized in Table 1. The two anions adopt extended conformations approximating to C_2 symmetry, in which each O_2S—N—S moiety displays an antiperiplanar and a synclinal O atom, denoted hereafter as O(*ap*) and O(*sc*), respectively. The molecular dimensions of the ions are normal and similar to those observed in (I) and other related structures [2-aminopyridinium: Henschel *et al.* (1999), and references therein; di(benzenesulfonyl)amidate (extended form): Henschel *et al.* (1997); di(benzenesulfonyl)amidate (folded form): Cotton & Stokely (1970) and Bombicz *et al.* (1996)]. A combination of N—H···N, N—H···O and C—H···O hydrogen bonds (Table 2) links the ions into a three-dimensional framework. It is noteworthy that the weak C—H···O bonds exhaustively satisfy all acceptors that are not involved in classical hydrogen bonds.

As is apparent from Fig. 1, the antidromic $R^2_2(8)$ motif observed in structure (I) neatly persists in the ion pairs of (II). There is no change in the way in which the oppositely charged ions are held together. In both crystals, the ring-forming hydrogen bonds connect the pyridinium donor to the amidate N acceptor and one of the amino donors to an O(*ap*) acceptor. The near planarity of the D_2A_2 systems in *A* and *B* is testimony to the robustness of the motif [dihedral angles: N2—N1—O1—N3 −3.55 (10)° and N2′—N1′—O1′—N3′ 8.13 (10)°; deviations of C and S ring atoms from the respective D_2A_2 mean plane: C3 0.055 (4), S1 −0.113 (2), C3′ −0.071 (4) and S1′ −0.246 (2) Å]. The amino donors not involved in ring formation serve to link alternating *A* and *B*

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[1] Part CXXXI: Moers, Blaschette & Jones (2000).
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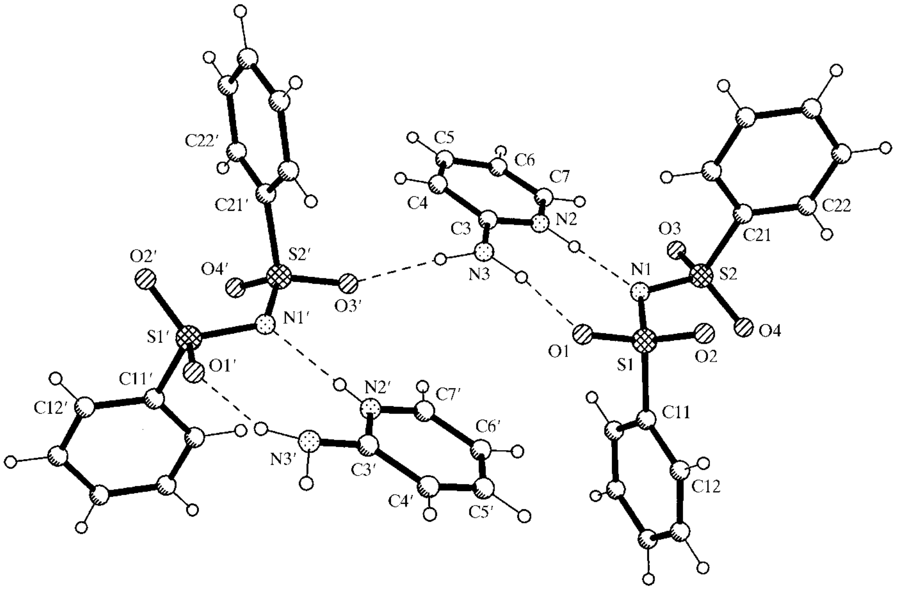

Figure 1
The asymmetric unit of the title compound. Hydrogen bonds are indicated by dashed lines. Radii are arbitrary.

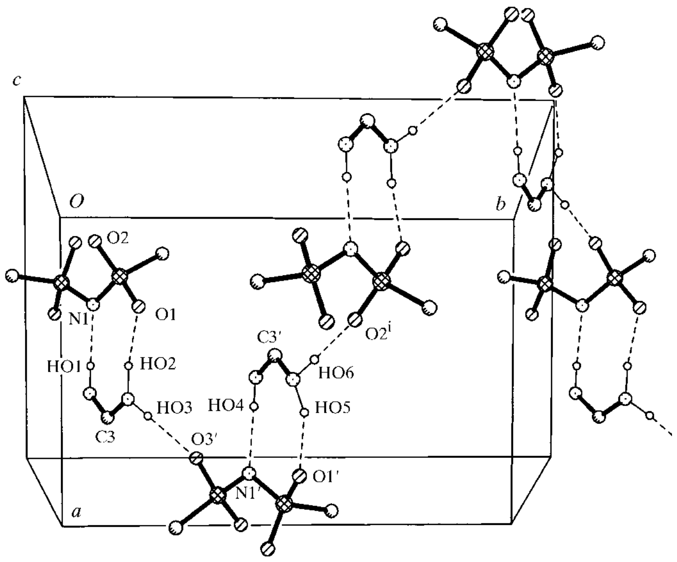

Figure 2
Packing diagram of the title compound, showing the formation of a strongly curved chain. For clarity, all ions are shown reduced to the fragments directly involved in catenation. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (i) $1-x, \frac{1}{2}+y, 2-z$.]

units into chains, which propagate parallel to the y direction and are generated by twofold screw axes (Fig. 2).

The structure is pseudosymmetric; the anions are related to a good approximation (mean deviation 0.09 Å) by an inversion centre at *ca* −0.257, 0.760, 0.252, but the cations are not. The pseudo-centre is automatically associated with a pseudo-glide plane and, accordingly, the reflections $h0l$ with $h+l$ odd are weak, but present. One clear topological difference between the two cations is shown by the NH_2 groups; that at N3 forms hydrogen bonds to two O(*ap*) atoms, but that at N3′ to one O(*ap*) and one O(*sc*) atom (see Figs. 1 and 2). Associated with this, the environment at N3 is essentially planar (angle sum 360°), whereas that at N3′ is pyramidalized (angle sum 346°).

On comparing the monoclinic crystal structures of (I) (space group $P2_1/c$, $Z' = 1$; Moers, Wijaya *et al.*, 2000) and (II) (space group $P2_1$, $Z' = 2$), the following similarities and discrepancies become apparent: (i) both assemblies contain the $R_2^2(8)$ target synthon; (ii) the differing shapes and volumes of the disulfonylamidate building blocks do not interfere with the donor–acceptor selectivity within the ring motifs [common pattern: $C_2N-H\cdots N$/$CN(H)-H\cdots O$(*ap*)]; (iii) the independent ion pairs, one in (I) and two in (II), are linked *via* the second amino donors into chains generated by 2_1 transformation in the y direction, but the c-glide plane (and concomitant inversion centre) operative in (I) is not maintained in (II); (iv) a striking contrast arises in the supramolecular catenation modi, so far as in (I) the chain-forming hydrogen bond is accepted by the O(*ap*) atom already pertaining to the ring motif, whereas in the present structure (Fig. 2), the catenation relies upon an O(*sc*) atom and an O(*ap*) acceptor that is not involved in the cyclic synthon; (v) the latter, apparently disparate, catenation mode clearly gives rise to a strongly meandering chain, which conveniently accommodates the bulky phenyl rings within spacious bays.

Experimental

Compound (II) was prepared by dissolving di(benzenesulfonyl)amine (0.60 g, 2.0 mmol) and 2-aminopyridine (0.19 g, 2.0 mmol) in acetonitrile (10 ml). Slow partial evaporation of the solvent at ambient temperature gave a yield of 0.68 g (86%) and crystals suitable for X-ray study (m.p. 403–408 K). A satisfactory elemental analysis was obtained.

Crystal data

$C_5H_7N_2^+\cdot C_{12}H_{10}NO_4S_2^-$
$M_r = 391.46$
Monoclinic, $P2_1$
$a = 10.643$ (3) Å
$b = 15.624$ (3) Å
$c = 11.349$ (3) Å
$\beta = 110.500$ (12)°
$V = 1767.5$ (7) Å^3
$Z = 4$

$D_x = 1.471$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 52 reflections
$\theta = 10.0$–11.5°
$\mu = 0.330$ mm^{-1}
$T = 143$ (2) K
Block, colourless
0.6 × 0.6 × 0.5 mm

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
11 932 measured reflections
8139 independent reflections
7516 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$

$\theta_{\rm max} = 27.54°$
$h = -13 \rightarrow 13$
$k = -20 \rightarrow 20$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.103$
$S = 1.044$
8139 reflections
494 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.7866P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.62 (6)

Table 1
Selected geometric parameters (Å, °).

N2—C3	1.342 (4)	N2′—C3′	1.347 (4)
N2—C7	1.353 (4)	N2′—C7′	1.345 (4)
N3—C3	1.326 (4)	N3′—C3′	1.329 (4)
N1—S1	1.597 (2)	N1′—S1′	1.595 (2)
S1—O1	1.443 (2)	S1′—O1′	1.442 (2)
N2—N3	2.311 (4)	N2′—N3′	2.316 (4)
N1—O1	2.428 (3)	N1′—O1′	2.413 (3)
C3—N2—C7	123.2 (3)	C3′—N2′—C7′	122.7 (3)
C3—N2—H01	116 (3)	C3′—N2′—H04	119 (2)
C7—N2—H01	120 (3)	C7′—N2′—H04	118 (2)
C3—N3—H02	127 (3)	C3′—N3′—H05	119 (3)
C3—N3—H03	124 (3)	C3′—N3′—H06	112 (3)
H02—N3—H03	109 (3)	H05—N3′—H06	115 (3)
N2—C3—N3	120.0 (3)	N2′—C3′—N3′	119.9 (3)
N1—S1—O1	105.90 (13)	N1′—S1′—O1′	105.14 (13)
S1—N1—S2	120.70 (13)	S2′—N1′—S1′	120.48 (14)
S2—N1—S1—O1	167.75 (15)	S2′—N1′—S1′—O1′	−166.13 (16)
S2—N1—S1—O2	39.6 (2)	S2′—N1′—S1′—O2′	−38.5 (2)
S1—N1—S2—O3	163.29 (16)	S1′—N1′—S2′—O3′	−173.12 (16)
S1—N1—S2—O4	34.7 (2)	S1′—N1′—S2′—O4′	−44.4 (2)
C11—S1—S2—C21	−147.86 (12)	C11′—S1′—S2′—C21′	139.69 (12)

The structure was refined as a racemic twin with components 0.62 (6) and 0.38 (6); 3930 Friedel pairs were available. H atoms bonded to N atoms were refined freely, but with chemically equivalent N—H and H···H distances of the NH_2 groups restrained to be approximately equal. The freely refined N—H distances were longer than expected but could not be satisfactorily restrained to standard values. We have observed this effect previously (Freytag & Jones, 1999). Other H atoms were refined using a riding model starting from calculated positions.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); 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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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H01···N1	0.89 (3)	2.01 (3)	2.890 (3)	172 (4)
N3—H02···O1	1.05 (3)	1.90 (3)	2.945 (4)	172 (5)
N3—H03···O3′	1.05 (3)	1.98 (4)	2.925 (4)	148 (5)
N2′—H04···N1′	0.87 (3)	2.05 (3)	2.907 (3)	168 (3)
N3′—H05···O1′	1.03 (3)	1.89 (3)	2.868 (4)	157 (4)
N3′—H06···O2^{i}	1.03 (3)	1.98 (3)	3.006 (4)	178 (5)
C25—H25···O2′^{ii}	0.95	2.63	3.227 (4)	121
C26—H26···O2′^{ii}	0.95	2.56	3.190 (3)	124
C5—H5···O4^{iii}	0.95	2.62	3.474 (4)	150
C6—H6···O4′^{iv}	0.95	2.53	3.422 (4)	155
C7—H7···O3	0.95	2.56	3.173 (4)	122
C12′—H12′···O1^{v}	0.95	2.65	3.447 (3)	141
C15′—H15′···O4^{vi}	0.95	2.68	3.250 (3)	119
C16′—H16′···O4^{vi}	0.95	2.51	3.166 (3)	126
C5′—H5′···O4′^{vii}	0.95	2.68	3.548 (4)	153

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1426). Services for accessing these data are described at the back of the journal.

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