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A quasi-diamondoid hydrogen-bonded framework in anhydrous sulfanilic acid

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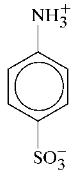
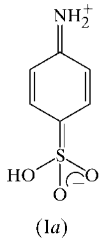
The title compound ($C_6H_7NO_3S$) exists as a zwitterion (4-ammoniobenzenesulfonate), $^+H_3NC_6H_4SO_3^-$, and these units are linked into a three-dimensional framework by two distinct two-centre N—H···O hydrogen bonds [H···O 1.84 and 1.87 Å; N···O 2.767 (2) and 2.746 (2) Å; N—H···O 166 and 172°] and a planar three-centre N—H···$(O)_2$ hydrogen bond [H···O 2.03 and 2.37 Å; N···O 2.816 (2) and 2.877 (2) Å; N—H···O 162 and 111°; O···H···O 86°].

Comment

The structures of 2-aminobenzenesulfonic acid [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode OTANAC (Hall & Maslen, 1967)] and 3-aminobenzenesulfonic acid (ANISAC; Hall & Maslen, 1965) were both reported many years ago but, somewhat surprisingly, the structure of isomeric 4-aminobenzenesulfonic acid (sulfanilic acid) has not previously been reported for the anhydrous form, although the structure has been reported for the monohydrate (SANACM; Rae & Maslen, 1962).



(I)



(I*a*)

Anhydrous 4-aminobenzenesulfonic acid exists in the crystalline state as a zwitterion, $^+H_3NC_6H_4SO_3^-$, (I) (Fig. 1), as was also observed for the OTANAC and ANISAC isomers. In the case of (I), this formulation was readily established by the straightforward identification of three H-atom sites adjacent to the N atom, all having full occupancy, and it is further supported by a number of metrical features (Table 1): first, the C—N distance is typical of those for $C_{aryl}—NH_3^+$ [mean value 1.465 (7) Å; Allen *et al.*, 1987], whereas the mean value for the $C_{aryl}—NH_2$ distance is 1.355 (20) Å for planar N and still only 1.394 (11) Å for pyramidal N; secondly, the three independent S—O distances are all rather similar, with no evidence for the presence of distinguishable single and double bonds; finally, the C—C distances show no evidence of quinonoid bond fixation, as might be expected for the form $H_2NC_6H_4SO_3H$ [*cf.* (I*a*) in the *Scheme* above].

The molecular units in (I) are linked by a number of hydrogen bonds (Table 2) into a three-dimensional quasi-diamondoid framework (Fig. 2). Two of the N—H bonds participate in two-centre N—H···O hydrogen bonds, while the third, involving H1*B*, participates in a planar but asymmetric three-centre N—H···$(O)_2$ system. Thus, each molecular unit is strongly linked to six others and rather weakly linked to a further two by the N—H···O interactions. The resulting framework structure is readily analyzed by means of the substructure approach (Gregson *et al.*, 2000). Each of the individual N—H···O interactions gives rise to a distinct *C*(8) chain running parallel to the [001] direction. The first and third of the interactions listed in Table 2 give chains generated by the *c*-glide planes at $x = \frac{1}{4}$ and $x = -\frac{1}{4}$, respectively, while the second and fourth interactions give chains generated by the 2_1 screw axes along $(0,0,z)$ and $(0,\frac{1}{2},z)$ respectively. In addition, two of the pairwise combinations of N—H···O interactions give rise to chains running parallel to [100] and [010]. Atom N1 at (x, y, z) acts as a hydrogen-bond donor, *via* H1*A*, to O41 at $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$, while O42 at $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$ accepts a hydrogen bond from N1 at $(1 + x, y, z)$, *via* H1*B*, so producing a $C_2^2(6)$ chain running parallel to [100]. Similarly, N1 acts as donor, *via* H1*C*, to O43 at $(-x, 1 - y, -\frac{1}{2} + z)$, while O41 at $(-x, 1 - y, -\frac{1}{2} + z)$ is an acceptor from N1 at $(x, 1 + y, z)$, *via* H1*B*, so producing a second $C_2^2(6)$ chain, this time running parallel to [010]. The combination of the [100], [010] and [001] chains generates the three-dimensional framework. If just the short strong N—H···O interactions are considered, a diamondoid structure is generated in which each unit mimics the action of a two-carbon fragment of the diamond structure, and its six strong N—H···O hydrogen bonds mimic the six covalent C—C bonds pendant from such a C_2 fragment.

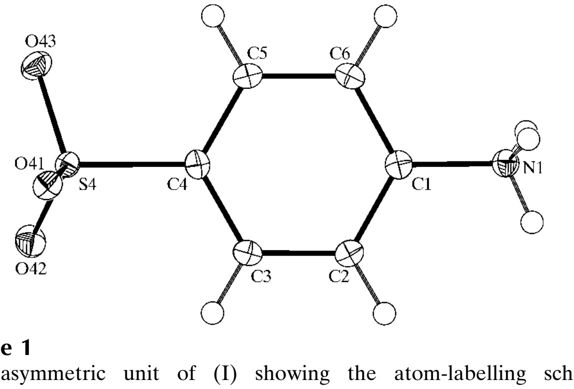


Figure 1
The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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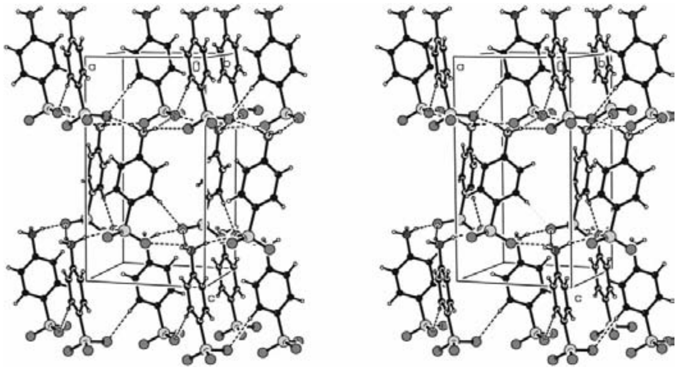

Figure 2
A stereoview of part of the crystal structure of (I) showing the formation of the quasi-diamondoid hydrogen-bonded framework.

However, the neat analogy is somewhat complicated not only by the weaker component of the three-centre hydrogen bond, but also by the single C—H$\cdots$O hydrogen bond (Table 2) which gives rise to a *C*(5) chain, running parallel to [100] and generated by the *a*-glide plane at $y = 0$. The supramolecular aggregation is completed by two C—H$\cdots\pi$ interactions.

Despite the extensive hydrogen bonding in (I), its density is significantly less than those of its two isomers. The density of the 2-isomer is 1.613 (2) Mg m^{-3} and here the zwitterions form a two-dimensional structure which is most readily envisaged as a chain of fused $R_2^2(12)$ rings involving two of the N—H$\cdots$O hydrogen bonds, with the chains being linked into sheets through the third hydrogen bond (Hall & Maslen, 1967); for the 3-isomer, which forms a three-dimensional framework structure, the density is 1.677 (1) Mg m^{-3}, and this high value is associated with the arrangement of the molecules across closely spaced mirror planes only *ca* 3.38 Å apart (Hall & Maslen, 1965). The monohydrate of sulfanilic acid also forms a three-dimensional hydrogen-bonded framework, but complete analysis is not possible as not all of the H atoms were located (Rae & Maslen, 1962).

The conformation of (I) (Fig. 1 and Table 2) is almost certainly determined by the hydrogen bonding. In this context, it is interesting to compare the conformation of (I) with that of the zwitterionic form of sulfamic acid, $^{+}H_3NSO_3^{-}$ (Sass, 1960; Cameron & Duncanson, 1976; Bats *et al.*, 1977), which may be regarded as related to (I) by notional removal of the arene ring. In sulfamic acid, there is almost perfect staggering about the S—N bond, giving effective C_{3v} ($3m$) molecular symmetry. Despite this, there is no crystallographically imposed symmetry, neither planes nor a threefold rotation axis, as this acid crystallizes in space group *Pbca* with $Z' = 1$. It is interesting to note that the N—H$\cdots$O hydrogen bonding in sulfamic acid comprises two three-centre N—H$\cdots$(O)$_2$ interactions and one two-centre interaction (Bats *et al.*, 1977).

Experimental

Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by recrystallization of a commercial sample (Aldrich) from water.

Crystal data

$C_6H_7NO_3S$
$M_r = 173.20$
Orthorhombic, $Pca2_1$
$a = 7.5113$ (14) Å
$b = 7.2791$ (13) Å
$c = 13.898$ (3) Å
$V = 759.9$ (3) Å^3
$Z = 4$
$D_x = 1.514$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1617 reflections
$\theta = 2.8$–$28.7°$
$\mu = 0.38$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
$0.20 \times 0.10 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.945$, $T_{\max} = 0.985$
4761 measured reflections
1617 independent reflections
1549 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 28.7°$
$h = -5 \rightarrow 10$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 17$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.069$
$S = 1.11$
1617 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.1146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Absolute structure: Flack (1983), 592 Friedel pairs
Flack parameter = 0.02 (7)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.384 (2)	C1—N1	1.461 (2)
C2—C3	1.387 (2)	C4—S4	1.774 (2)
C3—C4	1.389 (2)	S4—O41	1.4762 (10)
C4—C5	1.388 (2)	S4—O42	1.4454 (13)
C5—C6	1.395 (3)	S4—O43	1.4574 (12)
C6—C1	1.381 (2)		
C3—C4—S4—O41	76.94 (14)	C2—C1—N1—H1*A*	−110.8
C3—C4—S4—O42	−42.22 (15)	C2—C1—N1—H1*B*	2.7
C3—C4—S4—O43	−166.54 (13)	C2—C1—N1—H1*C*	121.2

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1*A*$\cdots$O41$^{\rm i}$	0.94	1.84	2.767 (2)	166
N1—H1*B*$\cdots$O41$^{\rm ii}$	0.88	2.03	2.877 (2)	162
N1—H1*B*$\cdots$O42$^{\rm iii}$	0.88	2.38	2.816 (2)	111
N1—H1*C*$\cdots$O43$^{\rm iv}$	0.88	1.87	2.746 (2)	172
C3—H3$\cdots$O41$^{\rm v}$	0.95	2.39	3.331 (3)	170
C2—H2$\cdots$*Cg*1$^{\rm v}$	0.95	3.16	3.949 (2)	142
C5—H5$\cdots$*Cg*1$^{\rm vi}$	0.95	3.18	3.979 (2)	143

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

Compound (I) crystallized in the orthorhombic system. The systematic absences permitted $Pca2_1$ and *Pcam* (= *Pbcm*) as possible space groups; $Pca2_1$was selected and confirmed by the analysis. H atoms were treated as riding atoms; those bonded to C atoms were placed in calculated positions with a C—H distance of 0.95 Å and those bonded to N atoms were allowed to ride at the positions determined from a difference map, with N—H distances in the range 0.88–0.94 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1537). Services for accessing these data are described at the back of the journal.

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