Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Polymorphism in ammonium 2,4,6-trimethylbenzenesulfonate

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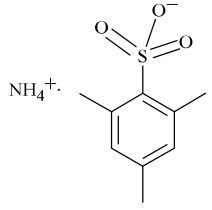
Received 9 November 2004
Accepted 23 December 2004
Online 12 February 2005

During investigations into sulfide- and selenide-amination reactions using the aminating agent *o*-mesitylsulfonylhydroxylamine, the monoclinic, (I), and orthorhombic, (II), polymorphs of ammonium 2,4,6-trimethylbenzenesulfonate, $NH_4^+\cdot C_9H_{11}O_3S^-$, have been crystallized. Investigation of the hydrogen-bonding motifs within the two polymorphs shows that both contain $N^+—H\cdots O^-$ hydrogen bonds between the ammonium cations and the 2,4,6-trimethylbenzenesulfonate anions. Polymorph (I) contains $R_4^4(12)$ and $R_4^2(8)$ graph-set ring motifs, while polymorph (II) contains the same $R_4^4(12)$ ring motif in combination with an $R_4^3(10)$ motif. The two hydrogen-bonding patterns result in slightly different packing structures for the two polymorphs, but both are based on a thick-sheet arrangement, in which the NH_4^+ cations are enveloped between two layers of 2,4,6-trimethylbenzenesulfonate anions. In (I), the aromatic rings of the anions are approximately coplanar, giving parallel sheets, whereas in (II) the sheets are antiparallel and the anions pack in a herringbone manner within the sheets, with angles of 78.76 (8)° between the planes of the aromatic rings.

Comment

Sulfonate anions have been used in the formation of hydrogen-bonding arrays (Haynes *et al.*, 2004; Russell & Ward, 1997), in particular in co-crystallization studies with the guanidinium cation, $[C(NH_2)_3]^+$. We present here the monoclinic, (I), and orthorhombic, (II), polymorphs of ammonium 2,4,6-trimethylbenzenesulfonate.

The polymorphs crystallize simultaneously as colourless columns and needles, respectively, upon slow diffusion of diethyl ether vapour into methanolic solutions of the crude mixtures resulting from two reactions utilizing the aminating agent *o*-mesitylsulfonylhydroxylamine (MSH). Preliminary evidence (mass spectrometry and ^{77}Se NMR spectroscopy) indicates that the first reaction, of Ph_2Se with MSH, results in the formation of $Ph_2SeNH_2^+\cdot$2,4,6-$Me_3C_6H_2SO_3^-$. Attempts to crystallize the compound have failed due to its high sensitivity to water, resulting in the hydrolysis of the cation to yield the title compound and, presumably, $Ph_2Se{=}O$. In the second reaction, amination of the thio crown ether [9]aneS_3(1,4,7-trithiacyclononane) leads to the formation of the [9]aneS-$(NH_2)S_2(\mu$-N)$\}^{2+}$ cation (in which an N atom bridges two of the S atoms), rather than the expected trisulfimidium cation, $\{[9\text{-ane}][S(NH_2)]_3\}^{3+}$, with the formation of the title compound as a stable by-product (Elsegood *et al.*, 2002).



(I) Monoclinic polymorph
(II) Orthorhombic polymorph

Both polymorphs crystallize with one formula unit in the asymmetric unit (Figs. 1 and 2). The geometry of the 2,4,6-trimethylbenzenesulfonate anion in (I) (Table 1) and (II) (Table 3) shows good agreement with that previously determined (for example, Russell & Ward, 1997, and references therein). In both polymorphs, the methyl group showing the greatest deviation from the least-squares plane of the aromatic ring in the anion is that *para* to the sulfonate group (C8), with values of 0.139 (2) Å in (I) and 0.096 (6) Å in (II). Atom S1 deviates from the plane of the aromatic ring by 0.2339 (17) Å in (I) and by 0.190 (5) Å in (II).

In both polymorphs, each NH_4^+ cation forms hydrogen bonds to four symmetry-related 2,4,6-trimethylbenzenesulfonate anions through $N^+—H\cdots O^-$ hydrogen bonds, using each of the N—H groups once. The geometries of the hydrogen bonds in polymorphs (I) and (II) are similar (Tables 2 and 4) and in both cases hydrogen bonds link the cations and anions into two-dimensional sheets.

The reason for the polymorphism observed in (I) and (II) is clearly seen in the hydrogen-bonding motifs within the structures. In the monoclinic polymorph, (I), two types of

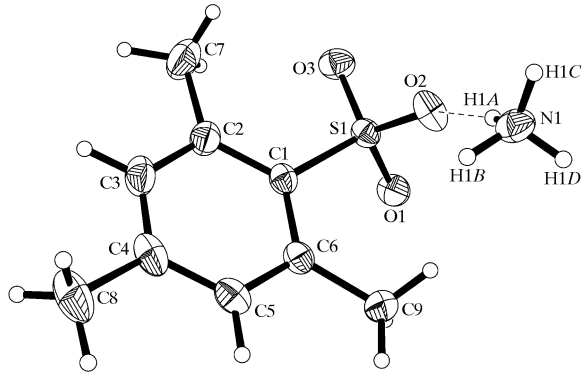


Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

  DOI: 10.1107/S0108270104034274

graph-set ring motif (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) are observed (Fig. 3). In the larger of the two ring motifs, two sulfonate groups and two NH_4^+ cations hydrogen bond together through $N^+—H\cdots O^-$ hydrogen bonds, using two acceptor O atoms from each sulfonate group and two N—H donor groups from each NH_4^+ cation, creating an $R_4^4(12)$ motif. A smaller $R_4^2(8)$ motif results from the hydrogen bonding of two sulfonate groups and two NH_4^+ cations, using two N—H groups from each cation and only one O-atom acceptor from each sulfonate group.

Polymorph (II) (Fig. 4) exhibits the same $R_4^4(12)$ motif as observed for (I), but in place of the second, motif seen in (I), *viz*. $R_4^2(8)$, there is an $R_4^3(10)$ motif, in which two NH_4^+ cations each donate two N—H groups, while one sulfonate group utilizes two acceptor O atoms and a second utilizes only one acceptor O atom in the hydrogen-bonding motif.

A recent study of supramolecular synthons in organic sulfonate structures in the Cambridge Structural Database (Haynes *et al.*, 2004) has highlighted the three hydrogen-bonded ring motifs seen in (I) and (II) as three of the most common ring motifs in sulfonate compounds containing NH donors. The $R_4^2(8)$, $R_4^3(10)$ and $R_4^4(12)$ motifs occur in 13.47, 13.64 and 17.85%, respectively, of all sulfonate/NH-donor crystal structures. The study also highlights an $R_6^6(18)$ ring motif built from three sulfonate groups providing two O donor atoms each, and three NH_x donors providing two NH donors each. This motif occurs in 12.29% of all sulfonate/NH-donor crystal structures and is observed in both polymorphs (I) and (II) as a combination of two smaller rings.

The differences in the hydrogen-bonding motifs observed in (I) and (II) result in differences in the packing of the two-dimensional sheets. Both contain the same two-dimensional sheet arrangement, in which, within the sheets, two layers of 2,4,6-trimethylbenzenesulfonate anions sandwich one layer of

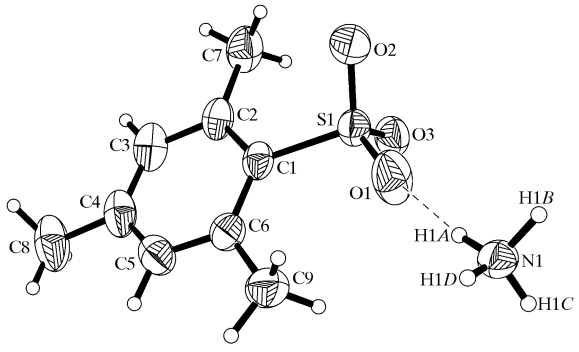


Figure 2
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

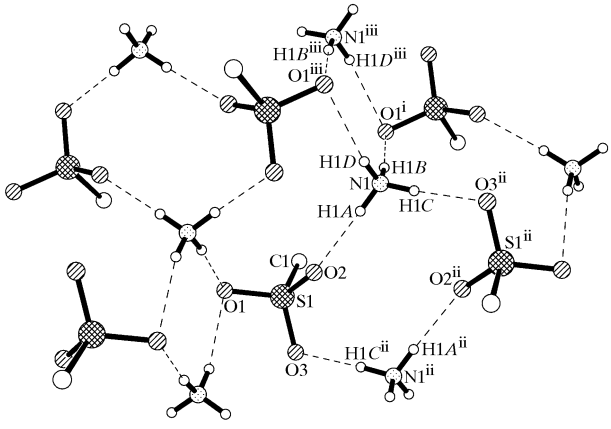


Figure 3
A view of the hydrogen-bonding array in (I). H atoms (except those bound to N atoms) and all C atoms (except C1) have been removed for clarity. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, -y, 1-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

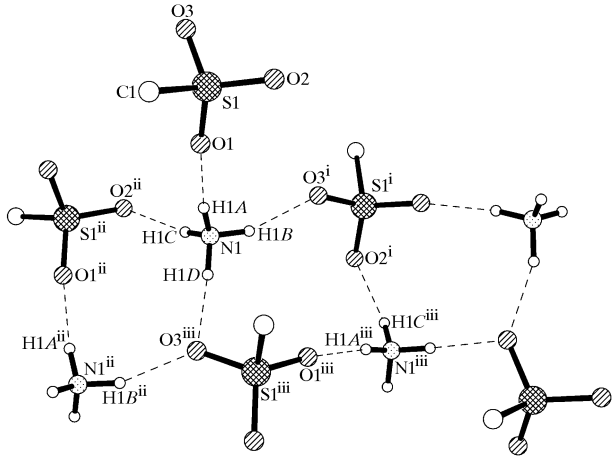


Figure 4
A view of the hydrogen-bonding array in (II). H atoms (except those bound to N atoms) and all C atoms (except C1) have been removed for clarity. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$.]

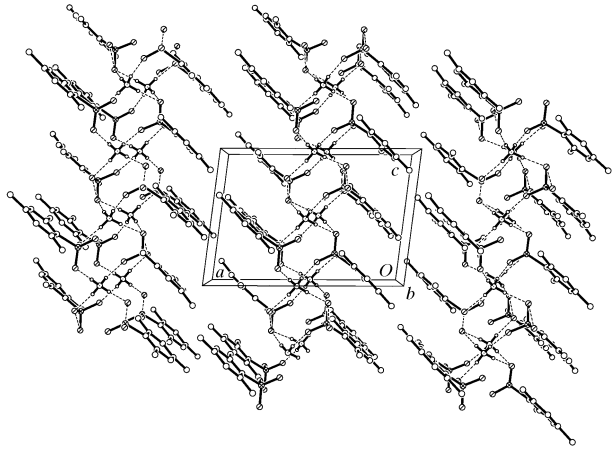


Figure 5
A packing plot of (I), viewed along the crystallographic *b* axis. H atoms not involved in hydrogen bonding have been omitted for clarity and hydrogen bonds are shown as dashed lines.

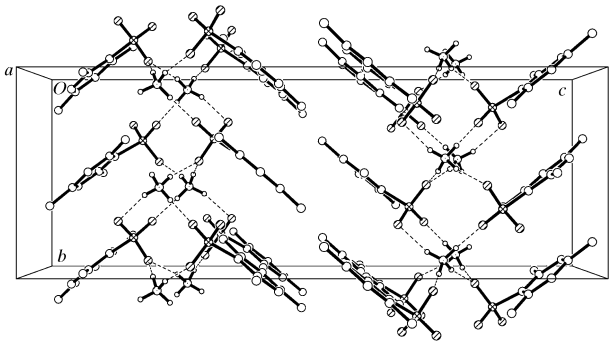


Figure 6
A packing plot of (II), viewed along the crystallographic *a* axis. H atoms not involved in hydrogen bonding have been omitted for clarity and hydrogen bonds are shown as dashed lines.

NH_4^+ cations, the charged NH_4^+ cations and SO_3^- groups of the anions being enveloped between layers of relatively hydrophobic aromatic rings. In the case of (I), the sheets are parallel and extend in the crystallographic *ac* plane, whereas in (II), the sheets are antiparallel and extend in the crystallographic *bc* plane. Figs. 5 and 6 show the result of the different hydrogen-bonding motifs in (I) and (II), in that the polymorphs pack with different alignments of the aromatic rings of the 2,4,6-trimethylbenzenesulfonate anions. In (I) (Fig. 5), all of the aromatic groups are approximately coplanar, with maximum angles of 5.74 (7)° between the least-squares planes of symmetry-related anions. In contrast, while the close-packed aromatic groups of adjacent sheets are approximately coplanar in (II), with maximum angles of 1.77 (19)° between the least-squares planes of symmetry-related anions (Fig. 6), the least-squares planes of the aromatic rings in the two different layers within each thick sheet are aligned at angles of 78.76 (8)° to each other, in a herring-bone manner.

In conclusion, small differences in the hydrogen-bonding motifs have led to the crystallization of two polymorphs of the title compound. In consideration of the frequency of the use of MSH as an aminating agent, we hope that the presentation of these results will aid researchers in the identification of crystals of their desired novel aminated compounds, rather than of the ammonium 2,4,6-trimethylbenzenesulfonate by-product. Indeed, in addition to the two aforementioned specific examples, we have noted the compound forming as a by-product in variable yield in other thio ether and mixed sulfide ligand amination reactions. This highlights the ubiquitous nature of the product in MSH amination reactions and thus serves to emphasize the need for its effective identification.

Experimental

Colourless columnar crystals of (I) and colourless needles of (II) crystallized simultaneously upon slow diffusion of diethyl ether vapour into a methanolic solution of a crude reaction mixture containing the title compound as either a by-product or a hydrolysis product (see *Comment* for further details).

Compound (I)

Crystal data

$NH_4^+\cdot C_9H_{11}O_3S^-$
M_r = 217.28
Monoclinic, $P2_1/c$
a = 13.7562 (15) Å
b = 8.4253 (9) Å
c = 9.4761 (10) Å
β = 97.368 (2)°
V = 1089.2 (2) Å^3
Z = 4
D_x = 1.325 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5637 reflections
θ = 2.8–28.4°
μ = 0.28 mm^{-1}
T = 150 (2) K
Column, colourless
0.76 × 0.19 × 0.13 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω rotation scans with narrow frame
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.816, T_{max} = 0.965
8693 measured reflections
2510 independent reflections
2202 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 28.5°
$h = -17 \rightarrow 17$
$k = -10 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.094
S = 1.04
2510 reflections
142 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.3258P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

S1—O1	1.4632 (10)	S1—O3	1.4557 (10)
S1—O2	1.4584 (10)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2	0.83 (2)	1.98 (2)	2.8124 (17)	171.5 (18)
N1—H1B···O1^{i}	0.92 (2)	1.91 (2)	2.8261 (17)	175.0 (17)
N1—H1C···O3^{ii}	0.87 (2)	1.96 (2)	2.8253 (16)	172.8 (18)
N1—H1D···O1^{iii}	0.83 (2)	2.18 (2)	2.9846 (16)	162.7 (18)

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

Compound (II)

Crystal data

$NH_4^+\cdot C_9H_{11}O_3S^-$
M_r = 217.29
Orthorhombic, *Pbca*
a = 8.4792 (13) Å
b = 9.6152 (15) Å
c = 26.864 (4) Å
V = 2190.2 (6) Å^3
Z = 8
D_x = 1.318 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2914 reflections
θ = 2.8–26.7°
μ = 0.28 mm^{-1}
T = 150 (2) K
Needle, colourless
0.45 × 0.04 × 0.02 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω rotation scans with narrow frame
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.885, T_{max} = 0.995
14 511 measured reflections
1929 independent reflections
1328 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.105P)^2 + 1.889P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.066$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.199$	$\Delta\rho_{max} = 0.78$ e Å^{-3}
$S = 1.15$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
1929 reflections	
142 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 3
Selected bond lengths (Å) for (II).

S1—O1	1.438 (3)	S1—O3	1.456 (3)
S1—O2	1.450 (3)	S1—C1	1.780 (4)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.90 (2)	1.86 (2)	2.755 (4)	173 (3)
N1—H1B···O3^{i}	0.93 (2)	1.84 (2)	2.734 (4)	160 (3)
N1—H1C···O2^{ii}	0.89 (2)	1.96 (2)	2.828 (4)	165 (3)
N1—H1D···O3^{iii}	0.92 (2)	1.95 (2)	2.861 (4)	167 (3)

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

Aromatic (C—H = 0.95 Å) and methyl (C—H = 0.98 Å) H atoms were placed in geometrically calculated positions and refined using a riding model. In (I), N-bound H atoms were located in a difference Fourier map and their coordinates refined freely. In (II), the N-bound H atoms were refined using restraints on the N—H bond length [target value = 0.90 (3) Å] and on the H—N—H angle (restrained to give similar 1,3-distances). In both structures, U_{iso}(H) values were set at $1.2U_{eq}$(C) for aryl H, and at $1.5U_{eq}$(N,C) for NH and methyl H atoms. Data for (II) were truncated at $2\theta = 50°$ as only statistically insignificant data were present above this limit.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepar material for publication: *SHELXTL* and local programs.

The authors acknowledge the EPSRC for Postdoctoral Research Assistant support (LMG and SMA).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1599). Services for accessing these data are described at the back of the journal.

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