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Dihydronium 3-nitrobenzenesulfonate

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.104
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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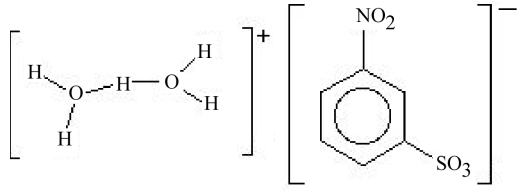
The title compound, $H_5O_2^+\cdot C_6H_4NO_5S^-$, crystallized slowly over a period of several years. It is stable and the dihydronium cation is well determined; all of the H-atom positions in the cation were refined. The strong hydrogen bond between the O atoms is nearly linear, with the H atom near the midpoint of the two O atoms. The refined O—H distances are 1.15 (2) and 1.27 (2) Å, respectively.

Comment

In the title compound, dihydronium 3-nitrobenzenesulfonate, (I), two water molecules are strongly hydrogen bonded, with an O···O separation of 2.411 (2) Å, forming a dihydronium ($H_5O_2^+$) cation. Each of the remaining H atoms in the cation participates in intermolecular hydrogen bonding with the sulfonate O atoms, and each sulfonate O atom acts as an acceptor, forming a three-dimensional network. There are a number of reports of dihydronium ions in the solid state. In the April 2002 release of the Cambridge Structural Database (Allen & Kennard, 1993), there are 36 occurrences in which the O···O separations are less than 2.6 Å between H_3O^+ and H_2O pairs. Some early examples are: bis[chloro(1,2-propanediamine-*N*,*N*′)cobalt] chloride hydrochloride hydronium (Saito & Iwasaki, 1962), and hydrogen chloride dihydrate (Lundgren & Olovsson, 1967).



(I)

In the current study, the data quality is sufficient to refine the dihydronium H-atom positions. The strong hydrogen bond between the water molecules is nearly linear, with the O—H···O angle equal to 177 (2)°. The hydrogen bonds between the ions are also nearly linear, with O—H···O angles in the range 174 (2)–179 (2)°. The central H atom in the cation has O—H distances of O1*S*—H1*C* = 1.15 (2) Å and O2*S*—H1*C* = 1.27 (2) Å. The dihydronium O atoms are pyramidal, with O1*S* 0.28 (2) Å out of the plane formed by atoms H1*A*, H1*B*, and H1*C*, and O2*S* 0.32 (2) Å out of the plane formed by atoms H2*A*, H2*B*, and H1*C*. The remaining cation O—H distances are O1*S*—H1*A* = 0.86 (2) Å, O1*S*—H1*B* = 0.83 (2) Å, O2*S*—H2*A* = 0.81 (2) Å and O2*S*—H2*B* = 0.81 (2) Å. The structure of the 3-nitrobenezenesulfonate anion has been reported in guanidinium 3-nitrobenezenesulfonate (Russell & Ward, 1997) and in (2-*p*-benzoquinonediimine)decaamminediru-

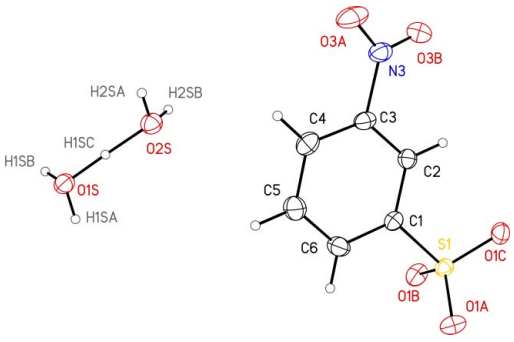


Figure 1
Displacement ellipsoid plot of dihydronium 3-nitrobenzenesulfonate, drawn at the 50% probability level.

thenium(II,III) pentakis(*m*-nitrobenzenesulfonate) pentahydrate (Joss *et al.*, 1985). Here, the nitro group is twisted out of the benzene plane; the torsion angle C2—C3—N3—O3*B* is 20.2 (2)°. The orientation of the sulfonate is defined by the torsion angle C2—C1—S1—O1*B* of −104.6 (1)°. The room-temperature (295 K) cell is *a* = 7.945 (4) Å, *b* = 8.119 (4) Å, *c* = 9.389 (5) Å, *α* = 90.42 (1), *β* = 94.70 (1) and *γ* = 119.08°(1).

Experimental

A Friedel–Crafts substitution on $PhCH_2CH_2Br$ with *m*-$ClSO_2$-$C_6H_4NO_2$, $AlCl_3$ and CH_2Cl_2 was worked-up by hydrolysis, drying of the organic layer, and distillation. The yellow distillate (383 K, vacuum) contained several products, from which dihydronium 3-nitrobenzenesulfonate, (I), crystallized over a period of several years. Apparently, (I) was formed from the hydrolysis of unreacted sulfonyl chloride.

Crystal data

$H_5O_2^+ \cdot C_6H_4NO_5S^-$
M_r = 239.20
Triclinic, $P\overline{1}$
a = 7.872 (2) Å
b = 7.986 (2) Å
c = 9.414 (2) Å
α = 90.456 (5)°
β = 95.284 (5)°
γ = 118.701 (5)°
V = 516.0 (1) Å^3
Z = 2
D_x = 1.540 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 3195 reflections
θ = 3.0–27.9°
μ = 0.33 mm^{-1}
T = 93 (2) K
Plate, yellow
0.52 × 0.43 × 0.18 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.845, T_{max} = 0.943
4192 measured reflections
2433 independent reflections
2086 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.2°
h = −9 → 10
k = −9 → 10
l = −12 → 12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.104
S = 1.08
2433 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.0567P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

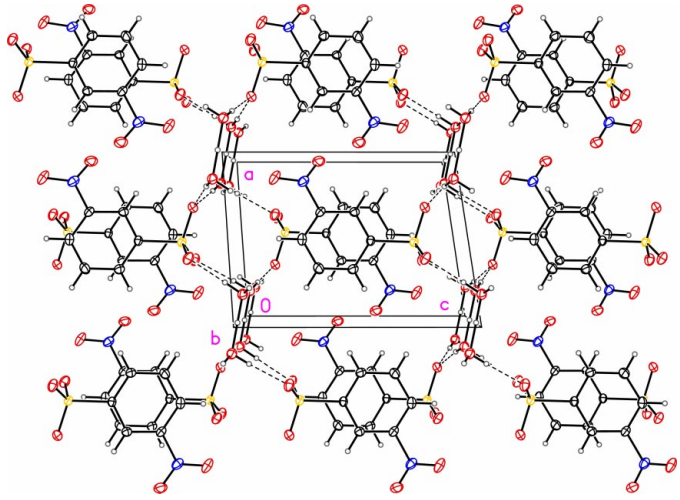


Figure 2
Packing diagram, viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*S*—H1*SC*···O2*S*	1.15 (2)	1.27 (2)	2.411 (2)	177 (2)
O1*S*—H1*SA*···O1*A*^{i}	0.86 (2)	1.79 (2)	2.643 (2)	177 (2)
O1*S*—H1*SB*···O1*C*^{ii}	0.83 (2)	1.87 (2)	2.696 (2)	174 (2)
O2*S*—H2*SA*···O1*B*^{iii}	0.81 (2)	1.85 (2)	2.656 (2)	177 (2)
O2*S*—H2*SB*···O1*C*^{iv}	0.81 (2)	1.85 (2)	2.663 (2)	179 (2)

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

Only the dihydronium H-atom positions were refined.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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