Bis(dimethylammonium) 2,5-dihydroxybenzene-1,4-disulfonate

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In the crystal of the title salt, $2C_2H_8N^+ \cdot C_6H_4O_8S_2^{2-}$, the anion lies on a center of inversion. The dimethylammonium cation forms one N—H···O hydrogen bond and another bifurcated N—H···O hydrogen bond. The hydroxy group links with the sulfonyl group *via* an intermolecular O—H···O hydrogen bond. These N—H···O and O—H···O hydrogen bonds generate a three-dimensional network.

Related literature

For the diethylammonium salt, see: Solans *et al.* (1982).
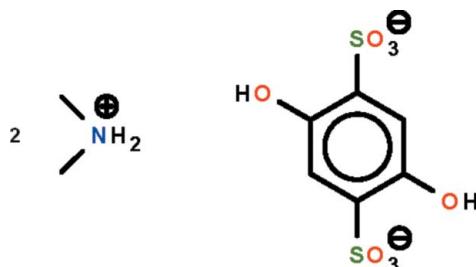
Experimental

Crystal data

$2C_2H_8N^+ \cdot C_6H_4O_8S_2^{2-}$
M_r = 360.40
Monoclinic, $P2_1/c$
a = 8.0136 (12) Å
b = 12.2741 (19) Å
c = 9.2061 (16) Å
β = 115.268 (5)°

V = 818.9 (2) Å³
Z = 2
Mo $K\alpha$ radiation
μ = 0.36 mm⁻¹
T = 293 K
0.25 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.770, T_{max} = 1.000

7785 measured reflections
1849 independent reflections
1675 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.115
S = 1.07
1849 reflections
112 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.78 e Å⁻³
$\Delta\rho_{min}$ = −0.25 e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O3ⁱ	0.83 (1)	1.85 (1)	2.670 (2)	175 (2)
N1—H1···O1	0.88 (1)	2.13 (2)	2.866 (2)	140 (2)
N1—H1···O1ⁱⁱ	0.88 (1)	2.21 (2)	2.921 (2)	138 (2)
N1—H2···O2ⁱⁱⁱ	0.89 (1)	2.07 (2)	2.837 (2)	143 (3)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalClear* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
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Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Solans, X., Plana, F. & Font-Altaba, M. (1982). *Acta Cryst.* B**38**, 651–653.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

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S1. Comment

Bis(diethylammonium) 2,5-dihydroxy-1,4-benzenedisulfonate is a commercial pharmacological chemical whose crystal structure has been described (Solans *et al.*, 1982). The title dimethyammonium salt (Scheme I) is an unexpected product of a hydrothermal synthesis involving 2,5-dihydroxy-1,4-benzenesulfonate in DMS solvent; the dimethylammonium cation probably resulted from the decomposition of DMF. The anion lies on a center-of-inversion (Fig. 1). The dimethyl-ammonium cation forms one N–H···O hydrogen bond and another bifurcated hydrogen bond. These N–H···O and O–H···O hydrogen bonds generate a three-dimensional network (Table 1).

S2. Experimental

DMF (8 ml), magnesium hydroxide (1 mmol) and 1,4-dihydroxy-2,5-benzenedisulfonic acid (1 mmol) were heated in a 23-ml, Teflon-lined, stainless-stell Parr bomb at 413 K for 3 days. Colorless crystals were isolated from the cool vessel.

S3. Refinement

The carbon-bound H-atoms were placed in a calculated position (C–H 0.93 and 0.96 Å) and were included in the refinement in the riding model approximation, U(H) set to 1.2U(C). The amino and hydroxy H-atoms were located in a difference Fourier map, and were refined with distance restraints of N–H 0.88±0.01 Å, O–H 0.84±0.01 Å; their temperature factors were refined.
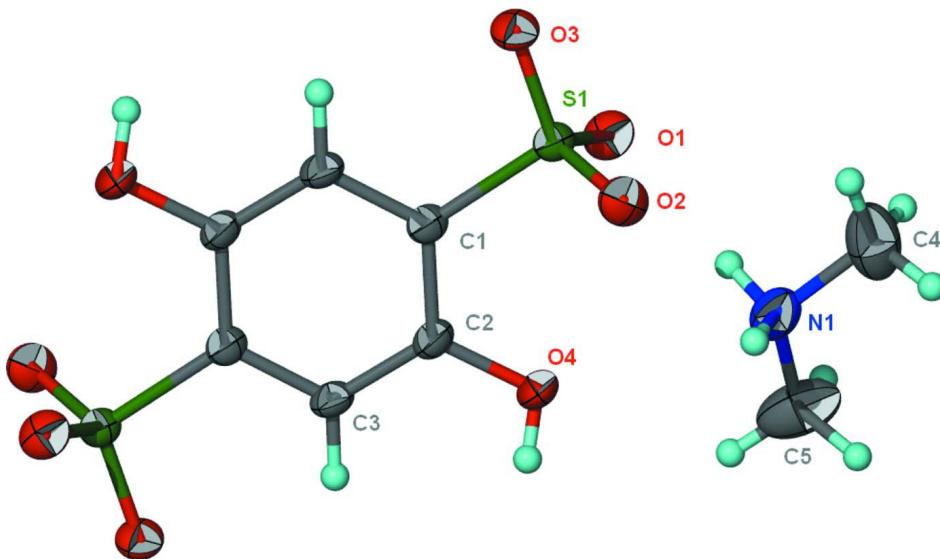
Figure 1
Thermal ellipsoid plot (Barbour, 2001) of $2(CH_3)_2NH_2 \cdot C_6H_2(OH)_2(SO_3)_2$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

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Crystal data
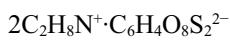
$2C_2H_8N^+ \cdot C_6H_4O_8S_2{}^{2-}$
$M_r = 360.40$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.0136$ (12) Å
$b = 12.2741$ (19) Å
$c = 9.2061$ (16) Å
$\beta = 115.268$ (5)°
$V = 818.9$ (2) Å^3
$Z = 2$

$F(000) = 380$
$D_x = 1.462$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5427 reflections
$\theta = 3.3$–27.4°
$\mu = 0.36$ mm^{-1}
$T = 293$ K
Prism, colorless
$0.25 \times 0.20 \times 0.15$ mm

Data collection

Rigaku R-AXIS RAPID IP
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scan
Absorption correction: multi-scan
    (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.770$, $T_{max} = 1.000$

7785 measured reflections
1849 independent reflections
1675 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.3°$
$h = -9 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.115$
$S = 1.07$
1849 reflections
112 parameters

3 restraints
Primary atom site location: structure-invariant
    direct methods
Secondary atom site location: difference Fourier
    map
Hydrogen site location: inferred from
    neighbouring sites

H atoms treated by a mixture of independent and constrained refinement		$(\Delta/\sigma)_{max} = 0.001$	
		$\Delta\rho_{max} = 0.78$ e Å^{-3}	
$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.1341P]$ where $P = (F_o^2 + 2F_c^2)/3$		$\Delta\rho_{min} = -0.25$ e Å^{-3}	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.31946 (5)	0.62757 (3)	0.66986 (4)	0.02663 (17)
O1	0.14241 (15)	0.57550 (9)	0.57815 (14)	0.0388 (3)
O2	0.44282 (17)	0.61906 (10)	0.59274 (16)	0.0405 (3)
O3	0.29844 (16)	0.73891 (8)	0.71461 (14)	0.0358 (3)
O4	0.4472 (2)	0.39499 (10)	0.71737 (15)	0.0439 (3)
H4	0.523 (2)	0.3448 (13)	0.742 (3)	0.047 (6)*
N1	0.1913 (2)	0.41948 (15)	0.3680 (2)	0.0466 (4)
H1	0.132 (3)	0.445 (2)	0.422 (3)	0.076 (8)*
H2	0.3121 (16)	0.432 (2)	0.410 (3)	0.085 (9)*
C1	0.4220 (2)	0.55462 (11)	0.85428 (17)	0.0274 (3)
C2	0.4752 (2)	0.44621 (12)	0.85763 (18)	0.0305 (3)
C3	0.5534 (2)	0.39234 (12)	1.00446 (19)	0.0308 (3)
H3	0.5897	0.3200	1.0083	0.037*
C4	0.1193 (3)	0.4894 (2)	0.2257 (3)	0.0727 (7)
H4A	0.1489	0.5640	0.2578	0.109*
H4B	−0.0122	0.4812	0.1710	0.109*
H4C	0.1741	0.4689	0.1551	0.109*
C5	0.1563 (3)	0.3028 (2)	0.3375 (4)	0.0769 (8)
H5A	0.2122	0.2637	0.4372	0.115*
H5B	0.2081	0.2784	0.2665	0.115*
H5C	0.0257	0.2898	0.2890	0.115*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0296 (2)	0.0240 (2)	0.0307 (3)	−0.00098 (12)	0.01698 (18)	0.00029 (12)
O1	0.0337 (6)	0.0388 (6)	0.0430 (7)	−0.0054 (5)	0.0156 (5)	−0.0072 (5)
O2	0.0418 (7)	0.0465 (7)	0.0445 (7)	0.0048 (5)	0.0293 (6)	0.0084 (5)
O3	0.0463 (6)	0.0230 (5)	0.0402 (6)	0.0005 (4)	0.0205 (5)	0.0012 (4)
O4	0.0667 (9)	0.0330 (6)	0.0303 (6)	0.0166 (6)	0.0192 (6)	−0.0040 (5)
N1	0.0400 (8)	0.0577 (10)	0.0451 (9)	0.0031 (7)	0.0211 (7)	−0.0086 (7)
C1	0.0334 (7)	0.0236 (7)	0.0302 (7)	−0.0008 (5)	0.0183 (6)	0.0001 (5)
C2	0.0409 (8)	0.0251 (7)	0.0300 (8)	0.0011 (6)	0.0194 (6)	−0.0040 (5)
C3	0.0423 (8)	0.0205 (6)	0.0346 (8)	0.0029 (6)	0.0211 (7)	−0.0017 (5)
C4	0.0601 (13)	0.110 (2)	0.0519 (13)	−0.0003 (14)	0.0279 (11)	0.0132 (13)
C5	0.0589 (13)	0.0636 (15)	0.120 (2)	−0.0071 (11)	0.0497 (15)	−0.0276 (14)

Geometric parameters (Å, º)

S1—O2	1.4462 (12)	C1—C2	1.394 (2)
S1—O1	1.4531 (11)	C2—C3	1.391 (2)

S1—O3	1.4577 (11)	C3—C1^i	1.391 (2)
S1—C1	1.7799 (15)	C3—H3	0.9300
O4—C2	1.3657 (18)	C4—H4A	0.9600
O4—H4	0.827 (9)	C4—H4B	0.9600
N1—C5	1.463 (3)	C4—H4C	0.9600
N1—C4	1.462 (3)	C5—H5A	0.9600
N1—H1	0.879 (10)	C5—H5B	0.9600
N1—H2	0.890 (10)	C5—H5C	0.9600
C1—C3^i	1.391 (2)		
O2—S1—O1	112.67 (8)	O4—C2—C1	119.56 (14)
O2—S1—O3	113.09 (7)	C3—C2—C1	118.83 (13)
O1—S1—O3	112.00 (7)	C2—C3—C1^i	120.76 (13)
O2—S1—C1	107.34 (7)	C2—C3—H3	119.6
O1—S1—C1	105.76 (7)	C1^i—C3—H3	119.6
O3—S1—C1	105.31 (7)	N1—C4—H4A	109.5
C2—O4—H4	106.1 (15)	N1—C4—H4B	109.5
C5—N1—C4	115.6 (2)	H4A—C4—H4B	109.5
C5—N1—H1	110.4 (19)	N1—C4—H4C	109.5
C4—N1—H1	101.2 (19)	H4A—C4—H4C	109.5
C5—N1—H2	110 (2)	H4B—C4—H4C	109.5
C4—N1—H2	103.1 (19)	N1—C5—H5A	109.5
H1—N1—H2	116 (3)	N1—C5—H5B	109.5
C3^i—C1—C2	120.41 (13)	H5A—C5—H5B	109.5
C3^i—C1—S1	118.67 (11)	N1—C5—H5C	109.5
C2—C1—S1	120.91 (11)	H5A—C5—H5C	109.5
O4—C2—C3	121.61 (13)	H5B—C5—H5C	109.5
O2—S1—C1—C3^i	126.33 (13)	C3^i—C1—C2—O4	178.89 (14)
O1—S1—C1—C3^i	−113.16 (13)	S1—C1—C2—O4	−0.5 (2)
O3—S1—C1—C3^i	5.58 (14)	C3^i—C1—C2—C3	−0.1 (3)
O2—S1—C1—C2	−54.28 (14)	S1—C1—C2—C3	−179.49 (11)
O1—S1—C1—C2	66.23 (14)	O4—C2—C3—C1^i	−178.87 (14)
O3—S1—C1—C2	−175.03 (12)	C1—C2—C3—C1^i	0.1 (3)

Symmetry code: (i) −x+1, −y+1, −z+2.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O4—H4⋯O3^{ii}	0.83 (1)	1.85 (1)	2.670 (2)	175 (2)
N1—H1⋯O1	0.88 (1)	2.13 (2)	2.866 (2)	140 (2)
N1—H1⋯O1^{iii}	0.88 (1)	2.21 (2)	2.921 (2)	138 (2)
N1—H2⋯O2^{iv}	0.89 (1)	2.07 (2)	2.837 (2)	143 (3)

Symmetry codes: (ii) −x+1, y−1/2, −z+3/2; (iii) −x, −y+1, −z+1; (iv) −x+1, −y+1, −z+1.