Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diethylammonium 2,5-dihydroxybenzenesulfonate

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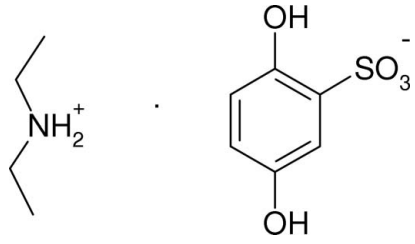
Received 14 November 2007; accepted 18 November 2007

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.079; data-to-parameter ratio = 20.8.

The title compound, $C_4H_{12}N^+\cdot C_6H_5O_5S^-$, also known as ethamsylate, is a molecular salt. Anion-to-anion O—H···O hydrogen bonds lead to helices containing $C(6)$ and $C(7)$ chains and further bonds of the same type cross-link the chains. Cation-to-anion N—H···O hydrogen bonds complete the structure.

Related literature

For a related structure, see: Solans *et al.* (1982). For background, see: Harrison *et al.* (2007); Hernandez *et al.* (2004); Garay *et al.* (2006). For reference structural data, see: Allen *et al.* (1987). For hydrogen-bonding motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_4H_{12}N^+\cdot C_6H_5O_5S^-$
M_r = 263.31
Trigonal, $P3_2$
a = 8.7006 (4) Å
c = 14.0732 (6) Å
V = 922.62 (7) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 291 (2) K
0.40 × 0.35 × 0.30 mm

Data collection

Bruker SMART1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.900, T_{max} = 0.926
7627 measured reflections
3516 independent reflections
3307 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.079
S = 1.08
3516 reflections
169 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), with 1734 Friedel pairs
Flack parameter: 0.03 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.85 (2)	2.02 (3)	2.8441 (17)	163 (2)
O2—H2···O4^{ii}	0.75 (3)	1.90 (3)	2.6480 (19)	174 (3)
N1—H3···O3	0.82 (3)	2.43 (3)	3.084 (2)	138 (2)
N1—H3···O2^{iii}	0.82 (3)	2.49 (3)	3.0691 (19)	129 (2)
N1—H4···O5^{iv}	0.96 (3)	1.94 (3)	2.888 (2)	171 (2)

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

MTS thanks Sambhram Institute of Technology for research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2077).

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  doi:10.1107/S1600536807060540

supplementary materials

Acta Cryst. (2007). E**63**, o4870 [**doi:10.1107/S1600536807060540**]

Diethylammonium 2,5-dihydroxybenzenesulfonate

W. T. A. Harrison, M. T. Swamy, H. S. Yathirajan, M. A. Ashok and B. Narayana

Comment

The title compound, (I), ethamsylate, or diethylammonium 2,5-dihydroxybenzenesulfonate, $C_4H_{12}N^+\cdot C_6H_5O_5S^-$, is a drug known to possess antihemorrhagic properties. It is said to correct abnormal platelet adhesion, thereby reducing capillary bleeding (Hernandez *et al.*, 2004; Garay *et al.*, 2006).

In continuation of our work on crystal structures of pharmaceutical compounds (Harrison *et al.*, 2007) and in view of the importance of (I), its crystal structure is now reported. The crystal structure of the related bis(diethylammonium) 2,5-dihydroxy-1,4-benzenedisulfonate, $(C_4H_{12}N^+)_2\cdot C_6H_4O_2S_2^{2-}$, was reported earlier (Solans *et al.*, 1982).

Compound (I) formally arises *via* proton transfer from the sulfonic acid group to the secondary amine N atom (Fig. 1) to yield a molecular salt. There are no previous crystal structures containg the 2,5-dihydroxybenzenesulfonate anion, but its individual bond lengths and angles are similar to the corresponding values in the related 2,5-dihydroxy-1,4-benzenedisulfonate (Solans *et al.*, 1982). Overall, the geomerical parameters of the two components in (I) may be regarded as normal (Allen *et al.*, 1987).

Compound (I) crystallizes in the chiral space group $P3_2$, with a well defined absolute structure (Flack, 1983). The constituents are achiral, so the enantiomorphic nature of the structure must arise from the packing, and an equal number of enantiomers (crystallizing in $P3_1$ and $P3_2$) must exist in the bulk sample. The packing is influenced by O—H···O and N—H···O hydrogen bonds (Table 1). Considered in isolation, both the O1—H1···O3^{i} and O2—H2···O4^{ii} bonds (see Table 1 for symmetry codes) lead to helical chains propagating in [001]. The first of these results in a C(6) chain, the second in a C(7) chain (Fig. 2). Together, the O—H···O bonds lead to a three-dimensional array. A strong, near linear N—H···O and a weak, bifurcated N—H···(O,*O*) hydrogen bond, which link the cation to adjacent anions, complete the structure.

Experimental

The title compound was obtained as a gift sample from Arvee Chem Pharma, Mysore, India. Crystals of (I) were grown by slow evaporation of an ethanol solution (m.p.: 400 K).

Refinement

The N– and O-bound H atoms were located in a difference map and their positions were freely refined with U_{iso}(H) = 1.2U_{eq}(carrier). The C-bound H atoms were geometrically placed (C—H = 0.93–0.98 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl C). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density.

Figures

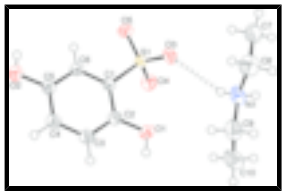

Fig. 1. View of the molecular structure of (I) showing 50% displacement ellipsoids (arbitrary sphere for the H atom). The hydrogen bond is shown as a double-dashed line.

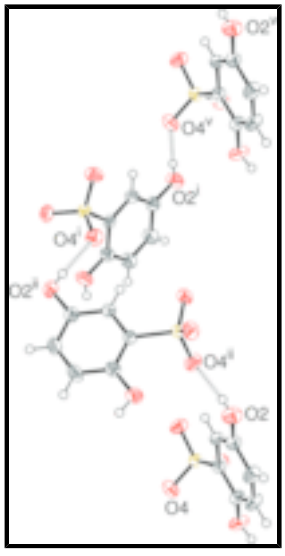

Fig. 2. Part of a helical chain on anions in the crystal structure of (I). The hydrogen bonds are shown as a double-dashed lines. Symmetry codes as in Table 1; additionally: (v) x, y, $z + 1$.

Diethylammonium 2,5-dihydroxybenzenesulfonate

Crystal data

$C_4H_{12}N^+·C_6H_5O_5S^-$	$Z = 3$
$M_r = 263.31$	$F_{000} = 420$
Trigonal, $P3_2$	$D_x = 1.422$ Mg m^{-3}
Hall symbol: P 32	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.7006$ (4) Å	Cell parameters from 5152 reflections
$b = 8.7006$ (4) Å	$\theta = 2.7$–29.9º
$c = 14.0732$ (6) Å	$\mu = 0.27$ mm^{-1}
$\alpha = 90$º	$T = 291$ (2) K
$\beta = 90$º	Chunk, colourless
$\gamma = 120$º	0.40 × 0.35 × 0.30 mm
$V = 922.62$ (7) Å^3	

Data collection

Bruker SMART1000 CCD diffractometer	3516 independent reflections
Radiation source: fine-focus sealed tube	3307 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.016$

T = 291(2) K	θ_{max} = 30.0º
ω scans	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Bruker, 1999)	h = −12→8
T_{min} = 0.900, T_{max} = 0.926	k = −10→12
7627 measured reflections	l = −19→19

Refinement

Refinement on F^2	Hydrogen site location: difmap and geom
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.0286P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.079	$(\Delta/\sigma)_{max} < 0.001$
S = 1.08	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
3516 reflections	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
169 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.028 (3)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 1734 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.03 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.92539 (18)	0.24787 (18)	0.04160 (9)	0.0255 (2)
C2	0.96186 (19)	0.3460 (2)	−0.04236 (11)	0.0303 (3)
C3	1.1272 (2)	0.4984 (2)	−0.05275 (13)	0.0379 (3)
H3A	1.1536	0.5643	−0.1084	0.046*
C4	1.2525 (2)	0.5526 (2)	0.01894 (12)	0.0379 (4)
H4A	1.3625	0.6544	0.0110	0.045*
C5	1.2151 (2)	0.45559 (19)	0.10314 (11)	0.0304 (3)
C6	1.05126 (19)	0.30364 (19)	0.11403 (10)	0.0268 (3)
H6	1.0251	0.2385	0.1700	0.032*

O1	0.83456 (17)	0.28992 (19)	−0.11154 (9)	0.0413 (3)
H1	0.879 (3)	0.367 (3)	−0.1556 (17)	0.050*
O2	1.34355 (16)	0.51443 (18)	0.17195 (9)	0.0413 (3)
H2	1.305 (4)	0.454 (4)	0.2142 (19)	0.050*
S1	0.72428 (4)	0.04463 (4)	0.05746 (2)	0.02561 (9)
O3	0.57761 (15)	0.08132 (17)	0.05299 (8)	0.0369 (3)
O4	0.71698 (18)	−0.07059 (17)	−0.02011 (9)	0.0399 (3)
O5	0.73716 (16)	−0.02270 (16)	0.14986 (8)	0.0383 (3)
C7	0.1436 (3)	−0.0537 (3)	0.03267 (17)	0.0538 (5)
H7A	0.0917	−0.0234	0.0844	0.081*
H7B	0.2264	−0.0862	0.0572	0.081*
H7C	0.0519	−0.1517	−0.0020	0.081*
C8	0.2377 (3)	0.1017 (3)	−0.03175 (17)	0.0551 (5)
H8A	0.1524	0.1297	−0.0592	0.066*
H8B	0.3221	0.2037	0.0049	0.066*
C9	0.4290 (3)	0.2214 (3)	−0.17701 (17)	0.0513 (5)
H9A	0.3551	0.2732	−0.1905	0.062*
H9B	0.5373	0.3120	−0.1473	0.062*
C10	0.4738 (3)	0.1650 (3)	−0.2678 (2)	0.0615 (6)
H10A	0.5233	0.2628	−0.3115	0.092*
H10B	0.3682	0.0682	−0.2946	0.092*
H10C	0.5588	0.1276	−0.2557	0.092*
N1	0.3328 (2)	0.0685 (2)	−0.10904 (12)	0.0427 (3)
H3	0.401 (4)	0.038 (4)	−0.0891 (18)	0.051*
H4	0.238 (4)	−0.038 (4)	−0.1357 (17)	0.051*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0235 (6)	0.0256 (6)	0.0259 (6)	0.0113 (5)	0.0015 (5)	0.0008 (5)
C2	0.0293 (7)	0.0332 (7)	0.0295 (6)	0.0165 (6)	0.0000 (5)	0.0052 (6)
C3	0.0343 (7)	0.0359 (8)	0.0384 (8)	0.0136 (6)	0.0028 (6)	0.0152 (6)
C4	0.0309 (7)	0.0303 (7)	0.0419 (8)	0.0073 (6)	−0.0002 (6)	0.0094 (6)
C5	0.0274 (7)	0.0290 (6)	0.0312 (6)	0.0113 (6)	−0.0017 (5)	0.0003 (6)
C6	0.0276 (6)	0.0274 (6)	0.0239 (6)	0.0127 (5)	−0.0003 (5)	0.0012 (5)
O1	0.0362 (6)	0.0485 (7)	0.0302 (5)	0.0144 (5)	−0.0053 (4)	0.0098 (5)
O2	0.0308 (6)	0.0401 (6)	0.0370 (6)	0.0058 (5)	−0.0081 (5)	−0.0009 (5)
S1	0.02316 (15)	0.02566 (15)	0.02480 (14)	0.00979 (12)	0.00046 (11)	−0.00058 (12)
O3	0.0266 (5)	0.0431 (6)	0.0429 (6)	0.0190 (5)	0.0036 (4)	0.0021 (5)
O4	0.0428 (6)	0.0370 (6)	0.0393 (6)	0.0195 (5)	−0.0030 (5)	−0.0125 (5)
O5	0.0373 (6)	0.0349 (6)	0.0320 (5)	0.0100 (5)	−0.0004 (4)	0.0096 (4)
C7	0.0437 (10)	0.0623 (13)	0.0535 (11)	0.0251 (9)	−0.0015 (9)	−0.0083 (9)
C8	0.0630 (13)	0.0535 (11)	0.0598 (12)	0.0373 (11)	−0.0016 (10)	−0.0107 (9)
C9	0.0430 (10)	0.0388 (9)	0.0690 (13)	0.0180 (8)	−0.0050 (9)	0.0055 (9)
C10	0.0509 (12)	0.0484 (11)	0.0776 (15)	0.0190 (10)	0.0137 (11)	0.0141 (11)
N1	0.0336 (7)	0.0376 (7)	0.0604 (10)	0.0204 (6)	0.0008 (7)	−0.0020 (7)

Geometric parameters (Å, °)

C1—C6	1.3937 (19)	C7—C8	1.488 (4)
C1—C2	1.3982 (19)	C7—H7A	0.9600
C1—S1	1.7732 (14)	C7—H7B	0.9600
C2—O1	1.3682 (18)	C7—H7C	0.9600
C2—C3	1.393 (2)	C8—N1	1.480 (3)
C3—C4	1.384 (2)	C8—H8A	0.9700
C3—H3A	0.9300	C8—H8B	0.9700
C4—C5	1.396 (2)	C9—C10	1.489 (4)
C4—H4A	0.9300	C9—N1	1.507 (3)
C5—O2	1.370 (2)	C9—H9A	0.9700
C5—C6	1.385 (2)	C9—H9B	0.9700
C6—H6	0.9300	C10—H10A	0.9600
O1—H1	0.85 (2)	C10—H10B	0.9600
O2—H2	0.75 (3)	C10—H10C	0.9600
S1—O5	1.4533 (12)	N1—H3	0.82 (3)
S1—O4	1.4618 (12)	N1—H4	0.96 (3)
S1—O3	1.4635 (13)		
C6—C1—C2	120.44 (13)	H7A—C7—H7B	109.5
C6—C1—S1	117.84 (10)	C8—C7—H7C	109.5
C2—C1—S1	121.65 (11)	H7A—C7—H7C	109.5
O1—C2—C3	122.09 (14)	H7B—C7—H7C	109.5
O1—C2—C1	119.18 (13)	N1—C8—C7	112.22 (18)
C3—C2—C1	118.74 (13)	N1—C8—H8A	109.2
C4—C3—C2	120.70 (14)	C7—C8—H8A	109.2
C4—C3—H3A	119.6	N1—C8—H8B	109.2
C2—C3—H3A	119.6	C7—C8—H8B	109.2
C3—C4—C5	120.46 (14)	H8A—C8—H8B	107.9
C3—C4—H4A	119.8	C10—C9—N1	112.02 (17)
C5—C4—H4A	119.8	C10—C9—H9A	109.2
O2—C5—C6	122.44 (14)	N1—C9—H9A	109.2
O2—C5—C4	118.29 (13)	C10—C9—H9B	109.2
C6—C5—C4	119.27 (14)	N1—C9—H9B	109.2
C5—C6—C1	120.39 (13)	H9A—C9—H9B	107.9
C5—C6—H6	119.8	C9—C10—H10A	109.5
C1—C6—H6	119.8	C9—C10—H10B	109.5
C2—O1—H1	105.5 (17)	H10A—C10—H10B	109.5
C5—O2—H2	108 (2)	C9—C10—H10C	109.5
O5—S1—O4	112.17 (8)	H10A—C10—H10C	109.5
O5—S1—O3	112.19 (7)	H10B—C10—H10C	109.5
O4—S1—O3	111.96 (7)	C8—N1—C9	114.35 (16)
O5—S1—C1	106.14 (7)	C8—N1—H3	112.5 (18)
O4—S1—C1	105.83 (7)	C9—N1—H3	109.5 (19)
O3—S1—C1	108.08 (7)	C8—N1—H4	100.4 (15)
C8—C7—H7A	109.5	C9—N1—H4	115.9 (15)
C8—C7—H7B	109.5	H3—N1—H4	104 (2)
C6—C1—C2—O1	−178.78 (14)	C2—C1—C6—C5	−1.0 (2)

S1—C1—C2—O1	4.4 (2)	S1—C1—C6—C5	176.03 (12)
C6—C1—C2—C3	1.1 (2)	C6—C1—S1—O5	0.19 (13)
S1—C1—C2—C3	−175.75 (13)	C2—C1—S1—O5	177.14 (12)
O1—C2—C3—C4	179.34 (17)	C6—C1—S1—O4	−119.17 (12)
C1—C2—C3—C4	−0.6 (3)	C2—C1—S1—O4	57.78 (13)
C2—C3—C4—C5	−0.2 (3)	C6—C1—S1—O3	120.73 (11)
C3—C4—C5—O2	179.88 (16)	C2—C1—S1—O3	−62.32 (13)
C3—C4—C5—C6	0.4 (3)	C7—C8—N1—C9	179.41 (18)
O2—C5—C6—C1	−179.29 (14)	C10—C9—N1—C8	−162.32 (19)
C4—C5—C6—C1	0.2 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.85 (2)	2.02 (3)	2.8441 (17)	163 (2)
O2—H2···O4^{ii}	0.75 (3)	1.90 (3)	2.6480 (19)	174 (3)
N1—H3···O3	0.82 (3)	2.43 (3)	3.084 (2)	138 (2)
N1—H3···O2^{iii}	0.82 (3)	2.49 (3)	3.0691 (19)	129 (2)
N1—H4···O5^{iv}	0.96 (3)	1.94 (3)	2.888 (2)	171 (2)

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

Fig. 1

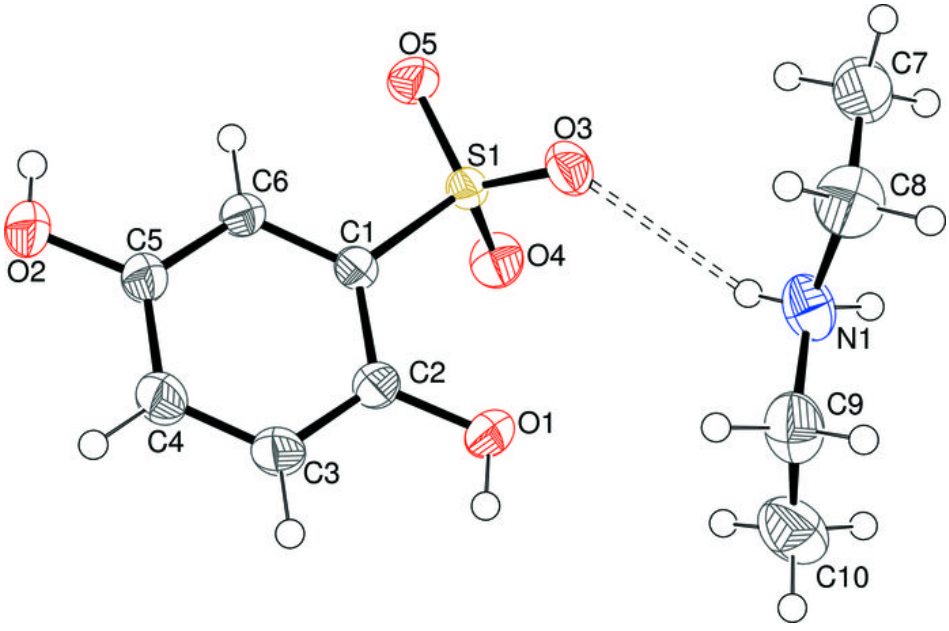

Fig. 2