

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-Guanidinobenzenesulfonic acid

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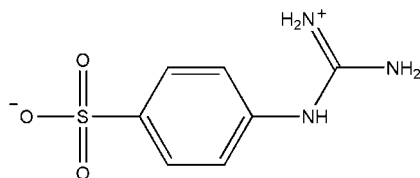
Received 20 February 2009; accepted 2 April 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.039; wR factor = 0.110; data-to-parameter ratio = 13.2.

In the zwitterionic title compound (systematic name: 4-[[amino(inimio)methyl]amino]benzenesulfonate), $\text{C}_7\text{H}_9\text{N}_3\text{O}_3\text{S}$, the dihedral angle between the plane of the guanidine grouping and the benzene ring system is $44.87(7)^\circ$. The crystal packing is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds involving all the potential donors.

Related literature

For the synthesis, see: Hofbans & Rath (1981). For the effect of guanidine salts on protein structure and their inhibitory effect on various physiological activities, see: Miyake *et al.* (2008).



Experimental

Crystal data

 $\text{C}_7\text{H}_9\text{N}_3\text{O}_3\text{S}$ $M_r = 215.24$ Orthorhombic, $Pbca$ $a = 7.9967(9)$ Å $b = 11.9200(13)$ Å $c = 19.721(2)$ Å $V = 1879.8(4)$ Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.33$ mm⁻¹ $T = 296$ K $0.35 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
 $T_{\min} = 0.902$, $T_{\max} = 0.944$

10292 measured reflections
2156 independent reflections
1544 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.110$
 $S = 1.02$
2156 reflections
163 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H5}\cdots\text{O2}^{\text{i}}$	0.80 (3)	2.00 (3)	2.802 (2)	171 (2)
$\text{N2}-\text{H6}\cdots\text{O2}^{\text{ii}}$	0.88 (3)	2.02 (3)	2.851 (2)	158 (2)
$\text{N2}-\text{H7}\cdots\text{O3}^{\text{iii}}$	0.89 (3)	2.07 (3)	2.913 (3)	160 (2)
$\text{N3}-\text{H8}\cdots\text{O1}^{\text{iii}}$	0.91 (3)	2.03 (3)	2.924 (3)	167 (3)
$\text{N3}-\text{H9}\cdots\text{O3}^{\text{iv}}$	0.83 (3)	2.34 (3)	2.928 (3)	129 (2)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to the Science Foundation of Jiangsu Education Bureau (05KJD 150039), the Professor Foundation of Huaiyin Teachers Collage (05 HSJS018) and the Science Foundation of Jiangsu Key Laboratory for the Chemistry of Low-Dimensional Materials (JSKC 06028) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2128).

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supplementary materials

Acta Cryst. (2009). E65, o980 [doi:10.1107/S1600536809012355]

4-Guanidinobenzenesulfonic acid

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Comment

Guanidine is known to interact strongly with various substances of biological origin in their molecules forming ionic pairs through ionic bonds and hydrogen bonding. Research on guanidine salts in the field of biochemistry have dealt mainly with their effect on protein structure and inhibitory effect on various physiological activities (Miyake *et al.*, 2008). The full molecule of the title compound, (I), (Fig. 1), is a big hyperconjugation system because the bond lengths of N1—C7 (1.329 (3)Å), C7—N2 (1.313 (3)Å) and C7—N3 (1.327 (3)Å) are averaged, and the bond lengths of S1—O1 (1.4546 (15)Å), S1—O2 (1.4619 (15)Å) and S1—O3 (1.4457 (15)Å) are also averaged. Meanwhile, the bond lengths of C3—N1 (1.327 (3)Å) and C6—S1 (1.770 (2)Å) become shorter than standard values (C—N = 1.47–1.50Å and C—S = 1.82Å). In addition, in (I) C2–C3–N1–C7 form a torsion angle of 42.3 (3)° and C1–C6–S1–O1 form a torsion angle of -69.91 (18)°. The dihedral angle between the plane of the guanidine group and the benzene ring system is 44.87 (7)°, while the dihedral angle between the benzene ring and the adjacent S1O1O2 group is 84.76 (7)°. The crystal packing is stabilized by intermolecular N—H···O hydrogen bonds involving all the potential donors.

Experimental

The title compound was synthesized by 4-aminobenzenesulfonic acid (3.5 g, 0.02 mol), 50% amino nitrile (3.5 g, 0.04 mol) and 37% hydrochloric acid (3.4 ml) in the ethanol boil point temperature for 24 h with stirring (Hofbens & Rath, 1981). The reaction mixture was reduced pressure distillation to obtain the rough solid, then dissolved in water. The solid residue was filtered and the filtrate was kept at room temperature. Colorless crystals of the title compound were obtained after a few days. The crystal used for data collection was obtained by slow evaporation from a saturated water solution at room temperature.

Refinement

All of the H atoms were located in a difference synthesis and refined isotropically [aromatic C—H = 0.90 (2)–0.97 (2)Å and N—H = 0.80 (3)–0.91 (3) Å].

Figures

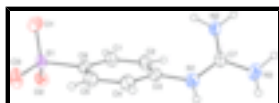


Fig. 1. The molecular structure of (I), with atom labels and 40% probability displacement ellipsoids for non-H atoms.

4-[[amino(inimio)methyl]amino]benzenesulfonate

Crystal data

C₇H₉N₃O₃S

$D_x = 1.521 \text{ Mg m}^{-3}$

supplementary materials

$M_r = 215.24$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 7.9967$ (9) Å

$b = 11.9200$ (13) Å

$c = 19.721$ (2) Å

$V = 1879.8$ (4) Å³

$Z = 8$

$F_{000} = 896$

Melting point > 300 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2125 reflections

$\theta = 3.2$ – 25.9°

$\mu = 0.33$ mm⁻¹

$T = 296$ K

Block, colourless

$0.35 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ K

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2000)

$T_{\min} = 0.902$, $T_{\max} = 0.944$

10292 measured reflections

2156 independent reflections

1544 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 3.2^\circ$

$h = -10 \rightarrow 10$

$k = -15 \rightarrow 13$

$l = -24 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.110$

$S = 1.02$

2156 reflections

163 parameters

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

$$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.6089P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.24$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Extinction correction: none

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0397 (3)	0.48689 (18)	0.26624 (10)	0.0329 (5)
C2	0.0470 (3)	0.53779 (18)	0.32882 (11)	0.0338 (5)
C3	0.1174 (2)	0.64333 (17)	0.33506 (10)	0.0316 (5)
C4	0.1778 (3)	0.69826 (18)	0.27833 (11)	0.0356 (5)
C5	0.1684 (3)	0.64822 (17)	0.21529 (11)	0.0346 (5)
C6	0.1005 (2)	0.54177 (16)	0.20961 (10)	0.0291 (4)
C7	0.1541 (3)	0.65879 (18)	0.45879 (10)	0.0349 (5)
H1	-0.006 (3)	0.4173 (19)	0.2604 (12)	0.044 (6)*
H2	-0.004 (3)	0.504 (2)	0.3685 (11)	0.043 (6)*
H3	0.230 (3)	0.765 (2)	0.2812 (11)	0.045 (7)*
H4	0.210 (3)	0.6900 (18)	0.1779 (13)	0.043 (6)*
H5	0.101 (3)	0.767 (2)	0.3958 (12)	0.049 (7)*
H6	0.253 (3)	0.523 (2)	0.4302 (14)	0.055 (8)*
H7	0.236 (3)	0.529 (2)	0.5062 (14)	0.058 (8)*
H8	0.178 (3)	0.700 (2)	0.5536 (15)	0.072 (9)*
H9	0.098 (3)	0.787 (2)	0.5079 (13)	0.052 (8)*
N1	0.1200 (3)	0.70124 (16)	0.39801 (10)	0.0412 (5)
N2	0.2066 (3)	0.55499 (17)	0.46566 (11)	0.0439 (5)
N3	0.1313 (3)	0.7218 (2)	0.51347 (11)	0.0532 (6)
O1	0.21174 (19)	0.38280 (13)	0.13149 (8)	0.0451 (4)
O2	-0.07907 (17)	0.43211 (12)	0.12279 (7)	0.0376 (4)
O3	0.1335 (2)	0.55807 (12)	0.07941 (8)	0.0494 (5)
S1	0.09167 (7)	0.47441 (4)	0.12971 (2)	0.03204 (18)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0413 (11)	0.0274 (11)	0.0300 (11)	-0.0057 (9)	-0.0014 (9)	0.0013 (8)
C2	0.0401 (10)	0.0355 (12)	0.0258 (11)	-0.0029 (9)	0.0007 (9)	0.0027 (9)
C3	0.0386 (10)	0.0276 (10)	0.0287 (11)	0.0059 (9)	-0.0034 (9)	-0.0024 (8)
C4	0.0467 (12)	0.0233 (10)	0.0368 (12)	-0.0024 (9)	-0.0033 (10)	-0.0017 (9)
C5	0.0451 (11)	0.0260 (11)	0.0327 (12)	-0.0013 (10)	0.0034 (10)	0.0034 (9)
C6	0.0348 (10)	0.0256 (10)	0.0268 (10)	0.0012 (8)	-0.0011 (8)	-0.0012 (8)
C7	0.0442 (11)	0.0343 (11)	0.0262 (11)	0.0069 (10)	-0.0028 (9)	-0.0045 (9)
N1	0.0665 (13)	0.0261 (10)	0.0311 (10)	0.0095 (9)	-0.0096 (9)	-0.0053 (8)
N2	0.0691 (13)	0.0396 (11)	0.0231 (10)	0.0176 (10)	-0.0035 (10)	-0.0027 (8)
N3	0.0846 (16)	0.0421 (13)	0.0329 (12)	0.0172 (12)	-0.0051 (11)	-0.0121 (10)
O1	0.0532 (9)	0.0373 (9)	0.0448 (10)	0.0100 (7)	0.0017 (7)	-0.0085 (7)
O2	0.0465 (8)	0.0309 (8)	0.0355 (9)	-0.0020 (7)	-0.0086 (7)	-0.0012 (6)
O3	0.0869 (12)	0.0336 (9)	0.0278 (8)	-0.0105 (9)	0.0088 (8)	0.0034 (6)
S1	0.0474 (3)	0.0247 (3)	0.0240 (3)	-0.0011 (2)	0.0010 (2)	-0.00080 (19)

supplementary materials

Geometric parameters (\AA , $^\circ$)

C1—C2	1.376 (3)	C7—N2	1.313 (3)
C1—C6	1.383 (3)	C7—N3	1.327 (3)
C1—H1	0.91 (2)	C7—N1	1.329 (3)
C2—C3	1.384 (3)	N1—H5	0.80 (3)
C2—H2	0.97 (2)	N2—H6	0.88 (3)
C3—C4	1.383 (3)	N2—H7	0.89 (3)
C3—N1	1.421 (3)	N3—H8	0.91 (3)
C4—C5	1.381 (3)	N3—H9	0.83 (3)
C4—H3	0.90 (2)	O1—S1	1.4546 (15)
C5—C6	1.385 (3)	O2—S1	1.4619 (15)
C5—H4	0.95 (2)	O3—S1	1.4457 (15)
C6—S1	1.770 (2)		
C2—C1—C6	120.1 (2)	N2—C7—N3	119.6 (2)
C2—C1—H1	122.0 (15)	N2—C7—N1	121.1 (2)
C6—C1—H1	117.9 (15)	N3—C7—N1	119.3 (2)
C1—C2—C3	119.9 (2)	C7—N1—C3	127.30 (19)
C1—C2—H2	121.6 (14)	C7—N1—H5	117.4 (18)
C3—C2—H2	118.4 (14)	C3—N1—H5	115.2 (18)
C4—C3—C2	120.0 (2)	C7—N2—H6	117.3 (17)
C4—C3—N1	118.13 (19)	C7—N2—H7	120.1 (17)
C2—C3—N1	121.70 (19)	H6—N2—H7	117 (2)
C5—C4—C3	120.3 (2)	C7—N3—H8	119.0 (18)
C5—C4—H3	117.6 (14)	C7—N3—H9	117.9 (19)
C3—C4—H3	122.0 (14)	H8—N3—H9	121 (3)
C4—C5—C6	119.3 (2)	O3—S1—O1	112.45 (10)
C4—C5—H4	116.9 (14)	O3—S1—O2	112.95 (10)
C6—C5—H4	123.7 (14)	O1—S1—O2	111.09 (9)
C1—C6—C5	120.40 (19)	O3—S1—C6	106.78 (9)
C1—C6—S1	119.37 (15)	O1—S1—C6	107.02 (9)
C5—C6—S1	120.22 (15)	O2—S1—C6	106.07 (9)
C6—C1—C2—C3	-0.9 (3)	N2—C7—N1—C3	6.7 (4)
C1—C2—C3—C4	1.1 (3)	N3—C7—N1—C3	-171.9 (2)
C1—C2—C3—N1	176.8 (2)	C4—C3—N1—C7	-141.9 (2)
C2—C3—C4—C5	-0.1 (3)	C2—C3—N1—C7	42.3 (3)
N1—C3—C4—C5	-176.0 (2)	C1—C6—S1—O3	169.46 (17)
C3—C4—C5—C6	-1.1 (3)	C5—C6—S1—O3	-10.8 (2)
C2—C1—C6—C5	-0.2 (3)	C1—C6—S1—O1	-69.91 (18)
C2—C1—C6—S1	179.46 (16)	C5—C6—S1—O1	109.79 (18)
C4—C5—C6—C1	1.2 (3)	C1—C6—S1—O2	48.76 (18)
C4—C5—C6—S1	-178.46 (16)	C5—C6—S1—O2	-131.54 (17)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H5 \cdots O2 ⁱ	0.80 (3)	2.00 (3)	2.802 (2)	171 (2)

N2—H6···O2 ⁱⁱ	0.88 (3)	2.02 (3)	2.851 (2)	158 (2)
N2—H7···O3 ⁱⁱⁱ	0.89 (3)	2.07 (3)	2.913 (3)	160 (2)
N3—H8···O1 ⁱⁱⁱ	0.91 (3)	2.03 (3)	2.924 (3)	167 (3)
N3—H9···O3 ^{iv}	0.83 (3)	2.34 (3)	2.928 (3)	129 (2)

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

Fig. 1

