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Glycinium 3-carboxy-4-hydroxybenzenesulfonate

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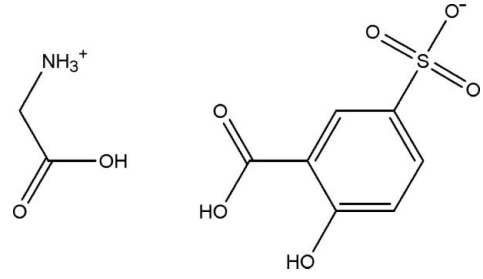
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.117; data-to-parameter ratio = 18.8.

In the anion of the title salt, $C_2H_6NO_2^+\cdot C_7H_5O_6S^-$, the dihedral angle between the carboxylic acid group and the benzene ring is 5.02 (12)°. In the crystal, the anions are linked into inversion dimers through pairs of O—H···O hydrogen bonds between the carboxylic acid groups and sulfonate O atoms. A pair of C—H···O interactions is also observed within each dimer. The anion dimers and the cations are linked into a three-dimensional network by N—H···O, O—H···O and C—H···O hydrogen bonds.

Related literature

For background to non-linear optical materials, see: Yang *et al.* (2005); Kumar *et al.* (2009). For related structures, see: Krishnakumar *et al.* (2012); Sudhahar *et al.* (2013).



Experimental

Crystal data

$C_2H_6NO_2^+\cdot C_7H_5O_6S^-$
M_r = 293.25
Monoclinic, $P2_1/c$
a = 5.3651 (3) Å
b = 24.7207 (15) Å
c = 8.6840 (5) Å
β = 90.170 (2)°
V = 1151.75 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 295 K
0.36 × 0.32 × 0.30 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.893, T_{max} = 0.910
21406 measured reflections
3694 independent reflections
3282 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.117
S = 1.20
3694 reflections
197 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6	0.82 (1)	1.89 (2)	2.631 (2)	150 (4)
N1—H1A···O6	0.86 (1)	2.27 (3)	2.878 (2)	127 (3)
N1—H1A···O7^{i}	0.86 (1)	2.46 (3)	3.134 (2)	135 (3)
N1—H1B···O3^{ii}	0.87 (1)	2.06 (2)	2.876 (2)	157 (3)
N1—H1C···O3^{iii}	0.87 (1)	1.98 (2)	2.811 (2)	161 (3)
O5—H5A···O4^{iv}	0.82 (1)	1.92 (2)	2.702 (2)	159 (3)
O7—H7···O2^{v}	0.82 (1)	1.84 (1)	2.646 (2)	169 (3)
C2—H2···O5^{iv}	0.93	2.45	3.370 (2)	168
C9—H9A···O4^{iv}	0.97	2.33	3.292 (2)	172
C6—H6···O8^{vi}	0.93	2.46	3.273 (2)	147
C9—H9B···O2^{vii}	0.97	2.37	3.324 (2)	167

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors thank the SAIF, IIT, Madras, for the data collection.

Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5343).

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supporting information

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Glycinium 3-carboxy-4-hydroxybenzenesulfonate

A. Thirunavukkarasu, A. Silambarasan, R. Mohan Kumar, P. R. Umarani and G. Chakkaravarthi

S1. Comment

Non-linear optical materials have recently invoked a large amount of interest due to their potential application in harmonic generation, optical information processing, optical storage and two photon pumped lasers (Yang *et al.*, 2005; Kumar *et al.*, 2009). We herein, report the crystal structure of the title compound (I), (Fig. 1). The geometric parameters of the title compound are comparable with the reported structures (Krishnakumar *et al.*, 2012; Sudhahar *et al.*, 2013).

In the molecular structure, the cation and anion are linked by N—H···O and O—H···O hydrogen bonds. In the anion, the dihedral angle between the carboxyl group and the benzene ring is 5.02 (12)°. The crystal structure exhibits intermolecular N—H···O, O—H···O and C—H···O (Table 1 & Fig. 2) interactions.

S2. Experimental

The title compound was obtained by slow evaporation from an aqueous solution of glycine ($C_2H_5NO_2$, 0.75 g) and 3-carboxy-4-hydroxybenzenesulfonic acid ($C_7H_6O_6S$, 2.18 g) at room temperature. The good quality crystals suitable for X-ray diffraction were collected in the period of 20 days.

S3. Refinement

H atoms of the NH_3 and OH groups were located in a difference Fourier map and refined freely, with bond-length restraints of N—H = 0.86 (1) Å and O—H = 0.82 (1) Å. The C-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and U_{iso}(H) = 1.2U_{eq}(C) for CH and C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for CH_2.

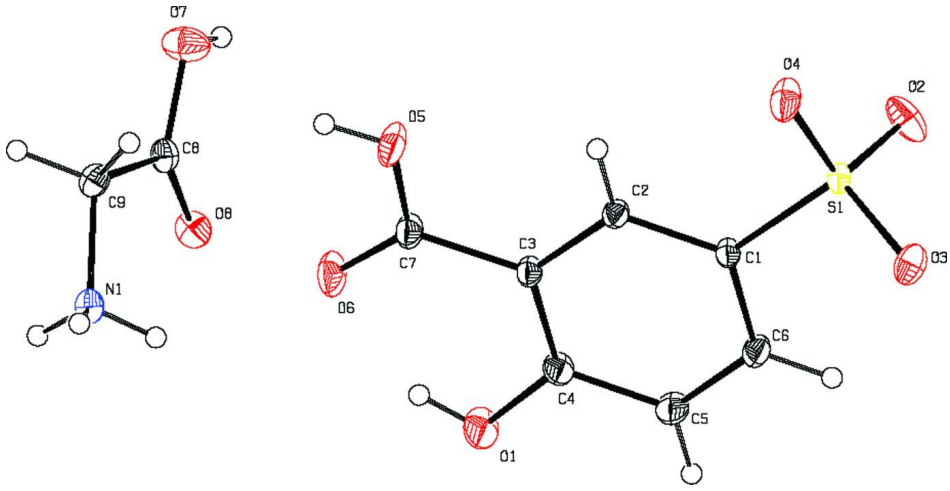

Figure 1

The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.

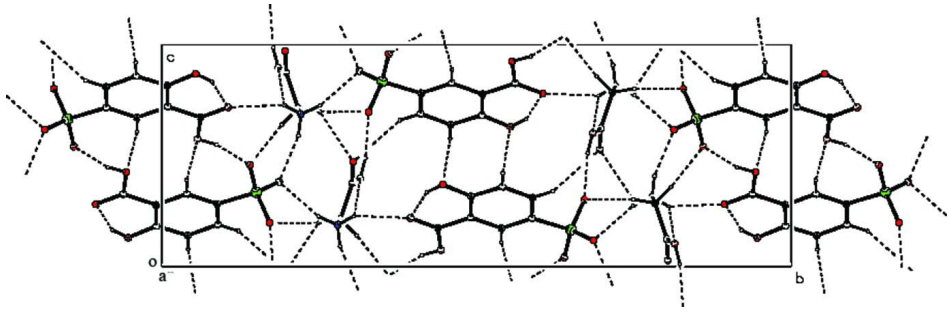

Figure 2

A packing diagram of the title compound, viewed down the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Glycinium 3-carboxy-4-hydroxybenzenesulfonate

Crystal data

$C_2H_6NO_2^+ \cdot C_7H_5O_6S^-$
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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
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b = 24.7207 (15) Å
c = 8.6840 (5) Å
β = 90.170 (2)°
V = 1151.75 (12) Å^3
Z = 4
$F(000)$ = 608
D_x = 1.691 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9634 reflections
θ = 2.5–32.0°
μ = 0.32 mm^{-1}
T = 295 K
Block, colourless
0.36 × 0.32 × 0.30 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.893, T_{max} = 0.910

21406 measured reflections
3694 independent reflections
3282 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 32.1°$, $\theta_{min} = 1.7°$
$h = -7 \rightarrow 7$
$k = -36 \rightarrow 36$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.117$
$S = 1.20$
3694 reflections
197 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.2564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.071 (3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5636 (3)	0.41186 (7)	0.7824 (2)	0.0177 (3)
C2	0.6669 (3)	0.46042 (7)	0.8273 (2)	0.0194 (3)
H2	0.8074	0.4607	0.8903	0.023*
C3	0.5608 (3)	0.50936 (7)	0.7784 (2)	0.0198 (3)
C4	0.3495 (4)	0.50846 (8)	0.6831 (2)	0.0244 (4)
C5	0.2445 (4)	0.45897 (8)	0.6403 (3)	0.0283 (4)
H5	0.1027	0.4583	0.5785	0.034*
C6	0.3505 (4)	0.41112 (8)	0.6893 (2)	0.0244 (4)
H6	0.2801	0.3783	0.6603	0.029*
C7	0.6683 (4)	0.56133 (7)	0.8269 (2)	0.0248 (4)
C8	0.8846 (4)	0.69748 (7)	0.6240 (2)	0.0213 (3)
C9	0.8379 (4)	0.71637 (8)	0.7865 (2)	0.0221 (3)
H9A	0.9096	0.6908	0.8589	0.026*
H9B	0.9166	0.7512	0.8028	0.026*
N1	0.5669 (3)	0.72092 (7)	0.81273 (19)	0.0219 (3)
O1	0.2384 (3)	0.55374 (7)	0.6301 (2)	0.0398 (4)
O2	0.8214 (3)	0.32854 (7)	0.69766 (18)	0.0377 (4)
O3	0.5004 (3)	0.31390 (6)	0.88206 (18)	0.0305 (3)
O4	0.8755 (3)	0.36047 (6)	0.9590 (2)	0.0364 (4)
O5	0.8540 (3)	0.55664 (6)	0.9256 (2)	0.0364 (4)
O6	0.5921 (3)	0.60513 (6)	0.7813 (2)	0.0380 (4)
O7	1.1214 (3)	0.68486 (8)	0.60241 (19)	0.0386 (4)
O8	0.7240 (3)	0.69592 (6)	0.52779 (16)	0.0278 (3)
S1	0.70129 (8)	0.349884 (16)	0.83495 (5)	0.01747 (12)
H1A	0.489 (6)	0.6942 (10)	0.771 (4)	0.059 (10)*
H1B	0.515 (6)	0.7512 (8)	0.774 (4)	0.059 (10)*
H1C	0.528 (6)	0.7171 (14)	0.9088 (15)	0.059 (10)*
H5A	0.910 (6)	0.5865 (7)	0.949 (4)	0.051 (9)*

H7	1.134 (6)	0.6766 (12)	0.5112 (15)	0.048 (9)*
H1	0.320 (6)	0.5791 (10)	0.665 (4)	0.064 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0206 (8)	0.0139 (7)	0.0186 (8)	−0.0001 (6)	−0.0015 (6)	−0.0008 (6)
C2	0.0198 (8)	0.0163 (7)	0.0219 (8)	−0.0006 (6)	−0.0050 (6)	−0.0003 (6)
C3	0.0229 (8)	0.0147 (7)	0.0218 (8)	−0.0006 (6)	−0.0037 (6)	0.0001 (6)
C4	0.0261 (9)	0.0201 (8)	0.0270 (9)	0.0030 (7)	−0.0065 (7)	0.0031 (7)
C5	0.0249 (9)	0.0258 (9)	0.0342 (11)	0.0013 (7)	−0.0141 (8)	−0.0010 (8)
C6	0.0249 (9)	0.0196 (8)	0.0286 (9)	−0.0025 (6)	−0.0071 (7)	−0.0034 (7)
C7	0.0292 (10)	0.0161 (7)	0.0291 (9)	−0.0014 (6)	−0.0055 (8)	0.0003 (7)
C8	0.0271 (9)	0.0181 (7)	0.0186 (8)	−0.0005 (6)	0.0015 (7)	0.0008 (6)
C9	0.0255 (9)	0.0238 (8)	0.0169 (8)	−0.0034 (7)	−0.0012 (6)	−0.0017 (6)
N1	0.0278 (8)	0.0198 (7)	0.0181 (7)	−0.0003 (6)	0.0008 (6)	−0.0003 (6)
O1	0.0426 (9)	0.0232 (7)	0.0534 (11)	0.0065 (7)	−0.0235 (8)	0.0052 (7)
O2	0.0510 (10)	0.0343 (8)	0.0279 (8)	0.0189 (7)	0.0124 (7)	0.0003 (6)
O3	0.0374 (8)	0.0217 (6)	0.0324 (8)	−0.0097 (6)	0.0019 (6)	0.0069 (6)
O4	0.0463 (9)	0.0209 (7)	0.0419 (9)	0.0003 (6)	−0.0261 (8)	−0.0003 (6)
O5	0.0452 (9)	0.0190 (7)	0.0449 (9)	−0.0059 (6)	−0.0232 (8)	−0.0013 (6)
O6	0.0492 (10)	0.0150 (6)	0.0496 (10)	0.0014 (6)	−0.0166 (8)	0.0022 (6)
O7	0.0282 (8)	0.0602 (11)	0.0274 (8)	0.0057 (7)	0.0009 (6)	−0.0083 (7)
O8	0.0328 (8)	0.0322 (7)	0.0183 (6)	0.0033 (6)	−0.0035 (5)	−0.0020 (5)
S1	0.0230 (2)	0.01263 (18)	0.0168 (2)	−0.00042 (14)	−0.00211 (14)	−0.00052 (13)

Geometric parameters (Å, º)

C1—C2	1.378 (2)	C8—O7	1.322 (2)
C1—C6	1.399 (3)	C8—C9	1.508 (3)
C1—S1	1.7605 (17)	C9—N1	1.477 (3)
C2—C3	1.402 (2)	C9—H9A	0.9700
C2—H2	0.9300	C9—H9B	0.9700
C3—C4	1.402 (3)	N1—H1A	0.863 (10)
C3—C7	1.470 (2)	N1—H1B	0.866 (10)
C4—O1	1.348 (2)	N1—H1C	0.865 (10)
C4—C5	1.397 (3)	O1—H1	0.823 (10)
C5—C6	1.379 (3)	O2—S1	1.4559 (15)
C5—H5	0.9300	O3—S1	1.4570 (14)
C6—H6	0.9300	O4—S1	1.4478 (15)
C7—O6	1.223 (2)	O5—H5A	0.822 (10)
C7—O5	1.317 (2)	O7—H7	0.821 (10)
C8—O8	1.199 (2)		
C2—C1—C6	120.16 (16)	O7—C8—C9	111.59 (17)
C2—C1—S1	121.11 (13)	N1—C9—C8	109.53 (15)
C6—C1—S1	118.69 (13)	N1—C9—H9A	109.8
C1—C2—C3	120.21 (16)	C8—C9—H9A	109.8

C1—C2—H2	119.9	N1—C9—H9B	109.8
C3—C2—H2	119.9	C8—C9—H9B	109.8
C4—C3—C2	119.48 (16)	H9A—C9—H9B	108.2
C4—C3—C7	119.94 (16)	C9—N1—H1A	111 (2)
C2—C3—C7	120.58 (16)	C9—N1—H1B	109 (2)
O1—C4—C5	117.33 (17)	H1A—N1—H1B	110 (3)
O1—C4—C3	122.96 (17)	C9—N1—H1C	112 (2)
C5—C4—C3	119.71 (17)	H1A—N1—H1C	102 (3)
C6—C5—C4	120.24 (18)	H1B—N1—H1C	113 (3)
C6—C5—H5	119.9	C4—O1—H1	106 (3)
C4—C5—H5	119.9	C7—O5—H5A	111 (2)
C5—C6—C1	120.18 (17)	C8—O7—H7	106 (2)
C5—C6—H6	119.9	O4—S1—O2	112.85 (11)
C1—C6—H6	119.9	O4—S1—O3	112.21 (10)
O6—C7—O5	122.70 (18)	O2—S1—O3	109.77 (10)
O6—C7—C3	123.42 (18)	O4—S1—C1	107.75 (8)
O5—C7—C3	113.88 (16)	O2—S1—C1	106.85 (9)
O8—C8—O7	125.65 (18)	O3—S1—C1	107.09 (9)
O8—C8—C9	122.73 (18)		

C6—C1—C2—C3	−0.8 (3)	C4—C3—C7—O6	−4.4 (3)
S1—C1—C2—C3	177.08 (14)	C2—C3—C7—O6	175.9 (2)
C1—C2—C3—C4	−0.2 (3)	C4—C3—C7—O5	175.01 (19)
C1—C2—C3—C7	179.42 (18)	C2—C3—C7—O5	−4.7 (3)
C2—C3—C4—O1	−179.32 (19)	O8—C8—C9—N1	11.5 (2)
C7—C3—C4—O1	1.0 (3)	O7—C8—C9—N1	−170.32 (16)
C2—C3—C4—C5	1.2 (3)	C2—C1—S1—O4	16.02 (18)
C7—C3—C4—C5	−178.49 (19)	C6—C1—S1—O4	−166.12 (16)
O1—C4—C5—C6	179.4 (2)	C2—C1—S1—O2	−105.50 (17)
C3—C4—C5—C6	−1.1 (3)	C6—C1—S1—O2	72.36 (17)
C4—C5—C6—C1	0.1 (3)	C2—C1—S1—O3	136.93 (15)
C2—C1—C6—C5	0.8 (3)	C6—C1—S1—O3	−45.21 (17)
S1—C1—C6—C5	−177.06 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O6	0.82 (1)	1.89 (2)	2.631 (2)	150 (4)
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Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+1, *y*+1/2, −*z*+3/2; (iii) −*x*+1, −*y*+1, −*z*+2; (iv) −*x*+2, −*y*+1, −*z*+2; (v) −*x*+2, −*y*+1, −*z*+1; (vi) −*x*+1, −*y*+1, −*z*+1; (vii) −*x*+2, *y*+1/2, −*z*+3/2.