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Creatinium 4-methylbenzenesulfonate

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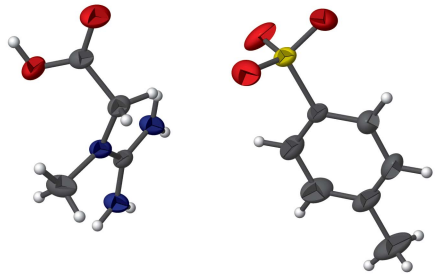
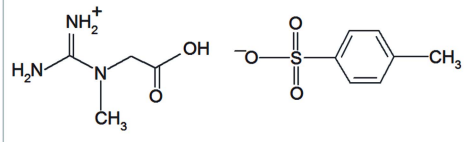
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_4H_{10}N_3O_2^+\cdot C_7H_7O_3S^-$ (systematic name: {amino[(carboxymethyl)(methyl)amino]methylidene}azanium 4-methylbenzenesulfonate), the OH group of the carboxylic acid and central N atom of the cation are close to being eclipsed [N—C—C—O = 11.6 (3)°]. In the crystal, C—H···O, O—H···O and N—H···O hydrogen bonds link the components into (001) sheets.

3D view



Chemical scheme



Structure description

Creatine is extracted from several kinds of muscle and it is endogenously synthesized by the liver and pancreas in humans (Walker, 1979). As part of our studies of creatine chemistry, the synthesis and structure of the title molecular salt are now described.

The asymmetric unit comprises a protonated creatinium cation and deprotonated 4-methylbenzenesulfonate anion (Fig. 1). The geometric parameters of the component ions agree well with those reported for similar structures (Ali *et al.*, 2012). In the anion, the O1—S1—C1—C2 torsion angle of 15.4 (2)° indicates that atom O1 lies close to the plane of the aromatic ring.

In the crystal, C—H···O, O—H···O and N—H···O hydrogen bonds (Fig. 2, Table 1) link the components into (001) sheets.

Synthesis and crystallization

Creatine (0.01 mol) was dissolved in 20 ml of de-ionized water and *p*-toluenesulfonic acid monohydrate (0.01 mol) was added slowly. The solution was stirred for 4 h. The solution was filtered and colourless blocks were obtained from the mother liquor after seven days. Yield = 95%.

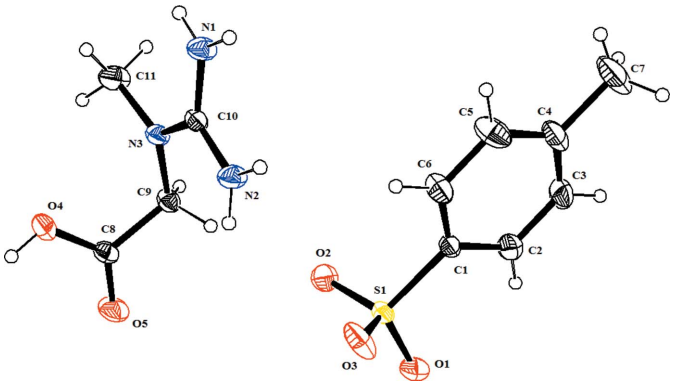


Figure 1
The molecular structure of the title compound, with 30% probability displacement ellipsoids for non-H atoms.

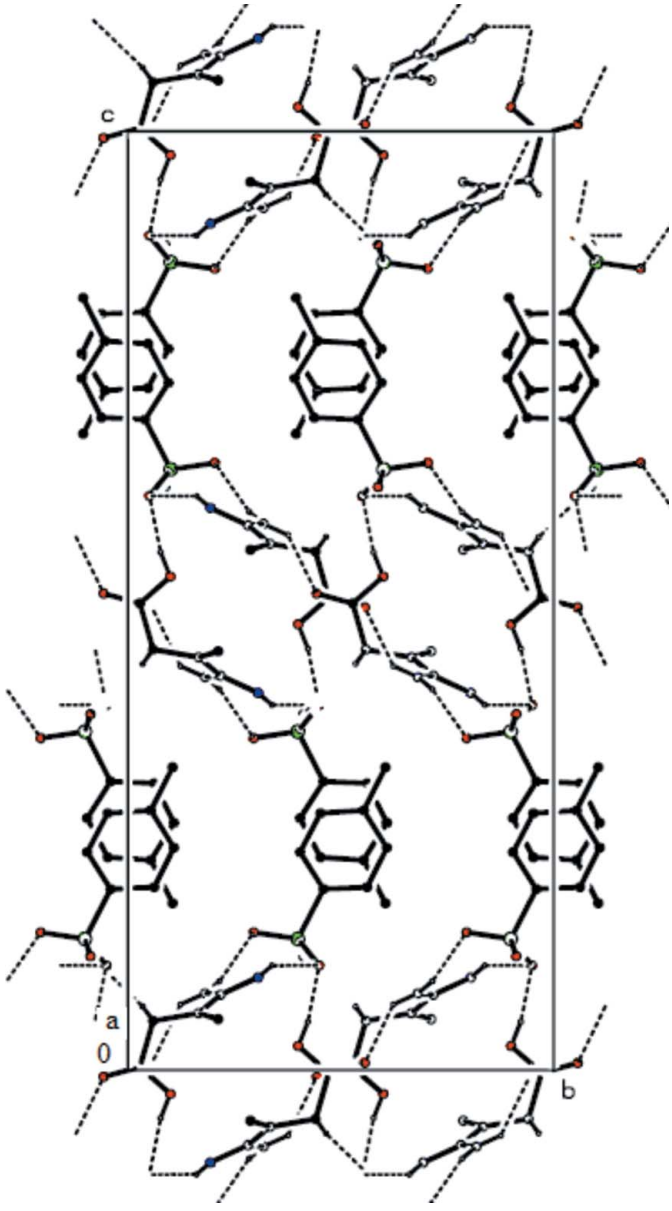


Figure 2
The packing, viewed along [100]. Hydrogen bonds are shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O2	0.97	2.45	3.297 (3)	146
O4—H4···O3^{i}	0.82	1.82	2.630 (2)	167
N2—H2B···O5^{i}	0.86	2.24	2.955 (2)	141
N1—H1A···O3^{ii}	0.86	2.33	3.121 (3)	154
N2—H2A···O1^{ii}	0.86	2.11	2.927 (2)	158

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_{10}N_3O_2^+\cdot C_7H_7O_3S^-$
M_r	303.34
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	295
a, b, c (Å)	7.1432 (2), 13.3500 (5), 29.4794 (10)
V (Å^3)	2811.21 (16)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	0.25 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.939, 0.951
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37602, 2469, 2118
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.108, 1.08
No. of reflections	2469
No. of parameters	185
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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References

Ali, A. J., Athimoolam, S. & Bahadur, S. A. (2012). *Acta Cryst.* E**68**, o416.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Walker, J. B. (1979). *Adv. Enzymol. Relat. Areas Mol. Med.* **50**, 177–242.

full crystallographic data

IUCrData (2016). **1**, x161622 [https://doi.org/10.1107/S2414314616016229]

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{Amino[(carboxymethyl)(methyl)amino]methylidene}azanium 4-methylbenzenesulfonate

Crystal data

$C_4H_{10}N_3O_2^+·C_7H_7O_3S^-$
M_r = 303.34
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 7.1432 (2) Å
b = 13.3500 (5) Å
c = 29.4794 (10) Å
V = 2811.21 (16) Å^3
Z = 8
F(000) = 1280
D_x = 1.433 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 2469 reflections
θ = 2.8–25.0°
μ = 0.25 mm^{-1}
T = 295 K
Block, colourless
0.25 × 0.25 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.939, T_{max} = 0.951
37602 measured reflections
2469 independent reflections
2118 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.0°, θ_{min} = 2.8°
h = −8→8
k = −15→15
l = −35→35

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
S = 1.08
2469 reflections
185 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 2.2285P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-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	0.82439 (7)	−0.10067 (4)	0.139590 (17)	0.03545 (19)
O1	0.7739 (3)	−0.20436 (14)	0.14653 (6)	0.0633 (6)
O2	1.0097 (2)	−0.08774 (13)	0.12117 (6)	0.0522 (5)

O3	0.6850 (3)	−0.05069 (16)	0.11132 (5)	0.0621 (6)
O4	1.2752 (3)	0.09972 (13)	−0.02547 (5)	0.0562 (5)
H4	1.2775	0.0770	−0.0513	0.084*
O5	1.2004 (3)	−0.05660 (12)	−0.00736 (6)	0.0524 (5)
N1	1.1562 (2)	0.30601 (13)	0.09852 (6)	0.0376 (4)
H1A	1.0666	0.3387	0.1112	0.045*
H1B	1.2672	0.3309	0.0979	0.045*
N2	0.9508 (2)	0.18133 (13)	0.08163 (6)	0.0394 (4)
H2A	0.8631	0.2151	0.0945	0.047*
H2B	0.9266	0.1239	0.0698	0.047*
N3	1.2622 (2)	0.16613 (12)	0.06048 (5)	0.0312 (4)
C1	0.8211 (3)	−0.04052 (16)	0.19269 (6)	0.0311 (4)
C2	0.8196 (4)	−0.0955 (2)	0.23192 (8)	0.0502 (6)
H2	0.8164	−0.1651	0.2306	0.060*
C3	0.8228 (4)	−0.0475 (2)	0.27340 (8)	0.0571 (7)
H3	0.8204	−0.0855	0.2998	0.069*
C4	0.8294 (3)	0.0539 (2)	0.27651 (8)	0.0515 (7)
C5	0.8338 (4)	0.1082 (2)	0.23673 (9)	0.0619 (8)
H5	0.8406	0.1777	0.2382	0.074*
C6	0.8284 (4)	0.06204 (18)	0.19472 (8)	0.0470 (6)
H6	0.8296	0.1000	0.1683	0.056*
C7	0.8319 (5)	0.1050 (3)	0.32238 (10)	0.0872 (12)
H7A	0.7168	0.0914	0.3380	0.131*
H7B	0.8454	0.1760	0.3183	0.131*
H7C	0.9351	0.0801	0.3399	0.131*
C8	1.2364 (3)	0.02815 (15)	0.00308 (7)	0.0327 (5)
C9	1.2474 (3)	0.05934 (15)	0.05220 (6)	0.0335 (5)
H9A	1.1367	0.0347	0.0676	0.040*
H9B	1.3549	0.0267	0.0658	0.040*
C10	1.1233 (3)	0.21775 (14)	0.08008 (6)	0.0289 (4)
C11	1.4454 (3)	0.21214 (19)	0.05409 (9)	0.0492 (6)
H11A	1.4299	0.2796	0.0434	0.074*
H11B	1.5155	0.1744	0.0322	0.074*
H11C	1.5116	0.2128	0.0824	0.074*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0350 (3)	0.0435 (3)	0.0279 (3)	−0.0040 (2)	0.0028 (2)	−0.0102 (2)
O1	0.0878 (14)	0.0527 (11)	0.0493 (10)	−0.0304 (10)	0.0037 (10)	−0.0147 (8)
O2	0.0440 (9)	0.0592 (10)	0.0534 (10)	−0.0044 (8)	0.0176 (8)	−0.0220 (8)
O3	0.0640 (12)	0.0919 (14)	0.0302 (8)	0.0234 (10)	−0.0108 (8)	−0.0151 (9)
O4	0.0903 (14)	0.0509 (10)	0.0274 (8)	−0.0180 (9)	0.0005 (9)	−0.0052 (7)
O5	0.0748 (12)	0.0355 (9)	0.0468 (9)	−0.0019 (8)	−0.0025 (8)	−0.0156 (7)
N1	0.0326 (9)	0.0343 (9)	0.0459 (10)	−0.0004 (8)	0.0039 (8)	−0.0138 (8)
N2	0.0333 (9)	0.0377 (10)	0.0470 (11)	−0.0043 (8)	0.0055 (8)	−0.0144 (8)
N3	0.0320 (9)	0.0312 (9)	0.0302 (9)	−0.0025 (7)	0.0020 (7)	−0.0091 (7)
C1	0.0266 (10)	0.0420 (11)	0.0248 (10)	−0.0016 (9)	0.0004 (8)	−0.0050 (8)

C2	0.0639 (16)	0.0525 (14)	0.0342 (12)	−0.0156 (12)	−0.0017 (11)	0.0028 (10)
C3	0.0621 (16)	0.083 (2)	0.0262 (12)	−0.0152 (15)	0.0002 (11)	0.0033 (12)
C4	0.0391 (13)	0.084 (2)	0.0317 (12)	0.0040 (13)	0.0005 (10)	−0.0203 (12)
C5	0.080 (2)	0.0487 (15)	0.0572 (17)	0.0140 (14)	−0.0059 (15)	−0.0211 (12)
C6	0.0644 (16)	0.0452 (13)	0.0315 (11)	0.0073 (12)	−0.0013 (11)	−0.0031 (10)
C7	0.076 (2)	0.137 (3)	0.0486 (17)	0.009 (2)	−0.0010 (15)	−0.0472 (19)
C8	0.0323 (10)	0.0333 (11)	0.0325 (10)	0.0029 (9)	−0.0012 (9)	−0.0089 (9)
C9	0.0416 (11)	0.0303 (10)	0.0286 (10)	0.0041 (9)	0.0002 (9)	−0.0041 (8)
C10	0.0340 (10)	0.0301 (10)	0.0225 (9)	0.0004 (8)	−0.0023 (8)	−0.0026 (8)
C11	0.0333 (12)	0.0552 (14)	0.0592 (15)	−0.0067 (11)	0.0086 (11)	−0.0237 (12)

Geometric parameters (Å, º)

S1—O2	1.4410 (17)	C1—C6	1.371 (3)
S1—O2	1.4410 (17)	C2—C3	1.381 (3)
S1—O1	1.4451 (19)	C2—H2	0.9300
S1—O3	1.4599 (18)	C3—C4	1.357 (4)
S1—C1	1.7596 (19)	C3—H3	0.9300
O2—O2	0.000 (4)	C4—C5	1.379 (4)
O4—C8	1.303 (3)	C4—C7	1.515 (3)
O4—H4	0.8200	C5—C6	1.384 (3)
O5—C8	1.200 (2)	C5—H5	0.9300
N1—C10	1.319 (2)	C6—H6	0.9300
N1—H1A	0.8600	C7—H7A	0.9600
N1—H1B	0.8600	C7—H7B	0.9600
N2—C10	1.325 (3)	C7—H7C	0.9600
N2—H2A	0.8600	C8—C9	1.509 (3)
N2—H2B	0.8600	C9—H9A	0.9700
N3—C10	1.339 (3)	C9—H9B	0.9700
N3—C9	1.450 (3)	C11—H11A	0.9600
N3—C11	1.458 (3)	C11—H11B	0.9600
C1—C2	1.370 (3)	C11—H11C	0.9600
O2—S1—O2	0.00 (13)	C5—C4—C7	121.4 (3)
O2—S1—O1	113.42 (12)	C4—C5—C6	121.7 (3)
O2—S1—O1	113.42 (12)	C4—C5—H5	119.1
O2—S1—O3	110.89 (11)	C6—C5—H5	119.1
O2—S1—O3	110.89 (11)	C1—C6—C5	119.0 (2)
O1—S1—O3	110.38 (12)	C1—C6—H6	120.5
O2—S1—C1	107.03 (9)	C5—C6—H6	120.5
O2—S1—C1	107.03 (9)	C4—C7—H7A	109.5
O1—S1—C1	107.93 (10)	C4—C7—H7B	109.5
O3—S1—C1	106.86 (10)	H7A—C7—H7B	109.5
O2—O2—S1	0 (10)	C4—C7—H7C	109.5
C8—O4—H4	109.5	H7A—C7—H7C	109.5
C10—N1—H1A	120.0	H7B—C7—H7C	109.5
C10—N1—H1B	120.0	O5—C8—O4	124.82 (19)
H1A—N1—H1B	120.0	O5—C8—C9	121.16 (19)

C10—N2—H2A	120.0	O4—C8—C9	113.98 (17)
C10—N2—H2B	120.0	N3—C9—C8	115.89 (17)
H2A—N2—H2B	120.0	N3—C9—H9A	108.3
C10—N3—C9	121.62 (17)	C8—C9—H9A	108.3
C10—N3—C11	120.28 (17)	N3—C9—H9B	108.3
C9—N3—C11	117.26 (17)	C8—C9—H9B	108.3
C2—C1—C6	119.9 (2)	H9A—C9—H9B	107.4
C2—C1—S1	120.43 (18)	N1—C10—N2	118.62 (18)
C6—C1—S1	119.60 (16)	N1—C10—N3	120.38 (18)
C1—C2—C3	119.9 (2)	N2—C10—N3	121.00 (17)
C1—C2—H2	120.0	N3—C11—H11A	109.5
C3—C2—H2	120.0	N3—C11—H11B	109.5
C4—C3—C2	121.6 (2)	H11A—C11—H11B	109.5
C4—C3—H3	119.2	N3—C11—H11C	109.5
C2—C3—H3	119.2	H11A—C11—H11C	109.5
C3—C4—C5	117.9 (2)	H11B—C11—H11C	109.5
C3—C4—C7	120.7 (3)		

O1—S1—O2—O2	0.0 (2)	C2—C3—C4—C7	179.7 (3)
O3—S1—O2—O2	0.0 (2)	C3—C4—C5—C6	1.2 (4)
C1—S1—O2—O2	0.0 (2)	C7—C4—C5—C6	−178.9 (3)
O2—S1—C1—C2	−107.0 (2)	C2—C1—C6—C5	−0.1 (4)
O2—S1—C1—C2	−107.0 (2)	S1—C1—C6—C5	−177.2 (2)
O1—S1—C1—C2	15.4 (2)	C4—C5—C6—C1	−1.0 (4)
O3—S1—C1—C2	134.1 (2)	C10—N3—C9—C8	112.1 (2)
O2—S1—C1—C6	70.1 (2)	C11—N3—C9—C8	−78.4 (2)
O2—S1—C1—C6	70.1 (2)	O5—C8—C9—N3	−170.6 (2)
O1—S1—C1—C6	−167.45 (19)	O4—C8—C9—N3	11.6 (3)
O3—S1—C1—C6	−48.7 (2)	C9—N3—C10—N1	161.24 (18)
C6—C1—C2—C3	0.9 (4)	C11—N3—C10—N1	−8.0 (3)
S1—C1—C2—C3	178.0 (2)	C9—N3—C10—N2	−18.3 (3)
C1—C2—C3—C4	−0.7 (4)	C11—N3—C10—N2	172.5 (2)
C2—C3—C4—C5	−0.3 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O2	0.97	2.45	3.297 (3)	146
O4—H4···O3^{i}	0.82	1.82	2.630 (2)	167
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Symmetry codes: (i) −*x*+2, −*y*, −*z*; (ii) −*x*+3/2, *y*+1/2, *z*.