IUCrData

ISSN 2414-3146

4-Methylanilinium 3-carboxy-4-hydroxybenzenesulfonate

S. Kalaiyarasi,[a] S. Suresh,[a] R. Akilan,[b] R. Mohan Kumar[a]* and G. Chakkaravarthi[c]*

[a]Department of Physics, Presidency College, Chennai 600 005, India, [b]Department of physics, Aksheyaa College of Engineering, Kancheepuram 603 314, India, and [c]Department of Physics, CPCL Polytechnic College, Chennai 600 068, India. *Correspondence e-mail: mohan66@hotmail.com, chakkaravarthi_2005@yahoo.com

Received 13 February 2017
Accepted 14 February 2017

Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

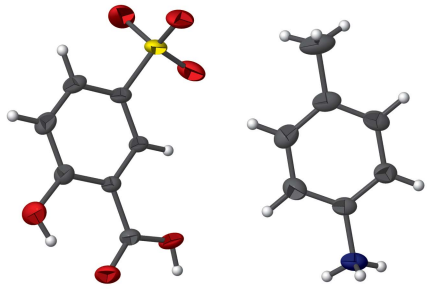
Keywords: crystal structure; molecular salt; hydrogen bonding.

CCDC reference: 1532573

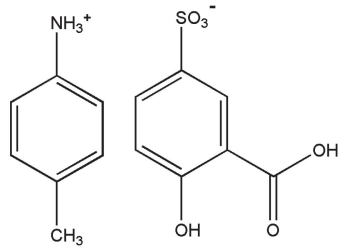
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_7H_{10}N^+\cdot C_7H_5O_6S^-$, the anion is deprotonated at the hydroxy O atom of the sulfonate group. In the anion, an intra-ionic O—H···O hydrogen bond generates an $S(6)$ graph-set motif. In the crystal, the inter-ionic N—H···O and O—H···O hydrogen bonds generate an $R_2^4(12)$ ring-set motif, linking the anions and cations into an infinite three-dimensional framework. The crystal structure also features C—H···π and π–π [centroid-to-centroid distance = 3.5946 (11) Å] interactions.

3D view



Chemical scheme



Structure description

Amino derivatives of benzoic acid are of considerable importance because of their use as anti-inflammatory and anti-cancer agents (Congiu *et al.*, 2005). We herein report the synthesis and the crystal structure of the title molecular salt (Fig. 1). The asymmetric unit contains a 4-methylanilinium cation and a 3-carboxy-4-hydroxybenzenesulfonate anion. The geometric parameters are comparable with those of reported similar structures for 4-methylanilinium (Benali-Cherif *et al.*, 2009) and 3-carboxy-4-hydroxybenzenesulfonate (Hemamalini & Fun, 2010). The cation is protonated at the amine atom N1 and the anion is deprotonated at the hydroxy atom O5. The O1—H1···O3 hydrogen bond generates an $S(6)$ graph-set motif (Fig. 1) in the anion.

A pair of inter-ionic N1—H1A···O6^{i} and N1—H1B···O4^{ii} hydrogen bonds (for symmetry codes, see Table 1) generate an $R_2^4(12)$ ring-set motif (Fig. 2). In the crystal structure, the inter-ionic N—H···O and O—H···O hydrogen bonds (Table 1 and Fig. 3) link the adjacent anions and cations into an infinite three-dimensional framework. The crystal structure is also influenced by weak C—H···π (Table 1) and π–π [$Cg1\cdots Cg1(1-x,1-y,1-z)$ = 3.5946 (11) Å; $Cg1$ is the centroid of the C8–C13 ring] interactions.

OPEN ACCESS

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

*Cg*2 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3	0.83 (1)	1.83 (2)	2.587 (2)	150 (3)
N1—H1*A*···O6^{i}	0.89	1.95	2.837 (3)	172
N1—H1*B*···O4^{ii}	0.89	1.94	2.821 (2)	169
O2—H2*A*···O5^{ii}	0.82 (1)	1.79 (1)	2.6159 (19)	176 (3)
N1—H1*C*···O3^{iii}	0.89	2.30	2.7548 (19)	112
N1—H1*C*···O5^{iv}	0.89	2.59	3.461 (3)	166
C10—H10···*Cg*2^{v}	0.93	2.66	3.549 (2)	160

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

Synthesis and crystallization

The title compound was synthesized from *p*-methyl aniline and 2-hydroxy-5-sulfobenzoic acid in a stoichiometric ratio and dissolved in a mixed solvent of water and acetone at ambient temperature. The solution was filtered and allowed to

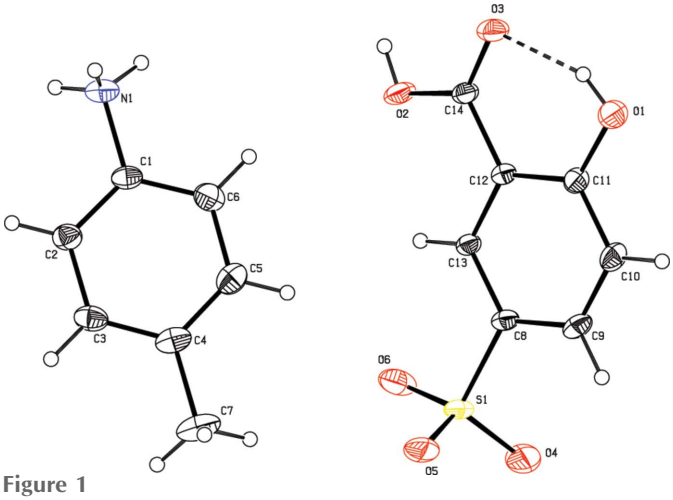


Figure 1
The molecular structure of the title molecular salt, with the atom labelling and 30% probability displacement ellipsoids.

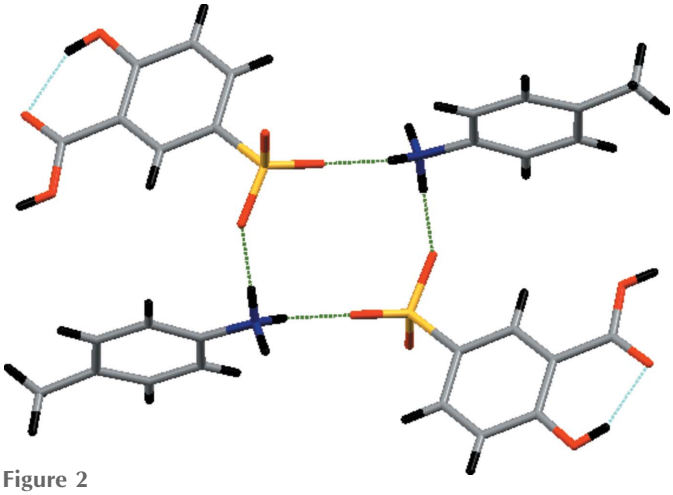


Figure 2
A partial view of the crystal packing showing the ring-set motif.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_{10}N^+\cdot C_7H_5O_6S^-$
M_r	325.33
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	295
a, *b*, *c* (Å)	9.5114 (8), 12.3080 (11), 12.5537 (11)
β (°)	98.962 (3)
V (Å^3)	1451.7 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	0.24 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII CCD Diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.609, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26625, 4730, 3474
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.738
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.142, 1.10
No. of reflections	4730
No. of parameters	208
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.76

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

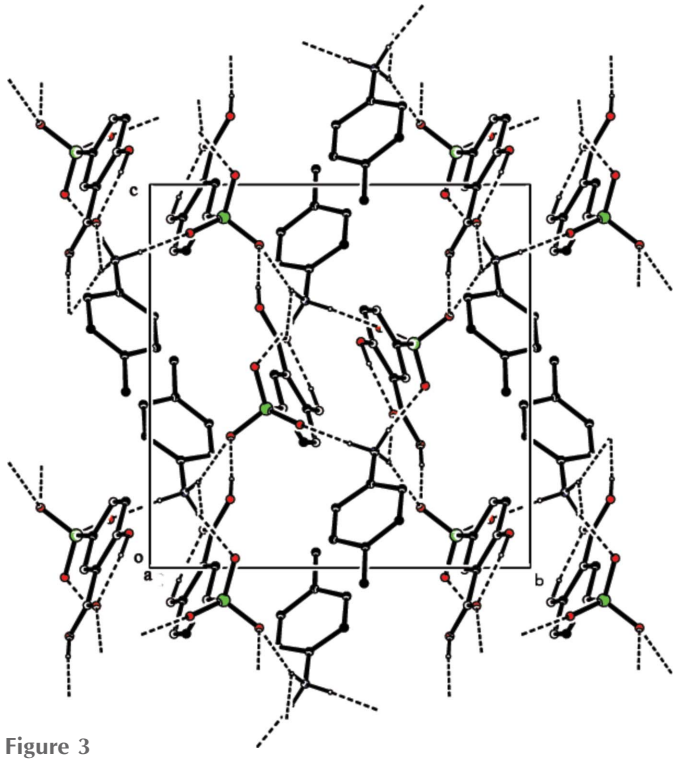


Figure 3
The crystal packing of the title molecular salt viewed along the *a* axis. The hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

evaporate and yielded crystals suitable for X-ray diffraction after two weeks.

Refinement

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

Acknowledgements

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

References

Benali-Cherif, N., Boussekine, H., Boutobba, Z. & Dadda, N. (2009). *Acta Cryst.* E**65**, o2744.
Bruker (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Congiu, C., Cocco, M. T., Lilliu, V. & Onnis, V. (2005). *J. Med. Chem.* **48**, 8245–8252.
Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o2153–o2154.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

full crystallographic data

IUCrData (2017). **2**, x170254 [https://doi.org/10.1107/S2414314617002541]

4-Methylanilinium 3-carboxy-4-hydroxybenzenesulfonate

S. Kalaiyarasi, S. Suresh, R. Akilan, R. Mohan Kumar and G. Chakkaravarthi

4-Methylanilinium 3-carboxy-4-hydroxybenzenesulfonate

Crystal data

$C_7H_{10}N^+·C_7H_5O_6S^-$
M_r = 325.33
Monoclinic, $P2_1/n$
a = 9.5114 (8) Å
b = 12.3080 (11) Å
c = 12.5537 (11) Å
β = 98.962 (3)°
V = 1451.7 (2) Å^3
Z = 4
$F(000)$ = 680
D_x = 1.489 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8665 reflections
θ = 2.3–31.5°
μ = 0.25 mm^{-1}
T = 295 K
Block, colourless
0.24 × 0.20 × 0.18 mm

Data collection

Bruker Kappa APEXII CCD Diffractometer
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.609, T_{max} = 0.746
26625 measured reflections
4730 independent reflections
3474 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 31.6°, θ_{min} = 2.3°
h = −14→13
k = −17→17
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.142
S = 1.10
4730 reflections
208 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.973P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}
Extinction correction: SHELXL2016 (Sheldrick, 2016), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.030 (2)

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.41299 (18)	1.08104 (15)	0.28078 (14)	0.0309 (4)
C2	0.3200 (2)	1.16342 (16)	0.29414 (16)	0.0352 (4)
H2	0.311647	1.223576	0.248763	0.042*
C3	0.2388 (2)	1.15537 (17)	0.37648 (16)	0.0387 (4)
H3	0.175095	1.210620	0.385736	0.046*
C4	0.2507 (2)	1.06667 (18)	0.44518 (15)	0.0385 (4)
C5	0.3410 (2)	0.98278 (19)	0.42574 (17)	0.0438 (5)
H5	0.346720	0.920894	0.468705	0.053*
C6	0.4227 (2)	0.98922 (18)	0.34377 (17)	0.0403 (4)
H6	0.482924	0.932553	0.331607	0.048*
C7	0.1721 (3)	1.0633 (2)	0.54056 (19)	0.0593 (7)
H7A	0.230980	1.093739	0.602444	0.089*
H7B	0.149500	0.989370	0.555340	0.089*
H7C	0.085869	1.104711	0.524619	0.089*
C8	0.36092 (18)	0.65002 (14)	0.58334 (13)	0.0283 (3)
C9	0.4344 (2)	0.59570 (16)	0.67204 (14)	0.0344 (4)
H9	0.389513	0.581016	0.731168	0.041*
C10	0.5734 (2)	0.56345 (16)	0.67298 (14)	0.0357 (4)
H10	0.621603	0.526240	0.732126	0.043*
C11	0.64165 (18)	0.58672 (15)	0.58512 (14)	0.0298 (3)
C12	0.56786 (17)	0.64118 (13)	0.49562 (12)	0.0250 (3)
C13	0.42673 (17)	0.67244 (14)	0.49550 (13)	0.0264 (3)
H13	0.377117	0.708411	0.436115	0.032*
C14	0.63914 (18)	0.66439 (15)	0.40202 (14)	0.0290 (3)
N1	0.50396 (18)	1.09139 (15)	0.19685 (14)	0.0400 (4)
H1A	0.457317	1.127520	0.140822	0.060*
H1B	0.526763	1.025568	0.175674	0.060*
H1C	0.582911	1.127370	0.223231	0.060*
O1	0.77811 (15)	0.55499 (14)	0.58997 (12)	0.0447 (4)
O2	0.55929 (15)	0.71141 (14)	0.32111 (11)	0.0442 (4)
O3	0.76397 (14)	0.64117 (14)	0.40068 (12)	0.0438 (4)
O4	0.11033 (19)	0.60551 (15)	0.62629 (18)	0.0701 (6)
O5	0.1984 (2)	0.78754 (13)	0.65703 (13)	0.0531 (4)
O6	0.12809 (16)	0.72387 (15)	0.47508 (13)	0.0517 (4)
S1	0.18523 (5)	0.69380 (4)	0.58472 (4)	0.03677 (15)
H1	0.804 (3)	0.576 (2)	0.5332 (13)	0.055*
H2A	0.601 (3)	0.715 (2)	0.2685 (15)	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0271 (8)	0.0397 (9)	0.0268 (8)	−0.0058 (7)	0.0066 (6)	−0.0079 (7)
C2	0.0398 (10)	0.0326 (9)	0.0351 (9)	−0.0034 (7)	0.0115 (8)	−0.0064 (7)
C3	0.0365 (9)	0.0413 (10)	0.0403 (10)	−0.0034 (8)	0.0121 (8)	−0.0140 (8)
C4	0.0346 (9)	0.0506 (11)	0.0315 (9)	−0.0148 (8)	0.0090 (7)	−0.0103 (8)

C5	0.0491 (12)	0.0487 (12)	0.0340 (10)	−0.0033 (9)	0.0072 (9)	0.0055 (9)
C6	0.0375 (10)	0.0463 (11)	0.0371 (10)	0.0067 (8)	0.0059 (8)	−0.0023 (8)
C7	0.0565 (14)	0.0821 (18)	0.0453 (13)	−0.0183 (13)	0.0266 (11)	−0.0090 (12)
C8	0.0302 (8)	0.0322 (8)	0.0250 (8)	−0.0026 (7)	0.0121 (6)	−0.0036 (6)
C9	0.0424 (10)	0.0411 (10)	0.0222 (8)	−0.0052 (8)	0.0122 (7)	0.0010 (7)
C10	0.0405 (10)	0.0416 (10)	0.0243 (8)	−0.0006 (8)	0.0034 (7)	0.0076 (7)
C11	0.0285 (8)	0.0321 (8)	0.0286 (8)	−0.0014 (7)	0.0041 (6)	0.0030 (7)
C12	0.0260 (7)	0.0284 (8)	0.0218 (7)	−0.0017 (6)	0.0077 (6)	−0.0006 (6)
C13	0.0276 (7)	0.0312 (8)	0.0216 (7)	0.0006 (6)	0.0081 (6)	0.0013 (6)
C14	0.0271 (7)	0.0343 (8)	0.0277 (8)	−0.0008 (6)	0.0107 (6)	0.0018 (7)
N1	0.0364 (8)	0.0490 (10)	0.0380 (9)	−0.0026 (7)	0.0170 (7)	−0.0066 (7)
O1	0.0306 (7)	0.0602 (10)	0.0437 (8)	0.0088 (6)	0.0067 (6)	0.0175 (7)
O2	0.0345 (7)	0.0713 (10)	0.0301 (7)	0.0101 (7)	0.0157 (5)	0.0189 (7)
O3	0.0292 (6)	0.0624 (10)	0.0435 (8)	0.0085 (6)	0.0170 (6)	0.0121 (7)
O4	0.0482 (9)	0.0539 (10)	0.1196 (17)	−0.0002 (8)	0.0485 (10)	0.0197 (11)
O5	0.0716 (11)	0.0506 (9)	0.0456 (9)	0.0087 (8)	0.0357 (8)	−0.0088 (7)
O6	0.0382 (8)	0.0744 (11)	0.0441 (9)	0.0165 (8)	0.0111 (6)	−0.0048 (8)
S1	0.0362 (2)	0.0396 (3)	0.0400 (3)	0.00331 (19)	0.02343 (19)	−0.00040 (19)

Geometric parameters (Å, º)

C1—C2	1.373 (3)	C9—H9	0.9300
C1—C6	1.374 (3)	C10—C11	1.394 (2)
C1—N1	1.469 (2)	C10—H10	0.9300
C2—C3	1.387 (3)	C11—O1	1.348 (2)
C2—H2	0.9300	C11—C12	1.400 (2)
C3—C4	1.385 (3)	C12—C13	1.396 (2)
C3—H3	0.9300	C12—C14	1.473 (2)
C4—C5	1.389 (3)	C13—H13	0.9300
C4—C7	1.508 (3)	C14—O3	1.224 (2)
C5—C6	1.385 (3)	C14—O2	1.305 (2)
C5—H5	0.9300	N1—H1A	0.8900
C6—H6	0.9300	N1—H1B	0.8900
C7—H7A	0.9600	N1—H1C	0.8900
C7—H7B	0.9600	O1—H1	0.829 (10)
C7—H7C	0.9600	O2—H2A	0.824 (10)
C8—C13	1.378 (2)	O4—S1	1.4411 (17)
C8—C9	1.390 (3)	O5—S1	1.4612 (16)
C8—S1	1.7585 (17)	O6—S1	1.4470 (17)
C9—C10	1.379 (3)		
C2—C1—C6	121.61 (17)	C9—C10—C11	119.87 (17)
C2—C1—N1	119.08 (17)	C9—C10—H10	120.1
C6—C1—N1	119.32 (17)	C11—C10—H10	120.1
C1—C2—C3	118.85 (19)	O1—C11—C10	117.93 (16)
C1—C2—H2	120.6	O1—C11—C12	122.28 (15)
C3—C2—H2	120.6	C10—C11—C12	119.78 (16)
C4—C3—C2	121.28 (19)	C13—C12—C11	119.65 (14)

C4—C3—H3	119.4	C13—C12—C14	120.50 (15)
C2—C3—H3	119.4	C11—C12—C14	119.84 (15)
C3—C4—C5	118.01 (17)	C8—C13—C12	120.03 (16)
C3—C4—C7	120.9 (2)	C8—C13—H13	120.0
C5—C4—C7	121.1 (2)	C12—C13—H13	120.0
C6—C5—C4	121.5 (2)	O3—C14—O2	122.76 (15)
C6—C5—H5	119.3	O3—C14—C12	122.26 (16)
C4—C5—H5	119.3	O2—C14—C12	114.99 (14)
C1—C6—C5	118.64 (19)	C1—N1—H1A	109.5
C1—C6—H6	120.7	C1—N1—H1B	109.5
C5—C6—H6	120.7	H1A—N1—H1B	109.5
C4—C7—H7A	109.5	C1—N1—H1C	109.5
C4—C7—H7B	109.5	H1A—N1—H1C	109.5
H7A—C7—H7B	109.5	H1B—N1—H1C	109.5
C4—C7—H7C	109.5	C11—O1—H1	106.3 (19)
H7A—C7—H7C	109.5	C14—O2—H2A	110.5 (19)
H7B—C7—H7C	109.5	O4—S1—O6	113.81 (13)
C13—C8—C9	120.18 (16)	O4—S1—O5	111.70 (11)
C13—C8—S1	119.83 (14)	O6—S1—O5	111.85 (10)
C9—C8—S1	119.97 (12)	O4—S1—C8	107.26 (10)
C10—C9—C8	120.47 (15)	O6—S1—C8	106.60 (8)
C10—C9—H9	119.8	O5—S1—C8	104.98 (10)
C8—C9—H9	119.8		

C6—C1—C2—C3	2.9 (3)	O1—C11—C12—C14	0.7 (3)
N1—C1—C2—C3	−177.26 (17)	C10—C11—C12—C14	−179.09 (17)
C1—C2—C3—C4	0.4 (3)	C9—C8—C13—C12	−0.4 (3)
C2—C3—C4—C5	−3.4 (3)	S1—C8—C13—C12	177.76 (13)
C2—C3—C4—C7	174.4 (2)	C11—C12—C13—C8	0.2 (3)
C3—C4—C5—C6	3.3 (3)	C14—C12—C13—C8	179.79 (16)
C7—C4—C5—C6	−174.5 (2)	C13—C12—C14—O3	177.70 (18)
C2—C1—C6—C5	−3.0 (3)	C11—C12—C14—O3	−2.7 (3)
N1—C1—C6—C5	177.11 (18)	C13—C12—C14—O2	−2.3 (3)
C4—C5—C6—C1	−0.1 (3)	C11—C12—C14—O2	177.28 (17)
C13—C8—C9—C10	−0.2 (3)	C13—C8—S1—O4	136.91 (17)
S1—C8—C9—C10	−178.34 (15)	C9—C8—S1—O4	−44.95 (19)
C8—C9—C10—C11	0.9 (3)	C13—C8—S1—O6	14.65 (18)
C9—C10—C11—O1	179.15 (18)	C9—C8—S1—O6	−167.20 (16)
C9—C10—C11—C12	−1.0 (3)	C13—C8—S1—O5	−104.14 (15)
O1—C11—C12—C13	−179.73 (17)	C9—C8—S1—O5	74.00 (17)
C10—C11—C12—C13	0.5 (3)		

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3	0.83 (1)	1.83 (2)	2.587 (2)	150 (3)
N1—H1*A*···O6^{i}	0.89	1.95	2.837 (3)	172

N1—H1*B*···O4^{ii}	0.89	1.94	2.821 (2)	169
O2—H2*A*···O5^{ii}	0.82 (1)	1.79 (1)	2.6159 (19)	176 (3)
N1—H1*C*···O3^{iii}	0.89	2.30	2.7548 (19)	112
N1—H1*C*···O5^{iv}	0.89	2.59	3.461 (3)	166
C10—H10···*Cg*2^{v}	0.93	2.66	3.549 (2)	160

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