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Crystal structure of piperazine-1,4-diium bis(4-aminobenzenesulfonate)

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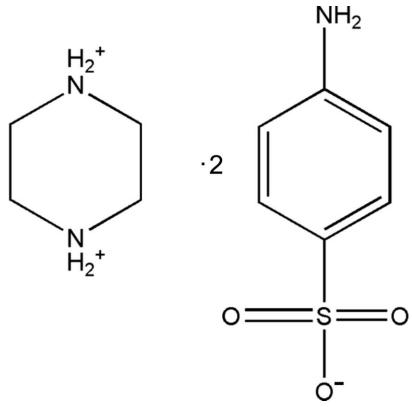
The asymmetric unit of the title salt, $C_4H_{12}N_2^{2+}\cdot 2C_6H_6NO_3S^-$, consists of half a piperazindiium dication, located about an inversion centre, and a 4-aminobenzenesulfonate anion. The piperazine ring adopts a chair conformation. In the crystal, the cations and anions are linked *via* N—H···O and C—H···O hydrogen bonds, forming a three-dimensional framework. Within the framework there are C—H···π interactions and the N—H···O hydrogen bonds result in the formation of $R_4^4(22)$ and $R_3^4(13)$ ring motifs.

Keywords: crystal structure; piperazine; 4-aminobenzenesulfonate; hydrogen bonding; three-dimensional framework.

CCDC reference: 1443504

1. Related literature

For examples of the the numerous biological activities of piperazines and their various salts, see: Kaur *et al.* (2010); Eswaran *et al.* (2010); Chou *et al.* (2010); Chen *et al.* (2004); Shingalapur *et al.* (2009); Shchekotikhin *et al.* (2005); Faist *et al.* (2012); Kulig *et al.* (2007). For a related structure, see: Wei (2011).



2. Experimental

2.1. Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_6H_6NO_3S^-$
M_r = 432.52
Orthorhombic, *Pbca*
a = 10.1709 (4) Å
b = 8.4461 (3) Å
c = 21.5569 (9) Å
V = 1851.83 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 293 K
0.25 × 0.22 × 0.19 mm

2.2. Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.920, T_{max} = 0.939
31521 measured reflections
2731 independent reflections
2130 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.107
S = 1.03
2731 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2^{i}	0.82 (3)	2.27 (3)	3.066 (2)	164 (2)
N1—H1B···O1^{ii}	0.86 (3)	2.49 (3)	3.296 (3)	156 (2)
N2—H2A···O3	0.85 (3)	1.92 (3)	2.764 (2)	175 (2)
N2—H2B···O2^{iii}	0.92 (3)	2.19 (2)	2.928 (2)	137 (2)
N2—H2B···O3^{iii}	0.92 (3)	2.54 (2)	3.328 (2)	145 (2)
C7—H7A···O1^{iv}	0.95 (2)	2.50 (2)	3.167 (2)	128 (2)
C6—H6···$Cg1^{ii}$	0.93	2.92	3.753 (2)	149

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*,

2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5262).

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Crystal structure of piperazine-1,4-diium bis(4-aminobenzenesulfonate)

K. Sathesh Kumar, S. Ranjith, S. Sudhakar, P. Srinivasan and M. N. Ponnuswamy

S1. Comment

Piperazine derivatives have wide range of applications in pharmaceuticals as antimalarial (Kaur *et al.*, 2010), anti-tuberculosis (Eswaran *et al.*, 2010), antitumor (Chou *et al.*, 2010), anticancer (Chen *et al.*, 2004) and antiviral (Shingalapur *et al.*, 2009) agents. The piperazine nucleus is capable of binding to multiple receptors with high affinity and therefore piperazine has been classified as a privileged structure. In the last decade, a number of piperazine derivatives have been synthesized and evaluated for their cytotoxic activity (Shchekotikhin *et al.*, 2005). The piperazine nucleus has been classified as a privileged structure and is frequently found in biologically active compounds across a number of different therapeutic areas (Faist *et al.*, 2012). Some of these therapeutic areas include antimicrobial, anti-tubercular, anti-convulsant, antidepressant, anti-inflammatory, cytotoxic, antimalarial, antiarrhythmic, antioxidant and antiviral activities *etc*. possessed by the compounds having piperazine nucleus (Kulig *et al.*, 2007). In view of the above said importance,the crystal structure of the title compound has been determined by crystallographic methods.

The molecular structure of the title salt is shown in Fig. 1. The crystallographic inversion centered piperazine ring adopts a chair conformation. The bond lengths N2—C7 and C4—S1 are comparable with the values observed in the related structure piperazine-1,4-diium naphthalene-1,5-disulfonate (Wei, 2011). In the anions atom S1 deviates from the benzene ring plane by −0.076 (1) Å. There is a short non-hydrogen contact involving atoms N2···O3 [2.764 Å] at *x*, *y*, *z*.

In the crystal, the N1—H1A···O2 and N1—H1B···O1 hydrogen bonds form an infinite chain leads to the formation of an $R_4^4(22)$ ring motif (Table 1 and Fig. 2). Similarly, the N2—H2···O hydrogen bonds in the molecular structure results in the formation of an $R_3^4(13)$ ring motif. These two motifs combine to form a hydrogen-bonded molecular ribbons running along *b* axis (Table 1 and Fig. 3). A C—H···π interaction is also observed involving atom C6 in the benzene ring of the anion and the centroid of another anion ring with an H···centroid distance of 2.92 Å (Table 1). The molecular structure is stabilized by strong N—H···O hydrogen bonds which form infinite one dimensional chains. These various interactions result finally in the formation of a three-dimensional framework structure (Table 1 and Fig. 4).

S2. Synthesis and crystallization

The title compound was synthesized by slow evaporation at room temperature of an aqueous mixture of piperazine (1.43 g) and sulfanilic acid (2.88 g). Colourless transparent crystals were obtained in a period of 7 days. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a solution in ethyl acetate at room temperature.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH_2 and methylene H atoms were located in difference Fourier maps and freely refined. The aromatic CH H atoms were fixed geometrically and treated as riding: C—H = 0.93 Å with U_{iso}(H) = 1.2U_{eq}(C)

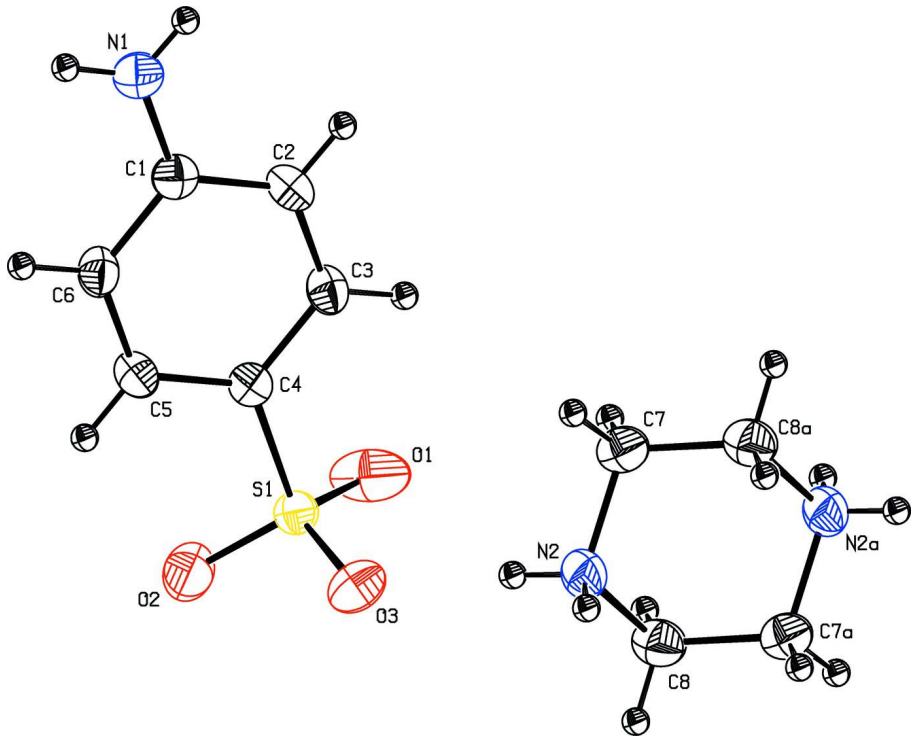

Figure 1

The molecular structure of the title salt, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The unlabelled atoms of the cation are related to the labelled atoms by inversion symmetry (- x + 2, − y, − z + 1).

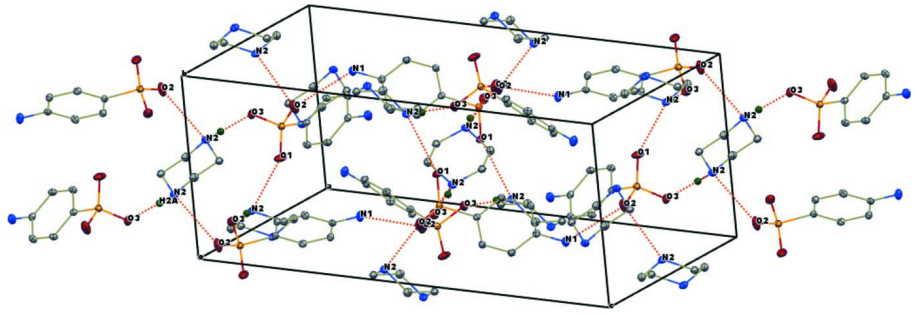

Figure 2

A partial view of the crystal packing of the title salt, viewed along the *a* axis. Hydrogen-bonded chains (dashed lines) run along the *a* and *c* axes (see Table 1).

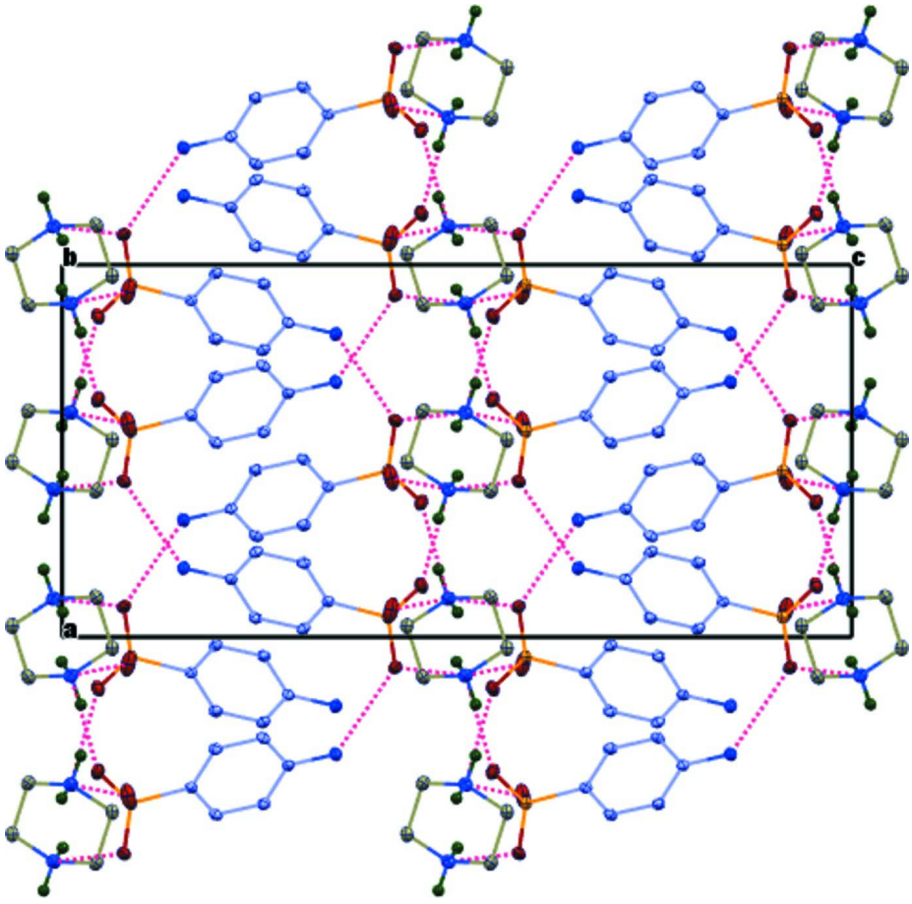

Figure 3

Crystal packing of the title salt, viewed along the *b* axis, illustrating the formation of the hydrogen-bonded (dashed lines) molecular ribbons running along the *b* axis direction (see Table 1). For the sake of clarity, H atoms not involved in hydrogen bonds have been omitted.

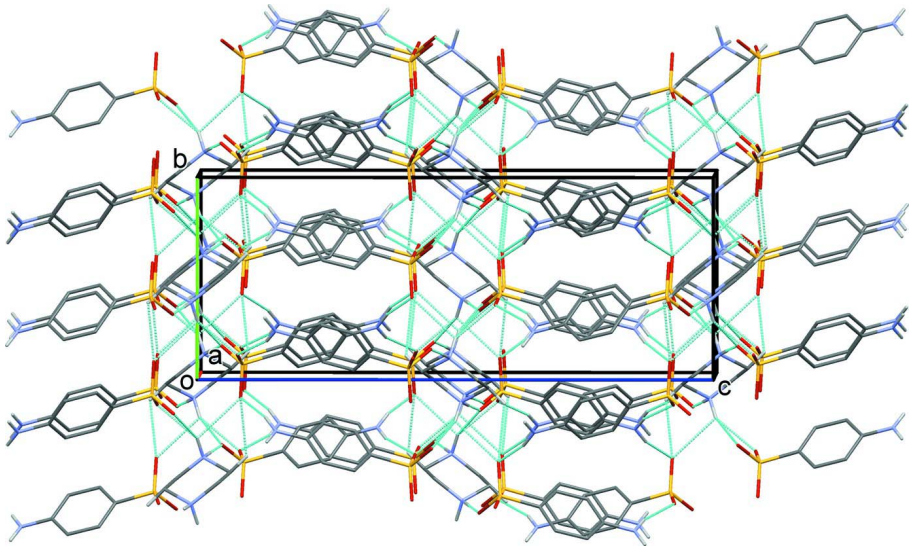

Figure 4

A view along the *a* axis of the crystal packing of the title salt. The hydrogen bonds are shown as dashed lines (Table 1), and H atoms not involved in these interactions have been omitted for clarity.

Piperazine-1,4-diium bis(4-aminobenzenesulfonate)

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_6H_6NO_3S^-$
M_r = 432.52
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 10.1709 (4) Å
b = 8.4461 (3) Å
c = 21.5569 (9) Å
V = 1851.83 (12) Å^3
Z = 4
F(000) = 912
D_x = 1.551 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2731 reflections
θ = 2.8–30.8°
μ = 0.33 mm^{-1}
T = 293 K
Block, white crystalline
0.25 × 0.22 × 0.19 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.920, T_{max} = 0.939
31521 measured reflections
2731 independent reflections
2130 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 30.8°, θ_{min} = 2.8°
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 10$
$l = -29 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.107
S = 1.03
2731 reflections
160 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 atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 1.5618P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0332 (17)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.65542 (16)	0.21272 (19)	0.21371 (7)	0.0266 (3)
C2	0.72879 (17)	0.09868 (19)	0.24541 (8)	0.0302 (3)
H2	0.7986	0.0490	0.2255	0.036*
C3	0.69927 (16)	0.05863 (19)	0.30585 (8)	0.0290 (3)
H3	0.7489	−0.0179	0.3262	0.035*
C4	0.59536 (15)	0.13233 (18)	0.33669 (7)	0.0245 (3)
C5	0.52268 (16)	0.24672 (19)	0.30563 (8)	0.0280 (3)
H5	0.4540	0.2976	0.3260	0.034*
C6	0.55133 (16)	0.2859 (2)	0.24479 (8)	0.0292 (3)
H6	0.5009	0.3615	0.2244	0.035*
C7	0.97012 (19)	0.0404 (2)	0.43662 (8)	0.0317 (4)
C8	0.8928 (2)	0.0027 (2)	0.54312 (9)	0.0358 (4)
N1	0.68534 (18)	0.2535 (2)	0.15357 (7)	0.0380 (4)
N2	0.89658 (17)	0.11265 (18)	0.48903 (7)	0.0331 (3)
O1	0.5723 (2)	−0.09171 (16)	0.41653 (7)	0.0586 (5)
O2	0.41824 (14)	0.1269 (2)	0.42189 (6)	0.0514 (4)
O3	0.63822 (14)	0.16386 (17)	0.45474 (6)	0.0413 (3)
S1	0.55342 (4)	0.07560 (5)	0.412784 (18)	0.02600 (14)
H2B	0.934 (2)	0.207 (3)	0.5007 (11)	0.046 (6)*
H1A	0.744 (2)	0.202 (3)	0.1367 (11)	0.042 (6)*
H7A	0.971 (2)	0.119 (3)	0.4049 (11)	0.042 (6)*
H1B	0.635 (2)	0.318 (3)	0.1336 (11)	0.047 (6)*
H8B	0.853 (2)	0.057 (3)	0.5758 (11)	0.046 (6)*
H2A	0.819 (3)	0.132 (3)	0.4765 (11)	0.046 (6)*
H7B	0.924 (2)	−0.044 (3)	0.4239 (10)	0.033 (5)*
H8A	0.842 (2)	−0.089 (3)	0.5299 (10)	0.045 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0248 (7)	0.0274 (7)	0.0278 (7)	−0.0045 (6)	−0.0003 (6)	−0.0017 (6)

C2	0.0275 (8)	0.0283 (7)	0.0349 (8)	0.0040 (6)	0.0058 (6)	−0.0030 (6)
C3	0.0274 (8)	0.0261 (7)	0.0336 (8)	0.0045 (6)	−0.0003 (6)	0.0024 (6)
C4	0.0249 (7)	0.0222 (7)	0.0266 (7)	−0.0019 (6)	0.0005 (6)	−0.0004 (6)
C5	0.0258 (7)	0.0261 (7)	0.0319 (8)	0.0030 (6)	0.0040 (6)	0.0009 (6)
C6	0.0258 (8)	0.0300 (8)	0.0318 (8)	0.0030 (6)	−0.0009 (6)	0.0064 (7)
C7	0.0423 (10)	0.0247 (7)	0.0282 (8)	−0.0012 (7)	−0.0005 (7)	−0.0003 (6)
C8	0.0379 (10)	0.0366 (9)	0.0328 (9)	0.0006 (8)	0.0060 (7)	−0.0005 (7)
N1	0.0366 (8)	0.0500 (10)	0.0275 (7)	0.0068 (8)	0.0036 (6)	0.0022 (7)
N2	0.0366 (8)	0.0265 (7)	0.0362 (8)	0.0072 (6)	−0.0033 (7)	−0.0028 (6)
O1	0.1135 (16)	0.0226 (7)	0.0395 (8)	0.0040 (8)	0.0162 (8)	0.0038 (5)
O2	0.0303 (7)	0.0879 (12)	0.0361 (7)	0.0069 (7)	0.0056 (6)	0.0168 (8)
O3	0.0462 (8)	0.0451 (8)	0.0327 (7)	−0.0063 (6)	−0.0078 (6)	−0.0035 (6)
S1	0.0292 (2)	0.0235 (2)	0.0252 (2)	0.00047 (14)	0.00009 (14)	0.00065 (14)

Geometric parameters (Å, º)

C1—N1	1.376 (2)	C7—H7A	0.95 (2)
C1—C6	1.397 (2)	C7—H7B	0.90 (2)
C1—C2	1.397 (2)	C8—N2	1.491 (2)
C2—C3	1.379 (2)	C8—C7^{i}	1.506 (3)
C2—H2	0.9300	C8—H8B	0.93 (2)
C3—C4	1.395 (2)	C8—H8A	0.98 (2)
C3—H3	0.9300	N1—H1A	0.82 (3)
C4—C5	1.389 (2)	N1—H1B	0.86 (3)
C4—S1	1.7614 (16)	N2—H2B	0.92 (3)
C5—C6	1.384 (2)	N2—H2A	0.85 (3)
C5—H5	0.9300	O1—S1	1.4285 (14)
C6—H6	0.9300	O2—S1	1.4548 (15)
C7—N2	1.486 (2)	O3—S1	1.4553 (13)
C7—C8^{i}	1.506 (3)	S1—O3	1.4553 (13)
N1—C1—C6	120.59 (16)	N2—C8—C7^{i}	110.69 (15)
N1—C1—C2	121.04 (16)	N2—C8—H8B	107.1 (15)
C6—C1—C2	118.37 (15)	C7^{i}—C8—H8B	107.5 (15)
C3—C2—C1	121.00 (15)	N2—C8—H8A	106.3 (13)
C3—C2—H2	119.5	C7^{i}—C8—H8A	112.6 (14)
C1—C2—H2	119.5	H8B—C8—H8A	113 (2)
C2—C3—C4	120.37 (15)	C1—N1—H1A	116.5 (16)
C2—C3—H3	119.8	C1—N1—H1B	119.8 (16)
C4—C3—H3	119.8	H1A—N1—H1B	123 (2)
C5—C4—C3	118.95 (15)	C7—N2—C8	110.61 (14)
C5—C4—S1	120.62 (12)	C7—N2—H2B	111.1 (15)
C3—C4—S1	120.39 (12)	C8—N2—H2B	109.7 (15)
C6—C5—C4	120.74 (15)	C7—N2—H2A	107.8 (16)
C6—C5—H5	119.6	C8—N2—H2A	110.2 (16)
C4—C5—H5	119.6	H2B—N2—H2A	107 (2)
C5—C6—C1	120.56 (15)	O1—S1—O2	114.48 (12)
C5—C6—H6	119.7	O1—S1—O3	113.06 (10)

C1—C6—H6	119.7	O2—S1—O3	108.89 (10)
N2—C7—C8^{i}	110.17 (15)	O1—S1—O3	113.06 (10)
N2—C7—H7A	105.4 (14)	O2—S1—O3	108.89 (10)
C8^{i}—C7—H7A	111.3 (14)	O1—S1—C4	106.80 (8)
N2—C7—H7B	107.0 (14)	O2—S1—C4	105.87 (8)
C8^{i}—C7—H7B	112.6 (14)	O3—S1—C4	107.21 (8)
H7A—C7—H7B	110.0 (19)	O3—S1—C4	107.21 (8)

N1—C1—C2—C3	179.55 (16)	O3—O3—S1—O1	0.00 (18)
C6—C1—C2—C3	0.2 (2)	O3—O3—S1—O2	0.00 (18)
C1—C2—C3—C4	−0.3 (3)	O3—O3—S1—C4	0.0 (2)
C2—C3—C4—C5	−0.2 (2)	C5—C4—S1—O1	140.98 (15)
C2—C3—C4—S1	177.43 (13)	C3—C4—S1—O1	−36.62 (17)
C3—C4—C5—C6	0.9 (2)	C5—C4—S1—O2	18.58 (16)
S1—C4—C5—C6	−176.76 (13)	C3—C4—S1—O2	−159.02 (14)
C4—C5—C6—C1	−1.0 (3)	C5—C4—S1—O3	−97.55 (15)
N1—C1—C6—C5	−178.90 (16)	C3—C4—S1—O3	84.85 (15)
C2—C1—C6—C5	0.5 (2)	C5—C4—S1—O3	−97.55 (15)
C8^{i}—C7—N2—C8	−57.3 (2)	C3—C4—S1—O3	84.85 (15)
C7^{i}—C8—N2—C7	57.6 (2)		

Symmetry code: (i) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2^{ii}	0.82 (3)	2.27 (3)	3.066 (2)	164 (2)
N1—H1*B*···O1^{iii}	0.86 (3)	2.49 (3)	3.296 (3)	156 (2)
N2—H2*A*···O3	0.85 (3)	1.92 (3)	2.764 (2)	175 (2)
N2—H2*B*···O2^{iv}	0.92 (3)	2.19 (2)	2.928 (2)	137 (2)
N2—H2*B*···O3^{iv}	0.92 (3)	2.54 (2)	3.328 (2)	145 (2)
C7—H7*A*···O1^{v}	0.95 (2)	2.50 (2)	3.167 (2)	128 (2)
C6—H6···*Cg*1^{iii}	0.93	2.92	3.753 (2)	149

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