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# Crystal structure of 2,4-diamino-6-oxo-3,6-dihydropyrimidin-1-ium *p*-toluenesulfonate

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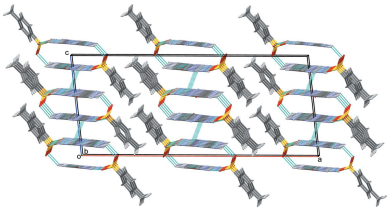
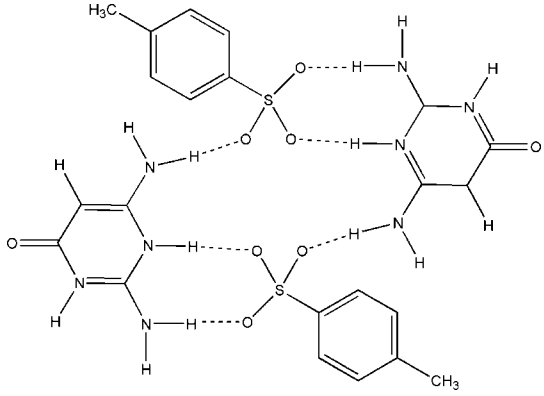
In the title salt, $C_4H_7N_4O^+\cdot C_7H_7O_3S^-$, the 2,6-diamino-4-oxo-1,3-dihydropyrimidin-1-ium cation interacts with the sulfonate group of the *p*-toluenesulfonate anion *via* a pair of N—H···O hydrogen bonds, forming a heterosynthon $R_2^2(8)$ that mimics the role of a carboxylate. The self-assembled cations form a homo-synthon $R_2^1(6)$ motif which is further linked with the sulfonate anion *via* N—H···O hydrogen bonds to generate an $R_3^2(10)$ ring motif. The three motifs are fused together and extended as supramolecular ribbons along the *b*-axis direction. Adjacent ribbons are further linked *via* N—H···O hydrogen bonds to form an annulus, with an $R_4^4(20)$ ring motif, resulting in a tunnel-like arrangement propagating along [010]. There are slipped parallel $\pi$–$\pi$ stacking interactions [inter-centroid distance = 3.6539 (7) Å], between the tunnel-like polymer chains, forming slabs parallel to (100).

## 1. Chemical context

Di- and tri-aminopyrimidines show various biological and pharmacological properties like tyrosine kinase (Thomas, 1995*a*,*b*), dihydrofolate reductase inhibitors (Ayer, 1991) and are used as antiviral and antiprotozoan agents. 2,6-Diamino-4-hydroxy pyrimidine (DAHP), an inhibitor of guanosine triphosphate cyclohydrolase I, blocks the synthesis of tetrahydrobiopterin which is a known cofactor of inducible nitric oxide synthesis (iNOS) (Bogdan *et al.*, 1995). The study of hydrogen-bonding patterns involving sulfonate groups in biological systems and metal complexes are of current interest (Gomathi & Muthiah, 2011; Wang, 2006). The present report deals with the supramolecular interactions exhibited by the title salt.





## 2. Structural commentary

The asymmetric unit of the title salt contains one 2,6-diamino-4-oxo-1,3-dihydropyrimidin-1-ium cation and one *p*-toluene

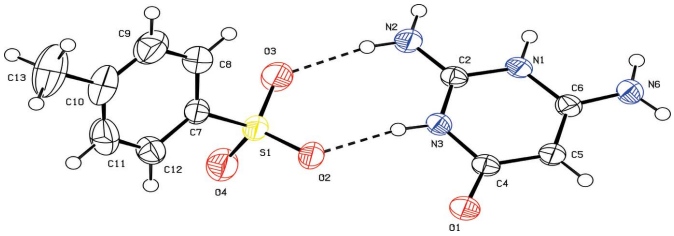



**Figure 1**
A view of the molecular structure of the title molecular salt, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

sulfonate anion (Fig. 1). The cation is protonated at the N3 position, which is reflected by the slight increase in the C2—N3—C4 bond angle to 123.2 (1)°. The dihedral angle between the cation and anion ring mean planes is 54.04 (6)°.

The three C—S—O angles, C7—S1—O3 [106.83 (7)°], C7—S1—O2 [105.89 (7)°] and C7—S1—O4 [106.91 (7)°], and the O—S—O angles, O3—S1—O2 [110.84 (7)°], O2—S1—O4 [111.93 (7)°] and O3—S1—O4 [113.91 (8)°], indicate that the geometry of the sulfonate group is slightly distorted from an ideal tetrahedral geometry.

## 3. Supramolecular features

The primary interaction between the cation and anion takes place *via* a pair of N—H···O hydrogen bonds, forming a robust six-membered hetero-synthon, $R_2^2(8)$, and here the sulfonate group mimics the role of a carboxylate. This motif links the protonated ring N atom, N3, and the 2-amino N atom, N2, of the cation with the sulfonate atoms O2 and O3 of the anion. Adjacent $R_2^2(8)$ ring motifs are connected *via* an N—H···O hydrogen bond by linking the 2-amino N atom, N2 with atom O3$^{i}$ [symmetry code: $x$, $y+1$, $z$]. The cation undergoes self-association *via* a pair of bifurcated N—H···(O,O) hydrogen bonds, forming a homo-synthon, $R_2^1(6)$. This motif involves ring N1 and the 6-amino N atoms and carbonyl atom O1$^{i}$ of the cation (Table 1). The self-assembled cations extend as a supramolecular chain propagating along [010]. The homo- and hetero-synthons [$R_2^2(8)$ and $R_2^1(6)$] are linked by an $R_3^2(10)$ ring motif. The three motifs are fused together continuously, forming supramolecular ribbons along [010]. Two such ribbons in adjacent planes are connected *via* N—H···O hydrogen bonds by linking the 6-amino N of the cation and the sulfonate atom O4$^{ii}$ [symmetry code: $-x+1$, $-y+1$, $-z+1$] of the anion, generating an annulus (Su *et al.*, 2007) with an $R_4^4(20)$ graph-set motif (Fig. 2). This motif extends in the direction of the supramolecular ribbons and generates a tunnel-like architecture along the *b*-axis direction (Figs. 2 and 3).

Adjacent tunnels interact by off-set aromatic $\pi$–$\pi$ stacking interactions which are observed between symmetry-related pyrimidine rings of the cations with a centroid–centroid distance $Cg\cdots Cg^{iii}$ of 3.6539 (7) Å [$Cg$ is the centroid of ring N1/C2/N3/C4–C6; the dihedral angle between the ring planes = 1.86 (6)°; perpendicular separation = 3.2501 (5) Å; symmetry code: (iii) $-x+1$, $y$, $-z+\frac{3}{2}$]. These interactions result in the formation of slabs parallel to (100); as shown in Fig. 3.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{i}$ | 0.86 | 1.86 | 2.6515 (14) | 152 |
| N2—H2$A$···O3 | 0.86 | 1.95 | 2.7935 (17) | 166 |
| N2—H2$B$···O2$^{i}$ | 0.86 | 2.01 | 2.8669 (16) | 175 |
| N3—H3···O2 | 0.86 | 1.92 | 2.7689 (14) | 169 |
| N6—H6$A$···O4$^{ii}$ | 0.86 | 2.25 | 2.9498 (18) | 139 |
| N6—H6$B$···O1$^{i}$ | 0.86 | 2.08 | 2.8201 (15) | 143 |

Symmetry codes: (i) $x$, $y+1$, $z$; (ii) $-x+1$, $-y+1$, $-z+1$.

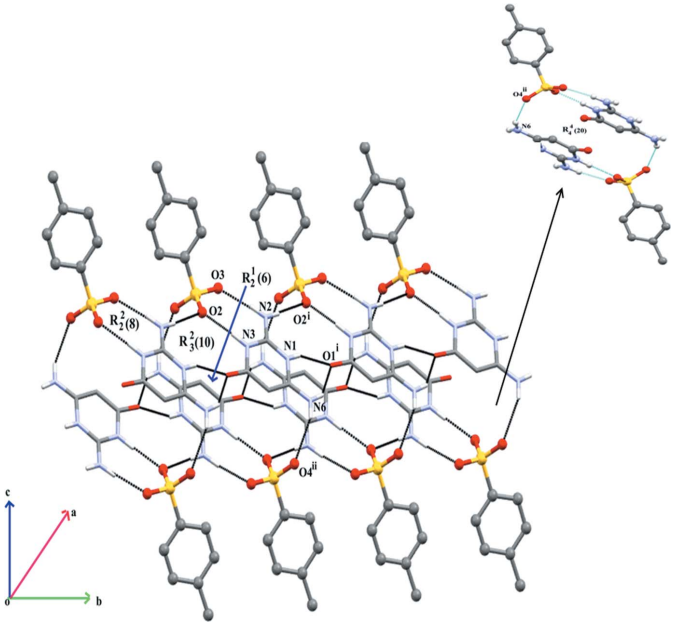



**Figure 2**
A view of the supramolecular tunnel-like architecture built by N—H···O hydrogen bonds [dashed lines; see Table 1 for details; symmetry codes: (i) $x$, $y+1$, $z$; (ii) $-x+1$, $-y+1$, $-z+1$], in the crystal structure of the title molecular salt.

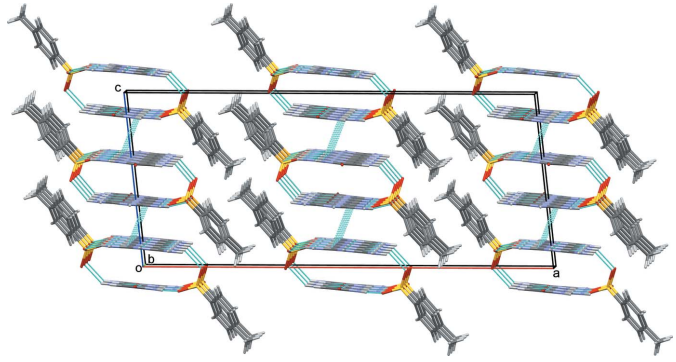



**Figure 3**
A view along the *b* axis of the crystal packing of the title molecular salt. Hydrogen bonds (see Table 1 for details) and $\pi$–$\pi$ interactions are shown as dashed lines.

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.36; Groom & Allen, 2014) revealed the presence of over 700 compounds involving *p*-toluene sulfonate but only three hits for the 2,6-diamino-4-oxo-1,3-dihydropyrimidin-1-ium cation. These include the sulfate monohydrate (ACEYUD; Muthiah *et al.*, 2004), the di(methanesulfanyl)amide (ESAQOE; Wijaya *et al.*, 2004) and the chloride dihydrate (SUZFOJ; Suleiman Gwaram *et al.*, 2010). In ACEYUD the cation is protonated at the N atom adjacent to the carbonyl group, as in the title compound, while in compounds ESAQOE and SUZFOJ it is the N atom *para* to the carbonyl group that is protonated. Otherwise, the bond distances in these three compounds are very similar and close to those observed for the title compound.

## 5. Synthesis and crystallization

A hot methanolic solution (20 ml) of 2,6-diamino-4-hydroxy pyrimidine (31.5 mg, Aldrich) and *p*-toluene sulfonic acid (43 mg, Loba chemie) was warmed at 323 K for 30 min over a water bath. The mixture was cooled slowly and kept at room temperature and after three weeks light-yellow needle-shaped crystals were obtained.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and refined using a riding model: N—H = 0.86 Å, C—H = 0.93–0.96 Å with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H atoms and 1.2$U_{eq}$(N,C) for other H atoms.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_4H_7N_4O^+\cdot C_7H_7O_3S^-$ |
| $M_r$ | 298.33 |
| Crystal system, space group | Monoclinic, *C*2/*c* |
| Temperature (K) | 296 |
| *a*, *b*, *c* (Å) | 30.8628 (7), 6.5559 (2), 13.1565 (3) |
| $\beta$ (°) | 96.428 (1) |
| *V* (Å$^3$) | 2645.27 (12) |
| *Z* | 8 |
| Radiation type | Mo *K*$\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.27 |
| Crystal size (mm) | 0.30 × 0.20 × 0.20 |
| | |
| Data collection | |
| Diffractometer | Bruker Kappa APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2004) |
| $T_{min}$, $T_{max}$ | 0.925, 0.949 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 14972, 3580, 2986 |
| $R_{int}$ | 0.022 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.687 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.037, 0.109, 1.06 |
| No. of reflections | 3580 |
| No. of parameters | 182 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.31, −0.25 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

## Acknowledgements

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# supporting information

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## Crystal structure of 2,4-diamino-6-oxo-3,6-dihydropyrimidin-1-ium *p*-toluenesulfonate

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### Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

### 2,4-Diamino-6-oxo-3,6-dihydropyrimidin-1-ium *p*-toluenesulfonate

*Crystal data*

$C_4H_7N_4O^+·C_7H_7O_3S^-$
$M_r$ = 298.33
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 30.8628 (7) Å
*b* = 6.5559 (2) Å
*c* = 13.1565 (3) Å
*β* = 96.428 (1)°
*V* = 2645.27 (12) Å$^3$
*Z* = 8
*F*(000) = 1248
$D_x$ = 1.498 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3580 reflections
*θ* = 2.7–29.3°
*μ* = 0.27 mm$^{-1}$
*T* = 296 K
Prism, colourless
0.30 × 0.20 × 0.20 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; Bruker, 2004)
$T_{min}$ = 0.925, $T_{max}$ = 0.949
14972 measured reflections
3580 independent reflections
2986 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022
$\theta_{max}$ = 29.2°, $\theta_{min}$ = 2.7°
*h* = −40→42
*k* = −9→7
*l* = −18→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.109
*S* = 1.06
3580 reflections
182 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

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 1.4509P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.31$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement**. Refinement on $F^2$ for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.37258 (1) | 0.33503 (6) | 0.60709 (3) | 0.0395 (1) |
| O2 | 0.41787 (3) | 0.26937 (17) | 0.63677 (10) | 0.0469 (4) |
| O3 | 0.36871 (4) | 0.55423 (17) | 0.61453 (11) | 0.0559 (4) |
| O4 | 0.35526 (4) | 0.2530 (2) | 0.50899 (10) | 0.0594 (4) |
| C7 | 0.34167 (4) | 0.2292 (2) | 0.69886 (12) | 0.0379 (4) |
| C8 | 0.33328 (5) | 0.3414 (3) | 0.78333 (14) | 0.0508 (5) |
| C9 | 0.30882 (6) | 0.2558 (4) | 0.85489 (15) | 0.0631 (7) |
| C10 | 0.29210 (5) | 0.0608 (4) | 0.84233 (15) | 0.0611 (7) |
| C11 | 0.30171 (6) | −0.0499 (3) | 0.75883 (16) | 0.0595 (6) |
| C12 | 0.32634 (5) | 0.0315 (3) | 0.68668 (14) | 0.0477 (5) |
| C13 | 0.26346 (7) | −0.0295 (5) | 0.9167 (2) | 0.0946 (12) |
| O1 | 0.52384 (3) | 0.28686 (15) | 0.61202 (10) | 0.0461 (4) |
| N1 | 0.50945 (3) | 0.88937 (16) | 0.62432 (8) | 0.0306 (3) |
| N2 | 0.43613 (4) | 0.84071 (18) | 0.63472 (10) | 0.0382 (3) |
| N3 | 0.48173 (3) | 0.56345 (16) | 0.62787 (9) | 0.0314 (3) |
| N6 | 0.58157 (4) | 0.95420 (18) | 0.60830 (11) | 0.0424 (4) |
| C2 | 0.47500 (4) | 0.76549 (19) | 0.62867 (9) | 0.0289 (3) |
| C4 | 0.52230 (4) | 0.4758 (2) | 0.61702 (10) | 0.0321 (3) |
| C5 | 0.55713 (4) | 0.6088 (2) | 0.61103 (11) | 0.0343 (4) |
| C6 | 0.55075 (4) | 0.8158 (2) | 0.61406 (10) | 0.0308 (3) |
| H8 | 0.34390 | 0.47360 | 0.79230 | 0.0610* |
| H9 | 0.30360 | 0.33110 | 0.91220 | 0.0760* |
| H11 | 0.29140 | −0.18290 | 0.75060 | 0.0710* |
| H12 | 0.33250 | −0.04600 | 0.63080 | 0.0570* |
| H13A | 0.23360 | 0.00590 | 0.89590 | 0.1420* |
| H13B | 0.27210 | 0.02330 | 0.98400 | 0.1420* |
| H13C | 0.26650 | −0.17530 | 0.91740 | 0.1420* |
| H1 | 0.50570 | 1.01900 | 0.62810 | 0.0370* |
| H2A | 0.41430 | 0.76020 | 0.63830 | 0.0460* |
| H2B | 0.43230 | 0.97070 | 0.63510 | 0.0460* |
| H3 | 0.46010 | 0.48390 | 0.63430 | 0.0380* |
| H5 | 0.58480 | 0.55720 | 0.60500 | 0.0410* |

| | | | | |
|---|---|---|---|---|
| H6A | 0.60780 | 0.91650 | 0.60220 | 0.0510* |
| H6B | 0.57530 | 1.08180 | 0.61070 | 0.0510* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0285 (2) | 0.0340 (2) | 0.0570 (2) | −0.0021 (1) | 0.0095 (1) | −0.0001 (2) |
| O2 | 0.0284 (5) | 0.0346 (5) | 0.0788 (8) | −0.0014 (4) | 0.0105 (5) | 0.0016 (5) |
| O3 | 0.0434 (6) | 0.0332 (6) | 0.0928 (10) | 0.0018 (5) | 0.0154 (6) | 0.0087 (6) |
| O4 | 0.0459 (6) | 0.0783 (9) | 0.0554 (7) | −0.0116 (6) | 0.0117 (5) | −0.0091 (6) |
| C7 | 0.0265 (6) | 0.0356 (7) | 0.0519 (8) | −0.0021 (5) | 0.0053 (5) | 0.0004 (6) |
| C8 | 0.0409 (8) | 0.0524 (10) | 0.0600 (10) | −0.0048 (7) | 0.0094 (7) | −0.0104 (8) |
| C9 | 0.0469 (9) | 0.0889 (15) | 0.0554 (10) | −0.0014 (10) | 0.0140 (8) | −0.0057 (10) |
| C10 | 0.0336 (7) | 0.0877 (15) | 0.0618 (11) | −0.0043 (8) | 0.0039 (7) | 0.0239 (10) |
| C11 | 0.0458 (9) | 0.0518 (11) | 0.0791 (13) | −0.0138 (8) | −0.0004 (8) | 0.0191 (9) |
| C12 | 0.0411 (7) | 0.0379 (8) | 0.0638 (10) | −0.0056 (6) | 0.0047 (7) | −0.0005 (7) |
| C13 | 0.0533 (11) | 0.149 (3) | 0.0824 (15) | −0.0176 (14) | 0.0114 (10) | 0.0509 (16) |
| O1 | 0.0415 (5) | 0.0209 (5) | 0.0767 (8) | 0.0010 (4) | 0.0104 (5) | 0.0001 (5) |
| N1 | 0.0338 (5) | 0.0190 (5) | 0.0395 (6) | −0.0006 (4) | 0.0066 (4) | 0.0008 (4) |
| N2 | 0.0333 (5) | 0.0271 (6) | 0.0552 (7) | 0.0018 (4) | 0.0092 (5) | 0.0027 (5) |
| N3 | 0.0307 (5) | 0.0221 (5) | 0.0417 (6) | −0.0022 (4) | 0.0061 (4) | 0.0018 (4) |
| N6 | 0.0353 (6) | 0.0269 (6) | 0.0665 (8) | −0.0041 (5) | 0.0126 (6) | −0.0005 (5) |
| C2 | 0.0332 (6) | 0.0244 (6) | 0.0293 (6) | −0.0003 (5) | 0.0042 (4) | 0.0014 (4) |
| C4 | 0.0346 (6) | 0.0230 (6) | 0.0388 (6) | 0.0009 (5) | 0.0040 (5) | 0.0010 (5) |
| C5 | 0.0316 (6) | 0.0256 (6) | 0.0462 (7) | 0.0008 (5) | 0.0068 (5) | 0.0001 (5) |
| C6 | 0.0328 (6) | 0.0261 (6) | 0.0338 (6) | −0.0020 (5) | 0.0055 (5) | 0.0008 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O2 | 1.4728 (10) | C7—C12 | 1.383 (2) |
| S1—O3 | 1.4462 (12) | C7—C8 | 1.381 (2) |
| S1—O4 | 1.4444 (14) | C8—C9 | 1.389 (3) |
| S1—C7 | 1.7628 (15) | C9—C10 | 1.382 (4) |
| O1—C4 | 1.2416 (16) | C10—C13 | 1.511 (3) |
| N1—C6 | 1.3835 (16) | C10—C11 | 1.376 (3) |
| N1—C2 | 1.3442 (16) | C11—C12 | 1.388 (3) |
| N2—C2 | 1.3077 (18) | C8—H8 | 0.9300 |
| N3—C2 | 1.3410 (16) | C9—H9 | 0.9300 |
| N3—C4 | 1.3994 (16) | C11—H11 | 0.9300 |
| N6—C6 | 1.3228 (18) | C12—H12 | 0.9300 |
| N1—H1 | 0.8600 | C13—H13C | 0.9600 |
| N2—H2A | 0.8600 | C13—H13A | 0.9600 |
| N2—H2B | 0.8600 | C13—H13B | 0.9600 |
| N3—H3 | 0.8600 | C4—C5 | 1.3932 (18) |
| N6—H6B | 0.8600 | C5—C6 | 1.3725 (19) |
| N6—H6A | 0.8600 | C5—H5 | 0.9300 |
| | | | |
| S1···H2A | 3.0800 | C5···O4$^{ii}$ | 3.4031 (18) |

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|---|---|---|---|
| S1···H2B$^{i}$ | 3.0100 | C6···N2$^{v}$ | 3.2886 (19) |
| S1···H3 | 2.8600 | C6···O1$^{iv}$ | 3.1973 (16) |
| O1···C6$^{i}$ | 3.1973 (16) | C6···C2$^{v}$ | 3.5776 (18) |
| O1···N1$^{i}$ | 2.6515 (14) | C13···O4$^{vi}$ | 3.298 (3) |
| O1···N6$^{i}$ | 2.8201 (15) | C4···H1$^{i}$ | 3.0400 |
| O1···C2$^{ii}$ | 3.1894 (18) | C4···H6B$^{i}$ | 3.0600 |
| O2···N3 | 2.7689 (14) | C7···H13A$^{vii}$ | 3.1000 |
| O2···N2$^{i}$ | 2.8669 (16) | C12···H13B$^{iii}$ | 3.0100 |
| O3···N2 | 2.7935 (17) | H1···H2B | 2.3000 |
| O4···C5$^{ii}$ | 3.4031 (18) | H1···H6B | 2.2200 |
| O4···N6$^{ii}$ | 2.9498 (18) | H1···C4$^{iv}$ | 3.0400 |
| O4···C13$^{iii}$ | 3.298 (3) | H1···O1$^{iv}$ | 1.8600 |
| O1···H6B$^{i}$ | 2.0800 | H2A···H3 | 2.3000 |
| O1···H1$^{i}$ | 1.8600 | H2A···S1 | 3.0800 |
| O2···H3 | 1.9200 | H2A···O3 | 1.9500 |
| O2···H2B$^{i}$ | 2.0100 | H2B···H1 | 2.3000 |
| O3···H12$^{iv}$ | 2.8700 | H2B···S1$^{iv}$ | 3.0100 |
| O3···H3 | 2.8400 | H2B···O2$^{iv}$ | 2.0100 |
| O3···H8 | 2.6000 | H3···S1 | 2.8600 |
| O3···H2A | 1.9500 | H3···H2A | 2.3000 |
| O4···H5$^{ii}$ | 2.8000 | H3···O2 | 1.9200 |
| O4···H13C$^{iii}$ | 2.9100 | H3···O3 | 2.8400 |
| O4···H6A$^{ii}$ | 2.2500 | H5···O4$^{ii}$ | 2.8000 |
| O4···H12 | 2.6800 | H5···H8$^{v}$ | 2.5100 |
| N1···O1$^{iv}$ | 2.6515 (14) | H5···H6A | 2.4600 |
| N1···C2$^{v}$ | 3.3319 (16) | H6A···O4$^{ii}$ | 2.2500 |
| N2···O3 | 2.7935 (17) | H6A···H5 | 2.4600 |
| N2···O2$^{iv}$ | 2.8669 (16) | H6B···C4$^{iv}$ | 3.0600 |
| N2···C6$^{v}$ | 3.2886 (19) | H6B···H1 | 2.2200 |
| N3···C5$^{ii}$ | 3.4276 (18) | H6B···O1$^{iv}$ | 2.0800 |
| N3···O2 | 2.7689 (14) | H8···H5$^{v}$ | 2.5100 |
| N3···N3$^{v}$ | 3.2844 (17) | H8···O3 | 2.6000 |
| N3···C4$^{v}$ | 3.4212 (18) | H9···H13B | 2.4700 |
| N3···C4$^{ii}$ | 3.2207 (18) | H11···H13C | 2.4100 |
| N6···O1$^{iv}$ | 2.8201 (15) | H12···O4 | 2.6800 |
| N6···O4$^{ii}$ | 2.9498 (18) | H12···H13B$^{iii}$ | 2.5300 |
| C2···N1$^{v}$ | 3.3319 (16) | H12···O3$^{i}$ | 2.8700 |
| C2···C2$^{v}$ | 3.3868 (17) | H13A···C7$^{viii}$ | 3.1000 |
| C2···C6$^{v}$ | 3.5776 (18) | H13B···H9 | 2.4700 |
| C2···O1$^{ii}$ | 3.1894 (18) | H13B···C12$^{vi}$ | 3.0100 |
| C4···N3$^{ii}$ | 3.2207 (18) | H13B···H12$^{vi}$ | 2.5300 |
| C4···C4$^{ii}$ | 3.2446 (18) | H13C···H11 | 2.4100 |
| C4···N3$^{v}$ | 3.4212 (18) | H13C···O4$^{vi}$ | 2.9100 |
| C5···N3$^{ii}$ | 3.4276 (18) | | |

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|---|---|---|---|
| O2—S1—O3 | 110.84 (7) | C7—C12—C11 | 119.19 (17) |
| O2—S1—O4 | 111.93 (7) | C9—C8—H8 | 120.00 |
| O2—S1—C7 | 105.89 (7) | C7—C8—H8 | 120.00 |

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|---|---|---|---|
| O3—S1—O4 | 113.91 (8) | C10—C9—H9 | 119.00 |
| O3—S1—C7 | 106.83 (7) | C8—C9—H9 | 119.00 |
| O4—S1—C7 | 106.91 (7) | C10—C11—H11 | 119.00 |
| C2—N1—C6 | 122.36 (11) | C12—C11—H11 | 119.00 |
| C2—N3—C4 | 123.20 (10) | C11—C12—H12 | 120.00 |
| C6—N1—H1 | 119.00 | C7—C12—H12 | 120.00 |
| C2—N1—H1 | 119.00 | C10—C13—H13C | 109.00 |
| C2—N2—H2B | 120.00 | H13B—C13—H13C | 109.00 |
| H2A—N2—H2B | 120.00 | C10—C13—H13A | 109.00 |
| C2—N2—H2A | 120.00 | C10—C13—H13B | 109.00 |
| C4—N3—H3 | 118.00 | H13A—C13—H13C | 109.00 |
| C2—N3—H3 | 118.00 | H13A—C13—H13B | 110.00 |
| C6—N6—H6A | 120.00 | N1—C2—N3 | 118.20 (11) |
| H6A—N6—H6B | 120.00 | N1—C2—N2 | 120.67 (12) |
| C6—N6—H6B | 120.00 | N2—C2—N3 | 121.13 (11) |
| S1—C7—C12 | 119.60 (12) | N3—C4—C5 | 116.98 (11) |
| C8—C7—C12 | 119.99 (15) | O1—C4—C5 | 125.95 (12) |
| S1—C7—C8 | 120.41 (11) | O1—C4—N3 | 117.07 (11) |
| C7—C8—C9 | 119.68 (18) | C4—C5—C6 | 120.20 (12) |
| C8—C9—C10 | 121.11 (19) | N1—C6—N6 | 116.28 (12) |
| C11—C10—C13 | 120.3 (2) | N1—C6—C5 | 118.97 (11) |
| C9—C10—C13 | 121.5 (2) | N6—C6—C5 | 124.76 (12) |
| C9—C10—C11 | 118.19 (18) | C4—C5—H5 | 120.00 |
| C10—C11—C12 | 121.79 (19) | C6—C5—H5 | 120.00 |

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|---|---|---|---|
| O2—S1—C7—C8 | 94.26 (13) | S1—C7—C12—C11 | −179.44 (13) |
| O2—S1—C7—C12 | −84.77 (13) | S1—C7—C8—C9 | 179.93 (13) |
| O3—S1—C7—C8 | −23.93 (14) | C12—C7—C8—C9 | −1.0 (2) |
| O3—S1—C7—C12 | 157.04 (12) | C8—C7—C12—C11 | 1.5 (2) |
| O4—S1—C7—C8 | −146.24 (13) | C7—C8—C9—C10 | −1.0 (3) |
| O4—S1—C7—C12 | 34.72 (14) | C8—C9—C10—C13 | −176.68 (19) |
| C6—N1—C2—N2 | −177.54 (12) | C8—C9—C10—C11 | 2.4 (3) |
| C6—N1—C2—N3 | 3.24 (18) | C13—C10—C11—C12 | 177.18 (19) |
| C2—N1—C6—N6 | 178.45 (12) | C9—C10—C11—C12 | −2.0 (3) |
| C2—N1—C6—C5 | −1.84 (19) | C10—C11—C12—C7 | 0.0 (3) |
| C2—N3—C4—O1 | −176.29 (13) | O1—C4—C5—C6 | 177.72 (14) |
| C2—N3—C4—C5 | 2.62 (19) | N3—C4—C5—C6 | −1.1 (2) |
| C4—N3—C2—N2 | 177.12 (12) | C4—C5—C6—N6 | −179.57 (14) |
| C4—N3—C2—N1 | −3.67 (18) | C4—C5—C6—N1 | 0.8 (2) |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O1$^{iv}$ | 0.86 | 1.86 | 2.6515 (14) | 152 |
| N2—H2*A*···O3 | 0.86 | 1.95 | 2.7935 (17) | 166 |
| N2—H2*B*···O2$^{iv}$ | 0.86 | 2.01 | 2.8669 (16) | 175 |

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|---|---|---|---|---|
| N3—H3···O2 | 0.86 | 1.92 | 2.7689 (14) | 169 |
| N6—H6*A*···O4$^{ii}$ | 0.86 | 2.25 | 2.9498 (18) | 139 |
| N6—H6*B*···O1$^{iv}$ | 0.86 | 2.08 | 2.8201 (15) | 143 |

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, *y*+1, *z*.