

Crystal structure and Hirshfeld surface analysis of 2,4-diamino-6-phenyl-1,3,5-triazin-1-ium 4-methylbenzenesulfonate

Ramalingam Sangeetha,^a Kasthuri Balasubramani,^{a*} Kaliyaperumal Thanigaimani^b and Savaridasson Jose Kavitha^c

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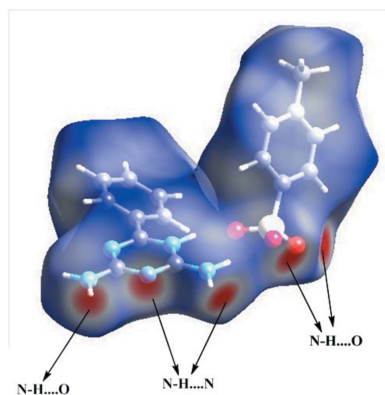
Supporting information: this article has supporting information at journals.iucr.org/e

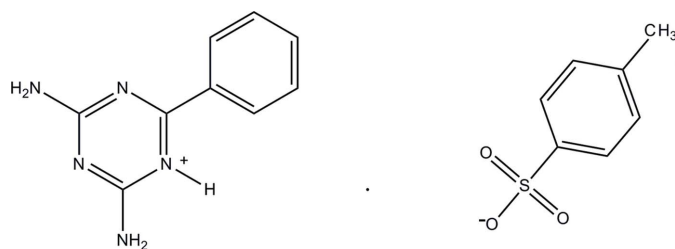
^aDepartment of Chemistry, Governemnt Arts College (Autonomous), Karur 639 005, Tamil Nadu, India, ^bDepartment of Chemistry, Government Arts College, Thiruchirappalli 620 022, Tamil Nadu, India, and ^cDepartment of Chemistry, Mother Teresa Womens University, Kodaikanal 624 102, Tamil Nadu, India. *Correspondence e-mail: manavaibala@gmail.com

In the title molecular salt, $C_9H_{10}N_5^+ \cdot C_7H_7O_3S^-$, the asymmetric unit consists of a 2,4-diamino-6-phenyl-1,3,5-triazin-1-ium cation and a 4-methylbenzenesulfonate anion. The cation is protonated at the N atom lying between the amine and phenyl substituents. The protonated N and amino-group N atoms are involved in hydrogen bonding with the sulfonate O atoms through a pair of intermolecular $N-H \cdots O$ hydrogen bonds, giving rise to a hydrogen-bonded cyclic motif with $R_2^2(8)$ graph-set notation. The inversion-related molecules are further linked by four $N-H \cdots O$ intermolecular interactions to produce a complementary *DDAA* (*D* = donor, *A* = acceptor) hydrogen-bonded array, forming $R_2^2(8)$, $R_4^2(8)$ and $R_2^2(8)$ ring motifs. The centrosymmetrically paired cations form $R_2^2(8)$ ring motifs through base-pairing *via* $N-H \cdots N$ hydrogen bonds. In addition, another $R_3^3(10)$ motif is formed between centrosymmetrically paired cations and a sulfonate anion *via* $N-H \cdots O$ hydrogen bonds. The crystal structure also features weak $S=O \cdots \pi$ and $\pi-\pi$ interactions. Hirshfeld surface and fingerprint plots were employed in order to further study the intermolecular interactions.

1. Chemical context

Triazine derivatives have been found to possess a wide variety of biological activities such as anticancer (El-Gendy *et al.*, 2001; Abdel-Rahman *et al.*, 1999), antitumour (Menicagli *et al.*, 2004) and anti-inflammatory (El-Massry *et al.*, 1999) activities. In addition, many *s*-triazine derivatives have been found to exhibit antibacterial (Jyoti *et al.*, 2003) and herbicidal activity. The 1,3,5-triazine moieties are of particular interest because of their potentially large non-linear optical response (Marchewka *et al.*, 2003). Triazine derivatives of melamine and benzoguanamine are used to manufacture resins (Ricciotti *et al.*, 2013). They are used as preservatives in oil-field applications and as disinfectants, industrial deodorants and as a biocide in water treatments. Triazine derivatives have been used appreciably as a valuable constructing unit of subtle architectures consisting of organic and inorganic hybrid frameworks (Mathias *et al.*, 1994; Zerkowski *et al.*, 1994; MacDonald & Whitesides, 1994; Guru Row *et al.*, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). Herein the crystal structure of 2,4-diamino-6-phenyl-1,3,5-triazine-1-ium-4-methylbenzene sulfonate is described. Hirshfeld surface analysis and two-dimensional fingerprint plots were employed to quantify the percentage contributions of the intermolecular interactions present in the molecule.





2. Structural commentary

The molecular structure with its atomic numbering scheme is shown in Fig. 1. The asymmetric unit comprises a 2,4-diamino-6-phenyl-1,3,5-triazin-1-ium cation and a 4-methylbenzene sulfonate anion. The cation is protonated at atom N5, which lies between the amine and phenyl substituents: this protonation is reflected by an increase in the bond angle at N5 [$\text{C8}-\text{N5}-\text{C10} = 119.43 (15)^\circ$] compared to the unprotonated atom N3 [$\text{C8}-\text{N3}-\text{C9} = 115.88 (15)^\circ$] and the corresponding angle of $113.7 (4)^\circ$ in neutral 2,4-diamino-6-phenyl-1,3,5-triazine (Díaz-Ortiz *et al.*, 2004). Otherwise, bond lengths and angles are in normal ranges (Allen *et al.*, 1987).

3. Supramolecular features

In the crystal, the protonated nitrogen (N5) and amino group nitrogen (N4) atoms are involved in hydrogen bonding with the 4-methylbenzene sulfonate oxygen atoms O2 and O3 through a pair of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, giving rise to a hydrogen-bonded $R_2^2(8)$ cyclic graph-set motif (Fig. 1, Table 1). Here the sulfonate oxygen atoms mimic the role of carboxylate oxygen atoms. The inversion-related molecules are further linked by four $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming an another $R_4^2(8)$ ring motif to produce a DDAA array of quadruple hydrogen bonds. This type of

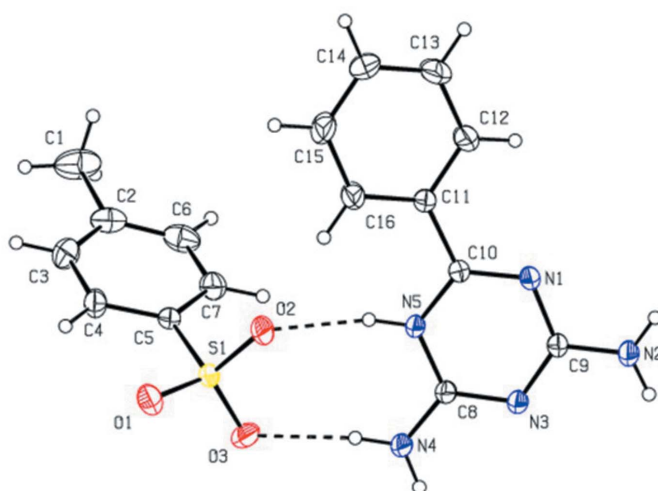


Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 40% probability level. $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (dashed lines) form an $R_2^2(8)$ ring motif between the 2,4-diamino-6-phenyl-1,3,5-triazin-1-ium cation and 4-methylbenzenesulfonate anion.

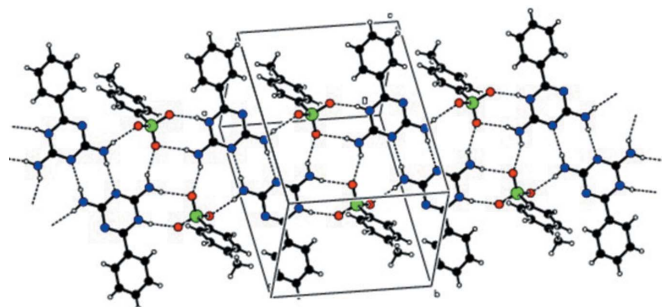


Figure 2

Crystal packing of the title compound viewed along the b axis. Dashed lines indicate $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, which form a complementary DDAA hydrogen bonded-array with $R_2^2(8)$, $R_4^2(8)$, $R_2^2(8)$ and $R_3^3(10)$ graph-set motifs, generating a one-dimensional hydrogen-bonded supramolecular structure. (Red = oxygen, green = sulfur).

conjoined hydrogen-bonded ring motifs can be represented as $R_2^2(8)$, $R_4^2(8)$ and $R_2^2(8)$, respectively (Fig. 2). The inversion-related triazinium bases are paired by two $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, generating an $R_2^2(8)$ graph-set motif. In addition, another $R_3^3(10)$ ring motif is formed between centrosymmetrically paired cations and a sulfonate anion *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. One of the sulfonate oxygen atoms acts as an acceptor of bifurcated hydrogen bonds. Overall, these hydrogen bonds generate chains along (100).

A weak intermolecular π -ring interaction between atom O1 of the anion and the π -system of the triazinium ring is observed in a slipped-parallel mode [$\text{S1}-\text{O1}\cdots\text{Cg1}$; $Y-X$, $\pi = 46.33^\circ$], (Fig. 3, Table 1). A similar interaction was observed in 1,3-dimethoxy-2-methylimidazolium bis(trifluoromethanesulfonyl)imide (Partl *et al.*, 2016). π - π interactions are also observed between the anionic rings, with a centroid-to-centroid distance of $3.9192 (13) \text{ \AA}$.

4. Hirshfeld surface analysis

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and two-dimensional fingerprint plots are useful tools for describing the surface characteristics of the crystal structure

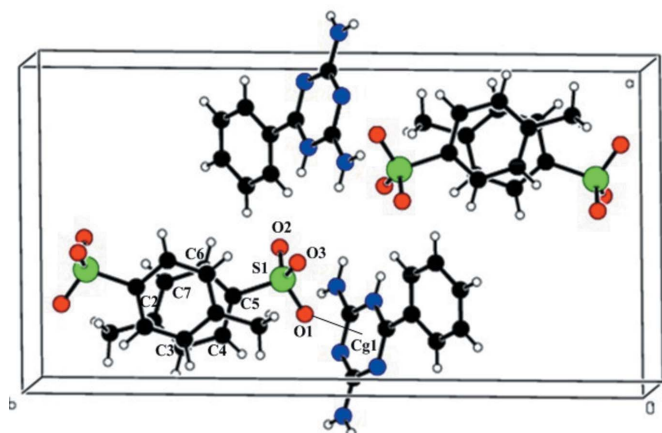


Figure 3

A packing view along the c axis showing the weak intermolecular $\text{S1}=\text{O1}\cdots\text{Cg1}$ (dashed line) and π - π interactions.

Table 1

Hydrogen-bond geometry (\AA , $^\circ$). Cg_1 and Cg_3 are the centroids of the N1/C9/N3/C8/N5/C10 and C2–C5/C6/C7 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4–H2N4 \cdots O3 ⁱ	0.86	2.10	2.877 (2)	150
N4–H1N4 \cdots O3	0.86	2.13	2.950 (2)	160
N2–H2N2 \cdots N3 ⁱⁱ	0.86	2.25	3.089 (2)	164
N2–H1N2 \cdots O1 ⁱⁱⁱ	0.86	2.05	2.895 (2)	169
N5–H1N5 \cdots O2	0.86	1.95	2.789 (2)	165
C16–H16 \cdots O2	0.93	2.40	3.210 (3)	146
S1–O1 \cdots Cg1 ^{iv}		2.93 (1)	4.1695 (8)	142 (1)
Cg_3-Cg_3			3.9192 (13)	

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

and were generated using *CrystalExplorer3.0* (Wolff *et al.*, 2012). The normalized contact distance (d_{norm}) is based on the distances from the nearest atom inside (d_i) and outside (d_e) the surface. The three-dimensional d_{norm} surface of the title compound is shown in Fig. 4. The red points represent closer contacts and negative d_{norm} values on the surface corresponding to N–H \cdots O and N–H \cdots N interactions. Two-dimensional fingerprint plots are shown in Fig. 5. The H \cdots H interactions (43.5%) and C \cdots H (18.7%) interactions make the highest contributions with the O \cdots H (15.9%) N \cdots H (10.9%), C \cdots C (3.9%), C \cdots O (2.3%), N \cdots O (1.6%) and O \cdots O (0.3%) contacts also making significant contributions to the Hirshfeld surface.

5. Database survey

A search of the Cambridge Structural Database (Version 5.37, update February 2016 Groom *et al.*, 2016) for 2,4-diamino-6-

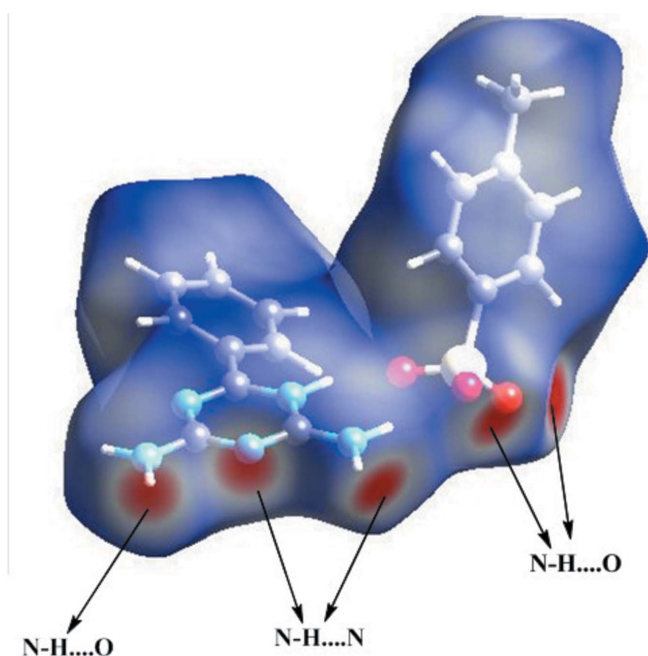


Figure 4
A view of the three-dimensional Hirshfeld surface of the title compound.

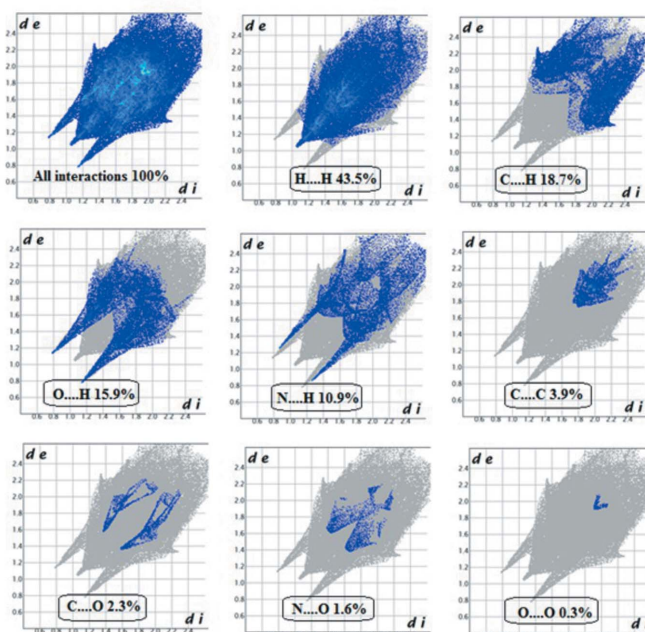


Figure 5
Two-dimensional fingerprint plots for the title compound.

phenyl-1,3,5-triazine yielded five crystal structures of proton-transfer salts with carboxylic acids: HEVQAB (with oxalic acid; Aghabozorg *et al.*, 2006), HEWFOG (with picric acid; Goel *et al.*, 2013), TEZNAP (with phthalic acid; Delori *et al.*, 2013), WEPBUP (with hydrogen chloride; Sheshmani *et al.*, 2006), and YOCZOH (with 2,3,5,6-tetrafluoroterephthalic acid; Wang *et al.*, 2014).

6. Synthesis and crystallization

The title compound was prepared by mixing a hot methanolic solution (20 ml) of 2,4-diamino-6-phenyl-1,3,5-triazine (0.187 g) and a hot methanolic solution (10 ml) of 4-methylbenzene sulfonic acid (0.172 g) in 1:1 molar ratio. The reaction mixture was warmed over a water bath for a few minutes. The resultant solution was then allowed to cool slowly at room temperature. After a few days, colourless block-shaped crystals were separated out.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C- and N-bound H atoms were placed in calculated positions and were included in the refinement in the riding-model approximation: C–H = 0.93 \AA and N–H = 0.86 \AA with $U_{\text{iso}}(\text{H})$ set to 1.2–1.5 $U_{\text{eq}}(\text{C})$ or 1.3 $U_{\text{eq}}(\text{N})$.

Acknowledgements

The authors wish to thank the SAIF–STIC, Cochin, Kerala, for the data collection.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{10}N_5^+ \cdot C_7H_7O_3S^-$
M_r	359.41
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	11.0060 (6), 20.7269 (11), 7.6213 (4)
β (°)	97.468 (2)
V (Å ³)	1723.83 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.21
Crystal size (mm)	0.35 × 0.35 × 0.30
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2004)
T_{\min}, T_{\max}	0.929, 0.939
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20842, 4273, 3325
R_{int}	0.033
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.151, 1.01
No. of reflections	4277
No. of parameters	227
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.49, -0.43

Computer programs: APEX2, SAINT and XPREP (Bruker, 2004), SHELXS97 and SHELXL97 (Sheldrick, 2008) and PLATON (Spek, 2009).

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Ramalingam Sangeetha, Kasthuri Balasubramani, Kaliyaperumal Thanigaimani and Savaridasson Jose Kavitha

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (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); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

2,4-Diamino-6-phenyl-1,3,5-triazin-1-ium 4-methylbenzenesulfonate

Crystal data

$C_9H_{10}N_5^+ \cdot C_7H_7O_3S^-$

$M_r = 359.41$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 11.0060$ (6) Å

$b = 20.7269$ (11) Å

$c = 7.6213$ (4) Å

$\beta = 97.468$ (2)°

$V = 1723.83$ (16) Å³

$Z = 4$

$F(000) = 752$

$D_x = 1.385$ Mg m⁻³

$D_m = 1.381$ Mg m⁻³

D_m measured by Not Measured

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6410 reflections

$\theta = 5.7\text{--}56.4^\circ$

$\mu = 0.21$ mm⁻¹

$T = 296$ K

Block, colourless

$0.35 \times 0.35 \times 0.30$ mm

Data collection

Bruker Kappa APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 18.4 pixels mm⁻¹

ω and ϕ scan

Absorption correction: multi-scan

(SADABS; Bruker, 2004)

$T_{\min} = 0.929$, $T_{\max} = 0.939$

20842 measured reflections

4273 independent reflections

3325 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -14 \rightarrow 14$

$k = -27 \rightarrow 24$

$l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.151$

$S = 1.01$

4277 reflections

227 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

$$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2 + 0.7378P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

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 esds 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.34811 (4)	0.91624 (2)	0.65382 (7)	0.0341 (2)
N1	0.90645 (14)	0.92499 (8)	0.5823 (2)	0.0331 (5)
N2	1.04787 (14)	0.97433 (9)	0.7826 (2)	0.0413 (5)
N3	0.85035 (14)	0.97568 (8)	0.8454 (2)	0.0328 (5)
N4	0.64605 (15)	0.97966 (9)	0.8776 (2)	0.0449 (6)
N5	0.70324 (13)	0.92814 (7)	0.6349 (2)	0.0306 (4)
O1	0.24577 (13)	0.95410 (7)	0.5729 (2)	0.0463 (5)
O2	0.45015 (13)	0.91551 (8)	0.5499 (2)	0.0506 (5)
O3	0.38962 (15)	0.93469 (8)	0.8365 (2)	0.0519 (5)
C8	0.73449 (16)	0.96182 (9)	0.7882 (2)	0.0313 (5)
C9	0.93250 (16)	0.95848 (9)	0.7378 (2)	0.0307 (5)
C10	0.79160 (16)	0.91143 (8)	0.5351 (2)	0.0295 (5)
C11	0.75537 (17)	0.87572 (10)	0.3686 (3)	0.0347 (5)
C12	0.8406 (2)	0.83807 (18)	0.3023 (4)	0.0817 (13)
C13	0.8094 (3)	0.8038 (2)	0.1478 (5)	0.1184 (18)
C14	0.6952 (3)	0.80698 (17)	0.0582 (4)	0.0729 (10)
C15	0.6098 (2)	0.84433 (17)	0.1229 (3)	0.0669 (9)
C16	0.6392 (2)	0.87874 (14)	0.2786 (3)	0.0541 (8)
C1	0.1803 (4)	0.63794 (13)	0.6294 (4)	0.0804 (13)
C2	0.2180 (3)	0.70767 (11)	0.6442 (3)	0.0510 (8)
C3	0.1408 (2)	0.75664 (11)	0.5771 (3)	0.0518 (8)
C4	0.17777 (18)	0.82075 (10)	0.5852 (3)	0.0407 (6)
C5	0.29530 (17)	0.83591 (9)	0.6579 (2)	0.0318 (5)
C6	0.3336 (3)	0.72421 (12)	0.7230 (3)	0.0560 (8)
C7	0.3737 (2)	0.78743 (11)	0.7282 (3)	0.0478 (7)
H2N4	0.66290	1.00070	0.97500	0.0540*
H1N4	0.57120	0.97030	0.83880	0.0540*
H2N2	1.06960	0.99530	0.87890	0.0500*
H1N2	1.10170	0.96380	0.71550	0.0500*
H1N5	0.62810	0.91760	0.60200	0.0370*

H12	0.91980	0.83550	0.36160	0.0980*
H13	0.86800	0.77810	0.10440	0.1420*
H14	0.67540	0.78390	-0.04630	0.0870*
H15	0.53090	0.84680	0.06220	0.0800*
H16	0.58000	0.90400	0.32220	0.0650*
H1A	0.21910	0.61750	0.53820	0.1200*
H1B	0.09300	0.63520	0.60040	0.1200*
H1C	0.20480	0.61660	0.74020	0.1200*
H3	0.06200	0.74650	0.52500	0.0620*
H4	0.12350	0.85320	0.54190	0.0490*
H6	0.38570	0.69210	0.77390	0.0670*
H7	0.45300	0.79740	0.77850	0.0570*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0234 (2)	0.0389 (3)	0.0409 (3)	-0.0040 (2)	0.0079 (2)	-0.0090 (2)
N1	0.0236 (7)	0.0420 (9)	0.0334 (8)	0.0026 (6)	0.0021 (6)	-0.0055 (6)
N2	0.0245 (8)	0.0586 (11)	0.0406 (9)	-0.0045 (7)	0.0039 (7)	-0.0133 (8)
N3	0.0253 (7)	0.0397 (9)	0.0335 (8)	-0.0046 (6)	0.0041 (6)	-0.0066 (6)
N4	0.0271 (8)	0.0616 (12)	0.0476 (10)	-0.0097 (7)	0.0107 (7)	-0.0249 (8)
N5	0.0222 (7)	0.0370 (8)	0.0325 (8)	-0.0047 (6)	0.0035 (6)	-0.0067 (6)
O1	0.0344 (8)	0.0381 (8)	0.0674 (10)	0.0022 (6)	0.0108 (7)	0.0063 (7)
O2	0.0286 (7)	0.0702 (11)	0.0558 (10)	-0.0100 (7)	0.0157 (7)	-0.0144 (8)
O3	0.0491 (9)	0.0605 (10)	0.0462 (9)	-0.0117 (8)	0.0070 (7)	-0.0225 (8)
C8	0.0267 (9)	0.0337 (9)	0.0341 (9)	-0.0044 (7)	0.0062 (7)	-0.0047 (7)
C9	0.0248 (8)	0.0346 (9)	0.0321 (9)	0.0003 (7)	0.0013 (7)	-0.0009 (7)
C10	0.0254 (8)	0.0310 (8)	0.0316 (9)	0.0018 (6)	0.0018 (7)	-0.0023 (7)
C11	0.0289 (9)	0.0420 (10)	0.0331 (9)	0.0006 (8)	0.0032 (7)	-0.0071 (8)
C12	0.0373 (13)	0.125 (3)	0.078 (2)	0.0236 (15)	-0.0105 (13)	-0.062 (2)
C13	0.0559 (18)	0.187 (4)	0.107 (3)	0.037 (2)	-0.0091 (17)	-0.106 (3)
C14	0.0574 (16)	0.104 (2)	0.0551 (16)	0.0007 (15)	-0.0010 (12)	-0.0444 (16)
C15	0.0394 (13)	0.115 (2)	0.0445 (13)	-0.0081 (14)	-0.0015 (10)	-0.0290 (15)
C16	0.0315 (11)	0.0896 (19)	0.0411 (12)	0.0025 (11)	0.0040 (9)	-0.0221 (12)
C1	0.127 (3)	0.0380 (13)	0.082 (2)	-0.0115 (15)	0.036 (2)	-0.0056 (13)
C2	0.0741 (17)	0.0371 (11)	0.0458 (12)	-0.0021 (11)	0.0234 (12)	-0.0037 (9)
C3	0.0452 (12)	0.0456 (12)	0.0647 (15)	-0.0135 (10)	0.0078 (11)	-0.0042 (11)
C4	0.0290 (9)	0.0396 (11)	0.0525 (12)	-0.0024 (8)	0.0014 (8)	0.0017 (9)
C5	0.0291 (9)	0.0363 (9)	0.0302 (9)	0.0009 (7)	0.0046 (7)	-0.0066 (7)
C6	0.0739 (17)	0.0424 (12)	0.0526 (14)	0.0203 (12)	0.0120 (12)	0.0052 (10)
C7	0.0408 (12)	0.0542 (13)	0.0454 (12)	0.0129 (10)	-0.0057 (9)	-0.0053 (10)

Geometric parameters (Å, °)

S1—O1	1.4437 (15)	C14—C15	1.359 (4)
S1—O2	1.4560 (15)	C15—C16	1.386 (4)
S1—O3	1.4588 (16)	C12—H12	0.9300
S1—C5	1.7651 (19)	C13—H13	0.9300

N1—C10	1.299 (2)	C14—H14	0.9300
N1—C9	1.371 (2)	C15—H15	0.9300
N2—C9	1.313 (2)	C16—H16	0.9300
N3—C8	1.324 (2)	C1—C2	1.504 (4)
N3—C9	1.345 (2)	C2—C3	1.379 (3)
N4—C8	1.312 (2)	C2—C6	1.378 (4)
N5—C10	1.355 (2)	C3—C4	1.389 (3)
N5—C8	1.366 (2)	C4—C5	1.376 (3)
N2—H2N2	0.8600	C5—C7	1.386 (3)
N2—H1N2	0.8600	C6—C7	1.382 (3)
N4—H2N4	0.8600	C1—H1A	0.9600
N4—H1N4	0.8600	C1—H1B	0.9600
N5—H1N5	0.8600	C1—H1C	0.9600
C10—C11	1.478 (3)	C3—H3	0.9300
C11—C12	1.367 (4)	C4—H4	0.9300
C11—C16	1.372 (3)	C6—H6	0.9300
C12—C13	1.380 (5)	C7—H7	0.9300
C13—C14	1.352 (5)		
O1—S1—O2	112.79 (9)	C11—C12—H12	120.00
O1—S1—O3	113.29 (9)	C13—C12—H12	120.00
O1—S1—C5	106.25 (9)	C12—C13—H13	119.00
O2—S1—O3	110.72 (9)	C14—C13—H13	119.00
O2—S1—C5	106.19 (9)	C15—C14—H14	120.00
O3—S1—C5	107.07 (9)	C13—C14—H14	120.00
C9—N1—C10	115.81 (15)	C14—C15—H15	120.00
C8—N3—C9	115.88 (15)	C16—C15—H15	120.00
C8—N5—C10	119.43 (15)	C15—C16—H16	120.00
C9—N2—H1N2	120.00	C11—C16—H16	120.00
C9—N2—H2N2	120.00	C1—C2—C3	121.9 (3)
H2N2—N2—H1N2	120.00	C1—C2—C6	120.1 (3)
C8—N4—H1N4	120.00	C3—C2—C6	117.9 (2)
H2N4—N4—H1N4	120.00	C2—C3—C4	121.7 (2)
C8—N4—H2N4	120.00	C3—C4—C5	119.42 (19)
C10—N5—H1N5	120.00	S1—C5—C4	120.19 (15)
C8—N5—H1N5	120.00	S1—C5—C7	120.05 (15)
N3—C8—N4	121.04 (16)	C4—C5—C7	119.71 (18)
N4—C8—N5	117.84 (16)	C2—C6—C7	121.5 (2)
N3—C8—N5	121.13 (16)	C5—C7—C6	119.7 (2)
N1—C9—N2	115.97 (16)	C2—C1—H1A	110.00
N1—C9—N3	125.41 (16)	C2—C1—H1B	109.00
N2—C9—N3	118.62 (15)	C2—C1—H1C	109.00
N1—C10—N5	122.18 (15)	H1A—C1—H1B	109.00
N5—C10—C11	118.46 (16)	H1A—C1—H1C	109.00
N1—C10—C11	119.35 (16)	H1B—C1—H1C	109.00
C12—C11—C16	118.8 (2)	C2—C3—H3	119.00
C10—C11—C12	118.80 (19)	C4—C3—H3	119.00
C10—C11—C16	122.43 (19)	C3—C4—H4	120.00

C11—C12—C13	120.2 (2)	C5—C4—H4	120.00
C12—C13—C14	121.2 (3)	C2—C6—H6	119.00
C13—C14—C15	119.1 (3)	C7—C6—H6	119.00
C14—C15—C16	120.6 (2)	C5—C7—H7	120.00
C11—C16—C15	120.2 (2)	C6—C7—H7	120.00
O1—S1—C5—C4	2.32 (18)	N1—C10—C11—C16	-156.7 (2)
O2—S1—C5—C4	-118.00 (16)	N5—C10—C11—C12	-155.5 (2)
O3—S1—C5—C4	123.67 (16)	C16—C11—C12—C13	-0.1 (4)
O1—S1—C5—C7	179.78 (16)	C10—C11—C16—C15	180.0 (2)
O2—S1—C5—C7	59.47 (17)	C10—C11—C12—C13	179.6 (3)
O3—S1—C5—C7	-58.87 (18)	C12—C11—C16—C15	-0.3 (4)
C10—N1—C9—N3	2.6 (3)	C11—C12—C13—C14	0.6 (6)
C10—N1—C9—N2	-177.59 (17)	C12—C13—C14—C15	-0.5 (6)
C9—N1—C10—N5	-1.3 (2)	C13—C14—C15—C16	0.0 (5)
C9—N1—C10—C11	179.67 (16)	C14—C15—C16—C11	0.4 (4)
C8—N3—C9—N2	176.08 (17)	C1—C2—C6—C7	175.7 (2)
C8—N3—C9—N1	-4.1 (3)	C1—C2—C3—C4	-177.5 (2)
C9—N3—C8—N5	4.3 (3)	C6—C2—C3—C4	1.0 (4)
C9—N3—C8—N4	-176.10 (17)	C3—C2—C6—C7	-2.9 (4)
C10—N5—C8—N4	177.08 (16)	C2—C3—C4—C5	1.7 (3)
C8—N5—C10—C11	-179.23 (16)	C3—C4—C5—C7	-2.5 (3)
C10—N5—C8—N3	-3.3 (3)	C3—C4—C5—S1	174.99 (16)
C8—N5—C10—N1	1.7 (3)	S1—C5—C7—C6	-176.79 (17)
N5—C10—C11—C16	24.2 (3)	C4—C5—C7—C6	0.7 (3)
N1—C10—C11—C12	23.6 (3)	C2—C6—C7—C5	2.1 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 and Cg3 are the centroids of the N1/C9/N3/C8/N5/C10 and C2—C5/C6/C7 rings, respectively.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N4—H2N4 \cdots O3 ⁱ	0.86	2.10	2.877 (2)	150
N4—H1N4 \cdots O3	0.86	2.13	2.950 (2)	160
N2—H2N2 \cdots N3 ⁱⁱ	0.86	2.25	3.089 (2)	164
N2—H1N2 \cdots O1 ⁱⁱⁱ	0.86	2.05	2.895 (2)	169
N5—H1N5 \cdots O2	0.86	1.95	2.789 (2)	165
C16—H16 \cdots O2	0.93	2.40	3.210 (3)	146
S1—O1 \cdots Cg1 ^{iv}		2.93 (1)	4.1695 (8)	142 (1)
Cg3—Cg3			3.9192 (13)	

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