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The imide tautomer of sulfasalazine

Alexander J. Blake,[a] Xiang Lin,[a] Martin Schröder,[a] Claire Wilson[a] and Rong-Xin Yuan[a,b]*

[a]School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England, and [b]Department of Chemistry, Changshu College, Changshu 215500, People's Republic of China
Correspondence e-mail: a.j.blake@nottingham.ac.uk

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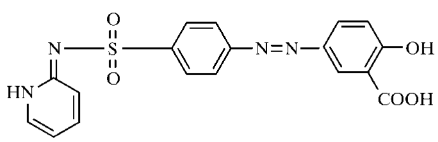
The title compound, 5-{4-[(2-pyridylideneamino)sulfonyl]-phenyldiazenyl}salicylic acid, $C_{18}H_{14}N_4O_5S$, crystallizes as the imide tautomer in the monoclinic space group $P2_1/c$. In addition to an intramolecular O—H···O hydrogen bond, intermolecular O—H···O interactions link adjacent molecules into helices, which are connected by pairwise N—H···N interactions into two-dimensional hydrogen-bonded layers. Both the molecular conformation and the packing differ from those seen in the triclinic amide form [Filip *et al.* (2001). *Acta Cryst.* C**57**, 435–436].

Comment

Crystal engineering of pharmaceutical solids represents a fertile emerging area of research (Walsh *et al.*, 2003; Oswald *et al.*, 2002). The impetus for discovery of diverse crystal forms of drugs stems from the critical need to balance stability, bioavailability and other performance characteristics, and also to provide valuable intellectual property protection. Sulfasalazine (synonyms: salazopyridine and salazosulfapyridine; abbreviated herein as SSZ) is a conjugate of 5-aminosalicylic acid and sulfapyridine possessing antimicrobial properties, and is used as a drug for treating inflammatory bowel disorders (Svartz, 1942; Das & Rubin, 1976) and rheumatoid arthritis (Pullar, 1989). It is also a known inhibitor of α-, μ- and π-class glutathione S-transferases, with concentrations of 28 µ*M* or less required to inhibit 50% of enzymatic activity (Ahmad *et al.*, 1992). We are investigating the interaction of this drug with metal ions, with a view to obtaining complexes with useful medicinal properties. In this paper, we report the crystal structure of the monoclinic form, (I), of SSZ and compare the hydrogen-bonding interactions observed in the two forms of SSZ, the structure of the triclinic amide form having been reported by Filip *et al.* (2001).

In the title phase, (I) (Fig. 1), both the C5—N2 [1.348 (4) Å] and the S1—N2 [1.586 (3) Å] bond lengths are much shorter than those observed in the triclinic amide form [1.425 (2) and 1.6539 (16) Å, respectively], indicating conjugation between the pyridine ring and the side chain. These bond lengths and the orange colour of the crystals of (I) identify the imide tautomeric form observed previously as a dimethylformamide–water mixed solvate by van der Sluis & Spek (1990) [C—N = 1.348 (7) and N—S = 1.600 (4) Å], rather than the triclinic amide phase reported by Filip *et al.* (2001). This conclusion was supported by competitive refinement of the occupancies of possible H-atom positions on N1 and N2, which clearly locates the H atom on the former. Other molecular geometry parameters are comparable with those found for the amide form.



(I)

The molecular conformation of (I) (Fig. 1) is different from that of the triclinic form. Although the aromatic rings linked by the –N═N– bridge are essentially coplanar in both forms, the relative orientations of the (2-pyridylamino)sulfonyl group differ markedly. In the triclinic form, the N—S—C—C torsion angles lie near 87°, while in the title phase, these torsions are about 44° (Table 1). In both forms, the bulk of the molecule (including the S atom, the phenyl ring, the azo bridge and the salicylic acid segment) is almost planar, as a result of extensive electron delocalization, with an intramolecular O3—H3O···O4 hydrogen bond (Table 2) directing the orientation of the carboxylic acid group; atom H3O lies within 0.075 (5) Å of the least-squares mean plane through the other atoms (O4/C12/C13/C14/O3) of the six-membered ring. The overall conformation is similar to that of one of the two independent molecules in the asymmetric unit of the solvate (Van der Sluis & Spek, 1990).

Analysis of the crystal packing of (I) shows the presence of intermolecular O—H···O and N—H···N hydrogen bonds in the structure (Table 2). The H atom of a carboxyl group forms an O5—H5O···O2[ii] interaction with an O atom of a sulfonyl group [symmetry code: (ii) $1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$]. These hydrogen bonds connect adjacent molecules into helices running along the *b* axis, with a pitch [6.0911 (11) Å] equal to

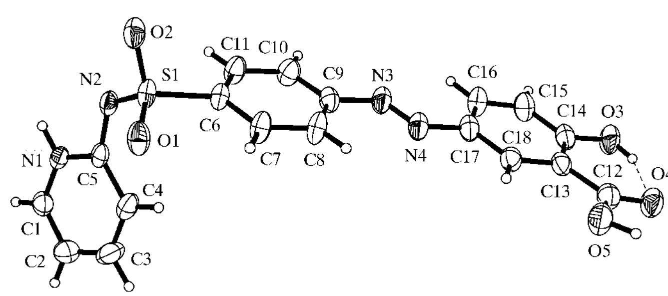


Figure 1
A view of (I) showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii. The dashed line identifies the intramolecular O3—H3O···O4 hydrogen bond.

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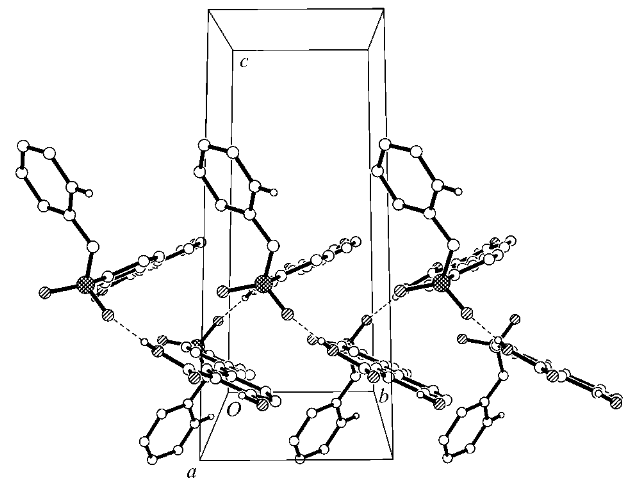

Figure 2
A side view of a helix formed in (I) *via* O5—H5O···O2 hydrogen bonds. The helix runs parallel to the *b* axis. Atoms are shown as plain for C, dotted for N, lined for O and cross-hatched for S.

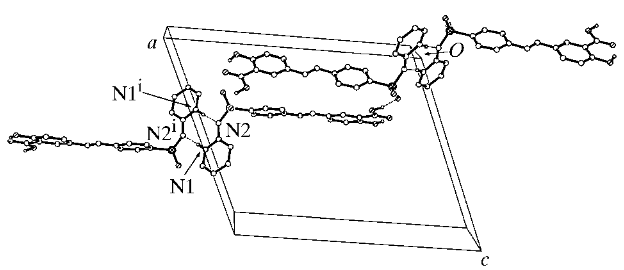

Figure 3
A view of representative parts of three helices in (I), showing the intermolecular N1—H1N···N2 interactions which link them. Atom shading is as in Fig. 2 [symmetry code: (i) $2 - x, 1 - y, 1 - z$].

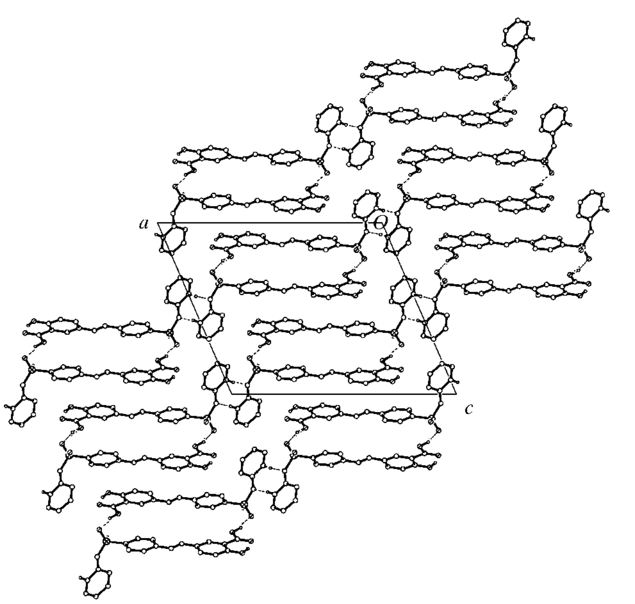

Figure 4
An overall view of the crystal packing in (I) along the *b* axis, showing a side view of the two-dimensional layers. Atom shading is as in Fig. 2.

its length (Fig. 2). Meanwhile, N1—H1N···N2^{i} interactions (Fig. 3) between pyridylamine moieties generate $R_2^2(8)$ rings (Etter, 1990; Etter *et al.*, 1990) and link the helices to form two-dimensional hydrogen-bonded sheets (Fig. 4) [symmetry code: (i) $2 - x, 2 - y, 1 - z$]. This packing contrasts with that of the amide tautomer (Filip *et al.*, 2001), which is characterized by a repeating unit consisting of a centrosymmetric dimer assembled through N—H···O hydrogen bonds between the pyridylamine and carboxylic acid moieties, and which exhibits aromatic π–π stacking between adjacent molecules.

We note that reaction under the same conditions but in the absence of the Zn^{II} ions, or under ambient conditions, did not result in the formation of (I), suggesting that the presence of these ions is important in obtaining the structure. As we have also obtained the same crystals in the presence of $Cu(ClO_4)_2$, $Zn(ClO_4)_2$ and $Cd(ClO_4)_2$, and the amide form was isolated from a reaction between SSZ and $CuCl_2$ (Filip *et al.*, 2001), it seems that the ions present play a structure-directing role in the system, although the origin of this effect remains unclear.

Experimental

A mixture of $Zn(ClO_4)_2\cdot 6H_2O$ (0.074 g, 0.2 mmol), SSZ (0.080 g, 0.2 mmol), ethanol (8 ml) and distilled water (2 ml) was sealed in a Teflon-lined stainless steel autoclave and heated at 393 K for 48 h under autogenous pressure and then cooled to room temperature. Orange lozenge-like crystals of (I) were obtained. Analysis calculated: C 54.3, H 3.5, N 14.1%; found: C 54.3, H 3.6, N 13.8%. Spectroscopic analysis, IR (KBr, ν, cm^{-1}): 3125 (*s*), 3059 (*s*), 3026 (*s*), 1677 (*m*), 1635 (*m*), 1617 (*m*), 1586 (*m*), 1393 (*m*), 1358 (*m*), 1270 (*m*), 1269 (*m*), 1199 (*m*), 1172 (*m*), 1127 (*m*), 1085 (*m*), 800 (*m*), 790 (*m*), 768 (*m*), 613 (*m*), 574 (*m*).

Crystal data

$C_{18}H_{14}N_4O_5S$
$M_r = 398.39$
Monoclinic, $P2_1/c$
$a = 19.308$ (3) Å
$b = 6.0911$ (11) Å
$c = 16.109$ (3) Å
$\beta = 113.405$ (3)°
$V = 1738.7$ (5) Å^3
$Z = 4$
$D_x = 1.522$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2040 reflections
$\theta = 2.5$–27.4°
$\mu = 0.23$ mm^{-1}
$T = 150$ (2) K
Column, orange
0.49 × 0.14 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.711$, $T_{max} = 1.000$
10 720 measured reflections
3950 independent reflections
2603 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.4°$
$h = -25 \rightarrow 24$
$k = -7 \rightarrow 4$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.195$
$S = 1.04$
3950 reflections
262 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.109P)^2 + 1.095P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.431 (3)	C12—O4	1.235 (4)
S1—O2	1.439 (3)	C12—O5	1.316 (5)
S1—N2	1.586 (3)	C14—O3	1.358 (4)
C5—N2	1.348 (4)	N3—N4	1.242 (4)
O1—S1—O2	116.79 (15)	N2—S1—C6	107.73 (14)
O1—S1—N2	113.77 (15)	C1—N1—C5	124.3 (3)
O2—S1—N2	104.12 (14)	C5—N2—S1	120.2 (2)
O1—S1—C6	106.96 (15)	N4—N3—C9	113.5 (3)
O2—S1—C6	107.00 (15)	N3—N4—C17	114.6 (3)
N2—S1—C6—C11	43.9 (3)	C10—C9—N3—N4	−179.6 (3)
N2—S1—C6—C7	−137.3 (3)	C8—C9—N3—N4	−2.1 (5)
O4—C12—C13—C18	177.8 (3)	C9—N3—N4—C17	178.6 (3)
C12—C13—C14—O3	1.7 (5)	C18—C17—N4—N3	−176.8 (3)
N1—C5—N2—S1	164.7 (2)	C16—C17—N4—N3	3.2 (5)
C4—C5—N2—S1	−15.8 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O4	0.91 (3)	1.75 (3)	2.612 (4)	157 (4)
N1—H1N···N2^{i}	0.90 (3)	1.98 (3)	2.878 (4)	173 (3)
O5—H5O···O2^{ii}	0.91 (3)	1.77 (3)	2.636 (4)	159 (4)

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

The highest difference electron-density peak (1.02 e Å^{-3}) lies 0.85 Å from atom S1. H atoms of the O—H and N—H groups were located from difference Fourier syntheses and thereafter refined with distance restraints of 0.90 (1) Å. C-bound H atoms were included at geometrically calculated positions and constrained to ride at distances of 0.93 Å from their parent atoms. For all H atoms, $U_{iso}(H) = 1.2U_{eq}(C)$. The location of an H atom on N1 rather than on N2 was established by competitive refinement of the occupancies of the two possible H-atom positions.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *enCIFer* (CCDC, 2003) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1702). Services for accessing these data are described at the back of the journal.

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supporting information

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Computing details

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$F(000)$ = 824
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Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2040 reflections
θ = 2.5–27.4°
μ = 0.23 mm^{-1}
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Column, orange
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θ_{max} = 27.4°, θ_{min} = 2.5°
$h = -25 \rightarrow 24$
$k = -7 \rightarrow 4$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.195
S = 1.04
3950 reflections
262 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: see text
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.109P)^2 + 1.095P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.02 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Special details

Geometry. Least-squares plane (*x*,*y*,*z* in crystal coordinates) through heavy atoms of the six-membered hydrogen bonded ring, and deviations from this plane (* indicates atom used to define plane)
0.1703 (0.0311) *x* − 2.5541 (0.0071) *y* + 13.3640 (0.0147) *z* = 3.7006 (0.0076)
* 0.0134 (0.0017) O4 * −0.0198 (0.0024) C12 * 0.0119 (0.0022) C13 * 0.0005 (0.0023) C14 * −0.0060 (0.0016) O3 − 0.0753 (0.0499) H3O
Rms deviation of fitted atoms = 0.0122

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
S1	0.84229 (4)	0.31088 (14)	0.35744 (6)	0.0306 (3)
C1	1.03415 (19)	0.1557 (6)	0.6604 (2)	0.0350 (8)
H1	1.0831	0.1870	0.7009	0.042*
C2	0.9951 (2)	−0.0084 (7)	0.6784 (3)	0.0451 (9)
H2	1.0171	−0.0945	0.7299	0.054*
C3	0.9215 (2)	−0.0451 (6)	0.6182 (3)	0.0463 (10)
H3	0.8930	−0.1528	0.6311	0.056*
C4	0.89000 (19)	0.0738 (6)	0.5405 (3)	0.0371 (8)
H4	0.8406	0.0462	0.5007	0.045*
C5	0.93222 (17)	0.2388 (5)	0.5205 (2)	0.0272 (7)
C6	0.76057 (16)	0.4047 (6)	0.3706 (2)	0.0290 (7)
C7	0.69737 (18)	0.2689 (6)	0.3419 (2)	0.0363 (8)
H7	0.6990	0.1302	0.3186	0.044*
C8	0.63203 (18)	0.3434 (6)	0.3486 (2)	0.0396 (9)
H8	0.5891	0.2557	0.3289	0.048*
C9	0.63090 (17)	0.5500 (6)	0.3848 (2)	0.0316 (7)
C10	0.6941 (2)	0.6799 (6)	0.4137 (3)	0.0386 (8)
H10	0.6929	0.8173	0.4383	0.046*
C11	0.75952 (19)	0.6089 (6)	0.4069 (2)	0.0378 (8)
H11B	0.8022	0.6976	0.4264	0.045*
C12	0.25593 (19)	0.3793 (7)	0.3446 (2)	0.0399 (9)
C13	0.32173 (18)	0.5223 (6)	0.3735 (2)	0.0334 (8)
C14	0.32089 (18)	0.7265 (6)	0.4117 (2)	0.0355 (8)
C15	0.38208 (19)	0.8644 (7)	0.4354 (3)	0.0421 (9)
H15	0.3808	1.0008	0.4607	0.051*
C16	0.44526 (19)	0.8016 (7)	0.4220 (2)	0.0410 (9)
H16	0.4862	0.8963	0.4372	0.049*
C17	0.44786 (17)	0.5955 (6)	0.3854 (2)	0.0349 (8)
C18	0.38714 (17)	0.4589 (6)	0.3610 (2)	0.0346 (8)
H18	0.3888	0.3226	0.3359	0.042*
N1	1.00235 (14)	0.2740 (5)	0.58389 (18)	0.0287 (6)
H1N	1.0288 (17)	0.379 (4)	0.570 (2)	0.034*
N2	0.91305 (13)	0.3695 (5)	0.44721 (18)	0.0292 (6)
N3	0.56743 (15)	0.6376 (5)	0.39784 (19)	0.0366 (7)
N4	0.51169 (15)	0.5139 (5)	0.37114 (19)	0.0363 (7)
O1	0.83263 (12)	0.0804 (4)	0.33919 (17)	0.0395 (6)
O2	0.85146 (12)	0.4462 (4)	0.28928 (15)	0.0391 (6)

O3	0.25995 (14)	0.7990 (5)	0.42586 (18)	0.0444 (7)
H3O	0.2268 (19)	0.688 (5)	0.400 (3)	0.053*
O4	0.19811 (13)	0.4243 (5)	0.35643 (17)	0.0457 (7)
O5	0.26400 (15)	0.1993 (5)	0.3041 (2)	0.0495 (7)
H5O	0.2179 (13)	0.134 (7)	0.278 (3)	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0191 (4)	0.0406 (5)	0.0327 (4)	−0.0020 (3)	0.0111 (3)	−0.0096 (4)
C1	0.0311 (17)	0.041 (2)	0.0356 (18)	0.0057 (14)	0.0157 (15)	0.0025 (16)
C2	0.050 (2)	0.045 (2)	0.047 (2)	0.0059 (18)	0.0257 (19)	0.0130 (18)
C3	0.054 (2)	0.039 (2)	0.057 (2)	−0.0074 (18)	0.034 (2)	0.0069 (19)
C4	0.0295 (17)	0.038 (2)	0.048 (2)	−0.0086 (15)	0.0196 (16)	−0.0072 (17)
C5	0.0237 (15)	0.0279 (17)	0.0348 (18)	0.0001 (12)	0.0167 (13)	−0.0080 (14)
C6	0.0204 (14)	0.0400 (19)	0.0275 (16)	−0.0015 (13)	0.0104 (12)	−0.0056 (14)
C7	0.0245 (16)	0.047 (2)	0.0384 (19)	−0.0070 (14)	0.0137 (14)	−0.0174 (16)
C8	0.0209 (15)	0.056 (2)	0.042 (2)	−0.0078 (15)	0.0125 (14)	−0.0132 (18)
C9	0.0266 (16)	0.040 (2)	0.0300 (17)	0.0060 (14)	0.0135 (13)	−0.0011 (15)
C10	0.0368 (19)	0.034 (2)	0.050 (2)	−0.0018 (15)	0.0231 (17)	−0.0093 (17)
C11	0.0297 (17)	0.036 (2)	0.051 (2)	−0.0074 (15)	0.0195 (16)	−0.0114 (17)
C12	0.0327 (18)	0.051 (2)	0.0373 (19)	0.0043 (16)	0.0150 (15)	0.0075 (17)
C13	0.0256 (16)	0.047 (2)	0.0268 (16)	0.0056 (14)	0.0097 (13)	0.0080 (15)
C14	0.0260 (16)	0.052 (2)	0.0287 (17)	0.0075 (15)	0.0109 (14)	0.0045 (16)
C15	0.0307 (18)	0.048 (2)	0.047 (2)	0.0045 (16)	0.0148 (16)	−0.0072 (18)
C16	0.0249 (16)	0.052 (2)	0.045 (2)	−0.0018 (15)	0.0122 (15)	−0.0079 (18)
C17	0.0246 (16)	0.049 (2)	0.0306 (17)	0.0040 (15)	0.0105 (13)	0.0004 (16)
C18	0.0275 (16)	0.043 (2)	0.0307 (18)	0.0008 (14)	0.0086 (14)	0.0032 (15)
N1	0.0244 (13)	0.0311 (15)	0.0348 (15)	−0.0022 (11)	0.0162 (12)	−0.0025 (12)
N2	0.0179 (12)	0.0335 (15)	0.0352 (15)	−0.0028 (11)	0.0095 (11)	−0.0021 (12)
N3	0.0253 (14)	0.0487 (19)	0.0382 (16)	0.0022 (13)	0.0151 (12)	−0.0008 (14)
N4	0.0248 (14)	0.0508 (19)	0.0336 (15)	0.0017 (13)	0.0120 (12)	−0.0017 (14)
O1	0.0281 (12)	0.0407 (15)	0.0488 (15)	−0.0011 (10)	0.0143 (11)	−0.0175 (12)
O2	0.0240 (11)	0.0605 (17)	0.0311 (12)	0.0035 (11)	0.0091 (10)	−0.0012 (12)
O3	0.0293 (13)	0.0609 (19)	0.0488 (16)	0.0042 (12)	0.0217 (12)	−0.0028 (13)
O4	0.0324 (13)	0.0668 (19)	0.0420 (14)	−0.0011 (12)	0.0190 (11)	0.0038 (13)
O5	0.0338 (14)	0.0503 (17)	0.0626 (18)	−0.0025 (12)	0.0173 (13)	−0.0058 (14)

Geometric parameters (Å, º)

S1—O1	1.431 (3)	C9—N3	1.427 (4)
S1—O2	1.439 (3)	C10—C11	1.380 (5)
S1—N2	1.586 (3)	C10—H10	0.9300
S1—C6	1.768 (3)	C11—H11B	0.9300
C1—N1	1.346 (4)	C12—O4	1.235 (4)
C1—C2	1.351 (5)	C12—O5	1.316 (5)
C1—H1	0.9300	C12—C13	1.456 (5)
C2—C3	1.384 (6)	C13—C14	1.390 (5)

C2—H2	0.9300	C13—C18	1.410 (5)
C3—C4	1.363 (5)	C14—O3	1.358 (4)
C3—H3	0.9300	C14—C15	1.374 (5)
C4—C5	1.410 (5)	C15—C16	1.376 (5)
C4—H4	0.9300	C15—H15	0.9300
C5—N2	1.348 (4)	C16—C17	1.396 (5)
C5—N1	1.351 (4)	C16—H16	0.9300
C6—C11	1.378 (5)	C17—C18	1.362 (5)
C6—C7	1.392 (5)	C17—N4	1.430 (4)
C7—C8	1.385 (4)	C18—H18	0.9300
C7—H7	0.9300	N1—H1N	0.90 (3)
C8—C9	1.391 (5)	N3—N4	1.242 (4)
C8—H8	0.9300	O3—H3O	0.91 (3)
C9—C10	1.372 (5)	O5—H5O	0.91 (3)

O1—S1—O2	116.79 (15)	C9—C10—H10	119.6
O1—S1—N2	113.77 (15)	C11—C10—H10	119.6
O2—S1—N2	104.12 (14)	C6—C11—C10	119.0 (3)
O1—S1—C6	106.96 (15)	C6—C11—H11B	120.5
O2—S1—C6	107.00 (15)	C10—C11—H11B	120.5
N2—S1—C6	107.73 (14)	O4—C12—O5	123.6 (4)
N1—C1—C2	120.1 (3)	O4—C12—C13	123.0 (4)
N1—C1—H1	119.9	O5—C12—C13	113.4 (3)
C2—C1—H1	119.9	C14—C13—C18	118.5 (3)
C1—C2—C3	118.4 (4)	C14—C13—C12	121.0 (3)
C1—C2—H2	120.8	C18—C13—C12	120.5 (3)
C3—C2—H2	120.8	O3—C14—C15	117.4 (3)
C4—C3—C2	121.1 (3)	O3—C14—C13	121.9 (3)
C4—C3—H3	119.5	C15—C14—C13	120.7 (3)
C2—C3—H3	119.5	C14—C15—C16	120.3 (4)
C3—C4—C5	120.1 (3)	C14—C15—H15	119.9
C3—C4—H4	119.9	C16—C15—H15	119.9
C5—C4—H4	119.9	C15—C16—C17	120.0 (3)
N2—C5—N1	114.4 (3)	C15—C16—H16	120.0
N2—C5—C4	129.7 (3)	C17—C16—H16	120.0
N1—C5—C4	115.9 (3)	C18—C17—C16	120.0 (3)
C11—C6—C7	121.2 (3)	C18—C17—N4	116.1 (3)
C11—C6—S1	120.4 (2)	C16—C17—N4	123.9 (3)
C7—C6—S1	118.3 (3)	C17—C18—C13	120.6 (3)
C8—C7—C6	119.0 (3)	C17—C18—H18	119.7
C8—C7—H7	120.5	C13—C18—H18	119.7
C6—C7—H7	120.5	C1—N1—C5	124.3 (3)
C7—C8—C9	119.7 (3)	C1—N1—H1N	121 (2)
C7—C8—H8	120.1	C5—N1—H1N	115 (2)
C9—C8—H8	120.1	C5—N2—S1	120.2 (2)
C10—C9—C8	120.3 (3)	N4—N3—C9	113.5 (3)
C10—C9—N3	115.8 (3)	N3—N4—C17	114.6 (3)
C8—C9—N3	123.9 (3)	C14—O3—H3O	100 (3)

C9—C10—C11	120.7 (3)	C12—O5—H5O	108 (3)
N1—C1—C2—C3	−2.4 (5)	C12—C13—C14—O3	1.7 (5)
C1—C2—C3—C4	3.1 (6)	C18—C13—C14—C15	1.0 (5)
C2—C3—C4—C5	−0.6 (6)	C12—C13—C14—C15	−177.3 (3)
C3—C4—C5—N2	177.9 (3)	O3—C14—C15—C16	−179.3 (3)
C3—C4—C5—N1	−2.6 (5)	C13—C14—C15—C16	−0.3 (6)
O1—S1—C6—C11	166.6 (3)	C14—C15—C16—C17	−1.0 (6)
O2—S1—C6—C11	−67.6 (3)	C15—C16—C17—C18	1.7 (5)
N2—S1—C6—C11	43.9 (3)	C15—C16—C17—N4	−178.4 (3)
O1—S1—C6—C7	−14.6 (3)	C16—C17—C18—C13	−1.0 (5)
O2—S1—C6—C7	111.3 (3)	N4—C17—C18—C13	179.1 (3)
N2—S1—C6—C7	−137.3 (3)	C14—C13—C18—C17	−0.4 (5)
C11—C6—C7—C8	1.2 (5)	C12—C13—C18—C17	178.0 (3)
S1—C6—C7—C8	−177.6 (3)	C2—C1—N1—C5	−1.0 (5)
C6—C7—C8—C9	−0.9 (6)	N2—C5—N1—C1	−177.0 (3)
C7—C8—C9—C10	0.0 (6)	C4—C5—N1—C1	3.4 (4)
C7—C8—C9—N3	−177.4 (3)	N1—C5—N2—S1	164.7 (2)
C8—C9—C10—C11	0.5 (6)	C4—C5—N2—S1	−15.8 (5)
N3—C9—C10—C11	178.1 (3)	O1—S1—N2—C5	−36.7 (3)
C7—C6—C11—C10	−0.6 (6)	O2—S1—N2—C5	−164.9 (2)
S1—C6—C11—C10	178.1 (3)	C6—S1—N2—C5	81.7 (3)
C9—C10—C11—C6	−0.2 (6)	C10—C9—N3—N4	−179.6 (3)
O4—C12—C13—C14	−3.9 (5)	C8—C9—N3—N4	−2.1 (5)
O5—C12—C13—C14	175.4 (3)	C9—N3—N4—C17	178.6 (3)
O4—C12—C13—C18	177.8 (3)	C18—C17—N4—N3	−176.8 (3)
O5—C12—C13—C18	−2.8 (5)	C16—C17—N4—N3	3.2 (5)
C18—C13—C14—O3	180.0 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O4	0.91 (3)	1.75 (3)	2.612 (4)	157 (4)
N1—H1*N*···N2^{i}	0.90 (3)	1.98 (3)	2.878 (4)	173 (3)
O5—H5*O*···O2^{ii}	0.91 (3)	1.77 (3)	2.636 (4)	159 (4)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1/2.