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(4-Aminosulfonylphenyl)[(2-oxidonaphthalen-1-yl)-imino]azanium

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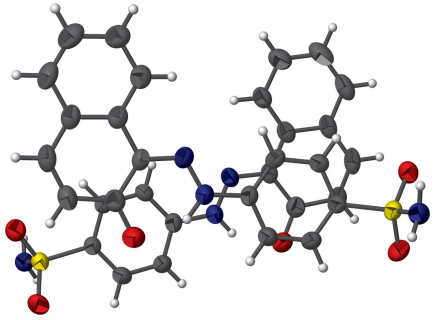
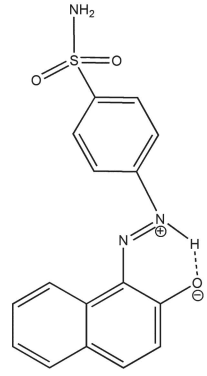
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title compound, $C_{16}H_{13}N_3O_3S$, shows that the two independent zwitterions in the asymmetric unit are approximately planar. Intramolecular N—H···O hydrogen bonds occur and the aromatic rings have a *trans* configuration with respect to the azo double bond. In the crystal, the molecules are linked *via* N—H···O hydrogen bonds and π–π stacking, forming a three-dimensional supramolecular network, the π–π stacking interactions between adjacent benzene and naphthalene rings having centroid-to-centroid distances of 3.764 (3) and 3.775 (3) Å.

3D view



Chemical scheme



Structure description

Dyes are natural or synthetic coloured chemical compounds. Usually organic in nature, they have the ability to permanently stain the material to which they are applied. Azo pigments are widely used for the colouration of coatings, plastics and printing inks, with an annual sales volume of more than one billion Euros (Biswas & Umapathy, 2000). In the literature, most azo pigments are drawn with an N=N double bond (Olivieri *et al.*, 1989). However, all commercial pigments based on β-naphthol adopt the hydrazone tautomeric form in the solid state, as proven by many X-ray structure determinations of β-naphthol pigments.

There are two independent molecules (*A* and *B*) in the asymmetric unit of the title compound (Fig. 1), each consisting of a benzene ring linked to the first nitrogen atom of the N=N chromophore and two aromatic rings of the core β-naphthol. The aromatic rings are in a *trans* configuration with respect to the azo double bond. The N1—C1 (molecule *A*) and N4—C17 (molecule *B*) bond lengths of 1.398 (3) and 1.393 (3) Å, respectively, indicate single-bond character. The N2—C7 (molecule *A*) and N5—C23 (molecule *B*) bond lengths of 1.332 (3) and 1.331 (3) Å, and the N=N bond lengths of

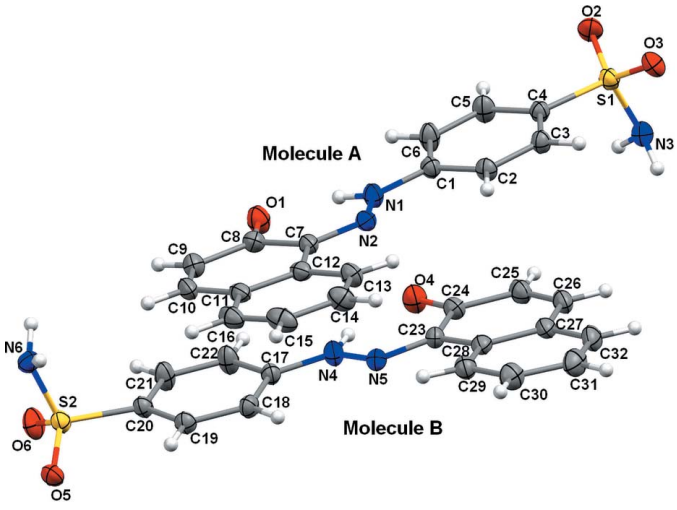


Figure 1
The asymmetric unit of the two independent molecules with 50% probability displacement ellipsoids and H atoms are drawn as small spheres of arbitrary radii.

1.313 (3) and 1.315 (3) Å in molecules *A* and *B*, respectively, are indicative of significant double-bond character.

In the crystal, the *A* and *B* molecules are linked *via* N—H···O hydrogen bonds, forming zigzag *–A–B–A–B–* chains propagating along the *b* axis (see Table 1 and Fig. 2). The chains are reinforced by π–π interactions, forming a three-dimensional network; see Fig. 3 [$Cg1\cdots Cg6^{i}$ = 3.775 (3) Å, where *Cg*1 and *Cg*6 are the centroids of rings C1–C6 and C23–C28, respectively; symmetry code: (i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$].

Synthesis and crystallization

For synthesis details, see: Jin *et al.* (2008); Lee *et al.* (2004). A mixture of 4-aminobenzenesulonamide (0.02 mol), water (40 ml) and concentrated hydrochloric acid (0.06 mol) was stirred. This solution was cooled to 273–278 K and a solution of sodium nitrite (0.02 mol) in water (10 ml) was added

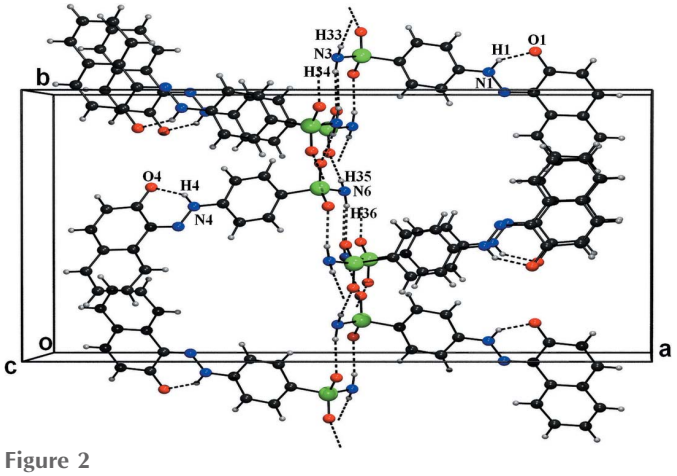


Figure 2
A view along the *b* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines and C-bound H atoms not involved in hydrogen bonding have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.88	1.75	2.520 (3)	145
N3—H33···O2^{i}	0.89	2.19	3.073 (4)	172
N3—H34···O3^{ii}	0.89	2.23	3.023 (3)	147
N4—H4···O4	0.92	1.73	2.525 (3)	142
N6—H35···O5^{iii}	0.93	2.09	2.993 (4)	162
N6—H36···O6^{iv}	0.90	2.11	3.009 (4)	179

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{13}N_3O_3S$
M_r	327.35
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	26.289 (5), 15.132 (5), 7.403 (5)
β (°)	95.179 (5)
V (Å^3)	2933 (2)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.24
Crystal size (mm)	0.09 × 0.04 × 0.02
Data collection	
Diffractometer	Enraf–Nonius FR590 CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8680, 5356, 3577
R_{int}	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.124, 1.06
No. of reflections	5356
No. of parameters	415
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.34

Computer programs: *APEX2* and *SAINT* (Bruker, 2006), *SHELXS97* (Sheldrick, 2008), *SHELXL2015* (Sheldrick, 2015), *ORTEP-3* for Windows (Farrugia, 2012) and *PLATON* (Spek, 2009).

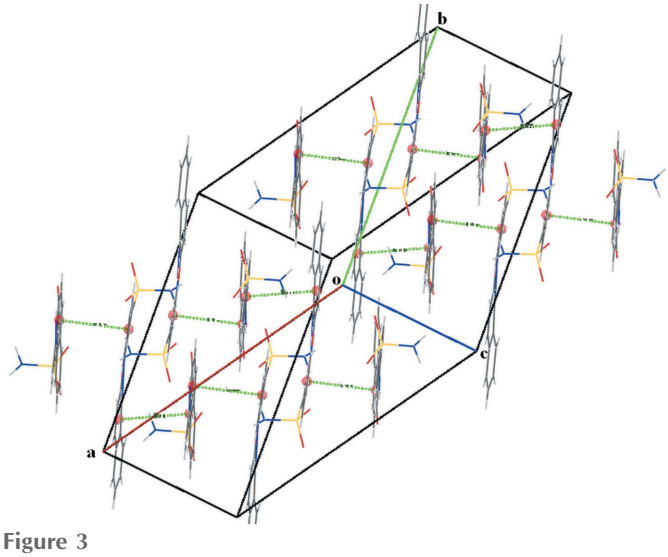


Figure 3
The packing of viewed along [010]. π–π interactions are shown as dashed lines, and C-bound H atoms not involved in hydrogen bonding have been omitted for clarity.

dropwise, while maintaining the temperature below 278 K. The resulting mixture was stirred for an additional 30 min in an ice bath and then buffered with solid sodium acetate. β-Naphthol (0.02 mol), dissolved with sodium hydroxide (0.02 mol) in water (10 ml), was cooled to 273–278 K in an ice bath and then gradually added to the above solution of 4-sulfamoylbenzenediazonium. The resulting mixture was stirred for 60 min. The crude precipitate was filtered off, washed several times with water and recrystallized from methanol. The compound was recrystallized from methanol to produce crystals of suitable quality for X-ray diffraction analysis.

IR spectroscopic data (ν, cm^{-1}): 3433.1 (O—H), 1616 (C═O), 3745 (O–H) and 1496 (Ar). UV–Vis measurements [λ (nm), log ε (l/mol cm), CH_2Cl_2]: 308.8 (0.093), 477.86 (0.203). ^{1}H NMR [500 MHz, DMSO-10 (1D 1H), σ]: 16 (*s*, 1H, NH), 740–7.85 (*m*, 10H, Ar), 2.29 (*s*, 3H, CH 3). ^{13}C NMR [500 MHz, DMSO-11(1D 13 C), σ]: 177(C═O), 115(C═N), 144(C—N), 125(C aromatic).

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160658 [doi:10.1107/S2414314616006581]

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(I)

Crystal data

$C_{16}H_{13}N_3O_3S$
M_r = 327.35
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 26.289 (5) Å
b = 15.132 (5) Å
c = 7.403 (5) Å
β = 95.179 (5)°
V = 2933 (2) Å^3
Z = 8
$F(000)$ = 1360
D_x = 1.483 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5463 reflections
θ = 2.9–25.4°
μ = 0.24 mm^{-1}
T = 293 K
Needle, colourless
0.09 × 0.04 × 0.02 mm

Data collection

Enraf–Nonius FR590 CCD diffractometer
Radiation source: fine-focus sealed tube
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images, thick slices scans
8680 measured reflections
5356 independent reflections
3577 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.4°, θ_{min} = 3.1°
h = −31→31
k = −18→15
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.124
S = 1.06
5356 reflections
415 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
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.988P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 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 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 $F^2 > 2\text{sigma}(F^2)$ 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	0.52672 (2)	0.13841 (4)	0.47978 (9)	0.0426 (2)
O1	0.81398 (8)	0.14154 (13)	0.9633 (3)	0.0613 (8)
O2	0.52403 (7)	0.22982 (12)	0.4290 (3)	0.0576 (7)
O3	0.50989 (7)	0.07261 (12)	0.3487 (2)	0.0521 (7)
N1	0.73795 (8)	0.06996 (14)	0.7901 (3)	0.0455 (8)
N2	0.76294 (8)	−0.00485 (14)	0.7818 (3)	0.0409 (7)
N3	0.49191 (8)	0.12714 (14)	0.6468 (3)	0.0459 (8)
C1	0.68829 (10)	0.08099 (17)	0.7085 (3)	0.0411 (9)
C2	0.65908 (9)	0.01275 (17)	0.6299 (3)	0.0416 (9)
C3	0.60995 (10)	0.03003 (17)	0.5570 (3)	0.0421 (9)
C4	0.59032 (9)	0.11517 (16)	0.5609 (3)	0.0393 (8)
C5	0.61962 (11)	0.18314 (18)	0.6383 (4)	0.0539 (10)
C6	0.66842 (11)	0.16604 (18)	0.7132 (4)	0.0550 (10)
C7	0.81068 (10)	−0.00709 (17)	0.8590 (3)	0.0401 (9)
C8	0.83656 (10)	0.06915 (19)	0.9463 (4)	0.0467 (10)
C9	0.88915 (11)	0.0587 (2)	1.0144 (4)	0.0538 (11)
C10	0.91382 (11)	−0.0178 (2)	0.9982 (4)	0.0540 (10)
C11	0.89000 (10)	−0.0945 (2)	0.9151 (3)	0.0464 (9)
C12	0.83819 (10)	−0.09042 (18)	0.8461 (3)	0.0430 (9)
C13	0.81554 (11)	−0.16598 (19)	0.7642 (4)	0.0504 (10)
C14	0.84370 (12)	−0.2420 (2)	0.7496 (4)	0.0591 (11)
C15	0.89420 (13)	−0.2463 (2)	0.8171 (4)	0.0640 (11)
C16	0.91724 (11)	−0.1738 (2)	0.8993 (4)	0.0573 (10)
S2	0.96326 (3)	0.11985 (4)	0.61220 (9)	0.0431 (2)
O4	0.66722 (8)	0.12662 (13)	0.2014 (3)	0.0610 (8)
O5	0.98563 (7)	0.04127 (12)	0.6943 (2)	0.0502 (7)
O6	0.96294 (8)	0.19919 (13)	0.7176 (3)	0.0618 (8)
N4	0.75208 (8)	0.05467 (15)	0.2964 (3)	0.0473 (8)
N5	0.73576 (8)	−0.02057 (14)	0.2236 (3)	0.0428 (8)
N6	0.99497 (8)	0.14091 (15)	0.4412 (3)	0.0488 (8)
C17	0.80156 (9)	0.06436 (17)	0.3787 (3)	0.0406 (9)
C18	0.83630 (10)	−0.00473 (17)	0.4023 (3)	0.0430 (9)
C19	0.88533 (10)	0.01125 (17)	0.4784 (3)	0.0417 (9)
C20	0.89966 (9)	0.09626 (17)	0.5320 (3)	0.0394 (8)
C21	0.86483 (11)	0.16454 (18)	0.5132 (4)	0.0546 (10)
C22	0.81611 (11)	0.14848 (18)	0.4370 (4)	0.0557 (10)
C23	0.68820 (10)	−0.02283 (17)	0.1450 (3)	0.0392 (8)
C24	0.65301 (10)	0.05225 (19)	0.1399 (4)	0.0462 (10)
C25	0.60133 (10)	0.0383 (2)	0.0648 (4)	0.0523 (10)

C26	0.58605 (11)	−0.0409 (2)	−0.0009 (4)	0.0523 (10)
C27	0.61932 (10)	−0.11560 (19)	−0.0043 (3)	0.0449 (9)
C28	0.67105 (10)	−0.10720 (18)	0.0631 (3)	0.0415 (9)
C29	0.70359 (11)	−0.17918 (19)	0.0507 (4)	0.0499 (10)
C30	0.68508 (12)	−0.2588 (2)	−0.0189 (4)	0.0579 (11)
C31	0.63398 (13)	−0.2678 (2)	−0.0781 (4)	0.0630 (11)
C32	0.60165 (12)	−0.1976 (2)	−0.0732 (4)	0.0567 (11)
H1	0.75520	0.11260	0.84890	0.0550*
H2	0.67240	−0.04410	0.62630	0.0500*
H3	0.58990	−0.01550	0.50510	0.0500*
H5	0.60650	0.24020	0.63980	0.0650*
H6	0.68820	0.21150	0.76720	0.0660*
H9	0.90640	0.10620	1.07100	0.0640*
H10	0.94800	−0.02130	1.04290	0.0650*
H13	0.78130	−0.16480	0.71940	0.0600*
H14	0.82830	−0.29140	0.69310	0.0710*
H15	0.91260	−0.29830	0.80680	0.0770*
H16	0.95130	−0.17690	0.94520	0.0690*
H33	0.49940	0.16570	0.73690	0.0550*
H34	0.48950	0.07340	0.69490	0.0550*
H4	0.72860	0.09980	0.29010	0.0570*
H18	0.82650	−0.06170	0.36690	0.0520*
H19	0.90870	−0.03490	0.49380	0.0500*
H21	0.87430	0.22120	0.55190	0.0660*
H22	0.79260	0.19450	0.42430	0.0670*
H25	0.57810	0.08480	0.06170	0.0630*
H26	0.55210	−0.04770	−0.04650	0.0630*
H29	0.73810	−0.17360	0.08950	0.0600*
H30	0.70710	−0.30650	−0.02590	0.0690*
H31	0.62160	−0.32210	−0.12160	0.0760*
H32	0.56750	−0.20410	−0.11590	0.0680*
H35	1.00100	0.09020	0.37420	0.0590*
H36	0.98490	0.18830	0.37420	0.0590*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0367 (4)	0.0394 (4)	0.0501 (4)	0.0035 (3)	−0.0045 (3)	0.0035 (3)
O1	0.0557 (13)	0.0468 (12)	0.0784 (15)	−0.0017 (10)	−0.0108 (11)	−0.0044 (10)
O2	0.0520 (12)	0.0417 (11)	0.0769 (14)	0.0070 (9)	−0.0055 (10)	0.0181 (10)
O3	0.0499 (12)	0.0551 (12)	0.0490 (11)	0.0023 (9)	−0.0086 (9)	−0.0075 (9)
N1	0.0361 (13)	0.0427 (13)	0.0561 (14)	0.0028 (10)	−0.0040 (10)	−0.0006 (11)
N2	0.0352 (13)	0.0427 (13)	0.0448 (12)	0.0041 (10)	0.0032 (9)	0.0063 (10)
N3	0.0413 (13)	0.0438 (13)	0.0524 (14)	0.0010 (10)	0.0031 (10)	−0.0055 (11)
C1	0.0334 (15)	0.0434 (16)	0.0458 (15)	0.0005 (12)	−0.0002 (11)	0.0017 (12)
C2	0.0369 (15)	0.0359 (14)	0.0515 (16)	0.0069 (12)	0.0014 (12)	−0.0011 (12)
C3	0.0383 (16)	0.0369 (15)	0.0502 (16)	−0.0013 (12)	−0.0003 (12)	−0.0023 (12)
C4	0.0344 (14)	0.0372 (15)	0.0456 (15)	0.0009 (12)	−0.0008 (11)	0.0017 (12)

C5	0.0443 (17)	0.0354 (15)	0.080 (2)	0.0062 (13)	−0.0057 (15)	−0.0015 (14)
C6	0.0429 (17)	0.0374 (16)	0.082 (2)	−0.0003 (13)	−0.0086 (15)	−0.0065 (15)
C7	0.0341 (15)	0.0482 (16)	0.0376 (14)	0.0003 (12)	0.0007 (11)	0.0055 (12)
C8	0.0443 (17)	0.0497 (18)	0.0454 (16)	−0.0022 (14)	−0.0002 (12)	0.0077 (13)
C9	0.0454 (18)	0.061 (2)	0.0531 (17)	−0.0085 (15)	−0.0057 (13)	0.0048 (15)
C10	0.0346 (16)	0.080 (2)	0.0454 (16)	−0.0032 (16)	−0.0069 (12)	0.0128 (16)
C11	0.0357 (15)	0.0646 (19)	0.0390 (15)	0.0061 (14)	0.0032 (11)	0.0128 (14)
C12	0.0384 (15)	0.0528 (17)	0.0379 (14)	0.0066 (13)	0.0047 (11)	0.0086 (13)
C13	0.0420 (17)	0.0536 (18)	0.0543 (17)	0.0081 (14)	−0.0028 (13)	0.0010 (14)
C14	0.063 (2)	0.0536 (19)	0.0597 (19)	0.0130 (16)	0.0002 (15)	−0.0014 (15)
C15	0.066 (2)	0.069 (2)	0.0569 (19)	0.0298 (18)	0.0046 (16)	0.0023 (17)
C16	0.0418 (17)	0.082 (2)	0.0480 (17)	0.0185 (17)	0.0034 (13)	0.0111 (17)
S2	0.0389 (4)	0.0396 (4)	0.0488 (4)	−0.0031 (3)	−0.0072 (3)	−0.0020 (3)
O4	0.0544 (13)	0.0439 (12)	0.0825 (15)	0.0029 (10)	−0.0064 (11)	−0.0047 (11)
O5	0.0459 (11)	0.0499 (12)	0.0525 (11)	0.0026 (9)	−0.0089 (9)	0.0091 (9)
O6	0.0572 (13)	0.0518 (12)	0.0737 (14)	−0.0058 (10)	−0.0087 (10)	−0.0245 (11)
N4	0.0364 (13)	0.0413 (13)	0.0623 (15)	−0.0011 (10)	−0.0054 (10)	−0.0037 (11)
N5	0.0391 (13)	0.0434 (13)	0.0450 (13)	−0.0053 (10)	−0.0004 (10)	0.0010 (10)
N6	0.0440 (14)	0.0416 (13)	0.0604 (15)	−0.0025 (10)	0.0028 (11)	0.0127 (11)
C17	0.0339 (15)	0.0414 (16)	0.0456 (15)	−0.0019 (12)	−0.0016 (11)	0.0015 (12)
C18	0.0440 (16)	0.0358 (15)	0.0483 (15)	−0.0073 (13)	−0.0015 (12)	−0.0035 (12)
C19	0.0405 (16)	0.0357 (14)	0.0479 (15)	0.0036 (12)	−0.0007 (12)	0.0001 (12)
C20	0.0389 (15)	0.0352 (14)	0.0427 (15)	−0.0004 (12)	−0.0044 (11)	−0.0019 (12)
C21	0.0476 (18)	0.0339 (15)	0.079 (2)	0.0006 (13)	−0.0131 (15)	−0.0085 (14)
C22	0.0426 (18)	0.0374 (16)	0.084 (2)	0.0048 (13)	−0.0113 (15)	−0.0054 (15)
C23	0.0330 (15)	0.0441 (15)	0.0400 (14)	−0.0062 (12)	0.0001 (11)	0.0021 (12)
C24	0.0422 (17)	0.0487 (17)	0.0471 (16)	0.0011 (13)	0.0012 (12)	0.0039 (14)
C25	0.0389 (17)	0.062 (2)	0.0550 (17)	0.0062 (14)	−0.0017 (13)	0.0024 (15)
C26	0.0350 (16)	0.072 (2)	0.0484 (17)	−0.0020 (15)	−0.0041 (12)	0.0029 (15)
C27	0.0399 (16)	0.0564 (17)	0.0376 (15)	−0.0071 (14)	−0.0008 (11)	0.0018 (13)
C28	0.0391 (15)	0.0493 (16)	0.0362 (14)	−0.0052 (13)	0.0045 (11)	0.0017 (12)
C29	0.0446 (17)	0.0550 (18)	0.0496 (17)	−0.0027 (14)	0.0009 (13)	−0.0024 (14)
C30	0.063 (2)	0.0517 (18)	0.0585 (19)	−0.0013 (16)	0.0029 (15)	−0.0093 (15)
C31	0.072 (2)	0.060 (2)	0.0562 (19)	−0.0182 (18)	0.0014 (16)	−0.0147 (16)
C32	0.0490 (18)	0.069 (2)	0.0502 (17)	−0.0163 (16)	−0.0067 (14)	−0.0080 (15)

Geometric parameters (Å, º)

S1—O2	1.434 (2)	C15—C16	1.369 (4)
S1—O3	1.432 (2)	C2—H2	0.9300
S1—N3	1.612 (3)	C3—H3	0.9300
S1—C4	1.760 (3)	C5—H5	0.9300
S2—O5	1.437 (2)	C6—H6	0.9300
S2—O6	1.432 (2)	C9—H9	0.9300
S2—N6	1.609 (3)	C10—H10	0.9300
S2—C20	1.760 (3)	C13—H13	0.9300
O1—C8	1.258 (4)	C14—H14	0.9300
O4—C24	1.258 (4)	C15—H15	0.9300

N1—C1	1.398 (3)	C16—H16	0.9300
N1—N2	1.313 (3)	C17—C18	1.389 (4)
N2—C7	1.332 (3)	C17—C22	1.387 (4)
N1—H1	0.8800	C18—C19	1.381 (4)
N3—H34	0.8900	C19—C20	1.388 (4)
N3—H33	0.8900	C20—C21	1.379 (4)
N4—N5	1.315 (3)	C21—C22	1.374 (4)
N4—C17	1.393 (3)	C23—C24	1.464 (4)
N5—C23	1.331 (3)	C23—C28	1.467 (4)
N4—H4	0.9200	C24—C25	1.436 (4)
N6—H35	0.9300	C25—C26	1.341 (4)
N6—H36	0.9000	C26—C27	1.431 (4)
C1—C2	1.383 (4)	C27—C32	1.405 (4)
C1—C6	1.391 (4)	C27—C28	1.411 (4)
C2—C3	1.379 (4)	C28—C29	1.393 (4)
C3—C4	1.389 (4)	C29—C30	1.382 (4)
C4—C5	1.378 (4)	C30—C31	1.382 (5)
C5—C6	1.375 (4)	C31—C32	1.363 (5)
C7—C8	1.460 (4)	C18—H18	0.9300
C7—C12	1.461 (4)	C19—H19	0.9300
C8—C9	1.437 (4)	C21—H21	0.9300
C9—C10	1.338 (4)	C22—H22	0.9300
C10—C11	1.431 (4)	C25—H25	0.9300
C11—C12	1.412 (4)	C26—H26	0.9300
C11—C16	1.408 (4)	C29—H29	0.9300
C12—C13	1.402 (4)	C30—H30	0.9300
C13—C14	1.378 (4)	C31—H31	0.9300
C14—C15	1.377 (5)	C32—H32	0.9300

O1···N1	2.520 (3)	C17···N2	3.403 (4)
O1···N2	2.861 (4)	C18···C12	3.528 (4)
O1···C17^{i}	3.333 (4)	C18···C8^{x}	3.557 (4)
O1···C21^{ii}	3.232 (4)	C18···C9^{x}	3.438 (4)
O1···C22^{ii}	3.184 (4)	C18···C7	3.507 (4)
O2···N3^{iii}	3.073 (4)	C19···C7	3.587 (4)
O3···O3^{iv}	3.214 (3)	C19···C9^{x}	3.520 (4)
O3···N3^{iv}	3.023 (3)	C19···C12	3.453 (4)
O3···C25	3.373 (4)	C19···C11	3.599 (4)
O4···C5^{iii}	3.157 (4)	C21···O1^{iii}	3.232 (4)
O4···N4	2.525 (3)	C22···O1^{iii}	3.184 (4)
O4···C6^{iii}	3.139 (4)	C23···C1^{x}	3.593 (4)
O4···N5	2.860 (4)	C23···N1^{x}	3.347 (4)
O5···C10	3.192 (4)	C24···C3	3.400 (4)
O5···N6^{v}	2.993 (4)	C24···C1^{x}	3.433 (4)
O5···C10^{vi}	3.348 (4)	C25···O3	3.373 (4)
O6···N6^{ii}	3.009 (4)	C26···C3^{x}	3.554 (4)
O1···H1	1.7500	C26···C2^{x}	3.573 (4)
O1···H21^{ii}	2.6600	C27···C2^{x}	3.565 (4)

O1···H22^{ii}	2.5500	C28···C31^{ix}	3.471 (5)
O2···H33^{iii}	2.1900	C29···C31^{ix}	3.529 (5)
O2···H5	2.5600	C29···C30^{ix}	3.399 (5)
O3···H3	2.6700	C30···C29^{viii}	3.399 (5)
O3···H26^{vii}	2.6700	C31···C28^{viii}	3.471 (5)
O3···H34^{iv}	2.2300	C31···C29^{viii}	3.529 (5)
O3···H25	2.9100	C8···H1	2.2900
O4···H4	1.7300	C16···H15^{ix}	3.0600
O4···H6^{iii}	2.5500	C24···H4	2.3000
O4···H5^{iii}	2.5900	C27···H31^{ix}	2.9800
O5···H19	2.6600	C28···H31^{ix}	2.9700
O5···H35^{v}	2.0900	H1···O1	1.7500
O5···H10^{vi}	2.5100	H1···H6	2.3500
O6···H21	2.5600	H1···C8	2.2900
O6···H36^{ii}	2.1100	H2···N2	2.6200
N1···O1	2.520 (3)	H3···O3	2.6700
N1···C23^{i}	3.347 (4)	H3···N3^{iv}	2.8800
N2···O1	2.861 (4)	H3···H34^{iv}	2.6000
N2···C17	3.403 (4)	H4···O4	1.7300
N3···O2^{ii}	3.073 (4)	H4···C24	2.3000
N3···O3^{iv}	3.023 (3)	H4···H22	2.3600
N4···O4	2.525 (3)	H5···O2	2.5600
N5···O4	2.860 (4)	H5···O4^{ii}	2.5900
N6···O5^{v}	2.993 (4)	H6···O4^{ii}	2.5500
N6···O6^{iii}	3.009 (4)	H6···H1	2.3500
N2···H2	2.6200	H10···O5^{vi}	2.5100
N2···H13	2.5200	H10···H16	2.4700
N3···H3^{iv}	2.8800	H13···N2	2.5200
N5···H29	2.5200	H13···H30^{ix}	2.5800
N5···H18	2.6000	H14···H18^{ix}	2.5700
C1···C23^{i}	3.593 (4)	H14···H29^{ix}	2.4800
C1···C24^{i}	3.433 (4)	H15···C16^{viii}	3.0600
C2···C27^{i}	3.565 (4)	H16···H10	2.4700
C2···C26^{i}	3.573 (4)	H18···N5	2.6000
C3···C24	3.400 (4)	H18···H14^{viii}	2.5700
C3···C26^{i}	3.554 (4)	H19···O5	2.6600
C5···O4^{ii}	3.157 (4)	H21···O6	2.5600
C6···O4^{ii}	3.139 (4)	H21···O1^{iii}	2.6600
C7···C18	3.507 (4)	H22···H4	2.3600
C7···C19	3.587 (4)	H22···O1^{iii}	2.5500
C8···C17^{i}	3.410 (4)	H25···O3	2.9100
C8···C18^{i}	3.557 (4)	H26···H32	2.4600
C9···C18^{i}	3.438 (4)	H26···O3^{vii}	2.6700
C9···C19^{i}	3.520 (4)	H29···N5	2.5200
C10···O5	3.192 (4)	H29···H14^{viii}	2.4800
C10···O5^{vi}	3.348 (4)	H30···H13^{viii}	2.5800
C11···C19	3.599 (4)	H31···C27^{viii}	2.9800
C12···C18	3.528 (4)	H31···C28^{viii}	2.9700

C12···C19	3.453 (4)	H32···H26	2.4600
C14···C15^{viii}	3.580 (5)	H33···O2^{ii}	2.1900
C15···C16^{viii}	3.425 (5)	H34···O3^{iv}	2.2300
C15···C14^{ix}	3.580 (5)	H34···H3^{iv}	2.6000
C16···C15^{ix}	3.425 (5)	H35···O5^{v}	2.0900
C17···C8^{x}	3.410 (4)	H36···O6^{iii}	2.1100
C17···O1^{x}	3.333 (4)		

O2—S1—O3	119.23 (12)	C5—C6—H6	120.00
O2—S1—N3	106.57 (12)	C10—C9—H9	119.00
O2—S1—C4	107.76 (11)	C8—C9—H9	119.00
O3—S1—N3	106.50 (11)	C9—C10—H10	119.00
O3—S1—C4	108.55 (11)	C11—C10—H10	119.00
N3—S1—C4	107.74 (11)	C12—C13—H13	120.00
N6—S2—C20	108.58 (11)	C14—C13—H13	120.00
O5—S2—C20	108.36 (12)	C15—C14—H14	119.00
O5—S2—O6	119.05 (12)	C13—C14—H14	119.00
O5—S2—N6	105.98 (11)	C14—C15—H15	120.00
O6—S2—N6	106.95 (12)	C16—C15—H15	120.00
O6—S2—C20	107.56 (13)	C11—C16—H16	120.00
N2—N1—C1	122.3 (2)	C15—C16—H16	120.00
N1—N2—C7	117.3 (2)	C18—C17—C22	119.5 (2)
N2—N1—H1	115.00	N4—C17—C22	116.9 (2)
C1—N1—H1	123.00	N4—C17—C18	123.6 (2)
H33—N3—H34	108.00	C17—C18—C19	119.9 (2)
S1—N3—H33	114.00	C18—C19—C20	119.9 (2)
S1—N3—H34	118.00	S2—C20—C19	120.63 (19)
N5—N4—C17	121.8 (2)	C19—C20—C21	120.3 (2)
N4—N5—C23	117.4 (2)	S2—C20—C21	119.0 (2)
N5—N4—H4	115.00	C20—C21—C22	119.7 (3)
C17—N4—H4	123.00	C17—C22—C21	120.7 (3)
S2—N6—H35	112.00	N5—C23—C28	116.4 (2)
S2—N6—H36	116.00	C24—C23—C28	119.7 (2)
H35—N6—H36	115.00	N5—C23—C24	123.9 (2)
N1—C1—C6	116.0 (2)	O4—C24—C23	121.3 (2)
N1—C1—C2	123.6 (2)	O4—C24—C25	120.7 (3)
C2—C1—C6	120.4 (2)	C23—C24—C25	118.0 (2)
C1—C2—C3	119.2 (2)	C24—C25—C26	120.9 (3)
C2—C3—C4	120.3 (2)	C25—C26—C27	123.3 (3)
S1—C4—C5	118.08 (19)	C26—C27—C32	121.4 (3)
S1—C4—C3	121.43 (19)	C28—C27—C32	119.0 (3)
C3—C4—C5	120.4 (2)	C26—C27—C28	119.6 (3)
C4—C5—C6	119.6 (2)	C23—C28—C29	122.7 (2)
C1—C6—C5	120.2 (3)	C27—C28—C29	119.0 (2)
N2—C7—C12	116.5 (2)	C23—C28—C27	118.4 (2)
N2—C7—C8	123.6 (2)	C28—C29—C30	120.6 (3)
C8—C7—C12	119.8 (2)	C29—C30—C31	120.3 (3)
O1—C8—C7	121.8 (2)	C30—C31—C32	120.4 (3)

C7—C8—C9	117.6 (2)	C27—C32—C31	120.8 (3)
O1—C8—C9	120.6 (3)	C17—C18—H18	120.00
C8—C9—C10	121.5 (3)	C19—C18—H18	120.00
C9—C10—C11	122.9 (3)	C18—C19—H19	120.00
C12—C11—C16	119.2 (3)	C20—C19—H19	120.00
C10—C11—C16	121.4 (2)	C20—C21—H21	120.00
C10—C11—C12	119.4 (3)	C22—C21—H21	120.00
C7—C12—C11	118.8 (2)	C17—C22—H22	120.00
C11—C12—C13	118.6 (3)	C21—C22—H22	120.00
C7—C12—C13	122.6 (2)	C24—C25—H25	120.00
C12—C13—C14	120.3 (3)	C26—C25—H25	119.00
C13—C14—C15	121.2 (3)	C25—C26—H26	118.00
C14—C15—C16	119.8 (3)	C27—C26—H26	118.00
C11—C16—C15	120.8 (3)	C28—C29—H29	120.00
C1—C2—H2	120.00	C30—C29—H29	120.00
C3—C2—H2	120.00	C29—C30—H30	120.00
C2—C3—H3	120.00	C31—C30—H30	120.00
C4—C3—H3	120.00	C30—C31—H31	120.00
C4—C5—H5	120.00	C32—C31—H31	120.00
C6—C5—H5	120.00	C27—C32—H32	120.00
C1—C6—H6	120.00	C31—C32—H32	120.00

O2—S1—C4—C3	−155.6 (2)	C10—C11—C12—C7	1.1 (3)
O2—S1—C4—C5	28.0 (2)	C10—C11—C12—C13	179.6 (2)
O3—S1—C4—C3	−25.2 (2)	C16—C11—C12—C7	−178.4 (2)
O3—S1—C4—C5	158.4 (2)	C12—C11—C16—C15	0.5 (4)
N3—S1—C4—C3	89.8 (2)	C16—C11—C12—C13	0.2 (4)
N3—S1—C4—C5	−86.7 (2)	C10—C11—C16—C15	−179.0 (3)
O6—S2—C20—C19	−158.62 (19)	C11—C12—C13—C14	−0.9 (4)
O5—S2—C20—C19	−28.7 (2)	C7—C12—C13—C14	177.6 (3)
O5—S2—C20—C21	155.0 (2)	C12—C13—C14—C15	1.1 (4)
N6—S2—C20—C21	−90.3 (2)	C13—C14—C15—C16	−0.5 (5)
O6—S2—C20—C21	25.1 (2)	C14—C15—C16—C11	−0.3 (5)
N6—S2—C20—C19	86.0 (2)	N4—C17—C18—C19	177.3 (2)
C1—N1—N2—C7	177.7 (2)	C22—C17—C18—C19	−1.9 (4)
N2—N1—C1—C2	7.4 (4)	N4—C17—C22—C21	−177.5 (3)
N2—N1—C1—C6	−174.0 (2)	C18—C17—C22—C21	1.8 (4)
N1—N2—C7—C8	−1.8 (4)	C17—C18—C19—C20	0.4 (3)
N1—N2—C7—C12	−179.1 (2)	C18—C19—C20—S2	−174.83 (18)
C17—N4—N5—C23	−178.7 (2)	C18—C19—C20—C21	1.4 (4)
N5—N4—C17—C18	−4.6 (4)	S2—C20—C21—C22	174.7 (2)
N5—N4—C17—C22	174.6 (2)	C19—C20—C21—C22	−1.6 (4)
N4—N5—C23—C24	−1.8 (4)	C20—C21—C22—C17	0.0 (4)
N4—N5—C23—C28	179.4 (2)	N5—C23—C24—O4	4.6 (4)
C6—C1—C2—C3	−0.3 (4)	N5—C23—C24—C25	−174.5 (2)
N1—C1—C6—C5	−179.2 (3)	C28—C23—C24—O4	−176.7 (2)
N1—C1—C2—C3	178.3 (2)	C28—C23—C24—C25	4.2 (4)
C2—C1—C6—C5	−0.5 (4)	N5—C23—C28—C27	173.3 (2)

C1—C2—C3—C4	0.7 (3)	N5—C23—C28—C29	−6.2 (4)
C2—C3—C4—C5	−0.3 (4)	C24—C23—C28—C27	−5.6 (3)
C2—C3—C4—S1	−176.65 (18)	C24—C23—C28—C29	174.9 (2)
S1—C4—C5—C6	176.0 (2)	O4—C24—C25—C26	180.0 (3)
C3—C4—C5—C6	−0.5 (4)	C23—C24—C25—C26	−0.9 (4)
C4—C5—C6—C1	0.9 (4)	C24—C25—C26—C27	−1.1 (5)
N2—C7—C12—C11	175.8 (2)	C25—C26—C27—C28	−0.4 (4)
N2—C7—C12—C13	−2.7 (4)	C25—C26—C27—C32	179.5 (3)
C8—C7—C12—C11	−1.6 (3)	C26—C27—C28—C23	3.7 (3)
C8—C7—C12—C13	179.9 (3)	C26—C27—C28—C29	−176.8 (2)
C12—C7—C8—O1	−178.6 (2)	C32—C27—C28—C23	−176.2 (2)
N2—C7—C8—O1	4.2 (4)	C32—C27—C28—C29	3.3 (4)
N2—C7—C8—C9	−176.3 (2)	C26—C27—C32—C31	179.0 (3)
C12—C7—C8—C9	0.9 (4)	C28—C27—C32—C31	−1.1 (4)
O1—C8—C9—C10	179.8 (3)	C23—C28—C29—C30	176.6 (3)
C7—C8—C9—C10	0.3 (4)	C27—C28—C29—C30	−2.9 (4)
C8—C9—C10—C11	−0.8 (5)	C28—C29—C30—C31	0.4 (4)
C9—C10—C11—C16	179.6 (3)	C29—C30—C31—C32	1.9 (5)
C9—C10—C11—C12	0.1 (4)	C30—C31—C32—C27	−1.5 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.88	1.75	2.520 (3)	145
N3—H33···O2^{ii}	0.89	2.19	3.073 (4)	172
N3—H34···O3^{iv}	0.89	2.23	3.023 (3)	147
N4—H4···O4	0.92	1.73	2.525 (3)	142
N6—H35···O5^{v}	0.93	2.09	2.993 (4)	162
N6—H36···O6^{iii}	0.90	2.11	3.009 (4)	179

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