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Crystal structure of 3-methoxy-4-[2-(thiazol-2-yl)-diazen-1-yl]aniline monohydrate

Nutchanikan Phiromphu,[a] Kittipong Chainok,[b] Apisit Songsasen[a] and Tanwawan Duangthongyou[a]*

[a]Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok, 10900, Thailand, and [b]Materials and Textile Technology, Faculty of Science and Technology, Thammasat, University, PathumThani 12120, Thailand. *Correspondence e-mail: fscitwd@ku.ac.th

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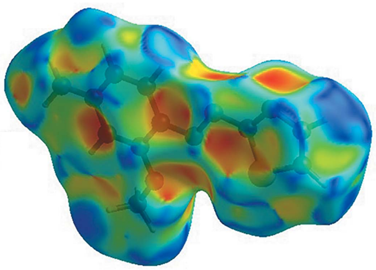
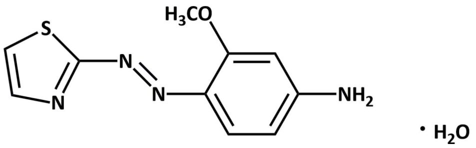
In the title hydrated azo dye, $C_{10}H_{10}N_4OS\cdot H_2O$, the benzene and thiazole, are nearly coplanar, with a dihedral angle between their mean planes of 4.69 (17)°. The aromatic rings on the –N═N– moiety exhibit a *trans* configuration. The crystal structure features many types of intermolecular interactions involving all the functional groups – strong hydrogen bonds (N⋯H and O⋯H), weak hydrogen bonds (C—H⋯O and C—H⋯N), C—H⋯π and π–π interactions – resulting in the formation of a three-dimensional framework.



1. Chemical context

Thiazolylazo compounds contain a thiazole ring and an azo group (–N═N–). Azo dyes have wide range applications in the cosmetic, food, textile industry, chemical sensing, and pharmaceutical (Weglarz-Tomczak & Gorecki, 2012) fields. 4-(2-Thiazolylazo) resorcinol (TAR) was the first thiazolylazo dye (Jensen, 1960). Changing the substituent groups on the azo bond (Hovind, 1975) changes the coordination properties with metal ions, as in the complexation of 1-(2-thiazolylazo)-2-naphthol (TAN) with transition metals (Omar *et al.*, 2005). Cleavage of the azo bond occurs in reductive metabolism of mammalian systems (Levine, 1991) that can decrease or increase any toxic or carcinogenic effects of the dyes. Sutthivaiyakit *et al.* (1998) described the preparation of a new chelating silica with 2-(2-thiazolylazo)-5-aminoanisole used for a stationary phase in high-pressure liquid chromatography. In this work, we report the structure of 3-methoxy-4-[2-(thiazol-2-yl)diazen-1-yl]aniline monohydrate, also known as 2-(2-thiazolylazo)-5-aminoanisole (*p*-amino TAA), (I). Future work will study its complexation with metal ions.



2. Structural commentary

The molecular structure of (I) is shown in Fig. 1. The thiazole and benzene rings are arranged *trans* to the azo bridge (–N2═N3–). The methoxy and amino groups on the benzene ring are co-planar with the ring with atoms O1 and N4 deviating by −0.010 (2) and −0.019 (4) Å, respectively. The

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N4—H4*A*⋯N2^{i}	0.87 (1)	2.30 (2)	3.137 (5)	162 (3)
N4—H4*B*⋯O3	0.87 (1)	2.08 (1)	2.946 (5)	173 (4)
O3—H3*A*⋯N1^{ii}	0.84 (1)	2.12 (2)	2.954 (5)	169 (6)
O3—H3*B*⋯N3^{iii}	0.84 (1)	2.43 (3)	3.186 (5)	150 (5)
C9—H9⋯N4^{iv}	0.93	2.69	3.587 (5)	162
C2—H2⋯N2^{v}	0.93	2.87	3.798 (5)	176
C8—H8⋯O1^{vi}	0.93	2.72	3.452 (5)	136
C1—H1⋯O3^{vii}	0.93	2.56	3.463 (5)	165
C10—H10*C*⋯C3^{ii}	0.96	2.89	3.655 (5)	137
C10—H10*A*⋯C6^{iii}	0.96	2.83	3.551 (5)	132
C10—H10*A*⋯C7^{iii}	0.96	2.86	3.502 (5)	125

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

dihedral angle between the thiazole and benzene rings is 4.69 (17)°, nearly coplanar.

3. Supramolecular features

In the crystal, three-dimensional structure is generated by contribution of strong and weak hydrogen bonding, C—H⋯π interactions and offset π–π interaction. The strong hydrogen bonds (Fig. 2*a*, Table 1), which involve the amine (NH_2), azo (–N═N–) and thiazole groups and the water molecule of crystallization [N4—H4*B*⋯O3, O3—H3*A*⋯N1^{ii}, O3—H3*B*⋯N3^{iii}, N4—H4*A*⋯N2^{i}] are the primary interactions responsible for the formation of the three dimensional structure. In addition, the crystal structure is supported by other intermolecular interactions as a secondary weak interactions, C—H⋯*X* (*X* = O and N), C—H⋯π and offset π—π interactions. The weak hydrogen bonds are formed between the C—H moieties in the benzene and thiazole rings with amine, azo, methoxy groups of adjacent molecules and water molecules [C1—H1⋯O3^{vii}, C2—H2⋯N2^{v}, C8—H8⋯O1^{vi} and C9—H9⋯N4^{iv}. The C—H⋯π interactions involve the methoxy group and ring carbon atoms [C10—H10*C*⋯C3^{ii}, C10—H10*A*⋯C6^{iii} and C10—H10*A*⋯C7^{iii} while the offset π–π interaction is formed between benzene and thiazole rings with a centroid–centroid distance of 3.850 (5) Å, symmetry operation $1-x, 2-y, 1-z$ (Fig. 2*b*, Table 1).

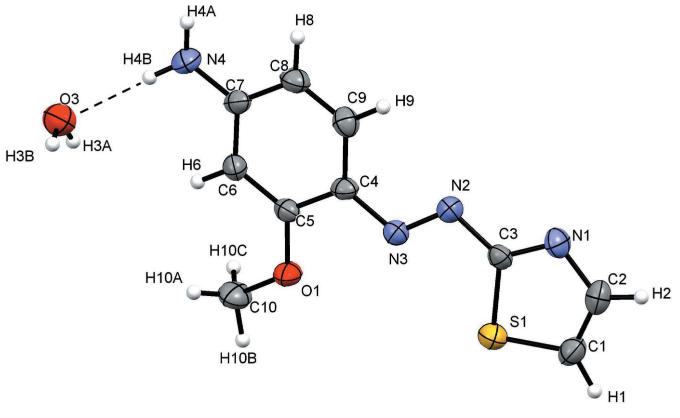


Figure 1
The molecular structure of compound (I) with the atom labelling and 50% probability displacement ellipsoids

4. Hirshfeld surface analysis

Hirshfeld surfaces and fingerprint plots were generated using *CrystalExplorer* (Hirshfeld, 1977; McKinnon *et al.*, 2004). Fig. 3 shows the Hirshfeld surface of compound (I) mapped over $d_{\rm norm}$ (−0.5129 to 1.1405 Å) and the shape index (−1.0 to 1.0 Å). The red spots in the Hirshfeld surface represent short N⋯H and O⋯H contacts and correspond to hydrogen-bonding interactions between (NH_2)N—H⋯N(azo), (H_2O)O—H⋯N(azo), (H_2O)O—H⋯N(thiazole) and (NH_2)N—H⋯O(H_2O). The pale-red spots result from the weak C—H⋯O(H_2O) and C—H⋯N(NH_2) hydrogen-bonding interactions. The white spots in Fig.3*a* represent long

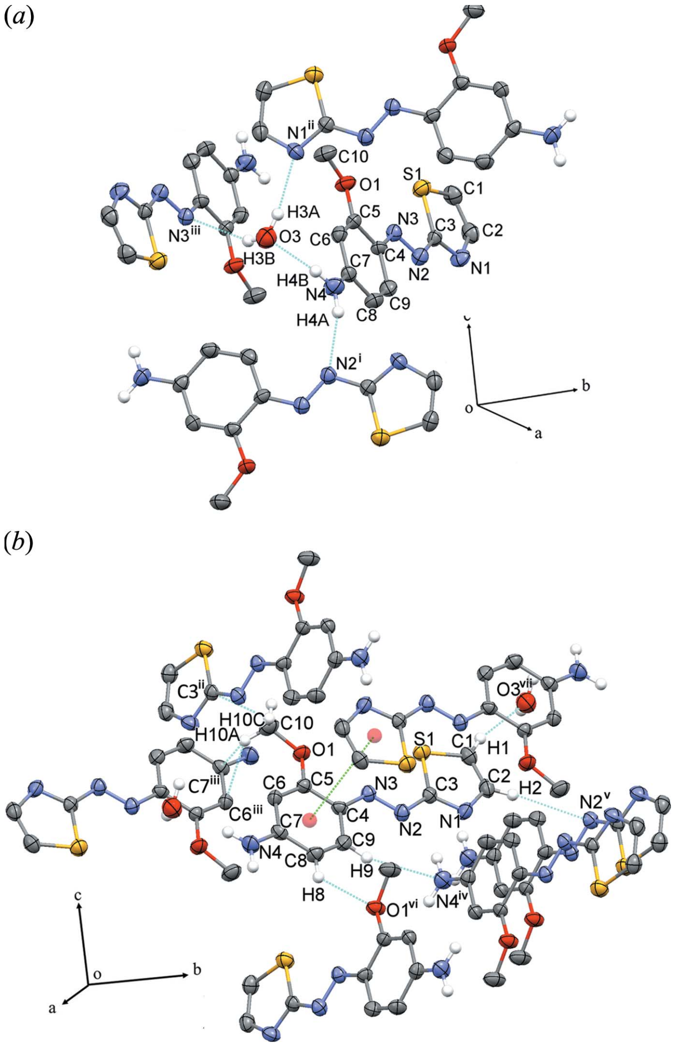


Figure 2
(*a*) The packing of the crystal by strong hydrogen bonds and (*b*) secondary interactions. Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (vii) $x-1, y+1, z$.

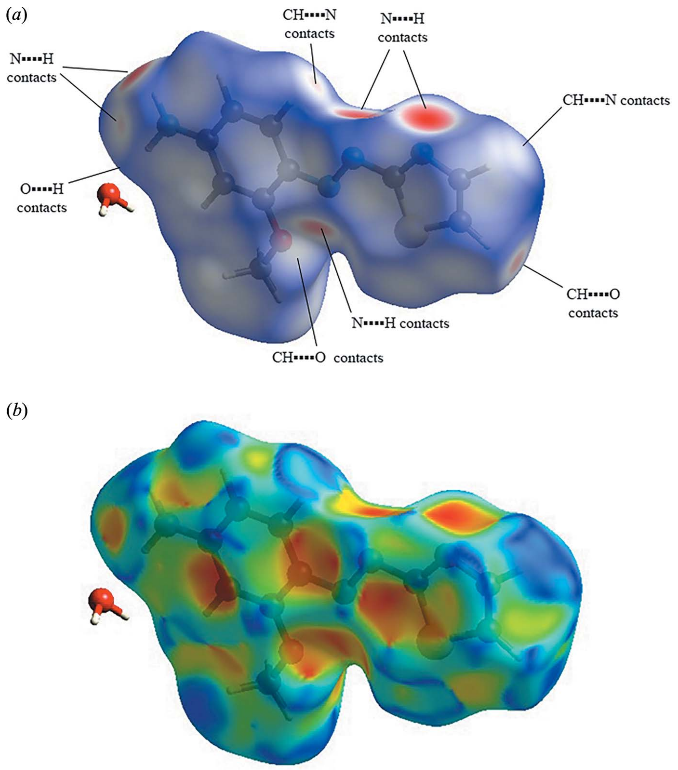


Figure 3
Hirshfeld surfaces for compound (I), mapped with (*a*) $d_{\rm norm}$ and (*b*) shape-index.

contacts [C—H···N(azo) and C—H···O(OCH$_3$)]. On the shape index surface (Fig. 3*b*), convex blue regions represent hydrogen-donor groups and concave red regions represent hydrogen-acceptor groups. In addition, concave red regions represent C—H···π and offset π–π interactions. The amino group behaves as both a donor and an acceptor. The methyl part of the methoxy group acts as a donor while the oxygen atom is an acceptor.

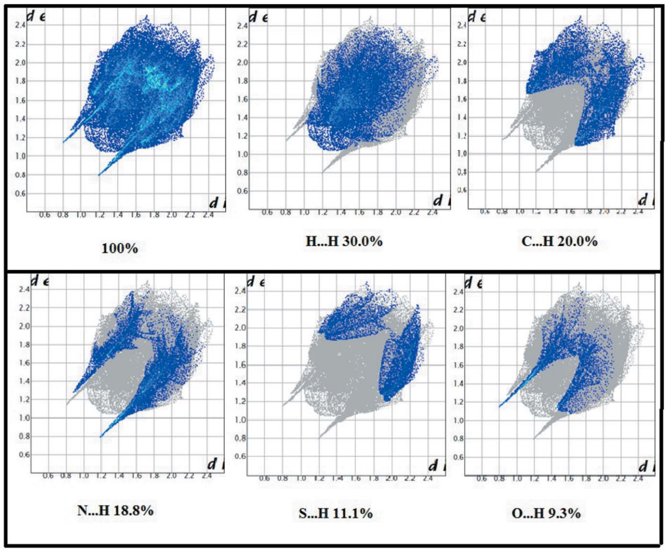


Figure 4
Two-dimensional fingerprints for compound (I), showing H···H, C···H, N···H, S···H and O···H contacts.

The two-dimensional fingerprint plots (Fig. 4) quantify the contributions of each type of intermolecular interaction to the Hirshfeld surface (McKinnon *et al.*, 2007). The largest contribution with 30.0% of the surface is from H···H contacts, which represent van der Waals interactions, followed by C···H contacts involved in C—H···π interactions (20.0%). In the N···H plot (18.8% contribution), the two sharp peaks correspond to strong hydrogen bonds. Finally, the O···H (9.3%), S···H (11.1%) and C···C (3.3%) contacts correspond to hydrogen bonds and offset π–π interactions, respectively.

5. Database survey

Related compounds to (I) are substituted thiazolylazo derivatives, for example 4-(2-thiazolylazo) resorcinol (TAR), 1-(2-thiazolylazo)-2-naphthol (TAN) and 2-(2-thiazolylazo)-4-methylphenol (TAC) (Jensen, 1960). These thiazolylazo derivatives are used as chelating agents with metal ions (Farias *et al.*, 1992). In the crystal structure of 1-(2-thiazolylazo)-2-naphthol (TAN; Kurahashi, 1976), the azo group adopts a *trans* configuration and the phenolic oxygen atom is linked to an azo nitrogen atom by intramolecular hydrogen bonding. The crystal structure features only van der Waals interactions. To form complexes with metal ions, both thiazole and naphthol rings are rotated by 180° to coordinate to the metal through the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring and the thiazole nitrogen atom, resulting the formation of five-membered chelate rings. Complexes of TAR and TAC are formed in a similar way due to the presence of a hydroxyl group in the structure (Karipcin *et al.*, 2010). 3-[2-(1,3-Thiazol-2-yl)diazen-1-yl]pyridine-2,6-diamine monohydrate (Chotima *et al.*, 2018) has been used as a chelating ligand to form a complex with Au$^{\rm III}$ ion (Piyasaengthong *et al.*, 2015). The crystal structure is stabilized by hydrogen bonding between the amine group, water and the thiazole nitrogen atom along with π–π interactions between pairs of pyridine rings and pairs of thiazole rings, resulting in the formation of a layered structure. In addition, weak C—H···S hydrogen bonds between adjacent thiazole rings further contribute to the crystal packing, generating a three-dimensional network.

6. Synthesis and crystallization

2-Aminothiazole (9.986 mmol) was dissolved in 6 *M* HCl (16 ml), and 8.236 mmol of sodium nitrate solution was added slowly under stirring at low temperature 268–273 K until the diazonium salt was obtained. *m*-Anisidine (1.12 ml in 40 ml of 4 *M* HCl) was slowly dropped into the mixture and stirred at a temperature between 268 and 273 K for 1 h. After the reaction was complete, conc. NH_3 was dropped into the mixture (pH 6) until the red–orange crude produce appeared. The products were filtered, washed with cold water, purified by column chromatography and recrystallized from an acetonitrile–water (1:1) mixture by vapour diffusion.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{10}N_4OS \cdot H_2O$
M_r	252.30
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, b, c (Å)	9.051 (5), 11.526 (5), 10.893 (6)
β (°)	90.345 (16)
V (Å^3)	1136.5 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.28
Crystal size (mm)	0.14 × 0.06 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
$T_{\min}$, $T_{\max}$	0.585, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13093, 2164, 995
$R_{\rm int}$	0.164
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.131, 0.93
No. of reflections	2164
No. of parameters	172
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.26, −0.26

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.806 (3H, *s*, H^c), 6.364 (1H, *dd*, H^f, $J = 8.7, 2.7$ Hz) , 6.374 (1H, *t*, H^d, $J = 2.8$ Hz), 7.546 (1H, *d*, H^g, $J = 8.9$ Hz) ,7.629 (1H, *d*, H^a, $J = 3.40$ Hz), 7.697 (2H, *s*, H^e), 7.883 (1H, *d*, H^b, $J = 3.42$ Hz). Mass spectroscopy: *m*/*z* 235.0654 [$C_{10}H_{11}N_4OS^+$], 205.0548 [$C_9H_9N_4S^{\cdot+}$], 150.0662 [$C_7H_8N_3O^{\cdot+}$], 122.0601 [$C_7H_8NO^{\cdot+}$]. IR (KBr cm^{-1}): 3,413 cm^{-1} (*s*, N—H); 821 cm^{-1} (*w*, NH$_2$); 1,617 (*m*, C═N); 1,222 cm^{-1} (*w*, C—N stretch aromatic amine); 1,103 cm^{-1} (*m*, C—N stretch amine); 1,152 cm^{-1} (*m*, C—S); 1,541cm^{-1} (*m*, N═N); 1,021 cm^{-1} (*w*, C—O stretch). Elemental analysis calculated for $C_{10}H_{10}N_4OS \cdot H_2O$: C, 51.27; H, 4.30; N, 23.92. Found: C, 51.34; H, 4.20; N, 23.98.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Water and amino H atoms were refined freely while those of aromatic and methyl groups were placed in calculated positions (C—H = 0.93 and 0.96 Å, respectively) and included in the cycles of refinement using a riding model with $U_{\rm iso} = 1.2\,U_{\rm eq}$(C-aromatic) and $1.5U_{\rm eq}$ (C-methyl).

Acknowledgements

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Crystal structure of 3-methoxy-4-[2-(thiazol-2-yl)diazen-1-yl]aniline monohydrate

Nutchanikan Phiromphu, Kittipong Chainok, Apisit Songsasen and Tanwawan Duangthongyou

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

3-Methoxy-4-[2-(thiazol-2-yl)diazen-1-yl]aniline monohydrate

Crystal data

$C_{10}H_{10}N_4OS\cdot H_2O$
$M_r = 252.30$
Monoclinic, $P2_1/n$
$a = 9.051$ (5) Å
$b = 11.526$ (5) Å
$c = 10.893$ (6) Å
$\beta = 90.345$ (16)°
$V = 1136.5$ (10) Å^3
$Z = 4$
$F(000) = 528$
$D_x = 1.475$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 395 reflections
$\theta = 2.9$–19.0°
$\mu = 0.28$ mm^{-1}
$T = 298$ K
Block, brown
0.14 × 0.06 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: microfocus sealed X-ray tube, Incoatec Iμs
Mirror optics monochromator
Detector resolution: 7.9 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{\min} = 0.585$, $T_{\max} = 0.745$
13093 measured reflections
2164 independent reflections
995 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.164$
$\theta_{\max} = 25.8°$, $\theta_{\min} = 2.6°$
$h = -10 \rightarrow 11$
$k = -14 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.131$
$S = 0.93$
2164 reflections
172 parameters
4 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Extinction correction: SHELXL2016 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.009 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
S1	0.22221 (11)	1.00037 (9)	0.49942 (9)	0.0393 (4)
O1	0.4757 (3)	0.6793 (2)	0.5996 (2)	0.0379 (7)
O3	0.8582 (4)	0.3028 (3)	0.5520 (4)	0.0512 (9)
N1	0.3051 (4)	1.0873 (3)	0.2927 (3)	0.0374 (9)
N2	0.4373 (3)	0.9181 (3)	0.3421 (3)	0.0324 (8)
N3	0.4436 (3)	0.8375 (3)	0.4254 (3)	0.0297 (8)
N4	0.8772 (4)	0.5020 (3)	0.3833 (4)	0.0421 (9)
C1	0.1384 (4)	1.1242 (3)	0.4478 (4)	0.0387 (11)
H1	0.063837	1.163516	0.488936	0.046*
C2	0.1954 (4)	1.1567 (3)	0.3399 (4)	0.0393 (11)
H2	0.162460	1.222749	0.298950	0.047*
C3	0.3298 (4)	1.0010 (3)	0.3686 (3)	0.0280 (9)
C4	0.5502 (4)	0.7542 (3)	0.4088 (3)	0.0283 (10)
C5	0.5698 (4)	0.6708 (3)	0.5038 (3)	0.0285 (9)
C6	0.6797 (4)	0.5880 (3)	0.4951 (3)	0.0313 (10)
H6	0.692487	0.534501	0.558164	0.038*
C7	0.7720 (4)	0.5838 (3)	0.3925 (4)	0.0304 (10)
C8	0.7527 (4)	0.6669 (3)	0.2975 (3)	0.0364 (11)
H8	0.813766	0.665287	0.229219	0.044*
C9	0.6462 (4)	0.7479 (3)	0.3060 (3)	0.0347 (10)
H9	0.634945	0.801384	0.242785	0.042*
C10	0.5045 (4)	0.6082 (3)	0.7052 (3)	0.0448 (12)
H10A	0.495963	0.527893	0.682871	0.067*
H10B	0.434175	0.625874	0.768158	0.067*
H10C	0.602526	0.623236	0.735301	0.067*
H4A	0.927 (4)	0.496 (3)	0.316 (2)	0.056 (14)*
H4B	0.877 (5)	0.446 (3)	0.437 (3)	0.078 (18)*
H3A	0.853 (7)	0.340 (5)	0.618 (3)	0.15 (3)*
H3B	0.776 (3)	0.276 (4)	0.530 (4)	0.10 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0428 (7)	0.0371 (6)	0.0381 (7)	0.0005 (6)	0.0105 (5)	0.0034 (6)
O1	0.0423 (18)	0.0405 (16)	0.0312 (18)	0.0105 (14)	0.0138 (14)	0.0063 (14)

O3	0.053 (3)	0.0464 (19)	0.055 (2)	−0.0033 (18)	0.010 (2)	−0.0018 (18)
N1	0.043 (2)	0.036 (2)	0.033 (2)	0.0055 (18)	0.0006 (17)	0.0102 (18)
N2	0.030 (2)	0.0297 (19)	0.037 (2)	0.0021 (16)	0.0040 (16)	0.0022 (17)
N3	0.028 (2)	0.0277 (18)	0.034 (2)	−0.0010 (16)	0.0017 (15)	0.0006 (17)
N4	0.045 (2)	0.038 (2)	0.044 (3)	0.010 (2)	0.016 (2)	0.000 (2)
C1	0.036 (3)	0.034 (2)	0.046 (3)	0.007 (2)	0.003 (2)	−0.005 (2)
C2	0.045 (3)	0.028 (2)	0.045 (3)	0.006 (2)	−0.005 (2)	−0.001 (2)
C3	0.026 (2)	0.026 (2)	0.032 (2)	−0.005 (2)	0.0027 (18)	0.000 (2)
C4	0.029 (2)	0.031 (2)	0.026 (3)	−0.002 (2)	0.008 (2)	−0.004 (2)
C5	0.031 (2)	0.028 (2)	0.027 (2)	−0.006 (2)	0.0057 (19)	−0.001 (2)
C6	0.037 (3)	0.025 (2)	0.032 (3)	0.001 (2)	0.004 (2)	0.0031 (19)
C7	0.027 (2)	0.029 (2)	0.035 (3)	−0.003 (2)	0.006 (2)	−0.006 (2)
C8	0.038 (3)	0.040 (2)	0.031 (3)	−0.003 (2)	0.010 (2)	0.002 (2)
C9	0.041 (3)	0.033 (2)	0.030 (3)	−0.001 (2)	−0.002 (2)	0.0031 (19)
C10	0.049 (3)	0.055 (3)	0.031 (3)	0.006 (2)	0.011 (2)	0.009 (2)

Geometric parameters (Å, º)

S1—C1	1.710 (4)	C1—C2	1.340 (5)
S1—C3	1.731 (4)	C2—H2	0.9300
O1—C5	1.355 (4)	C4—C5	1.422 (5)
O1—C10	1.435 (4)	C4—C9	1.423 (5)
O3—H3A	0.842 (10)	C5—C6	1.382 (5)
O3—H3B	0.840 (10)	C6—H6	0.9300
N1—C2	1.377 (5)	C6—C7	1.401 (5)
N1—C3	1.312 (4)	C7—C8	1.420 (5)
N2—N3	1.299 (4)	C8—H8	0.9300
N2—C3	1.396 (4)	C8—C9	1.345 (5)
N3—C4	1.374 (4)	C9—H9	0.9300
N4—C7	1.344 (5)	C10—H10A	0.9600
N4—H4A	0.865 (10)	C10—H10B	0.9600
N4—H4B	0.868 (10)	C10—H10C	0.9600
C1—H1	0.9300		

C1—S1—C3	88.6 (2)	O1—C5—C4	115.8 (3)
C5—O1—C10	117.7 (3)	O1—C5—C6	123.9 (3)
H3A—O3—H3B	112 (5)	C6—C5—C4	120.2 (3)
C3—N1—C2	109.0 (3)	C5—C6—H6	119.6
N3—N2—C3	111.9 (3)	C5—C6—C7	120.8 (3)
N2—N3—C4	115.8 (3)	C7—C6—H6	119.6
C7—N4—H4A	120 (3)	N4—C7—C6	120.7 (4)
C7—N4—H4B	118 (3)	N4—C7—C8	120.2 (4)
H4A—N4—H4B	121 (4)	C6—C7—C8	119.1 (3)
S1—C1—H1	124.8	C7—C8—H8	119.9
C2—C1—S1	110.5 (3)	C9—C8—C7	120.2 (4)
C2—C1—H1	124.8	C9—C8—H8	119.9
N1—C2—H2	121.7	C4—C9—H9	119.0
C1—C2—N1	116.6 (3)	C8—C9—C4	122.1 (4)

C1—C2—H2	121.7	C8—C9—H9	119.0
N1—C3—S1	115.3 (3)	O1—C10—H10A	109.5
N1—C3—N2	120.4 (3)	O1—C10—H10B	109.5
N2—C3—S1	124.3 (3)	O1—C10—H10C	109.5
N3—C4—C5	117.5 (3)	H10A—C10—H10B	109.5
N3—C4—C9	124.9 (3)	H10A—C10—H10C	109.5
C5—C4—C9	117.6 (3)	H10B—C10—H10C	109.5

S1—C1—C2—N1	0.2 (5)	C3—S1—C1—C2	−0.2 (3)
O1—C5—C6—C7	179.3 (3)	C3—N1—C2—C1	−0.1 (5)
N2—N3—C4—C5	174.2 (3)	C3—N2—N3—C4	−177.8 (3)
N2—N3—C4—C9	−3.2 (5)	C4—C5—C6—C7	−0.8 (5)
N3—N2—C3—S1	2.3 (4)	C5—C4—C9—C8	−0.2 (5)
N3—N2—C3—N1	−178.1 (3)	C5—C6—C7—N4	−178.9 (3)
N3—C4—C5—O1	2.8 (5)	C5—C6—C7—C8	0.8 (5)
N3—C4—C5—C6	−177.0 (3)	C6—C7—C8—C9	−0.5 (6)
N3—C4—C9—C8	177.1 (3)	C7—C8—C9—C4	0.2 (6)
N4—C7—C8—C9	179.2 (4)	C9—C4—C5—O1	−179.6 (3)
C1—S1—C3—N1	0.2 (3)	C9—C4—C5—C6	0.5 (5)
C1—S1—C3—N2	179.7 (3)	C10—O1—C5—C4	−171.3 (3)
C2—N1—C3—S1	−0.1 (4)	C10—O1—C5—C6	8.6 (5)
C2—N1—C3—N2	−179.7 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···N2$^{\rm i}$	0.87 (1)	2.30 (2)	3.137 (5)	162 (3)
N4—H4*B*···O3	0.87 (1)	2.08 (1)	2.946 (5)	173 (4)
O3—H3*A*···N1$^{\rm ii}$	0.84 (1)	2.12 (2)	2.954 (5)	169 (6)
O3—H3*B*···N3$^{\rm iii}$	0.84 (1)	2.43 (3)	3.186 (5)	150 (5)
C9—H9···N4$^{\rm iv}$	0.93	2.69	3.587 (5)	162
C2—H2···N2$^{\rm v}$	0.93	2.87	3.798 (5)	176
C8—H8···O1$^{\rm vi}$	0.93	2.72	3.452 (5)	136
C1—H1···O3$^{\rm vii}$	0.93	2.56	3.463 (5)	165
C10—H10*C*···C3$^{\rm ii}$	0.96	2.89	3.655 (5)	137
C10—H10*A*···C6$^{\rm iii}$	0.96	2.83	3.551 (5)	132
C10—H10*A*···C7$^{\rm iii}$	0.96	2.86	3.502 (5)	125

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