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3a,11b-Dihydroxy-3a,11b-dihydro-1*H*-imidazo[4,5-*f*][1,10]phenanthroline-2(3*H*)-thione

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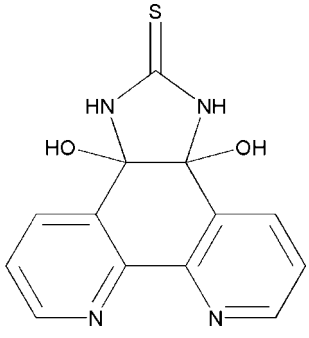
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.061; wR factor = 0.161; data-to-parameter ratio = 15.9.

The title compound, $C_{13}H_{10}N_4O_2S$, was prepared through a cyclization reaction of 1,10-phenanthroline-5,6-dione and thiourea. The dihedral angle between the pyridine rings is 8.22 (2)°. In the crystal, molecules are connected by N—H···O, O—H···N, N—H···S and O—H···S hydrogen bonds, forming a three-dimensional network.

Related literature

For related structures, see: Liu *et al.* (2008); Wang *et al.* (2011); Cong *et al.* (2009).



Experimental

Crystal data

$C_{13}H_{10}N_4O_2S$
M_r = 286.31
Monoclinic, $P2_1/c$
a = 11.259 (4) Å
b = 12.815 (4) Å
c = 8.565 (3) Å
β = 100.382 (5)°
V = 1215.6 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 293 K
0.18 × 0.14 × 0.12 mm

Data collection

Bruker SMART APEXII CCD detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.952, T_{max} = 0.968
9690 measured reflections
3035 independent reflections
1325 reflections with $I > 2\sigma(I)$
R_{int} = 0.107

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.161
S = 0.94
3035 reflections
191 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3*N*···O1^{i}	0.93 (4)	2.08 (4)	2.980 (4)	162 (3)
O2—H2*O*···S1^{ii}	0.82	2.49	3.276 (3)	160
N4—H4*N*···S1^{iii}	0.90 (4)	2.48 (4)	3.365 (4)	166 (3)
O1—H1*O*···N1^{iv}	0.82	2.33	2.930 (4)	130
O1—H1*O*···N2^{iv}	0.82	2.26	3.032 (4)	158

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

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2329).

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3a,11b-Dihydroxy-3a,11b-dihydro-1*H*-imidazo[4,5-*f*][1,10]phenanthroline-2(3*H*)-thione

Hua Wang, Peng Mei, Wen-Yi Chu, Zhi-Zhong Sun and Yan-Jun Hou

S1. Comment

Considerable interest have been paid to the reactions of various metal salts with multi-carboxylate ligands and 1,10-phenanthroline-5,6-dione and the influence of the reaction pH on the structure of the resultant complexes (Liu *et al.*, 2008; Wang *et al.*, 2011; Cong *et al.*, 2009). We prepare 3a,11*b*-dihydroxy-3,3a-dihydro-1*H*-imidazo [4,5-*f*] [1,10]phenanthroline-2(11bH)-thione as a precursor of 1,10-phenanthroline-5,6-dione for precise control of the reaction pH.

As shown in Fig. 1, The dihedral angle between the pyridine rings (C1-C5/N1) (C6-C7/C10-C12/N2) is 8.22 (2)°. The neighboring molecules are connected by N-H···O, O-H···N, N-H···Si and O-H···Si hydrogen bonds to form an infinite three-dimensional network (Table 1. and Fig. 2).

S2. Experimental

40 ml 98% H_2SO_4 and 20 ml 69% HNO_3 were mixed in a flask and cooled to 273 K. Then A mixture of 1,10-phenanthroline (4 g, 22.2 mmol) and KBr (4 g, 33.6 mmol) was slowly added while keeping the temperature below 279 K. The resulting solution was refluxed for 4 hr and finally cooled to room temperature. The contents of the flask were poured onto 100 g crushed ice and neutralized with 40% sodium hydroxide solution. The yellow precipitate of 1,10-phenanthroline-5,6-dione was collected by filtration and washed with water. The filtrate was extracted with EtOAc, the organic phase was dried over magnesium sulfate and the solvent was evaporated off under vacuum. All of the crude product was then recrystallized from 100 mL EtOH to give 2.6 g of 1,10-phenanthroline-5,6-dione as yellow needles. The product of the reaction mentioned above was reacted with thiourea (13 g, 217 mmol) in 50 ml methanol for 5 hr under reflux. After cooling, the precipitated product was separated and recrystallized from EtOH to give 2.1 g (63%) of 1,11*b*-dihydro-3a,11*b*-dihydroxy-1*H*-imidazo[4,5-*f*][1,10] phenanthroline-2(11bH)-thione as white powder. Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from methanol at room temperature in a total yield of 24%. Anal. Calcd. for $C_{13}H_{10}N_4O_2S$: C, 54.54; H, 3.52; N, 19.57. Found(%):*C*, 54.60; H, 3.58; N, 19.66. IR(KBr) ^{1}H NMR (400 MHz, DMSO-d^6): 9.47 (s, 2H), 8.71 (dd, *J* = 4.6, 1.7 Hz, 2H), 8.23 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.53 (dd, *J* = 7.9, 4.6 Hz, 2H), 6.83 (s, 2H), 3.31 (s, 2H).

S3. Refinement

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms with C—H = 0.93 Å (aromatic C), and with U_{iso}(H) = 1.2Ueq(C). H atoms bound to O atoms were placed in calculated positions and treated as riding on their parent atoms, with O—H = 0.82 Å and with U_{iso}(H) = 1.5Ueq(O). H atoms bound to N atoms were located in the difference-Fourier map and refined isotropically.

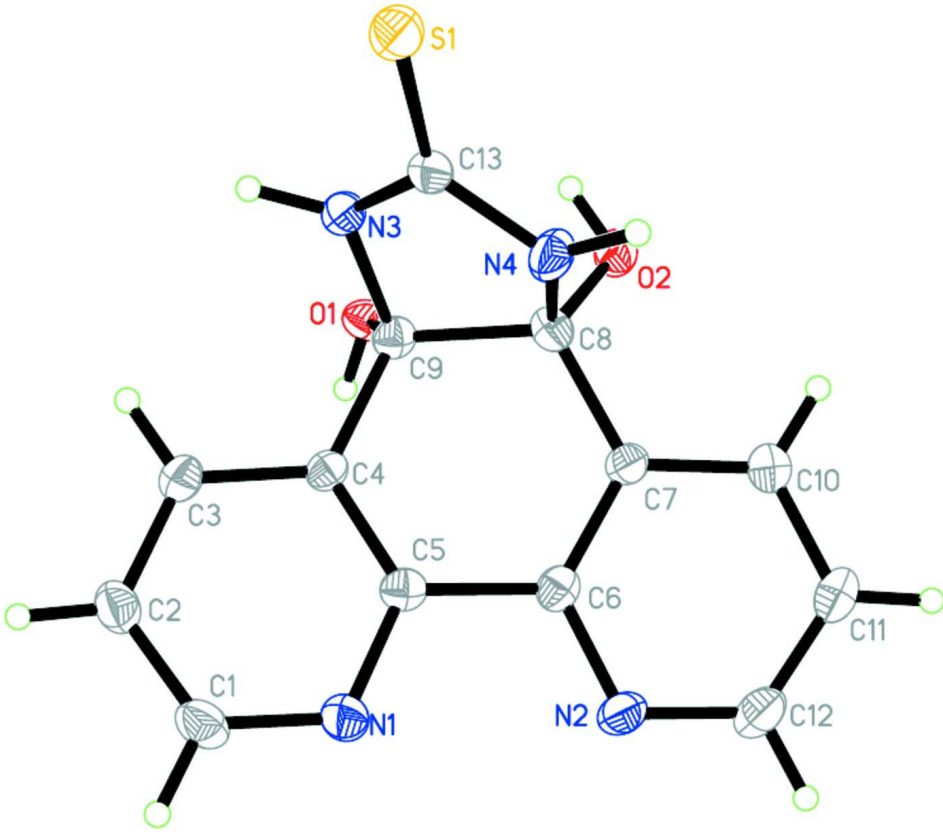

Figure 1

The molecular structure of the title compound I, with displacement ellipsoids drawn at the 50% probability level.

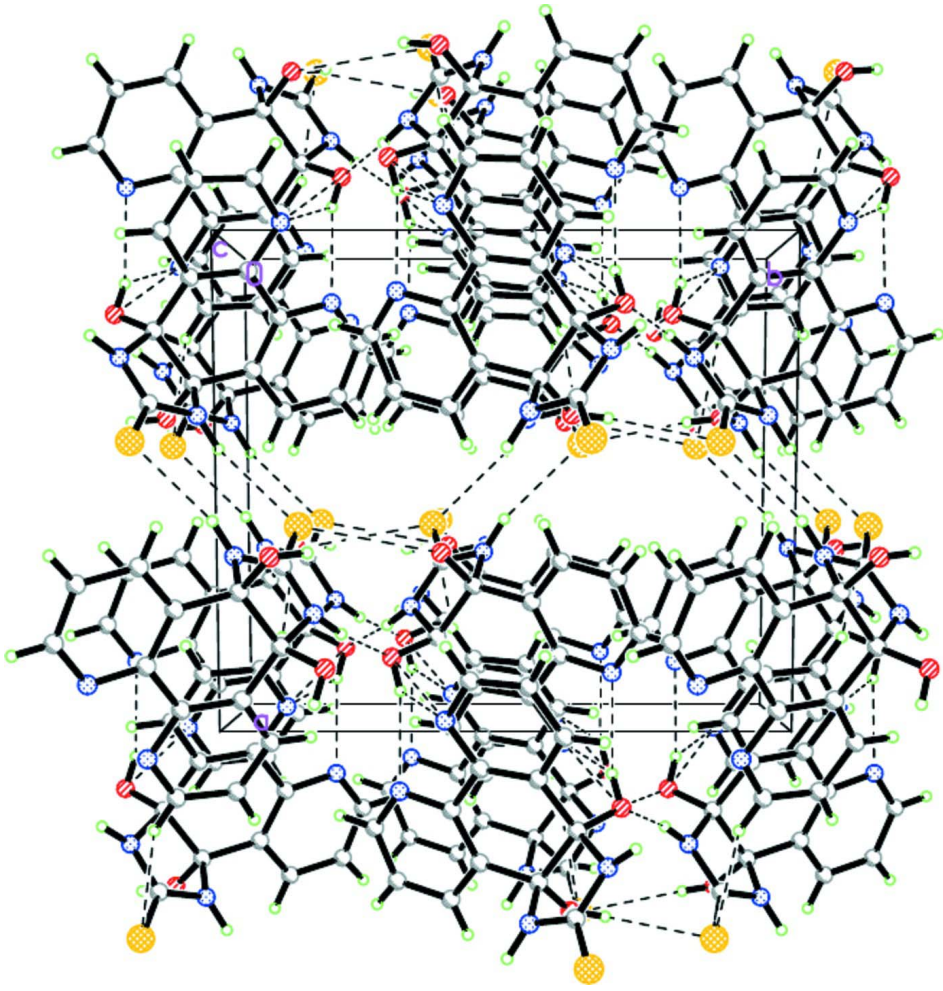

Figure 2

Part of the packing of the title compound, viewed down the c-axis. Dashed lines indicate hydrogen bonds.

2,6-dihydroxy-11,14-diazatetracyclo[11.4.0.0^{2,6}.0^{7,12}]heptadeca- 1(13),7(12),8,10,14,16-hexaene-4-thione

Crystal data

$C_{13}H_{10}N_4O_2S$
M_r = 286.31
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.259 (4) Å
b = 12.815 (4) Å
c = 8.565 (3) Å
β = 100.382 (5)°
V = 1215.6 (7) Å^3
Z = 4
$F(000)$ = 592
D_x = 1.564 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 512 reflections
θ = 2.4–19.3°
μ = 0.27 mm^{-1}
T = 293 K
Block, colorless
0.18 × 0.14 × 0.12 mm

Data collection

Bruker SMART APEXII CCD detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.952, T_{max} = 0.968

9690 measured reflections
3035 independent reflections
1325 reflections with $I > 2\sigma(I)$
$R_{int} = 0.107$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.4°$
$h = -14 \rightarrow 15$
$k = -17 \rightarrow 10$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.161$
$S = 0.94$
3035 reflections
191 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *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	0.41534 (9)	0.63611 (8)	0.62203 (12)	0.0424 (3)
O1	0.1477 (2)	0.70072 (19)	0.1051 (3)	0.0370 (7)
H1O	0.0819	0.6850	0.0525	0.055*
O2	0.3623 (2)	0.6130 (2)	0.0847 (3)	0.0452 (7)
H2O	0.3702	0.6733	0.1168	0.068*
N1	−0.0346 (3)	0.3969 (2)	0.1943 (4)	0.0387 (8)
N2	0.1205 (3)	0.3145 (2)	0.0259 (4)	0.0378 (8)
N3	0.2442 (3)	0.6720 (3)	0.3648 (4)	0.0351 (8)
N4	0.3596 (3)	0.5401 (3)	0.3380 (4)	0.0412 (9)
C5	0.0627 (3)	0.4558 (3)	0.1826 (4)	0.0301 (8)
C9	0.1854 (3)	0.6227 (3)	0.2162 (4)	0.0302 (8)
C4	0.0789 (3)	0.5553 (3)	0.2417 (4)	0.0269 (8)
C7	0.2619 (3)	0.4546 (3)	0.0946 (4)	0.0310 (9)
C6	0.1524 (3)	0.4060 (3)	0.0979 (4)	0.0305 (9)
C8	0.2935 (3)	0.5569 (3)	0.1767 (4)	0.0337 (9)
C3	−0.0097 (3)	0.5981 (3)	0.3175 (4)	0.0357 (9)
H3	−0.0016	0.6652	0.3591	0.043*
C13	0.3384 (3)	0.6167 (3)	0.4379 (4)	0.0326 (9)
C10	0.3448 (3)	0.4034 (3)	0.0190 (5)	0.0447 (11)
H10	0.4196	0.4331	0.0152	0.054*

C2	−0.1093 (3)	0.5385 (3)	0.3291 (4)	0.0405 (10)
H2A	−0.1703	0.5651	0.3777	0.049*
C1	−0.1175 (3)	0.4392 (3)	0.2681 (5)	0.0428 (10)
H1A	−0.1846	0.3992	0.2788	0.051*
C12	0.2019 (4)	0.2682 (3)	−0.0466 (5)	0.0458 (11)
H12	0.1808	0.2051	−0.0978	0.055*
C11	0.3136 (4)	0.3072 (3)	−0.0505 (5)	0.0503 (11)
H11	0.3680	0.2701	−0.0988	0.060*
H4N	0.428 (3)	0.503 (3)	0.356 (4)	0.043 (11)*
H3N	0.203 (3)	0.717 (3)	0.421 (4)	0.047 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0378 (5)	0.0448 (7)	0.0423 (6)	0.0060 (5)	0.0008 (4)	−0.0064 (5)
O1	0.0349 (14)	0.0285 (16)	0.0458 (16)	−0.0037 (12)	0.0027 (12)	0.0078 (13)
O2	0.0439 (16)	0.0358 (17)	0.0624 (19)	−0.0067 (14)	0.0269 (14)	−0.0091 (14)
N1	0.0371 (18)	0.032 (2)	0.049 (2)	−0.0024 (15)	0.0144 (16)	0.0008 (15)
N2	0.0457 (19)	0.0283 (19)	0.0409 (19)	−0.0063 (15)	0.0117 (15)	−0.0059 (15)
N3	0.0282 (17)	0.035 (2)	0.0402 (19)	0.0029 (15)	0.0013 (14)	−0.0086 (16)
N4	0.0374 (19)	0.039 (2)	0.043 (2)	0.0132 (17)	−0.0035 (16)	−0.0121 (17)
C5	0.0320 (19)	0.027 (2)	0.0303 (19)	−0.0002 (17)	0.0027 (15)	0.0040 (17)
C9	0.0324 (19)	0.025 (2)	0.0322 (19)	0.0015 (16)	0.0043 (16)	0.0023 (17)
C4	0.0304 (19)	0.022 (2)	0.0281 (19)	0.0016 (16)	0.0040 (15)	0.0004 (16)
C7	0.031 (2)	0.028 (2)	0.033 (2)	−0.0005 (16)	0.0037 (16)	−0.0034 (17)
C6	0.034 (2)	0.029 (2)	0.0282 (19)	0.0040 (17)	0.0030 (16)	0.0005 (16)
C8	0.0274 (19)	0.036 (2)	0.038 (2)	0.0007 (17)	0.0055 (16)	−0.0004 (19)
C3	0.037 (2)	0.029 (2)	0.042 (2)	0.0031 (17)	0.0081 (17)	−0.0049 (18)
C13	0.0277 (19)	0.029 (2)	0.041 (2)	−0.0016 (16)	0.0061 (17)	−0.0037 (18)
C10	0.037 (2)	0.044 (3)	0.056 (3)	−0.0013 (19)	0.016 (2)	−0.011 (2)
C2	0.032 (2)	0.040 (3)	0.051 (3)	0.0043 (19)	0.0135 (18)	0.002 (2)
C1	0.038 (2)	0.039 (3)	0.054 (3)	−0.0058 (19)	0.0148 (19)	0.009 (2)
C12	0.061 (3)	0.032 (3)	0.047 (2)	−0.001 (2)	0.016 (2)	−0.008 (2)
C11	0.053 (3)	0.040 (3)	0.062 (3)	0.005 (2)	0.019 (2)	−0.014 (2)

Geometric parameters (Å, º)

S1—C13	1.676 (4)	C9—C4	1.524 (5)
O1—C9	1.393 (4)	C9—C8	1.568 (5)
O1—H1O	0.8200	C4—C3	1.397 (5)
O2—C8	1.399 (4)	C7—C6	1.387 (5)
O2—H2O	0.8200	C7—C10	1.392 (5)
N1—C1	1.333 (4)	C7—C8	1.499 (5)
N1—C5	1.349 (4)	C3—C2	1.375 (5)
N2—C12	1.335 (5)	C3—H3	0.9300
N2—C6	1.343 (4)	C10—C11	1.386 (5)
N3—C13	1.334 (4)	C10—H10	0.9300
N3—C9	1.467 (4)	C2—C1	1.372 (5)

N3—H3N	0.93 (4)	C2—H2A	0.9300
N4—C13	1.351 (4)	C1—H1A	0.9300
N4—C8	1.463 (5)	C12—C11	1.360 (5)
N4—H4N	0.90 (4)	C12—H12	0.9300
C5—C4	1.372 (5)	C11—H11	0.9300
C5—C6	1.489 (5)		

C9—O1—H1O	109.5	O2—C8—N4	111.6 (3)
C8—O2—H2O	109.5	O2—C8—C7	107.0 (3)
C1—N1—C5	117.1 (3)	N4—C8—C7	110.6 (3)
C12—N2—C6	116.9 (3)	O2—C8—C9	112.1 (3)
C13—N3—C9	112.0 (3)	N4—C8—C9	99.1 (3)
C13—N3—H3N	121 (2)	C7—C8—C9	116.4 (3)
C9—N3—H3N	122 (2)	C2—C3—C4	118.4 (3)
C13—N4—C8	111.9 (3)	C2—C3—H3	120.8
C13—N4—H4N	122 (2)	C4—C3—H3	120.8
C8—N4—H4N	121 (2)	N3—C13—N4	107.8 (3)
N1—C5—C4	123.3 (3)	N3—C13—S1	126.6 (3)
N1—C5—C6	115.3 (3)	N4—C13—S1	125.7 (3)
C4—C5—C6	121.4 (3)	C11—C10—C7	118.7 (4)
O1—C9—N3	108.6 (3)	C11—C10—H10	120.7
O1—C9—C4	110.7 (3)	C7—C10—H10	120.7
N3—C9—C4	111.3 (3)	C1—C2—C3	119.2 (4)
O1—C9—C8	113.0 (3)	C1—C2—H2A	120.4
N3—C9—C8	99.9 (3)	C3—C2—H2A	120.4
C4—C9—C8	112.8 (3)	N1—C1—C2	123.5 (4)
C5—C4—C3	118.5 (3)	N1—C1—H1A	118.2
C5—C4—C9	122.0 (3)	C2—C1—H1A	118.2
C3—C4—C9	119.4 (3)	N2—C12—C11	124.3 (4)
C6—C7—C10	118.1 (3)	N2—C12—H12	117.8
C6—C7—C8	121.3 (3)	C11—C12—H12	117.8
C10—C7—C8	120.5 (3)	C12—C11—C10	118.7 (4)
N2—C6—C7	123.2 (3)	C12—C11—H11	120.6
N2—C6—C5	116.7 (3)	C10—C11—H11	120.6
C7—C6—C5	120.1 (3)		

C1—N1—C5—C4	−0.3 (5)	C10—C7—C8—O2	37.4 (4)
C1—N1—C5—C6	−179.4 (3)	C6—C7—C8—N4	92.5 (4)
C13—N3—C9—O1	−142.9 (3)	C10—C7—C8—N4	−84.4 (4)
C13—N3—C9—C4	95.0 (3)	C6—C7—C8—C9	−19.5 (5)
C13—N3—C9—C8	−24.4 (4)	C10—C7—C8—C9	163.6 (3)
N1—C5—C4—C3	−0.1 (5)	O1—C9—C8—O2	25.6 (4)
C6—C5—C4—C3	178.9 (3)	N3—C9—C8—O2	−89.6 (3)
N1—C5—C4—C9	−175.5 (3)	C4—C9—C8—O2	152.1 (3)
C6—C5—C4—C9	3.5 (5)	O1—C9—C8—N4	143.4 (3)
O1—C9—C4—C5	106.4 (4)	N3—C9—C8—N4	28.3 (3)
N3—C9—C4—C5	−132.8 (3)	C4—C9—C8—N4	−90.0 (3)
C8—C9—C4—C5	−21.4 (4)	O1—C9—C8—C7	−98.1 (4)

O1—C9—C4—C3	−69.0 (4)	N3—C9—C8—C7	146.8 (3)
N3—C9—C4—C3	51.9 (4)	C4—C9—C8—C7	28.5 (4)
C8—C9—C4—C3	163.2 (3)	C5—C4—C3—C2	−0.1 (5)
C12—N2—C6—C7	2.5 (5)	C9—C4—C3—C2	175.4 (3)
C12—N2—C6—C5	−178.3 (3)	C9—N3—C13—N4	8.9 (4)
C10—C7—C6—N2	−3.1 (5)	C9—N3—C13—S1	−169.8 (3)
C8—C7—C6—N2	179.9 (3)	C8—N4—C13—N3	12.8 (4)
C10—C7—C6—C5	177.7 (3)	C8—N4—C13—S1	−168.6 (3)
C8—C7—C6—C5	0.7 (5)	C6—C7—C10—C11	0.7 (6)
N1—C5—C6—N2	8.0 (5)	C8—C7—C10—C11	177.7 (4)
C4—C5—C6—N2	−171.1 (3)	C4—C3—C2—C1	0.8 (5)
N1—C5—C6—C7	−172.7 (3)	C5—N1—C1—C2	1.1 (6)
C4—C5—C6—C7	8.1 (5)	C3—C2—C1—N1	−1.3 (6)
C13—N4—C8—O2	91.6 (4)	C6—N2—C12—C11	0.6 (6)
C13—N4—C8—C7	−149.3 (3)	N2—C12—C11—C10	−2.8 (6)
C13—N4—C8—C9	−26.5 (4)	C7—C10—C11—C12	2.1 (6)
C6—C7—C8—O2	−145.7 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···O1^{i}	0.93 (4)	2.08 (4)	2.980 (4)	162 (3)
O2—H2*O*···S1^{ii}	0.82	2.49	3.276 (3)	160
N4—H4*N*···S1^{iii}	0.90 (4)	2.48 (4)	3.365 (4)	166 (3)
O1—H1*O*···N1^{iv}	0.82	2.33	2.930 (4)	130
O1—H1*O*···N2^{iv}	0.82	2.26	3.032 (4)	158

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