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(4*S*,5*S*)-2,2-Dimethyl-4,5-bis(3-methyl-2-thioxo-2,3-dihydro-1*H*-imidazol-1-ylmethyl)-1,3-dioxolane

Colin Marshall and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

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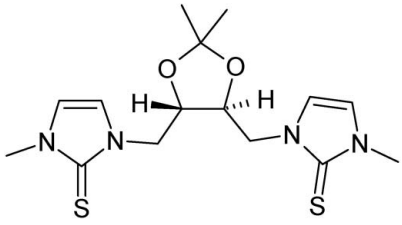
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.105; data-to-parameter ratio = 15.7.

In the chiral title compound, $C_{15}H_{22}N_4O_2S_2$, there are two molecules in the asymmetric unit with distinctly different conformations, as quantified by torsion angles. The dihedral angles between the thioimidazole rings are 81.59 (5) and 67.04 (4)°. One molecule exhibits local twofold rotation symmetry, while the other displays no local symmetry. Intermolecular C—H···O and C—H···S interactions are observed.

Related literature

For background, see: Marshall *et al.* (2004); Williamson *et al.* (2006).



Experimental

Crystal data

$C_{15}H_{22}N_4O_2S_2$
M_r = 354.49
Monoclinic, $P2_1$
a = 10.462 (2) Å
b = 8.6043 (17) Å
c = 20.249 (4) Å
β = 103.19 (3)°
V = 1774.7 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 123 (2) K
0.18 × 0.16 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
13494 measured reflections
6651 independent reflections
6047 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.105
S = 1.02
6651 reflections
423 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Absolute structure: Flack (1983), 2303 Friedel pairs
Flack parameter: 0.06 (5)

Table 1
Selected torsion angles (°).

C2—N2—C5—C6	109.2 (2)	C21—C20—N6—C17	−75.4 (3)
C7—C11—N3—C12	104.4 (2)	C25—C26—N7—C27	−72.9 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···S4	0.95	2.86	3.797 (2)	170
C5—H5*B*···O4	0.99	2.50	3.470 (3)	166
C11—H11*B*···O3^{i}	0.99	2.58	3.500 (3)	154
C13—H13···S3^{i}	0.95	2.83	3.715 (2)	156
C28—H28···S1^{ii}	0.95	2.87	3.749 (2)	155

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997), *HKL SCALEPACK* and *SORTAV* (Blessing 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2249).

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(4*S*,5*S*)-2,2-Dimethyl-4,5-bis(3-methyl-2-thioxo-2,3-dihydro-1*H*-imidazol-1-ylmethyl)-1,3-dioxolane

Colin Marshall and William T. A. Harrison

S1. Comment

As part of our ongoing investigations of chiral, C_2-symmetric catalysts (Marshall *et al.*, 2004), the title compound, $C_{15}H_{22}N_4O_2S_2$, an intermediate in such materials, has been synthesized and structurally characterized.

There are two molecules in the asymmetric unit (Figs. 1 & 2), both of which show the same, expected, atomic chirality: atoms C6, C7, C21 and C25 all have an *S* configuration. However, their conformations are distinctly different, as indicated by a comparison of C—C—N—C side-chain torsion angles for the two molecules (Table 1). The dihedral angles between the thio-imidazole rings are 81.59 (5)° and 67.04 (4)°, for the C1 and C16-containing molecules, respectively. This means that the C1 molecule shows no local symmetry, whereas the C16 molecule possesses local C_2 symmetry about the axis running through C22 and the mid-point of the C21—C25 bond. The thio-imidazole rings of both molecules display typical geometrical parameters, with the C—S bond lengths significantly longer than that of an isolated C?S double bond (~1.60 Å), which can be correlated with the contribution of resonance structures involving the lone pair electrons of the adjacent N atoms (Williamson *et al.*, 2006). Otherwise, the geometries of the two molecules may be regarded as normal.

The crystal packing exhibits intermolecular C—H···O and C—H···S contacts (Table 2), giving pseudo (100) sheets of molecules in the crystal (Fig. 3).

S2. Experimental

A mixture of (4*S*,5*S*)-4,5-bis(1-methylimidazolium-3-methyl)-2,2-dimethyl-1,3- dioxolane dibromide (0.67 g, 1.48 mmol), sulfur (0.14 g, 4.45 mmol), methanol (17 ml), pyridine (1.5 ml) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1 g, 6.53 mmol) was heated at 338 K for 18 h. Once cooled to room temperature, water (50 ml) was added, and the mixture was extracted with chloroform (3 × 20 ml). The combined extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure to leave a brown residue. The crude product was purified by column chromatography (SiO_2, ethyl acetate, loaded as a dichloromethane solution) to give the dithione (0.37 g, 70%) as a colourless solid which was recrystallized from ethanol to give colourless blocks (m.p. 442 K).

S3. Refinement

The H atoms were placed in calculated positions (C—H = 0.95–1.00 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The methyl groups were allowed to rotate about their local threefold axes to give the best fit to the electron density.

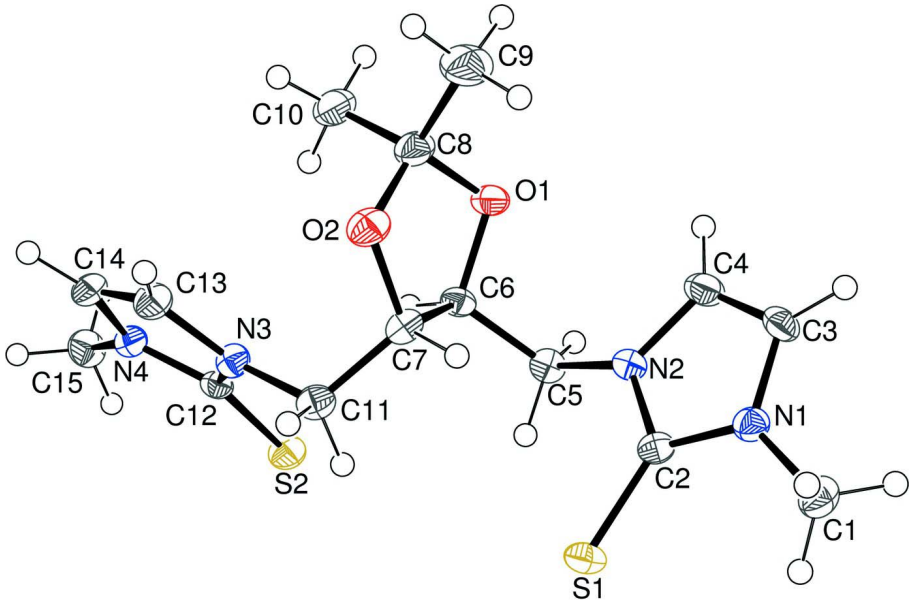

Figure 1

View of the molecular structures of C1 molecule showing 50% displacement ellipsoids. The H atoms are drawn as spheres of arbitrary radius.

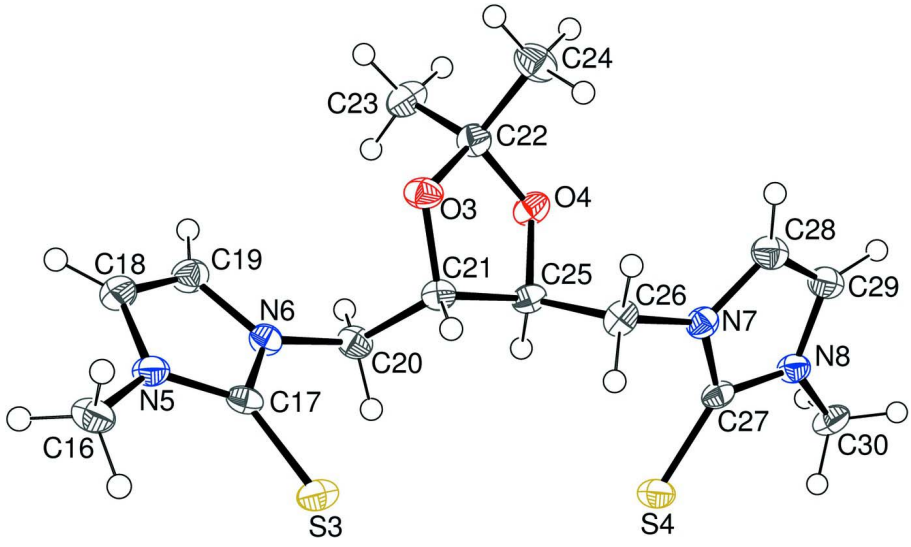

Figure 2

View of the molecular structures of C16 molecule of showing 50% displacement ellipsoids. The H atoms are drawn as spheres of arbitrary radius.

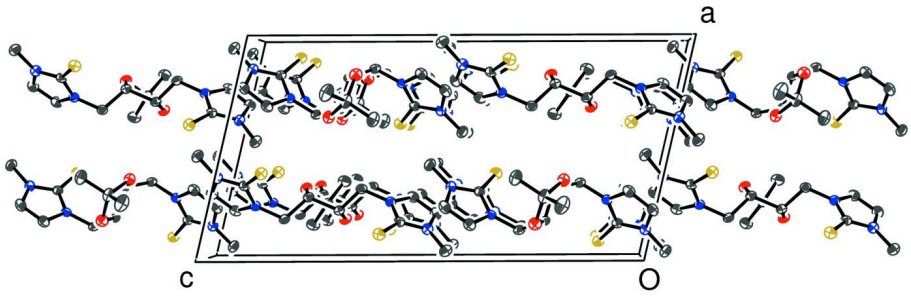

Figure 3

Unit-cell packing with H atoms omitted for clarity.

(4*S*,5*S*)-2,2-Dimethyl-4,5-bis(3-methyl-2-thioxo-2,3-dihydro-1*H*-\ imidazol-1-ylmethyl)-1,3-dioxolane

Crystal data

$C_{15}H_{22}N_4O_2S_2$
$M_r = 354.49$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 10.462\ (2)$ Å
$b = 8.6043\ (17)$ Å
$c = 20.249\ (4)$ Å
$\beta = 103.19\ (3)°$
$V = 1774.7\ (6)$ Å^3
$Z = 4$
$F(000) = 752$
$D_x = 1.327$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9330 reflections
$\theta = 2.9–27.5°$
$\mu = 0.31$ mm^{-1}
$T = 123$ K
Block, colourless
0.18 × 0.16 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
13494 measured reflections
6651 independent reflections
6047 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -13\rightarrow13$
$k = -10\rightarrow11$
$l = -24\rightarrow26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.105$
$S = 1.03$
6651 reflections
423 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Absolute structure: Flack (1983), with 2303 Friedel pairs
Absolute structure parameter: 0.06 (5)

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	0.08821 (5)	1.00232 (6)	0.11169 (3)	0.02403 (14)
S2	0.38790 (5)	0.99782 (6)	0.37475 (3)	0.02505 (14)
O1	0.36101 (14)	0.55181 (18)	0.22141 (7)	0.0253 (4)
O2	0.17411 (15)	0.52668 (19)	0.26106 (8)	0.0277 (4)
N1	0.14301 (16)	0.8059 (2)	0.01597 (9)	0.0217 (4)
N2	0.27338 (16)	0.7767 (2)	0.11545 (8)	0.0194 (4)
N3	0.20925 (15)	0.7609 (2)	0.36360 (8)	0.0200 (4)
N4	0.33053 (16)	0.7879 (2)	0.46509 (9)	0.0218 (4)
C1	0.0455 (2)	0.8683 (3)	−0.04072 (10)	0.0272 (5)
H1A	0.0778	0.8597	−0.0823	0.041*
H1B	0.0293	0.9778	−0.0321	0.041*
H1C	−0.0365	0.8095	−0.0459	0.041*
C2	0.16862 (19)	0.8611 (2)	0.08012 (10)	0.0186 (4)
C3	0.2295 (2)	0.6852 (3)	0.01103 (11)	0.0238 (5)
H3	0.2311	0.6262	−0.0284	0.029*
C4	0.3105 (2)	0.6679 (3)	0.07280 (11)	0.0264 (5)
H4	0.3800	0.5948	0.0849	0.032*
C5	0.34737 (19)	0.8156 (3)	0.18340 (10)	0.0211 (5)
H5A	0.3228	0.9217	0.1948	0.025*
H5B	0.4421	0.8166	0.1836	0.025*
C6	0.32494 (19)	0.7044 (3)	0.23752 (10)	0.0196 (4)
H6	0.3800	0.7364	0.2826	0.024*
C7	0.18308 (19)	0.6860 (3)	0.24267 (10)	0.0205 (5)
H7	0.1242	0.7039	0.1969	0.025*
C8	0.2924 (2)	0.4465 (3)	0.25547 (11)	0.0282 (5)
C9	0.2571 (3)	0.3041 (3)	0.21235 (13)	0.0435 (6)
H9A	0.2092	0.2313	0.2350	0.065*
H9B	0.3374	0.2544	0.2055	0.065*
H9C	0.2017	0.3337	0.1683	0.065*
C10	0.3730 (2)	0.4109 (3)	0.32569 (11)	0.0332 (5)
H10A	0.3213	0.3467	0.3500	0.050*
H10B	0.3973	0.5083	0.3505	0.050*
H10C	0.4526	0.3547	0.3222	0.050*
C11	0.1421 (2)	0.7934 (3)	0.29347 (10)	0.0226 (5)
H11A	0.1605	0.9021	0.2825	0.027*

H11B	0.0462	0.7836	0.2890	0.027*
C12	0.30930 (19)	0.8479 (2)	0.40141 (10)	0.0189 (4)
C13	0.1689 (2)	0.6502 (3)	0.40400 (11)	0.0257 (5)
H13	0.1007	0.5764	0.3898	0.031*
C14	0.2442 (2)	0.6661 (3)	0.46713 (12)	0.0266 (5)
H14	0.2393	0.6057	0.5057	0.032*
C15	0.4273 (2)	0.8457 (3)	0.52392 (11)	0.0284 (5)
H15A	0.3898	0.8430	0.5640	0.043*
H15B	0.4511	0.9528	0.5155	0.043*
H15C	0.5058	0.7800	0.5317	0.043*
S3	0.87712 (5)	0.39985 (7)	0.39791 (3)	0.02640 (14)
S4	0.60998 (5)	0.40522 (7)	0.10499 (3)	0.02620 (14)
O3	0.81983 (14)	0.88017 (18)	0.30275 (7)	0.0240 (3)
O4	0.67952 (14)	0.88153 (18)	0.19686 (7)	0.0240 (3)
N5	0.86003 (17)	0.6053 (2)	0.49936 (9)	0.0223 (4)
N6	0.73945 (16)	0.6687 (2)	0.40117 (9)	0.0205 (4)
N7	0.75542 (16)	0.6655 (2)	0.09850 (9)	0.0208 (4)
N8	0.63092 (17)	0.6032 (2)	0.00141 (9)	0.0217 (4)
C16	0.9544 (2)	0.5263 (3)	0.55250 (11)	0.0275 (5)
H16A	0.9245	0.5306	0.5949	0.041*
H16B	1.0400	0.5774	0.5588	0.041*
H16C	0.9622	0.4176	0.5396	0.041*
C17	0.8268 (2)	0.5597 (3)	0.43322 (11)	0.0203 (5)
C18	0.7935 (2)	0.7417 (3)	0.50761 (12)	0.0263 (5)
H18	0.7998	0.7971	0.5488	0.032*
C19	0.7189 (2)	0.7803 (3)	0.44683 (11)	0.0253 (5)
H19	0.6625	0.8679	0.4370	0.030*
C20	0.68137 (19)	0.6688 (3)	0.32881 (10)	0.0229 (5)
H20A	0.6037	0.7379	0.3195	0.027*
H20B	0.6514	0.5624	0.3143	0.027*
C21	0.77773 (19)	0.7232 (3)	0.28799 (10)	0.0204 (4)
H21	0.8562	0.6534	0.2977	0.024*
C22	0.74960 (16)	0.9822 (3)	0.25008 (9)	0.0227 (5)
C23	0.6504 (2)	1.0807 (3)	0.27491 (13)	0.0309 (6)
H23A	0.6958	1.1457	0.3128	0.046*
H23B	0.5874	1.0130	0.2901	0.046*
H23C	0.6036	1.1471	0.2379	0.046*
C24	0.8486 (2)	1.0810 (3)	0.22528 (13)	0.0310 (6)
H24A	0.8983	1.1437	0.2629	0.046*
H24B	0.8027	1.1497	0.1889	0.046*
H24C	0.9090	1.0136	0.2079	0.046*
C25	0.71825 (19)	0.7234 (3)	0.21188 (10)	0.0204 (4)
H25	0.6386	0.6554	0.2020	0.024*
C26	0.8143 (2)	0.6675 (3)	0.17078 (10)	0.0224 (5)
H26A	0.8919	0.7367	0.1795	0.027*
H26B	0.8445	0.5614	0.1857	0.027*
C27	0.66460 (19)	0.5591 (3)	0.06785 (11)	0.0202 (4)
C28	0.7787 (2)	0.7730 (3)	0.05187 (12)	0.0256 (5)

H28	0.8382	0.8580	0.0608	0.031*
C29	0.7014 (2)	0.7348 (3)	−0.00841 (12)	0.0258 (5)
H29	0.6958	0.7879	−0.0501	0.031*
C30	0.5324 (2)	0.5260 (3)	−0.05076 (10)	0.0264 (5)
H30A	0.5588	0.5308	−0.0941	0.040*
H30B	0.4476	0.5782	−0.0552	0.040*
H30C	0.5245	0.4171	−0.0381	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0243 (3)	0.0177 (3)	0.0285 (3)	0.0034 (3)	0.0029 (2)	−0.0032 (3)
S2	0.0272 (3)	0.0182 (3)	0.0301 (3)	−0.0057 (3)	0.0073 (2)	0.0003 (3)
O1	0.0306 (8)	0.0188 (9)	0.0259 (8)	0.0057 (6)	0.0048 (6)	0.0006 (6)
O2	0.0298 (8)	0.0205 (9)	0.0319 (8)	−0.0071 (7)	0.0054 (7)	0.0011 (7)
N1	0.0245 (9)	0.0183 (9)	0.0218 (9)	−0.0009 (8)	0.0039 (7)	0.0002 (8)
N2	0.0185 (8)	0.0178 (10)	0.0219 (9)	0.0010 (7)	0.0048 (7)	−0.0012 (8)
N3	0.0166 (8)	0.0209 (10)	0.0230 (9)	−0.0018 (7)	0.0057 (7)	0.0021 (8)
N4	0.0252 (9)	0.0190 (10)	0.0214 (9)	0.0005 (8)	0.0056 (7)	0.0012 (8)
C1	0.0301 (12)	0.0260 (13)	0.0222 (11)	−0.0031 (10)	−0.0008 (9)	0.0006 (9)
C2	0.0182 (10)	0.0139 (11)	0.0234 (10)	−0.0045 (8)	0.0039 (8)	0.0005 (8)
C3	0.0295 (11)	0.0179 (11)	0.0266 (11)	−0.0019 (9)	0.0118 (9)	−0.0061 (9)
C4	0.0279 (11)	0.0212 (12)	0.0321 (12)	0.0046 (10)	0.0111 (10)	−0.0013 (10)
C5	0.0173 (10)	0.0219 (11)	0.0229 (10)	−0.0015 (9)	0.0020 (8)	−0.0021 (9)
C6	0.0169 (10)	0.0185 (11)	0.0226 (10)	0.0039 (8)	0.0028 (8)	−0.0008 (9)
C7	0.0167 (10)	0.0205 (12)	0.0225 (10)	−0.0029 (9)	0.0007 (8)	0.0036 (9)
C8	0.0391 (13)	0.0186 (12)	0.0249 (11)	−0.0020 (11)	0.0031 (9)	−0.0001 (9)
C9	0.0619 (17)	0.0253 (14)	0.0379 (14)	−0.0018 (13)	0.0005 (12)	−0.0070 (12)
C10	0.0450 (13)	0.0236 (12)	0.0285 (11)	0.0000 (11)	0.0034 (10)	0.0041 (10)
C11	0.0170 (10)	0.0239 (12)	0.0253 (11)	0.0021 (9)	0.0014 (8)	0.0023 (10)
C12	0.0181 (10)	0.0164 (11)	0.0228 (10)	0.0033 (8)	0.0059 (8)	−0.0005 (9)
C13	0.0278 (11)	0.0199 (12)	0.0310 (12)	−0.0052 (9)	0.0098 (9)	0.0009 (10)
C14	0.0339 (12)	0.0181 (12)	0.0310 (12)	−0.0002 (10)	0.0142 (10)	0.0059 (10)
C15	0.0286 (12)	0.0314 (14)	0.0229 (11)	0.0019 (10)	0.0010 (9)	−0.0035 (10)
S3	0.0292 (3)	0.0172 (3)	0.0332 (3)	−0.0004 (3)	0.0078 (2)	−0.0030 (2)
S4	0.0305 (3)	0.0180 (3)	0.0292 (3)	−0.0008 (3)	0.0048 (2)	0.0018 (2)
O3	0.0226 (8)	0.0207 (9)	0.0260 (8)	−0.0050 (7)	−0.0001 (6)	0.0003 (7)
O4	0.0235 (8)	0.0215 (9)	0.0243 (7)	0.0050 (7)	0.0000 (6)	−0.0027 (7)
N5	0.0254 (9)	0.0160 (10)	0.0253 (9)	0.0001 (8)	0.0056 (8)	0.0002 (8)
N6	0.0199 (8)	0.0200 (10)	0.0221 (9)	−0.0016 (8)	0.0057 (7)	0.0013 (8)
N7	0.0191 (8)	0.0209 (10)	0.0223 (9)	−0.0007 (8)	0.0044 (7)	−0.0029 (8)
N8	0.0244 (9)	0.0175 (10)	0.0219 (9)	0.0012 (8)	0.0028 (7)	0.0000 (8)
C16	0.0285 (11)	0.0221 (13)	0.0291 (11)	−0.0027 (10)	0.0010 (9)	0.0059 (10)
C17	0.0190 (10)	0.0160 (11)	0.0263 (11)	−0.0039 (8)	0.0060 (9)	0.0025 (9)
C18	0.0306 (11)	0.0218 (13)	0.0279 (11)	0.0010 (10)	0.0095 (9)	−0.0026 (10)
C19	0.0249 (11)	0.0217 (12)	0.0308 (12)	0.0013 (9)	0.0096 (9)	−0.0017 (10)
C20	0.0193 (10)	0.0235 (12)	0.0253 (11)	−0.0030 (9)	0.0040 (9)	0.0014 (9)
C21	0.0184 (10)	0.0190 (11)	0.0227 (11)	−0.0001 (9)	0.0025 (8)	−0.0002 (9)

C22	0.0222 (11)	0.0219 (14)	0.0230 (11)	0.0011 (8)	0.0031 (9)	0.0005 (8)
C23	0.0268 (12)	0.0281 (14)	0.0387 (13)	−0.0025 (10)	0.0091 (11)	−0.0107 (11)
C24	0.0272 (12)	0.0279 (13)	0.0388 (13)	0.0041 (10)	0.0097 (11)	0.0093 (11)
C25	0.0186 (10)	0.0178 (11)	0.0236 (11)	−0.0005 (8)	0.0023 (8)	−0.0029 (9)
C26	0.0184 (10)	0.0250 (12)	0.0218 (10)	0.0031 (9)	0.0007 (8)	−0.0029 (9)
C27	0.0202 (10)	0.0154 (11)	0.0252 (11)	0.0034 (8)	0.0055 (9)	−0.0028 (9)
C28	0.0222 (11)	0.0230 (13)	0.0328 (12)	0.0003 (9)	0.0089 (9)	0.0011 (10)
C29	0.0265 (11)	0.0218 (13)	0.0299 (12)	−0.0003 (10)	0.0078 (9)	0.0021 (10)
C30	0.0309 (11)	0.0199 (12)	0.0252 (11)	0.0017 (10)	−0.0003 (9)	−0.0064 (9)

Geometric parameters (Å, º)

S1—C2	1.685 (2)	S3—C17	1.689 (2)
S2—C12	1.684 (2)	S4—C27	1.686 (2)
O1—C6	1.425 (3)	O3—C21	1.431 (3)
O1—C8	1.427 (3)	O3—C22	1.446 (3)
O2—C7	1.429 (3)	O4—C25	1.433 (3)
O2—C8	1.444 (3)	O4—C22	1.445 (3)
N1—C2	1.351 (3)	N5—C17	1.362 (3)
N1—C3	1.396 (3)	N5—C18	1.394 (3)
N1—C1	1.454 (3)	N5—C16	1.452 (3)
N2—C2	1.372 (3)	N6—C17	1.366 (3)
N2—C4	1.387 (3)	N6—C19	1.384 (3)
N2—C5	1.456 (2)	N6—C20	1.452 (3)
N3—C12	1.370 (3)	N7—C27	1.363 (3)
N3—C13	1.383 (3)	N7—C28	1.383 (3)
N3—C11	1.460 (3)	N7—C26	1.453 (3)
N4—C12	1.359 (3)	N8—C27	1.364 (3)
N4—C14	1.390 (3)	N8—C29	1.390 (3)
N4—C15	1.463 (3)	N8—C30	1.457 (3)
C1—H1A	0.980	C16—H16A	0.980
C1—H1B	0.980	C16—H16B	0.980
C1—H1C	0.980	C16—H16C	0.980
C3—C4	1.349 (3)	C18—C19	1.340 (3)
C3—H3	0.950	C18—H18	0.950
C4—H4	0.950	C19—H19	0.950
C5—C6	1.513 (3)	C20—C21	1.516 (3)
C5—H5A	0.990	C20—H20A	0.990
C5—H5B	0.990	C20—H20B	0.990
C6—C7	1.520 (3)	C21—C25	1.525 (3)
C6—H6	1.000	C21—H21	1.000
C7—C11	1.516 (3)	C22—C24	1.512 (3)
C7—H7	1.000	C22—C23	1.512 (3)
C8—C9	1.501 (3)	C23—H23A	0.980
C8—C10	1.510 (3)	C23—H23B	0.980
C9—H9A	0.980	C23—H23C	0.980
C9—H9B	0.980	C24—H24A	0.980
C9—H9C	0.980	C24—H24B	0.980

C10—H10A	0.980	C24—H24C	0.980
C10—H10B	0.980	C25—C26	1.521 (3)
C10—H10C	0.980	C25—H25	1.000
C11—H11A	0.990	C26—H26A	0.990
C11—H11B	0.990	C26—H26B	0.990
C13—C14	1.347 (3)	C28—C29	1.342 (3)
C13—H13	0.950	C28—H28	0.950
C14—H14	0.950	C29—H29	0.950
C15—H15A	0.980	C30—H30A	0.980
C15—H15B	0.980	C30—H30B	0.980
C15—H15C	0.980	C30—H30C	0.980

C6—O1—C8	106.59 (16)	C21—O3—C22	109.79 (16)
C7—O2—C8	109.22 (16)	C25—O4—C22	109.89 (16)
C2—N1—C3	109.93 (17)	C17—N5—C18	109.75 (18)
C2—N1—C1	125.35 (19)	C17—N5—C16	124.85 (19)
C3—N1—C1	124.62 (18)	C18—N5—C16	125.36 (19)
C2—N2—C4	109.65 (17)	C17—N6—C19	110.39 (18)
C2—N2—C5	124.06 (17)	C17—N6—C20	124.06 (18)
C4—N2—C5	125.43 (17)	C19—N6—C20	125.51 (18)
C12—N3—C13	110.06 (17)	C27—N7—C28	110.58 (18)
C12—N3—C11	125.14 (18)	C27—N7—C26	123.91 (18)
C13—N3—C11	124.29 (18)	C28—N7—C26	125.46 (18)
C12—N4—C14	110.34 (18)	C27—N8—C29	109.96 (18)
C12—N4—C15	125.21 (19)	C27—N8—C30	124.70 (19)
C14—N4—C15	124.42 (19)	C29—N8—C30	125.32 (19)
N1—C1—H1A	109.5	N5—C16—H16A	109.5
N1—C1—H1B	109.5	N5—C16—H16B	109.5
H1A—C1—H1B	109.5	H16A—C16—H16B	109.5
N1—C1—H1C	109.5	N5—C16—H16C	109.5
H1A—C1—H1C	109.5	H16A—C16—H16C	109.5
H1B—C1—H1C	109.5	H16B—C16—H16C	109.5
N1—C2—N2	105.93 (18)	N5—C17—N6	105.20 (18)
N1—C2—S1	127.72 (16)	N5—C17—S3	128.06 (17)
N2—C2—S1	126.35 (16)	N6—C17—S3	126.71 (16)
C4—C3—N1	107.20 (19)	C19—C18—N5	107.5 (2)
C4—C3—H3	126.4	C19—C18—H18	126.2
N1—C3—H3	126.4	N5—C18—H18	126.2
C3—C4—N2	107.28 (19)	C18—C19—N6	107.1 (2)
C3—C4—H4	126.4	C18—C19—H19	126.4
N2—C4—H4	126.4	N6—C19—H19	126.4
N2—C5—C6	113.73 (18)	N6—C20—C21	111.90 (17)
N2—C5—H5A	108.8	N6—C20—H20A	109.2
C6—C5—H5A	108.8	C21—C20—H20A	109.2
N2—C5—H5B	108.8	N6—C20—H20B	109.2
C6—C5—H5B	108.8	C21—C20—H20B	109.2
H5A—C5—H5B	107.7	H20A—C20—H20B	107.9
O1—C6—C5	108.90 (17)	O3—C21—C20	112.87 (18)

O1—C6—C7	103.50 (15)	O3—C21—C25	104.21 (15)
C5—C6—C7	115.53 (16)	C20—C21—C25	112.49 (18)
O1—C6—H6	109.6	O3—C21—H21	109.0
C5—C6—H6	109.6	C20—C21—H21	109.0
C7—C6—H6	109.6	C25—C21—H21	109.0
O2—C7—C11	111.25 (17)	O4—C22—O3	105.8 (2)
O2—C7—C6	103.95 (16)	O4—C22—C24	111.03 (16)
C11—C7—C6	114.51 (17)	O3—C22—C24	108.37 (16)
O2—C7—H7	109.0	O4—C22—C23	108.29 (16)
C11—C7—H7	109.0	O3—C22—C23	111.51 (16)
C6—C7—H7	109.0	C24—C22—C23	111.7 (2)
O1—C8—O2	105.64 (18)	C22—C23—H23A	109.5
O1—C8—C9	108.73 (19)	C22—C23—H23B	109.5
O2—C8—C9	109.5 (2)	H23A—C23—H23B	109.5
O1—C8—C10	110.47 (18)	C22—C23—H23C	109.5
O2—C8—C10	109.11 (18)	H23A—C23—H23C	109.5
C9—C8—C10	113.1 (2)	H23B—C23—H23C	109.5
C8—C9—H9A	109.5	C22—C24—H24A	109.5
C8—C9—H9B	109.5	C22—C24—H24B	109.5
H9A—C9—H9B	109.5	H24A—C24—H24B	109.5
C8—C9—H9C	109.5	C22—C24—H24C	109.5
H9A—C9—H9C	109.5	H24A—C24—H24C	109.5
H9B—C9—H9C	109.5	H24B—C24—H24C	109.5
C8—C10—H10A	109.5	O4—C25—C26	111.97 (18)
C8—C10—H10B	109.5	O4—C25—C21	104.23 (15)
H10A—C10—H10B	109.5	C26—C25—C21	112.61 (18)
C8—C10—H10C	109.5	O4—C25—H25	109.3
H10A—C10—H10C	109.5	C26—C25—H25	109.3
H10B—C10—H10C	109.5	C21—C25—H25	109.3
N3—C11—C7	113.29 (18)	N7—C26—C25	111.96 (17)
N3—C11—H11A	108.9	N7—C26—H26A	109.2
C7—C11—H11A	108.9	C25—C26—H26A	109.2
N3—C11—H11B	108.9	N7—C26—H26B	109.2
C7—C11—H11B	108.9	C25—C26—H26B	109.2
H11A—C11—H11B	107.7	H26A—C26—H26B	107.9
N4—C12—N3	105.17 (17)	N7—C27—N8	105.00 (18)
N4—C12—S2	127.51 (17)	N7—C27—S4	126.63 (16)
N3—C12—S2	127.32 (16)	N8—C27—S4	128.35 (17)
C14—C13—N3	107.47 (19)	C29—C28—N7	107.1 (2)
C14—C13—H13	126.3	C29—C28—H28	126.5
N3—C13—H13	126.3	N7—C28—H28	126.5
C13—C14—N4	106.9 (2)	C28—C29—N8	107.4 (2)
C13—C14—H14	126.5	C28—C29—H29	126.3
N4—C14—H14	126.5	N8—C29—H29	126.3
N4—C15—H15A	109.5	N8—C30—H30A	109.5
N4—C15—H15B	109.5	N8—C30—H30B	109.5
H15A—C15—H15B	109.5	H30A—C30—H30B	109.5
N4—C15—H15C	109.5	N8—C30—H30C	109.5

H15A—C15—H15C	109.5	H30A—C30—H30C	109.5
H15B—C15—H15C	109.5	H30B—C30—H30C	109.5
C3—N1—C2—N2	1.1 (2)	C18—N5—C17—N6	−0.1 (2)
C1—N1—C2—N2	−175.43 (18)	C16—N5—C17—N6	−178.01 (18)
C3—N1—C2—S1	−177.95 (15)	C18—N5—C17—S3	−178.07 (16)
C1—N1—C2—S1	5.5 (3)	C16—N5—C17—S3	4.0 (3)
C4—N2—C2—N1	−0.9 (2)	C19—N6—C17—N5	0.0 (2)
C5—N2—C2—N1	168.98 (18)	C20—N6—C17—N5	177.77 (18)
C4—N2—C2—S1	178.19 (16)	C19—N6—C17—S3	178.02 (16)
C5—N2—C2—S1	−11.9 (3)	C20—N6—C17—S3	−4.2 (3)
C2—N1—C3—C4	−0.9 (2)	C17—N5—C18—C19	0.1 (3)
C1—N1—C3—C4	175.6 (2)	C16—N5—C18—C19	178.1 (2)
N1—C3—C4—N2	0.3 (2)	N5—C18—C19—N6	−0.1 (2)
C2—N2—C4—C3	0.3 (2)	C17—N6—C19—C18	0.1 (2)
C5—N2—C4—C3	−169.37 (19)	C20—N6—C19—C18	−177.65 (19)
C2—N2—C5—C6	109.2 (2)	C21—C20—N6—C17	−75.4 (3)
C7—C11—N3—C12	104.4 (2)	C25—C26—N7—C27	−72.9 (3)
C4—N2—C5—C6	−82.5 (2)	C19—N6—C20—C21	102.0 (2)
C8—O1—C6—C5	−157.40 (16)	C22—O3—C21—C20	−101.23 (19)
C8—O1—C6—C7	−33.99 (19)	C22—O3—C21—C25	21.1 (2)
N2—C5—C6—O1	58.9 (2)	N6—C20—C21—O3	−62.6 (2)
N2—C5—C6—C7	−57.0 (2)	N6—C20—C21—C25	179.80 (17)
C8—O2—C7—C11	−133.47 (17)	C25—O4—C22—O3	−7.34 (18)
C8—O2—C7—C6	−9.7 (2)	C25—O4—C22—C24	110.0 (2)
O1—C6—C7—O2	26.5 (2)	C25—O4—C22—C23	−127.0 (2)
C5—C6—C7—O2	145.48 (17)	C21—O3—C22—O4	−9.39 (18)
O1—C6—C7—C11	148.13 (17)	C21—O3—C22—C24	−128.53 (19)
C5—C6—C7—C11	−92.9 (2)	C21—O3—C22—C23	108.1 (2)
C6—O1—C8—O2	28.40 (19)	C22—O4—C25—C26	−102.18 (19)
C6—O1—C8—C9	145.9 (2)	C22—O4—C25—C21	19.8 (2)
C6—O1—C8—C10	−89.5 (2)	O3—C21—C25—O4	−24.7 (2)
C7—O2—C8—O1	−10.7 (2)	C20—C21—C25—O4	97.95 (19)
C7—O2—C8—C9	−127.6 (2)	O3—C21—C25—C26	96.94 (19)
C7—O2—C8—C10	108.05 (19)	C20—C21—C25—C26	−140.5 (2)
C13—N3—C11—C7	−84.7 (2)	C28—N7—C26—C25	104.3 (2)
O2—C7—C11—N3	51.3 (2)	O4—C25—C26—N7	−64.0 (2)
C6—C7—C11—N3	−66.2 (2)	C21—C25—C26—N7	178.92 (17)
C14—N4—C12—N3	−0.5 (2)	C28—N7—C27—N8	−0.5 (2)
C15—N4—C12—N3	−178.67 (19)	C26—N7—C27—N8	177.06 (18)
C14—N4—C12—S2	178.97 (16)	C28—N7—C27—S4	178.30 (16)
C15—N4—C12—S2	0.8 (3)	C26—N7—C27—S4	−4.1 (3)
C13—N3—C12—N4	0.6 (2)	C29—N8—C27—N7	0.4 (2)
C11—N3—C12—N4	172.64 (18)	C30—N8—C27—N7	−177.74 (18)
C13—N3—C12—S2	−178.82 (16)	C29—N8—C27—S4	−178.38 (16)
C11—N3—C12—S2	−6.8 (3)	C30—N8—C27—S4	3.5 (3)
C12—N3—C13—C14	−0.6 (2)	C27—N7—C28—C29	0.4 (2)
C11—N3—C13—C14	−172.64 (19)	C26—N7—C28—C29	−177.09 (19)

N3—C13—C14—N4	0.2 (2)	N7—C28—C29—N8	−0.2 (2)
C12—N4—C14—C13	0.2 (2)	C27—N8—C29—C28	−0.1 (2)
C15—N4—C14—C13	178.4 (2)	C30—N8—C29—C28	178.0 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···S4	0.95	2.86	3.797 (2)	170
C5—H5*B*···O4	0.99	2.50	3.470 (3)	166
C11—H11*B*···O3^{i}	0.99	2.58	3.500 (3)	154
C13—H13···S3^{i}	0.95	2.83	3.715 (2)	156
C28—H28···S1^{ii}	0.95	2.87	3.749 (2)	155

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.