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(4*S*,5*S*)-4,5-Bis(3-cyclohexyl-2-thioxo-benzimidazol-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane from synchrotron data

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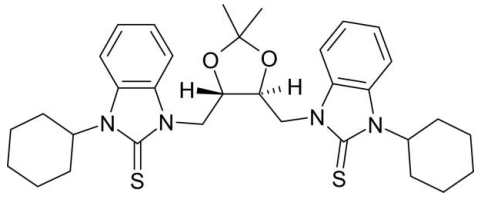
Key indicators: single-crystal synchrotron study; T = 120 K; mean σ(C–C) = 0.005 Å; R factor = 0.055; wR factor = 0.128; data-to-parameter ratio = 20.2.

In the chiral title compound, $C_{33}H_{42}N_4O_2S_2$, the dihedral angle between the imidazole ring planes is 79.47 (17)°. The packing is consolidated by van der Waals forces and weak C—H···S interactions.

Related literature

For background, see: Marshall & Harrison (2007); Williamson *et al.* (2006). For reference structural data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{33}H_{42}N_4O_2S_2$
M_r = 590.83
Monoclinic, $C2$
a = 21.876 (6) Å
b = 10.652 (3) Å
c = 14.120 (4) Å
β = 95.398 (6)°
V = 3275.5 (16) Å^3
Z = 4
Synchrotron radiation
λ = 0.6871 Å
μ = 0.20 mm^{-1}
T = 120 (2) K
0.05 × 0.04 × 0.03 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: none
11222 measured reflections
7522 independent reflections
5903 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.128
S = 1.00
7522 reflections
372 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}
Absolute structure: Flack (1983), 3144 Friedel pairs
Flack parameter: 0.07 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14B···S2^{i}	0.99	2.86	3.806 (3)	160
C18—H18···S1^{i}	0.95	2.78	3.633 (4)	150

Symmetry code: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+2$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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*.

We thank the EPSRC UK National Crystallography Service (Newcastle University and Daresbury Laboratory) for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2390).

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supplementary materials

Acta Cryst. (2007). E**63**, o4502 [**doi:10.1107/S1600536807053342**]

(4*S*,5*S*)-4,5-Bis(3-cyclohexyl-2-thioxobenzimidazol-1-ylmethyl)-2,2-dimethyl-1,3-dioxolane from synchrotron data

C. Marshall and W. T. A. Harrison

Comment

As part of our ongoing investigations of chiral, C_2-symmetric catalysts (Marshall & Harrison, 2007), the title compound, (I), an intermediate in the synthesis of such materials, has been synthesized and structurally characterized. There is a single molecule in the asymmetric unit of (I) (Fig. 1), with C9 and C13 showing the expected atomic chirality (both have S configuration). The dihedral angle between the imidazole rings (N1/N2/C1/C2/C7 and N3/N4/C15/C16/C21) is 79.47 (17)°.

Both the thio-imidazole ring systems 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). The terminal cyclohexane rings are normal chairs. Otherwise, the geometry of the molecule may be regarded as normal (Allen *et al.*, 1995).

The crystal packing for (I) is consolidated by van der Walls forces and weak C—H···S interactions. (Table 2).

Experimental

A mixture of (4*S*,5S)-4,5-bis(1-cyclohexylimidazolium-3-methyl)-2,2- dimethyl-1,3-dioxolane dibromide (1.29 g, 1.9 mmol), sulfur (0.18 g, 5.6 mmol), methanol (20 ml), pyridine (1.8 ml) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.26 g, 8.3 mmol) was heated at 338 K for 18 h. Once cooled to room temperature the mixture was opened to water (50 ml) and 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:petroleum ether *v*/*v* = 1:1, loaded as a dichloromethane solution) to give the title compound (0.92 g, 83%) as a colourless foam that was recrystallized from methanol to give colourless needles of (I); mp 470 K (from MeOH).

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, but not to tip, to best fit the electron density.

Figures

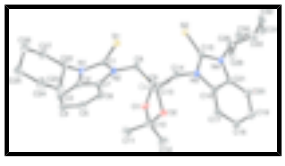


Fig. 1. View of the molecular structures of (I) showing 50% displacement ellipsoids. All the H atoms except H9 and H13 (drawn as spheres of arbitrary radius) are omitted for clarity.

(4*S*,5S)-4,5-Bis(3-cyclohexyl-2-thioxobenzimidazol-1-ylmethyl)-2,2-dimethyl-\ 1,3-dioxolane

Crystal data

$C_{33}H_{42}N_4O_2S_2$	F_{000} = 1264
M_r = 590.83	D_x = 1.198 Mg m^{-3}
Monoclinic, *C*2	Synchrotron radiation λ = 0.68710 Å
Hall symbol: C 2y	Cell parameters from 3328 reflections
a = 21.876 (6) Å	θ = 2.2–27.8º
b = 10.652 (3) Å	μ = 0.20 mm^{-1}
c = 14.120 (4) Å	*T* = 120 (2) K
β = 95.398 (6)º	Block, colourless
V = 3275.5 (16) Å^3	0.05 × 0.04 × 0.03 mm
Z = 4	

Data collection

Bruker SMART CCD diffractometer	5903 reflections with $I > 2\sigma(I)$
Radiation source: Daresbury synchrotron	R_{int} = 0.036
Monochromator: silicon	θ_{max} = 27.5º
T = 120(2) K	θ_{min} = 1.8º
ω scans	*h* = −29→23
Absorption correction: none	*k* = −14→14
11222 measured reflections	*l* = −15→18
7522 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.1687P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.128	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.00	$\Delta\rho_{max}$ = 0.36 e Å^{-3}
7522 reflections	$\Delta\rho_{min}$ = −0.40 e Å^{-3}
372 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 3144 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.07 (7)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.73086 (4)	0.02150 (7)	0.70554 (5)	0.02164 (17)
S2	0.84007 (4)	0.22570 (7)	0.94868 (5)	0.02080 (16)
O1	0.89848 (10)	−0.2189 (2)	0.86999 (15)	0.0234 (5)
O2	0.81855 (10)	−0.24757 (18)	0.96132 (14)	0.0217 (5)
N1	0.77308 (12)	−0.1591 (2)	0.58975 (18)	0.0201 (5)
N2	0.84145 (11)	−0.0936 (2)	0.70315 (16)	0.0164 (5)
N3	0.81917 (11)	0.0130 (2)	1.04818 (16)	0.0174 (5)
N4	0.88379 (11)	0.1442 (2)	1.12569 (17)	0.0187 (5)
C1	0.78195 (14)	−0.0793 (3)	0.6658 (2)	0.0164 (6)
C2	0.82764 (15)	−0.2231 (3)	0.5778 (2)	0.0205 (6)
C3	0.84320 (15)	−0.3128 (3)	0.5124 (2)	0.0219 (6)
H3	0.8139	−0.3437	0.4641	0.026*
C4	0.90343 (16)	−0.3548 (3)	0.5210 (2)	0.0262 (7)
H4	0.9154	−0.4165	0.4779	0.031*
C5	0.94693 (16)	−0.3094 (3)	0.5909 (2)	0.0278 (7)
H5	0.9880	−0.3389	0.5930	0.033*
C6	0.93160 (14)	−0.2220 (3)	0.6575 (2)	0.0239 (7)
H6	0.9610	−0.1918	0.7059	0.029*
C7	0.87146 (14)	−0.1811 (3)	0.6498 (2)	0.0191 (6)
C8	0.86992 (14)	−0.0265 (3)	0.7861 (2)	0.0189 (6)
H8A	0.8482	0.0541	0.7923	0.023*
H8B	0.9130	−0.0071	0.7757	0.023*
C9	0.86904 (13)	−0.0998 (3)	0.8785 (2)	0.0176 (6)
H9	0.8922	−0.0512	0.9308	0.021*
C10	0.86347 (16)	−0.3145 (3)	0.9129 (2)	0.0255 (7)
C11	0.83314 (18)	−0.3989 (3)	0.8362 (3)	0.0346 (8)
H11A	0.8645	−0.4352	0.7993	0.052*
H11B	0.8041	−0.3498	0.7940	0.052*
H11C	0.8111	−0.4664	0.8657	0.052*
C12	0.90456 (19)	−0.3837 (4)	0.9875 (3)	0.0381 (9)
H12A	0.9374	−0.4260	0.9573	0.057*
H12B	0.8804	−0.4462	1.0187	0.057*
H12C	0.9225	−0.3239	1.0349	0.057*

C13	0.80586 (14)	−0.1337 (3)	0.9095 (2)	0.0170 (6)
H13	0.7769	−0.1515	0.8520	0.020*
C14	0.77648 (14)	−0.0399 (3)	0.9730 (2)	0.0188 (6)
H14A	0.7583	0.0294	0.9330	0.023*
H14B	0.7427	−0.0821	1.0024	0.023*
C15	0.84741 (14)	0.1273 (3)	1.0423 (2)	0.0183 (6)
C16	0.83756 (14)	−0.0426 (3)	1.1360 (2)	0.0191 (6)
C17	0.82177 (15)	−0.1563 (3)	1.1748 (2)	0.0233 (7)
H17	0.7937	−0.2123	1.1413	0.028*
C18	0.84907 (16)	−0.1842 (3)	1.2649 (2)	0.0287 (8)
H18	0.8390	−0.2608	1.2941	0.034*
C19	0.89093 (17)	−0.1029 (3)	1.3140 (2)	0.0302 (8)
H19	0.9093	−0.1262	1.3752	0.036*
C20	0.90623 (15)	0.0113 (3)	1.2752 (2)	0.0251 (7)
H20	0.9344	0.0671	1.3089	0.030*
C21	0.87863 (14)	0.0410 (3)	1.1848 (2)	0.0200 (6)
C22	0.71324 (14)	−0.1752 (3)	0.5341 (2)	0.0218 (6)
H22	0.6845	−0.1130	0.5590	0.026*
C23	0.68706 (15)	−0.3058 (3)	0.5503 (2)	0.0258 (7)
H23A	0.6841	−0.3191	0.6191	0.031*
H23B	0.7147	−0.3706	0.5279	0.031*
C24	0.62329 (16)	−0.3178 (4)	0.4961 (3)	0.0334 (8)
H24A	0.5946	−0.2588	0.5233	0.040*
H24B	0.6076	−0.4041	0.5035	0.040*
C25	0.62588 (16)	−0.2890 (3)	0.3902 (2)	0.0303 (8)
H25A	0.6512	−0.3533	0.3619	0.036*
H25B	0.5839	−0.2934	0.3574	0.036*
C26	0.65257 (16)	−0.1606 (3)	0.3747 (3)	0.0322 (8)
H26A	0.6247	−0.0956	0.3963	0.039*
H26B	0.6558	−0.1478	0.3059	0.039*
C27	0.71624 (16)	−0.1458 (3)	0.4289 (2)	0.0266 (7)
H27A	0.7456	−0.2034	0.4019	0.032*
H27B	0.7310	−0.0587	0.4218	0.032*
C28	0.92048 (14)	0.2584 (3)	1.1462 (2)	0.0193 (6)
H28	0.9126	0.3145	1.0896	0.023*
C29	0.98903 (14)	0.2306 (3)	1.1566 (2)	0.0268 (7)
H29A	1.0007	0.1868	1.0991	0.032*
H29B	0.9993	0.1753	1.2122	0.032*
C30	1.02441 (17)	0.3547 (3)	1.1699 (3)	0.0340 (8)
H30A	1.0689	0.3366	1.1810	0.041*
H30B	1.0175	0.4051	1.1109	0.041*
C31	1.00441 (16)	0.4309 (3)	1.2535 (3)	0.0329 (8)
H31A	1.0163	0.3854	1.3136	0.040*
H31B	1.0260	0.5127	1.2565	0.040*
C32	0.93546 (15)	0.4532 (3)	1.2439 (2)	0.0261 (7)
H32A	0.9244	0.5087	1.1887	0.031*
H32B	0.9237	0.4961	1.3016	0.031*
C33	0.89993 (16)	0.3299 (3)	1.2304 (2)	0.0268 (7)
H33A	0.9071	0.2781	1.2886	0.032*

H33B	0.8554	0.3477	1.2196	0.032*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0258 (4)	0.0213 (4)	0.0178 (4)	0.0050 (3)	0.0019 (3)	0.0001 (3)
S2	0.0281 (4)	0.0170 (3)	0.0171 (4)	0.0009 (3)	0.0014 (3)	0.0027 (3)
O1	0.0274 (12)	0.0237 (11)	0.0200 (11)	0.0070 (9)	0.0066 (9)	0.0056 (9)
O2	0.0342 (13)	0.0171 (11)	0.0148 (10)	0.0016 (9)	0.0082 (9)	0.0032 (8)
N1	0.0248 (14)	0.0191 (12)	0.0160 (13)	−0.0019 (10)	−0.0007 (10)	0.0004 (10)
N2	0.0195 (13)	0.0182 (11)	0.0116 (12)	−0.0025 (10)	0.0025 (10)	0.0003 (10)
N3	0.0219 (12)	0.0180 (11)	0.0126 (11)	−0.0025 (11)	0.0033 (9)	0.0008 (10)
N4	0.0255 (14)	0.0158 (11)	0.0149 (12)	−0.0022 (10)	0.0025 (10)	0.0005 (10)
C1	0.0224 (15)	0.0143 (13)	0.0122 (14)	−0.0013 (11)	0.0004 (11)	0.0035 (11)
C2	0.0289 (16)	0.0178 (13)	0.0151 (15)	−0.0030 (13)	0.0032 (12)	0.0031 (12)
C3	0.0326 (17)	0.0199 (14)	0.0136 (14)	−0.0034 (13)	0.0038 (12)	0.0002 (12)
C4	0.042 (2)	0.0213 (15)	0.0175 (16)	0.0037 (14)	0.0125 (14)	−0.0002 (13)
C5	0.0313 (18)	0.0289 (16)	0.0252 (17)	0.0111 (14)	0.0127 (14)	0.0073 (14)
C6	0.0236 (16)	0.0340 (16)	0.0145 (15)	0.0007 (13)	0.0036 (12)	0.0015 (13)
C7	0.0269 (16)	0.0191 (14)	0.0117 (14)	−0.0003 (12)	0.0039 (12)	0.0025 (11)
C8	0.0190 (15)	0.0217 (14)	0.0154 (14)	−0.0024 (12)	−0.0015 (11)	−0.0010 (12)
C9	0.0202 (15)	0.0202 (14)	0.0122 (13)	0.0002 (12)	0.0005 (11)	0.0002 (11)
C10	0.0372 (19)	0.0206 (14)	0.0197 (16)	0.0054 (13)	0.0069 (14)	0.0013 (13)
C11	0.050 (2)	0.0259 (17)	0.0290 (19)	−0.0014 (16)	0.0083 (17)	−0.0079 (15)
C12	0.054 (2)	0.0331 (19)	0.0275 (19)	0.0147 (18)	0.0066 (17)	0.0080 (16)
C13	0.0241 (16)	0.0171 (13)	0.0094 (13)	−0.0017 (11)	−0.0012 (11)	0.0017 (11)
C14	0.0198 (15)	0.0196 (14)	0.0171 (14)	−0.0009 (12)	0.0029 (11)	−0.0010 (12)
C15	0.0204 (15)	0.0181 (14)	0.0170 (14)	0.0020 (12)	0.0054 (11)	−0.0021 (12)
C16	0.0234 (16)	0.0199 (14)	0.0143 (14)	−0.0019 (12)	0.0037 (11)	−0.0004 (11)
C17	0.0308 (18)	0.0232 (15)	0.0167 (15)	−0.0066 (13)	0.0059 (13)	−0.0015 (13)
C18	0.044 (2)	0.0247 (16)	0.0182 (16)	−0.0057 (15)	0.0040 (14)	0.0038 (13)
C19	0.045 (2)	0.0281 (16)	0.0172 (16)	−0.0042 (15)	0.0001 (14)	0.0040 (14)
C20	0.0354 (18)	0.0248 (15)	0.0148 (14)	−0.0046 (14)	0.0003 (12)	0.0019 (13)
C21	0.0264 (15)	0.0175 (14)	0.0165 (14)	−0.0040 (12)	0.0041 (11)	−0.0018 (12)
C22	0.0253 (16)	0.0219 (15)	0.0172 (15)	0.0017 (12)	−0.0024 (12)	−0.0040 (12)
C23	0.0271 (17)	0.0295 (17)	0.0201 (16)	−0.0028 (13)	−0.0015 (13)	0.0039 (13)
C24	0.0300 (19)	0.0405 (19)	0.0289 (19)	−0.0083 (15)	−0.0010 (15)	−0.0035 (16)
C25	0.0331 (18)	0.0292 (18)	0.0265 (17)	0.0027 (15)	−0.0081 (14)	−0.0047 (15)
C26	0.038 (2)	0.0299 (17)	0.0252 (18)	0.0029 (15)	−0.0129 (15)	−0.0015 (15)
C27	0.0336 (19)	0.0256 (16)	0.0188 (15)	−0.0077 (14)	−0.0079 (13)	0.0045 (13)
C28	0.0226 (15)	0.0168 (14)	0.0184 (14)	−0.0042 (11)	0.0016 (11)	0.0004 (11)
C29	0.0256 (16)	0.0272 (15)	0.0287 (17)	−0.0027 (15)	0.0080 (12)	−0.0100 (15)
C30	0.0288 (18)	0.0373 (19)	0.037 (2)	−0.0118 (16)	0.0098 (15)	−0.0145 (17)
C31	0.0301 (19)	0.0334 (18)	0.034 (2)	−0.0080 (15)	−0.0030 (15)	−0.0124 (16)
C32	0.0312 (18)	0.0215 (15)	0.0251 (17)	−0.0009 (14)	−0.0008 (14)	−0.0075 (14)
C33	0.0271 (17)	0.0235 (15)	0.0297 (18)	0.0001 (13)	0.0029 (14)	−0.0040 (14)

Geometric parameters (Å, °)

S1—C1	1.684 (3)	C16—C17	1.387 (4)
S2—C15	1.683 (3)	C16—C21	1.399 (4)
O1—C9	1.433 (4)	C17—C18	1.386 (4)
O1—C10	1.441 (4)	C17—H17	0.9500
O2—C13	1.430 (3)	C18—C19	1.396 (5)
O2—C10	1.438 (4)	C18—H18	0.9500
N1—C1	1.369 (4)	C19—C20	1.388 (5)
N1—C2	1.399 (4)	C19—H19	0.9500
N1—C22	1.472 (4)	C20—C21	1.396 (4)
N2—C1	1.366 (4)	C20—H20	0.9500
N2—C7	1.400 (4)	C22—C27	1.525 (4)
N2—C8	1.460 (4)	C22—C23	1.530 (4)
N3—C15	1.372 (4)	C22—H22	1.0000
N3—C16	1.399 (4)	C23—C24	1.532 (5)
N3—C14	1.459 (4)	C23—H23A	0.9900
N4—C15	1.369 (4)	C23—H23B	0.9900
N4—C21	1.391 (4)	C24—C25	1.533 (5)
N4—C28	1.471 (4)	C24—H24A	0.9900
C2—C3	1.393 (4)	C24—H24B	0.9900
C2—C7	1.404 (4)	C25—C26	1.510 (5)
C3—C4	1.386 (5)	C25—H25A	0.9900
C3—H3	0.9500	C25—H25B	0.9900
C4—C5	1.391 (5)	C26—C27	1.533 (5)
C4—H4	0.9500	C26—H26A	0.9900
C5—C6	1.386 (5)	C26—H26B	0.9900
C5—H5	0.9500	C27—H27A	0.9900
C6—C7	1.381 (4)	C27—H27B	0.9900
C6—H6	0.9500	C28—C33	1.515 (4)
C8—C9	1.523 (4)	C28—C29	1.522 (4)
C8—H8A	0.9900	C28—H28	1.0000
C8—H8B	0.9900	C29—C30	1.534 (5)
C9—C13	1.532 (4)	C29—H29A	0.9900
C9—H9	1.0000	C29—H29B	0.9900
C10—C12	1.512 (5)	C30—C31	1.530 (5)
C10—C11	1.512 (5)	C30—H30A	0.9900
C11—H11A	0.9800	C30—H30B	0.9900
C11—H11B	0.9800	C31—C32	1.520 (5)
C11—H11C	0.9800	C31—H31A	0.9900
C12—H12A	0.9800	C31—H31B	0.9900
C12—H12B	0.9800	C32—C33	1.529 (5)
C12—H12C	0.9800	C32—H32A	0.9900
C13—C14	1.524 (4)	C32—H32B	0.9900
C13—H13	1.0000	C33—H33A	0.9900
C14—H14A	0.9900	C33—H33B	0.9900
C14—H14B	0.9900		
C9—O1—C10	109.2 (2)	C16—C17—H17	121.7

C13—O2—C10	106.6 (2)	C17—C18—C19	122.0 (3)
C1—N1—C2	109.8 (2)	C17—C18—H18	119.0
C1—N1—C22	123.0 (3)	C19—C18—H18	119.0
C2—N1—C22	127.2 (3)	C20—C19—C18	121.2 (3)
C1—N2—C7	110.2 (2)	C20—C19—H19	119.4
C1—N2—C8	125.0 (2)	C18—C19—H19	119.4
C7—N2—C8	124.8 (2)	C19—C20—C21	117.4 (3)
C15—N3—C16	109.6 (2)	C19—C20—H20	121.3
C15—N3—C14	124.0 (2)	C21—C20—H20	121.3
C16—N3—C14	126.4 (2)	N4—C21—C20	132.5 (3)
C15—N4—C21	109.8 (2)	N4—C21—C16	107.0 (2)
C15—N4—C28	122.7 (2)	C20—C21—C16	120.5 (3)
C21—N4—C28	127.5 (2)	N1—C22—C27	112.2 (3)
N2—C1—N1	107.1 (2)	N1—C22—C23	110.7 (2)
N2—C1—S1	125.5 (2)	C27—C22—C23	112.6 (3)
N1—C1—S1	127.4 (2)	N1—C22—H22	107.0
C3—C2—N1	132.8 (3)	C27—C22—H22	107.0
C3—C2—C7	120.4 (3)	C23—C22—H22	107.0
N1—C2—C7	106.8 (3)	C22—C23—C24	109.7 (3)
C4—C3—C2	116.9 (3)	C22—C23—H23A	109.7
C4—C3—H3	121.5	C24—C23—H23A	109.7
C2—C3—H3	121.5	C22—C23—H23B	109.7
C3—C4—C5	122.1 (3)	C24—C23—H23B	109.7
C3—C4—H4	119.0	H23A—C23—H23B	108.2
C5—C4—H4	119.0	C23—C24—C25	110.8 (3)
C6—C5—C4	121.4 (3)	C23—C24—H24A	109.5
C6—C5—H5	119.3	C25—C24—H24A	109.5
C4—C5—H5	119.3	C23—C24—H24B	109.5
C7—C6—C5	116.7 (3)	C25—C24—H24B	109.5
C7—C6—H6	121.7	H24A—C24—H24B	108.1
C5—C6—H6	121.7	C26—C25—C24	111.9 (3)
C6—C7—N2	131.3 (3)	C26—C25—H25A	109.2
C6—C7—C2	122.4 (3)	C24—C25—H25A	109.2
N2—C7—C2	106.2 (3)	C26—C25—H25B	109.2
N2—C8—C9	113.4 (2)	C24—C25—H25B	109.2
N2—C8—H8A	108.9	H25A—C25—H25B	107.9
C9—C8—H8A	108.9	C25—C26—C27	111.5 (3)
N2—C8—H8B	108.9	C25—C26—H26A	109.3
C9—C8—H8B	108.9	C27—C26—H26A	109.3
H8A—C8—H8B	107.7	C25—C26—H26B	109.3
O1—C9—C8	109.9 (2)	C27—C26—H26B	109.3
O1—C9—C13	103.9 (2)	H26A—C26—H26B	108.0
C8—C9—C13	116.8 (2)	C22—C27—C26	110.1 (3)
O1—C9—H9	108.7	C22—C27—H27A	109.6
C8—C9—H9	108.7	C26—C27—H27A	109.6
C13—C9—H9	108.7	C22—C27—H27B	109.6
O2—C10—O1	105.3 (2)	C26—C27—H27B	109.6
O2—C10—C12	107.4 (3)	H27A—C27—H27B	108.1
O1—C10—C12	109.4 (3)	N4—C28—C33	111.9 (2)

O2—C10—C11	111.2 (3)	N4—C28—C29	111.8 (2)
O1—C10—C11	109.5 (3)	C33—C28—C29	112.7 (3)
C12—C10—C11	113.6 (3)	N4—C28—H28	106.7
C10—C11—H11A	109.5	C33—C28—H28	106.7
C10—C11—H11B	109.5	C29—C28—H28	106.7
H11A—C11—H11B	109.5	C28—C29—C30	108.9 (3)
C10—C11—H11C	109.5	C28—C29—H29A	109.9
H11A—C11—H11C	109.5	C30—C29—H29A	109.9
H11B—C11—H11C	109.5	C28—C29—H29B	109.9
C10—C12—H12A	109.5	C30—C29—H29B	109.9
C10—C12—H12B	109.5	H29A—C29—H29B	108.3
H12A—C12—H12B	109.5	C31—C30—C29	112.0 (3)
C10—C12—H12C	109.5	C31—C30—H30A	109.2
H12A—C12—H12C	109.5	C29—C30—H30A	109.2
H12B—C12—H12C	109.5	C31—C30—H30B	109.2
O2—C13—C14	109.1 (2)	C29—C30—H30B	109.2
O2—C13—C9	102.1 (2)	H30A—C30—H30B	107.9
C14—C13—C9	117.1 (2)	C32—C31—C30	111.6 (3)
O2—C13—H13	109.4	C32—C31—H31A	109.3
C14—C13—H13	109.4	C30—C31—H31A	109.3
C9—C13—H13	109.4	C32—C31—H31B	109.3
N3—C14—C13	113.8 (2)	C30—C31—H31B	109.3
N3—C14—H14A	108.8	H31A—C31—H31B	108.0
C13—C14—H14A	108.8	C31—C32—C33	111.4 (3)
N3—C14—H14B	108.8	C31—C32—H32A	109.3
C13—C14—H14B	108.8	C33—C32—H32A	109.3
H14A—C14—H14B	107.7	C31—C32—H32B	109.3
N4—C15—N3	107.1 (2)	C33—C32—H32B	109.3
N4—C15—S2	126.8 (2)	H32A—C32—H32B	108.0
N3—C15—S2	126.1 (2)	C28—C33—C32	110.1 (3)
C17—C16—N3	131.2 (3)	C28—C33—H33A	109.6
C17—C16—C21	122.3 (3)	C32—C33—H33A	109.6
N3—C16—C21	106.6 (2)	C28—C33—H33B	109.6
C18—C17—C16	116.6 (3)	C32—C33—H33B	109.6
C18—C17—H17	121.7	H33A—C33—H33B	108.2
C7—N2—C1—N1	1.2 (3)	C28—N4—C15—N3	−178.7 (2)
C8—N2—C1—N1	−179.4 (2)	C21—N4—C15—S2	−178.5 (2)
C7—N2—C1—S1	−177.2 (2)	C28—N4—C15—S2	3.0 (4)
C8—N2—C1—S1	2.3 (4)	C16—N3—C15—N4	0.3 (3)
C2—N1—C1—N2	−0.9 (3)	C14—N3—C15—N4	−179.9 (2)
C22—N1—C1—N2	176.6 (3)	C16—N3—C15—S2	178.6 (2)
C2—N1—C1—S1	177.4 (2)	C14—N3—C15—S2	−1.6 (4)
C22—N1—C1—S1	−5.1 (4)	C15—N3—C16—C17	179.8 (3)
C1—N1—C2—C3	−179.9 (3)	C14—N3—C16—C17	0.1 (5)
C22—N1—C2—C3	2.7 (5)	C15—N3—C16—C21	−0.3 (3)
C1—N1—C2—C7	0.3 (3)	C14—N3—C16—C21	179.9 (3)
C22—N1—C2—C7	−177.1 (3)	N3—C16—C17—C18	179.5 (3)
N1—C2—C3—C4	178.7 (3)	C21—C16—C17—C18	−0.4 (5)
C7—C2—C3—C4	−1.5 (4)	C16—C17—C18—C19	−0.7 (5)

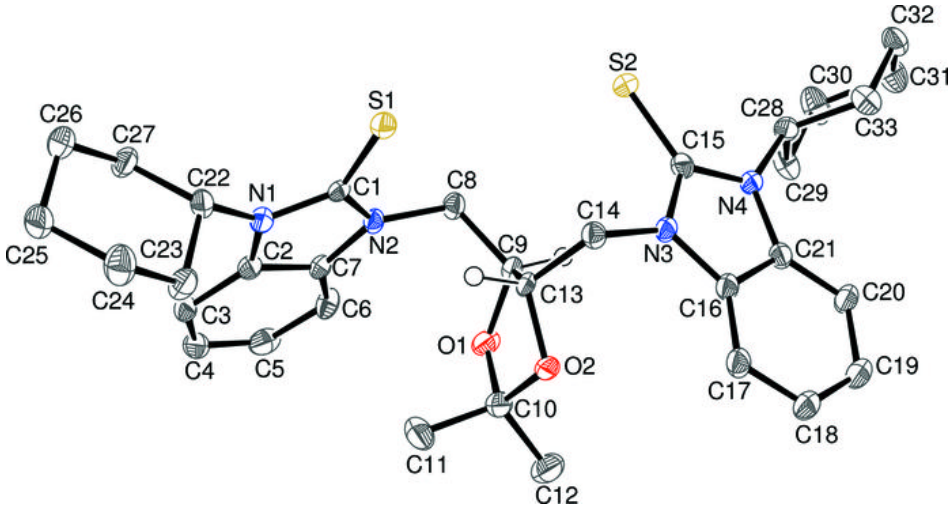
C2—C3—C4—C5	−0.6 (5)	C17—C18—C19—C20	1.3 (6)
C3—C4—C5—C6	1.9 (5)	C18—C19—C20—C21	−0.7 (5)
C4—C5—C6—C7	−1.0 (5)	C15—N4—C21—C20	179.0 (3)
C5—C6—C7—N2	−178.7 (3)	C28—N4—C21—C20	−2.6 (5)
C5—C6—C7—C2	−1.1 (5)	C15—N4—C21—C16	0.0 (3)
C1—N2—C7—C6	176.9 (3)	C28—N4—C21—C16	178.4 (3)
C8—N2—C7—C6	−2.5 (5)	C19—C20—C21—N4	−179.2 (3)
C1—N2—C7—C2	−1.0 (3)	C19—C20—C21—C16	−0.4 (5)
C8—N2—C7—C2	179.6 (2)	C17—C16—C21—N4	−180.0 (3)
C3—C2—C7—C6	2.4 (5)	N3—C16—C21—N4	0.2 (3)
N1—C2—C7—C6	−177.7 (3)	C17—C16—C21—C20	0.9 (5)
C3—C2—C7—N2	−179.4 (3)	N3—C16—C21—C20	−178.9 (3)
N1—C2—C7—N2	0.4 (3)	C1—N1—C22—C27	122.3 (3)
C1—N2—C8—C9	95.4 (3)	C2—N1—C22—C27	−60.7 (4)
C7—N2—C8—C9	−85.2 (3)	C1—N1—C22—C23	−111.1 (3)
C10—O1—C9—C8	−138.1 (2)	C2—N1—C22—C23	66.0 (4)
C10—O1—C9—C13	−12.4 (3)	N1—C22—C23—C24	176.9 (3)
N2—C8—C9—O1	56.6 (3)	C27—C22—C23—C24	−56.6 (4)
N2—C8—C9—C13	−61.3 (3)	C22—C23—C24—C25	55.6 (4)
C13—O2—C10—O1	29.6 (3)	C23—C24—C25—C26	−56.2 (4)
C13—O2—C10—C12	146.1 (3)	C24—C25—C26—C27	55.6 (4)
C13—O2—C10—C11	−89.0 (3)	N1—C22—C27—C26	−178.5 (3)
C9—O1—C10—O2	−9.5 (3)	C23—C22—C27—C26	55.9 (4)
C9—O1—C10—C12	−124.6 (3)	C25—C26—C27—C22	−54.6 (4)
C9—O1—C10—C11	110.2 (3)	C15—N4—C28—C33	116.4 (3)
C10—O2—C13—C14	−160.9 (2)	C21—N4—C28—C33	−61.8 (4)
C10—O2—C13—C9	−36.4 (3)	C15—N4—C28—C29	−116.1 (3)
O1—C9—C13—O2	29.6 (3)	C21—N4—C28—C29	65.7 (4)
C8—C9—C13—O2	150.7 (2)	N4—C28—C29—C30	175.5 (3)
O1—C9—C13—C14	148.7 (2)	C33—C28—C29—C30	−57.4 (4)
C8—C9—C13—C14	−90.2 (3)	C28—C29—C30—C31	55.1 (4)
C15—N3—C14—C13	97.8 (3)	C29—C30—C31—C32	−54.7 (4)
C16—N3—C14—C13	−82.4 (3)	C30—C31—C32—C33	54.2 (4)
O2—C13—C14—N3	72.7 (3)	N4—C28—C33—C32	−175.1 (2)
C9—C13—C14—N3	−42.5 (3)	C29—C28—C33—C32	57.8 (4)
C21—N4—C15—N3	−0.2 (3)	C31—C32—C33—C28	−55.2 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14B···S2^{i}	0.99	2.86	3.806 (3)	160
C18—H18···S1^{i}	0.95	2.78	3.633 (4)	150

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

Fig. 1


C32
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C11
C12