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A thiophene-based azacryptand Mannich base: 18,24-bis(*p*-tolylsulfonamido)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diazatricyclo[24.3.0.0]nonacosa-1(26),12(16),13,28-tetraene

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.108
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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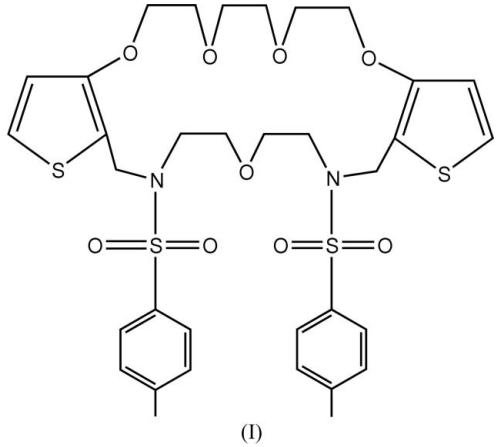
The title compound, $C_{34}H_{42}N_2O_9S_4$, is composed of two thiophene rings bridged by an $-O-(CH_2)_2-O-(CH_2)_2-O-$ chain and a trisubstitued diamine with pendent tosyl rings. In the crystal structure, the molecules are stabilized by several intra- and intermolecular C—H···O interactions, forming a two-dimensional network arranged in the *ac* plane.

Comment

The title compound, (I), is similar to the macrocycle reported by Halfpenny & Sloman (2000), in that the bulky tosyl substituents may have a major effect on the macrocyclic ring geometry. Considering the important steric restrictions imposed in (I) by the thiophene and the tosyl rings, the flexibility must be even lower and the selectivity of this macrocycle higher than the benzyl analogue reported by Halfpenny & Sloman (2000) and Barker *et al.* (1993).



(I)

The molecule (I) can be divided into two similar parts through a local approximate C_2 axis passing through atom O5 and the mid-point of the C7—C8 bond (Fig. 1). The macrocyclic ring shows a non-planar conformation; the longest intramolecular distance between the two thiophene rings is 13.479 (4) Å for C4···C14 and the longest between the two tosyl rings is 9.983 (3) Å for C25···C29. The large separation of the two tosyl rings influences the geometry of the macrocyclic cavity by ensuring that the thiophene rings and therefore the O and N atoms do not lie in the same plane. The largest cross-cavity distances are N1···O1 = 7.472 (3) Å, N2···O4 = 7.458 (3) Å and O1···O4 = 7.798 (3) Å. The macrocyclic cavity can be divided in two smaller distorted tetrahedral cavities, defined by the potential donor atoms O5/N1/O4/O3 and O5/N2/O1/O2. Their largest cross-cavity distances are N1···O3 = 5.085 (3) Å, O4···O5 = 4.619 (3) Å,

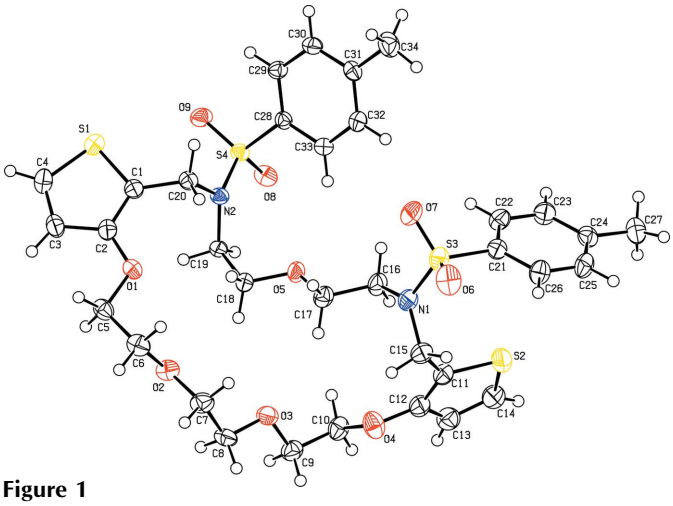


Figure 1
A view of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

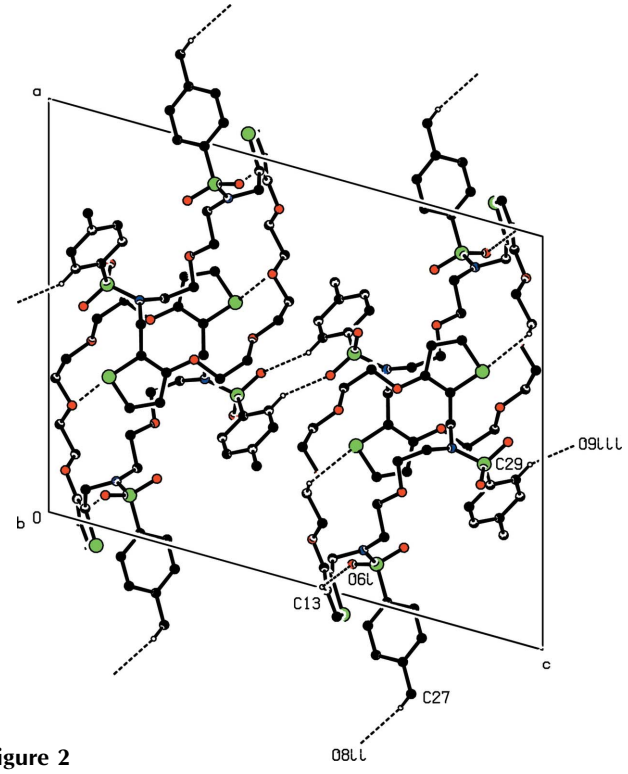


Figure 2
The molecular packing of (I), viewed down the *b* axis. H atoms have been omitted unless these are involved in C—H···O interactions (dashed lines). [Symmetry codes: (i) $x, 1+y, z$; (ii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $1-x, -y, 2-z$.]

N2···O2 = 5.304 (3) Å and O1···O5 = 4.597 (2) Å. The macrocycle conformation of (I) is stabilized by intramolecular C—H···O interactions (Table 2). The molecules are linked by C—H···O interactions, forming a two-dimensional network in the *ac* plane (Fig. 2).

Experimental

Compound (I) was synthesized according to the procedure described by Chaffin *et al.* (2002). Crystals suitable for X-ray analysis were grown from a cyclohexane/methanol solution (1:1 *v*/*v*) by slow evaporation at 278 K.

Crystal data

$C_{34}H_{42}N_2O_9S_4$
M_r = 750.94
Monoclinic, $P2_1/c$
a = 18.2875 (13) Å
b = 9.0910 (5) Å
c = 22.6813 (17) Å
β = 105.619 (9)°
V = 3631.6 (4) Å^3
Z = 4
D_x = 1.373 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 153 (2) K
Block, colourless
0.50 × 0.50 × 0.30 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: none
27910 measured reflections
7077 independent reflections
4692 reflections with $I > 2\sigma(I)$
R_{int} = 0.116
θ_{max} = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.108
S = 0.88
7077 reflections
444 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C4	1.708 (3)	S3—N1	1.620 (2)
S1—C1	1.722 (2)	S3—C21	1.762 (2)
S2—C11	1.712 (3)	S4—N2	1.6200 (19)
S2—C14	1.719 (3)	S4—C28	1.768 (2)
C4—S1—C1	92.06 (12)	C20—C1—S1	123.41 (17)
C11—S2—C14	92.06 (14)	C12—C11—C15	125.9 (2)
C2—C1—C20	126.3 (2)	C15—C11—S2	123.7 (2)
O1—C5—C6—O2	71.3 (3)	N1—C16—C17—O5	−168.6 (2)
O2—C7—C8—O3	−84.8 (3)	O5—C18—C19—N2	68.5 (2)
O3—C9—C10—O4	−72.1 (3)	S1—C1—C20—N2	92.0 (2)
S2—C11—C15—N1	−72.0 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*A*···O4	0.99	2.54	2.941 (3)	104
C15—H15*B*···O6	0.99	2.45	2.914 (4)	108
C16—H16*A*···O7	0.99	2.36	2.828 (4)	108
C19—H19*B*···O8	0.99	2.34	2.859 (3)	112
C26—H26*A*···O6	0.95	2.56	2.923 (3)	103
C29—H29*A*···O9	0.95	2.50	2.885 (3)	104
C32—H32*A*···O7	0.95	2.57	3.386 (3)	145
C33—H33*A*···O5	0.95	2.59	3.450 (3)	151
C13—H13*A*···O6^{i}	0.95	2.53	3.245 (4)	132
C27—H27*B*···O8^{ii}	0.98	2.58	3.463 (3)	149
C29—H29*A*···O9^{iii}	0.95	2.48	3.221 (3)	135

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

H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.95–0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl groups.

Data collection: *IPDS-I* (Stoe & Cie, 2000); cell refinement: *IPDS-I*; data reduction: *IPDS-I*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

We thank Professor Helen Stoeckli-Evans (Neuchâtel) for making available the Stoe IPDS diffractometer for data collection.

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supporting information

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A thiophene-based azacryptand Mannich base: 18,24-bis(*p*-tolylsulfonamido)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diazatricyclo[24.3.0.0]nonacosa-1(26),12(16),13,28-tetraene

Gaël Labat and Joan Halfpenny

18,24-bis(*p*-tolylsulfonamide)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diazatricyclo[24.3.0.0]nonacosa-1(26),12 (16),13,28-tetraene

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$C_{34}H_{42}N_2O_9S_4$
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Hall symbol: -P 2ybc
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c = 22.6813 (17) Å
β = 105.619 (9)°
V = 3631.6 (4) Å^3
Z = 4
$F(000)$ = 1584
D_x = 1.373 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8001 reflections
θ = 1.7–26.1°
μ = 0.32 mm^{-1}
T = 153 K
Block, colorless
0.50 × 0.50 × 0.30 mm

Data collection

Stoe IPDS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.81Å pixels mm^{-1}
φ oscillation scans
27910 measured reflections
7077 independent reflections
4692 reflections with $I > 2\sigma(I)$
R_{int} = 0.116
θ_{max} = 26.0°, θ_{min} = 2.3°
h = −22→22
k = −11→11
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.108
S = 0.88
7077 reflections
444 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
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 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	0.63246 (4)	0.10947 (9)	0.87786 (3)	0.03915 (18)
S2	−0.04945 (4)	0.11148 (9)	0.59600 (4)	0.0465 (2)
S3	0.09481 (3)	−0.23262 (7)	0.66381 (3)	0.03410 (16)
S4	0.40997 (3)	0.15930 (6)	0.88159 (2)	0.02415 (14)
O1	0.53364 (9)	0.0928 (2)	0.70555 (7)	0.0335 (4)
O2	0.44238 (10)	0.18169 (19)	0.58657 (7)	0.0329 (4)
O3	0.27322 (9)	0.2796 (2)	0.54703 (8)	0.0336 (4)
O4	0.11196 (11)	0.2617 (2)	0.53383 (9)	0.0426 (5)
O5	0.28638 (8)	0.1333 (2)	0.71479 (7)	0.0303 (4)
O6	0.07829 (11)	−0.3366 (2)	0.61450 (10)	0.0474 (5)
O7	0.15329 (10)	−0.2638 (2)	0.71908 (9)	0.0456 (5)
O8	0.35785 (10)	0.28003 (19)	0.87440 (8)	0.0323 (4)
O9	0.47933 (10)	0.1675 (2)	0.92982 (7)	0.0342 (4)
N1	0.11995 (11)	−0.0815 (2)	0.63687 (9)	0.0328 (5)
N2	0.42678 (10)	0.1321 (2)	0.81587 (8)	0.0237 (4)
C1	0.55972 (13)	0.0801 (3)	0.81273 (11)	0.0269 (5)
C2	0.58368 (13)	0.1095 (3)	0.76200 (11)	0.0281 (5)
C3	0.66082 (14)	0.1556 (3)	0.77493 (13)	0.0351 (6)
H3A	0.6858	0.1818	0.7447	0.042*
C4	0.69394 (15)	0.1571 (3)	0.83619 (13)	0.0414 (7)
H4A	0.7457	0.1818	0.8539	0.050*
C5	0.56219 (14)	0.1112 (3)	0.65329 (11)	0.0315 (5)
H5B	0.6067	0.0466	0.6566	0.038*
H5A	0.5781	0.2145	0.6504	0.038*
C6	0.49965 (15)	0.0714 (3)	0.59777 (12)	0.0344 (6)
H6B	0.5203	0.0623	0.5618	0.041*
H6A	0.4775	−0.0247	0.6043	0.041*
C7	0.38147 (15)	0.1422 (3)	0.53506 (11)	0.0362 (6)
H7A	0.3530	0.0589	0.5462	0.043*
H7B	0.4023	0.1096	0.5012	0.043*
C8	0.32842 (15)	0.2690 (3)	0.51376 (11)	0.0347 (6)
H8A	0.3580	0.3615	0.5187	0.042*
H8B	0.3025	0.2567	0.4697	0.042*
C9	0.21918 (14)	0.3906 (3)	0.52223 (12)	0.0346 (6)
H9B	0.1972	0.3729	0.4779	0.041*

H9A	0.2445	0.4879	0.5272	0.041*
C10	0.15743 (14)	0.3907 (3)	0.55385 (12)	0.0355 (6)
H10B	0.1793	0.3883	0.5988	0.043*
H10A	0.1260	0.4805	0.5431	0.043*
C11	0.03290 (14)	0.1058 (3)	0.57380 (11)	0.0356 (6)
C12	0.05090 (14)	0.2431 (3)	0.55734 (11)	0.0359 (6)
C13	−0.00160 (15)	0.3533 (3)	0.56282 (12)	0.0417 (7)
H13A	0.0030	0.4542	0.5534	0.050*
C14	−0.05897 (16)	0.2977 (3)	0.58306 (14)	0.0458 (7)
H14A	−0.0997	0.3547	0.5894	0.055*
C15	0.07899 (14)	−0.0320 (3)	0.57464 (11)	0.0358 (6)
H15B	0.0447	−0.1118	0.5540	0.043*
H15A	0.1163	−0.0142	0.5509	0.043*
C16	0.16578 (13)	0.0277 (3)	0.67937 (12)	0.0337 (6)
H16A	0.1746	−0.0074	0.7220	0.040*
H16B	0.1378	0.1220	0.6755	0.040*
C17	0.24085 (13)	0.0515 (3)	0.66539 (11)	0.0320 (6)
H17A	0.2651	−0.0441	0.6615	0.038*
H17B	0.2336	0.1064	0.6266	0.038*
C18	0.35816 (12)	0.1711 (3)	0.70649 (10)	0.0284 (5)
H18A	0.3518	0.2420	0.6724	0.034*
H18B	0.3837	0.0822	0.6965	0.034*
C19	0.40534 (12)	0.2390 (3)	0.76533 (10)	0.0243 (5)
H19A	0.4520	0.2816	0.7581	0.029*
H19B	0.3762	0.3200	0.7774	0.029*
C20	0.48397 (12)	0.0195 (3)	0.81353 (11)	0.0261 (5)
H20B	0.4644	−0.0413	0.7764	0.031*
H20A	0.4908	−0.0459	0.8495	0.031*
C21	0.01010 (13)	−0.2021 (3)	0.68490 (11)	0.0292 (5)
C22	0.01297 (14)	−0.1313 (3)	0.73938 (11)	0.0356 (6)
H22A	0.0605	−0.1029	0.7660	0.043*
C23	−0.05321 (14)	−0.1021 (3)	0.75498 (12)	0.0371 (6)
H23A	−0.0507	−0.0540	0.7926	0.045*
C24	−0.12381 (14)	−0.1414 (3)	0.71681 (12)	0.0321 (6)
C25	−0.12502 (14)	−0.2143 (3)	0.66265 (13)	0.0372 (6)
H25A	−0.1724	−0.2443	0.6364	0.045*
C26	−0.05956 (14)	−0.2442 (3)	0.64603 (12)	0.0359 (6)
H26A	−0.0618	−0.2930	0.6085	0.043*
C27	−0.19559 (15)	−0.1047 (3)	0.73362 (14)	0.0429 (7)
H27C	−0.1871	−0.1147	0.7780	0.064*
H27B	−0.2360	−0.1722	0.7125	0.064*
H27A	−0.2105	−0.0034	0.7213	0.064*
C28	0.36361 (12)	−0.0038 (3)	0.89398 (10)	0.0232 (5)
C29	0.39360 (13)	−0.0892 (3)	0.94540 (10)	0.0259 (5)
H29A	0.4395	−0.0610	0.9742	0.031*
C30	0.35604 (13)	−0.2159 (3)	0.95433 (11)	0.0276 (5)
H30A	0.3762	−0.2736	0.9899	0.033*
C31	0.28951 (13)	−0.2605 (3)	0.91229 (11)	0.0279 (5)

C32	0.26032 (13)	−0.1730 (3)	0.86087 (11)	0.0323 (6)
H32A	0.2145	−0.2016	0.8320	0.039*
C33	0.29661 (13)	−0.0453 (3)	0.85100 (11)	0.0298 (5)
H33A	0.2763	0.0130	0.8156	0.036*
C34	0.25128 (16)	−0.4027 (3)	0.92084 (14)	0.0429 (7)
H34C	0.2421	−0.4039	0.9614	0.064*
H34B	0.2841	−0.4856	0.9173	0.064*
H34A	0.2028	−0.4111	0.8894	0.064*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0286 (3)	0.0524 (5)	0.0337 (3)	−0.0024 (3)	0.0038 (3)	0.0044 (3)
S2	0.0328 (3)	0.0528 (5)	0.0558 (5)	0.0022 (3)	0.0152 (3)	0.0148 (4)
S3	0.0279 (3)	0.0323 (4)	0.0419 (4)	0.0020 (3)	0.0092 (3)	−0.0024 (3)
S4	0.0272 (3)	0.0234 (3)	0.0215 (3)	−0.0020 (2)	0.0062 (2)	−0.0005 (2)
O1	0.0303 (9)	0.0433 (11)	0.0295 (9)	−0.0016 (8)	0.0127 (7)	0.0032 (8)
O2	0.0397 (10)	0.0302 (10)	0.0290 (9)	0.0060 (7)	0.0099 (7)	−0.0031 (8)
O3	0.0358 (9)	0.0366 (11)	0.0298 (9)	0.0036 (8)	0.0113 (7)	0.0059 (8)
O4	0.0433 (10)	0.0415 (12)	0.0466 (11)	−0.0146 (8)	0.0184 (9)	−0.0138 (9)
O5	0.0227 (8)	0.0421 (11)	0.0252 (8)	−0.0060 (7)	0.0047 (6)	−0.0054 (7)
O6	0.0498 (11)	0.0368 (11)	0.0597 (13)	−0.0017 (9)	0.0222 (10)	−0.0179 (10)
O7	0.0286 (9)	0.0518 (13)	0.0529 (12)	0.0109 (8)	0.0048 (8)	0.0113 (10)
O8	0.0421 (10)	0.0248 (9)	0.0341 (9)	0.0052 (7)	0.0173 (8)	0.0001 (7)
O9	0.0373 (10)	0.0334 (10)	0.0266 (9)	−0.0105 (8)	−0.0006 (7)	0.0019 (8)
N1	0.0298 (10)	0.0367 (13)	0.0286 (11)	−0.0085 (9)	0.0024 (8)	−0.0053 (9)
N2	0.0259 (9)	0.0220 (11)	0.0241 (9)	0.0040 (8)	0.0083 (7)	0.0043 (8)
C1	0.0268 (12)	0.0245 (13)	0.0300 (12)	0.0019 (9)	0.0088 (10)	0.0019 (10)
C2	0.0256 (11)	0.0218 (13)	0.0372 (13)	0.0016 (9)	0.0091 (10)	0.0020 (11)
C3	0.0282 (12)	0.0324 (15)	0.0479 (16)	−0.0007 (11)	0.0159 (11)	0.0063 (13)
C4	0.0253 (13)	0.0496 (18)	0.0482 (16)	−0.0038 (12)	0.0079 (11)	0.0022 (14)
C5	0.0342 (13)	0.0286 (14)	0.0365 (13)	0.0043 (10)	0.0179 (11)	0.0022 (11)
C6	0.0423 (14)	0.0297 (15)	0.0360 (14)	0.0077 (11)	0.0185 (12)	−0.0010 (11)
C7	0.0415 (14)	0.0412 (17)	0.0260 (12)	0.0033 (12)	0.0088 (11)	−0.0032 (11)
C8	0.0420 (14)	0.0390 (16)	0.0254 (12)	0.0004 (12)	0.0130 (11)	0.0058 (11)
C9	0.0342 (13)	0.0304 (15)	0.0353 (14)	−0.0016 (11)	0.0027 (11)	0.0035 (11)
C10	0.0318 (13)	0.0318 (15)	0.0396 (14)	−0.0060 (11)	0.0039 (11)	−0.0059 (12)
C11	0.0292 (12)	0.0454 (17)	0.0296 (13)	−0.0040 (11)	0.0037 (10)	−0.0007 (12)
C12	0.0324 (13)	0.0455 (18)	0.0274 (12)	−0.0064 (11)	0.0042 (10)	−0.0052 (12)
C13	0.0411 (15)	0.0424 (18)	0.0393 (15)	−0.0028 (12)	0.0071 (12)	0.0017 (13)
C14	0.0375 (15)	0.0486 (19)	0.0514 (17)	0.0078 (13)	0.0122 (13)	0.0115 (14)
C15	0.0352 (13)	0.0421 (16)	0.0271 (13)	−0.0035 (11)	0.0033 (11)	−0.0038 (11)
C16	0.0277 (12)	0.0408 (16)	0.0302 (13)	−0.0071 (11)	0.0033 (10)	−0.0090 (12)
C17	0.0290 (13)	0.0350 (15)	0.0292 (13)	−0.0039 (10)	0.0032 (10)	−0.0059 (11)
C18	0.0227 (11)	0.0359 (14)	0.0261 (12)	−0.0018 (10)	0.0056 (9)	0.0011 (11)
C19	0.0245 (11)	0.0229 (13)	0.0249 (11)	−0.0010 (9)	0.0055 (9)	0.0046 (10)
C20	0.0276 (12)	0.0223 (13)	0.0295 (12)	0.0023 (9)	0.0096 (10)	0.0026 (10)
C21	0.0294 (12)	0.0234 (14)	0.0341 (13)	−0.0007 (9)	0.0072 (10)	0.0016 (10)

C22	0.0323 (13)	0.0397 (16)	0.0312 (13)	−0.0022 (11)	0.0026 (10)	−0.0010 (12)
C23	0.0361 (14)	0.0428 (17)	0.0325 (13)	−0.0006 (12)	0.0094 (11)	−0.0051 (12)
C24	0.0326 (13)	0.0248 (14)	0.0395 (14)	−0.0030 (10)	0.0110 (11)	0.0045 (11)
C25	0.0275 (13)	0.0343 (15)	0.0453 (15)	−0.0079 (11)	0.0019 (11)	−0.0056 (12)
C26	0.0330 (13)	0.0337 (16)	0.0394 (14)	−0.0040 (11)	0.0070 (11)	−0.0088 (12)
C27	0.0336 (14)	0.0433 (17)	0.0548 (17)	−0.0035 (12)	0.0171 (13)	0.0008 (14)
C28	0.0231 (11)	0.0255 (13)	0.0218 (11)	−0.0018 (9)	0.0077 (9)	−0.0017 (9)
C29	0.0282 (12)	0.0268 (13)	0.0215 (11)	−0.0009 (9)	0.0046 (9)	−0.0013 (10)
C30	0.0315 (12)	0.0266 (13)	0.0252 (12)	0.0021 (10)	0.0085 (10)	0.0046 (10)
C31	0.0278 (12)	0.0281 (14)	0.0309 (12)	−0.0002 (10)	0.0134 (10)	0.0007 (10)
C32	0.0255 (12)	0.0387 (15)	0.0304 (13)	−0.0063 (10)	0.0037 (10)	0.0008 (11)
C33	0.0276 (12)	0.0359 (15)	0.0252 (12)	−0.0006 (10)	0.0059 (10)	0.0066 (11)
C34	0.0395 (15)	0.0365 (17)	0.0542 (17)	−0.0084 (12)	0.0151 (13)	0.0038 (14)

Geometric parameters (Å, º)

S1—C4	1.708 (3)	C11—C15	1.507 (4)
S1—C1	1.722 (2)	C12—C13	1.416 (4)
S2—C11	1.712 (3)	C13—C14	1.352 (4)
S2—C14	1.719 (3)	C13—H13A	0.9500
S3—O6	1.433 (2)	C14—H14A	0.9500
S3—O7	1.4399 (19)	C15—H15B	0.9900
S3—N1	1.620 (2)	C15—H15A	0.9900
S3—C21	1.762 (2)	C16—C17	1.506 (3)
S4—O8	1.4339 (17)	C16—H16A	0.9900
S4—O9	1.4365 (17)	C16—H16B	0.9900
S4—N2	1.6200 (19)	C17—H17A	0.9900
S4—C28	1.768 (2)	C17—H17B	0.9900
O1—C2	1.367 (3)	C18—C19	1.512 (3)
O1—C5	1.428 (3)	C18—H18A	0.9900
O2—C6	1.423 (3)	C18—H18B	0.9900
O2—C7	1.426 (3)	C19—H19A	0.9900
O3—C8	1.417 (3)	C19—H19B	0.9900
O3—C9	1.419 (3)	C20—H20B	0.9900
O4—C12	1.371 (3)	C20—H20A	0.9900
O4—C10	1.439 (3)	C21—C22	1.382 (4)
O5—C17	1.414 (3)	C21—C26	1.394 (3)
O5—C18	1.418 (3)	C22—C23	1.375 (4)
N1—C16	1.477 (3)	C22—H22A	0.9500
N1—C15	1.479 (3)	C23—C24	1.394 (4)
N2—C19	1.473 (3)	C23—H23A	0.9500
N2—C20	1.475 (3)	C24—C25	1.391 (4)
C1—C2	1.363 (3)	C24—C27	1.500 (4)
C1—C20	1.496 (3)	C25—C26	1.375 (4)
C2—C3	1.424 (3)	C25—H25A	0.9500
C3—C4	1.358 (4)	C26—H26A	0.9500
C3—H3A	0.9500	C27—H27C	0.9800
C4—H4A	0.9500	C27—H27B	0.9800

C5—C6	1.500 (4)	C27—H27A	0.9800
C5—H5B	0.9900	C28—C29	1.385 (3)
C5—H5A	0.9900	C28—C33	1.397 (3)
C6—H6B	0.9900	C29—C30	1.384 (3)
C6—H6A	0.9900	C29—H29A	0.9500
C7—C8	1.500 (4)	C30—C31	1.389 (3)
C7—H7A	0.9900	C30—H30A	0.9500
C7—H7B	0.9900	C31—C32	1.394 (3)
C8—H8A	0.9900	C31—C34	1.507 (4)
C8—H8B	0.9900	C32—C33	1.385 (4)
C9—C10	1.492 (4)	C32—H32A	0.9500
C9—H9B	0.9900	C33—H33A	0.9500
C9—H9A	0.9900	C34—H34C	0.9800
C10—H10B	0.9900	C34—H34B	0.9800
C10—H10A	0.9900	C34—H34A	0.9800
C11—C12	1.368 (4)		

C4—S1—C1	92.06 (12)	N1—C15—C11	113.8 (2)
C11—S2—C14	92.06 (14)	N1—C15—H15B	108.8
O6—S3—O7	120.03 (13)	C11—C15—H15B	108.8
O6—S3—N1	106.67 (12)	N1—C15—H15A	108.8
O7—S3—N1	106.00 (12)	C11—C15—H15A	108.8
O6—S3—C21	107.44 (12)	H15B—C15—H15A	107.7
O7—S3—C21	107.21 (12)	N1—C16—C17	110.4 (2)
N1—S3—C21	109.18 (12)	N1—C16—H16A	109.6
O8—S4—O9	118.07 (11)	C17—C16—H16A	109.6
O8—S4—N2	107.29 (10)	N1—C16—H16B	109.6
O9—S4—N2	111.17 (10)	C17—C16—H16B	109.6
O8—S4—C28	109.12 (11)	H16A—C16—H16B	108.1
O9—S4—C28	106.58 (10)	O5—C17—C16	106.51 (19)
N2—S4—C28	103.66 (10)	O5—C17—H17A	110.4
C2—O1—C5	117.53 (18)	C16—C17—H17A	110.4
C6—O2—C7	110.12 (19)	O5—C17—H17B	110.4
C8—O3—C9	110.92 (19)	C16—C17—H17B	110.4
C12—O4—C10	116.1 (2)	H17A—C17—H17B	108.6
C17—O5—C18	113.02 (17)	O5—C18—C19	108.10 (18)
C16—N1—C15	118.1 (2)	O5—C18—H18A	110.1
C16—N1—S3	119.51 (17)	C19—C18—H18A	110.1
C15—N1—S3	119.73 (17)	O5—C18—H18B	110.1
C19—N2—C20	118.20 (17)	C19—C18—H18B	110.1
C19—N2—S4	122.60 (15)	H18A—C18—H18B	108.4
C20—N2—S4	116.82 (15)	N2—C19—C18	112.76 (19)
C2—C1—C20	126.3 (2)	N2—C19—H19A	109.0
C2—C1—S1	110.14 (17)	C18—C19—H19A	109.0
C20—C1—S1	123.41 (17)	N2—C19—H19B	109.0
C1—C2—O1	118.8 (2)	C18—C19—H19B	109.0
C1—C2—C3	114.2 (2)	H19A—C19—H19B	107.8
O1—C2—C3	127.0 (2)	N2—C20—C1	114.4 (2)

C4—C3—C2	111.0 (2)	N2—C20—H20B	108.7
C4—C3—H3A	124.5	C1—C20—H20B	108.7
C2—C3—H3A	124.5	N2—C20—H20A	108.7
C3—C4—S1	112.64 (19)	C1—C20—H20A	108.7
C3—C4—H4A	123.7	H20B—C20—H20A	107.6
S1—C4—H4A	123.7	C22—C21—C26	120.1 (2)
O1—C5—C6	107.58 (19)	C22—C21—S3	119.44 (18)
O1—C5—H5B	110.2	C26—C21—S3	120.4 (2)
C6—C5—H5B	110.2	C23—C22—C21	119.7 (2)
O1—C5—H5A	110.2	C23—C22—H22A	120.1
C6—C5—H5A	110.2	C21—C22—H22A	120.1
H5B—C5—H5A	108.5	C22—C23—C24	121.5 (2)
O2—C6—C5	109.7 (2)	C22—C23—H23A	119.2
O2—C6—H6B	109.7	C24—C23—H23A	119.2
C5—C6—H6B	109.7	C25—C24—C23	117.6 (2)
O2—C6—H6A	109.7	C25—C24—C27	121.6 (2)
C5—C6—H6A	109.7	C23—C24—C27	120.9 (2)
H6B—C6—H6A	108.2	C26—C25—C24	121.9 (2)
O2—C7—C8	111.4 (2)	C26—C25—H25A	119.1
O2—C7—H7A	109.3	C24—C25—H25A	119.1
C8—C7—H7A	109.3	C25—C26—C21	119.1 (2)
O2—C7—H7B	109.3	C25—C26—H26A	120.4
C8—C7—H7B	109.3	C21—C26—H26A	120.4
H7A—C7—H7B	108.0	C24—C27—H27C	109.5
O3—C8—C7	111.8 (2)	C24—C27—H27B	109.5
O3—C8—H8A	109.2	H27C—C27—H27B	109.5
C7—C8—H8A	109.2	C24—C27—H27A	109.5
O3—C8—H8B	109.2	H27C—C27—H27A	109.5
C7—C8—H8B	109.2	H27B—C27—H27A	109.5
H8A—C8—H8B	107.9	C29—C28—C33	120.7 (2)
O3—C9—C10	110.3 (2)	C29—C28—S4	120.37 (17)
O3—C9—H9B	109.6	C33—C28—S4	118.95 (18)
C10—C9—H9B	109.6	C30—C29—C28	119.3 (2)
O3—C9—H9A	109.6	C30—C29—H29A	120.3
C10—C9—H9A	109.6	C28—C29—H29A	120.3
H9B—C9—H9A	108.1	C29—C30—C31	121.3 (2)
O4—C10—C9	107.2 (2)	C29—C30—H30A	119.3
O4—C10—H10B	110.3	C31—C30—H30A	119.3
C9—C10—H10B	110.3	C30—C31—C32	118.4 (2)
O4—C10—H10A	110.3	C30—C31—C34	120.9 (2)
C9—C10—H10A	110.3	C32—C31—C34	120.7 (2)
H10B—C10—H10A	108.5	C33—C32—C31	121.4 (2)
C12—C11—C15	125.9 (2)	C33—C32—H32A	119.3
C12—C11—S2	110.4 (2)	C31—C32—H32A	119.3
C15—C11—S2	123.7 (2)	C32—C33—C28	118.8 (2)
C11—C12—O4	120.0 (2)	C32—C33—H33A	120.6
C11—C12—C13	113.8 (2)	C28—C33—H33A	120.6
O4—C12—C13	126.1 (3)	C31—C34—H34C	109.5

C14—C13—C12	111.8 (3)	C31—C34—H34B	109.5
C14—C13—H13A	124.1	H34C—C34—H34B	109.5
C12—C13—H13A	124.1	C31—C34—H34A	109.5
C13—C14—S2	112.0 (2)	H34C—C34—H34A	109.5
C13—C14—H14A	124.0	H34B—C34—H34A	109.5
S2—C14—H14A	124.0		

O6—S3—N1—C16	−158.31 (18)	C12—C11—C15—N1	106.0 (3)
O7—S3—N1—C16	−29.3 (2)	S2—C11—C15—N1	−72.0 (3)
C21—S3—N1—C16	85.9 (2)	C15—N1—C16—C17	−79.4 (3)
O6—S3—N1—C15	40.5 (2)	S3—N1—C16—C17	119.1 (2)
O7—S3—N1—C15	169.51 (19)	C18—O5—C17—C16	−176.9 (2)
C21—S3—N1—C15	−75.3 (2)	N1—C16—C17—O5	−168.6 (2)
O8—S4—N2—C19	13.3 (2)	C17—O5—C18—C19	−172.3 (2)
O9—S4—N2—C19	−117.22 (18)	C20—N2—C19—C18	71.6 (2)
C28—S4—N2—C19	128.63 (18)	S4—N2—C19—C18	−126.44 (18)
O8—S4—N2—C20	175.43 (16)	O5—C18—C19—N2	68.5 (2)
O9—S4—N2—C20	44.96 (19)	C19—N2—C20—C1	60.6 (3)
C28—S4—N2—C20	−69.19 (18)	S4—N2—C20—C1	−102.4 (2)
C4—S1—C1—C2	−1.1 (2)	C2—C1—C20—N2	−93.3 (3)
C4—S1—C1—C20	174.4 (2)	S1—C1—C20—N2	92.0 (2)
C20—C1—C2—O1	4.8 (4)	O6—S3—C21—C22	166.3 (2)
S1—C1—C2—O1	−179.89 (17)	O7—S3—C21—C22	36.0 (2)
C20—C1—C2—C3	−175.2 (2)	N1—S3—C21—C22	−78.4 (2)
S1—C1—C2—C3	0.1 (3)	O6—S3—C21—C26	−16.0 (2)
C5—O1—C2—C1	−174.4 (2)	O7—S3—C21—C26	−146.3 (2)
C5—O1—C2—C3	5.6 (4)	N1—S3—C21—C26	99.3 (2)
C1—C2—C3—C4	1.2 (3)	C26—C21—C22—C23	−0.2 (4)
O1—C2—C3—C4	−178.8 (2)	S3—C21—C22—C23	177.5 (2)
C2—C3—C4—S1	−2.0 (3)	C21—C22—C23—C24	−0.4 (4)
C1—S1—C4—C3	1.8 (2)	C22—C23—C24—C25	1.3 (4)
C2—O1—C5—C6	173.8 (2)	C22—C23—C24—C27	−178.2 (3)
C7—O2—C6—C5	−178.0 (2)	C23—C24—C25—C26	−1.5 (4)
O1—C5—C6—O2	71.3 (3)	C27—C24—C25—C26	177.9 (3)
C6—O2—C7—C8	−167.9 (2)	C24—C25—C26—C21	0.9 (4)
C9—O3—C8—C7	−174.1 (2)	C22—C21—C26—C25	0.0 (4)
O2—C7—C8—O3	−84.8 (3)	S3—C21—C26—C25	−177.7 (2)
C8—O3—C9—C10	174.6 (2)	O8—S4—C28—C29	−124.30 (19)
C12—O4—C10—C9	−179.0 (2)	O9—S4—C28—C29	4.2 (2)
O3—C9—C10—O4	−72.1 (3)	N2—S4—C28—C29	121.62 (19)
C14—S2—C11—C12	0.0 (2)	O8—S4—C28—C33	56.0 (2)
C14—S2—C11—C15	178.3 (2)	O9—S4—C28—C33	−175.48 (19)
C15—C11—C12—O4	6.4 (4)	N2—S4—C28—C33	−58.1 (2)
S2—C11—C12—O4	−175.32 (18)	C33—C28—C29—C30	−0.7 (3)
C15—C11—C12—C13	−178.0 (2)	S4—C28—C29—C30	179.58 (18)
S2—C11—C12—C13	0.2 (3)	C28—C29—C30—C31	1.0 (4)
C10—O4—C12—C11	−140.3 (2)	C29—C30—C31—C32	−1.0 (4)
C10—O4—C12—C13	44.7 (3)	C29—C30—C31—C34	176.8 (2)

C11—C12—C13—C14	−0.4 (3)	C30—C31—C32—C33	0.7 (4)
O4—C12—C13—C14	174.9 (3)	C34—C31—C32—C33	−177.1 (2)
C12—C13—C14—S2	0.3 (3)	C31—C32—C33—C28	−0.4 (4)
C11—S2—C14—C13	−0.2 (2)	C29—C28—C33—C32	0.4 (4)
C16—N1—C15—C11	−49.6 (3)	S4—C28—C33—C32	−179.87 (19)
S3—N1—C15—C11	111.8 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*A*···O4	0.99	2.54	2.941 (3)	104
C15—H15*B*···O6	0.99	2.45	2.914 (4)	108
C16—H16*A*···O7	0.99	2.36	2.828 (4)	108
C19—H19*B*···O8	0.99	2.34	2.859 (3)	112
C26—H26*A*···O6	0.95	2.56	2.923 (3)	103
C29—H29*A*···O9	0.95	2.50	2.885 (3)	104
C32—H32*A*···O7	0.95	2.57	3.386 (3)	145
C33—H33*A*···O5	0.95	2.59	3.450 (3)	151
C13—H13*A*···O6^{i}	0.95	2.53	3.245 (4)	132
C27—H27*B*···O8^{ii}	0.98	2.58	3.463 (3)	149
C29—H29*A*···O9^{iii}	0.95	2.48	3.221 (3)	135

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