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(5,7-Dimethyl-2-oxo-2*H*-chromen-4-yl)methyl morpholine-4-carbodithioate

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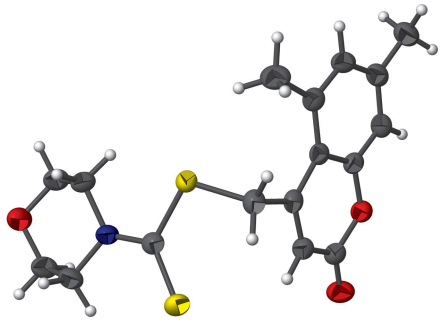
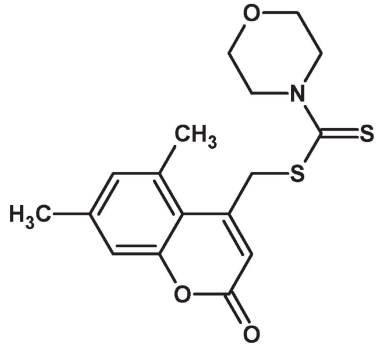
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{17}H_{19}NO_3S_2$, the 2*H*-chromene ring system is nearly planar, with a maximum deviation of 0.080 (2) Å, and the morpholine ring adopts a chair conformation. The bond-angle sum at the N atom is 358°. The coumarin unit makes dihedral angle of 86.34 (9)° with the morpholine ring. A short intramolecular C—H···S contact generates an *S*(7) ring. In the crystal, inversion dimers linked by pairs of weak C—H···O hydrogen bonds generate $R_2^2(16)$ loops. Aromatic π–π interactions interactions [shortest centroid–centroid distance = 3.8599 (13) Å] also occur.

3D view



Chemical scheme



Structure description

Recently, dithiocarbamic acid esters, a common class of organic molecules, have also attracted attention due to their anti-cancer action (Scozzafava *et al.*, 2000) in derivatives such as thalidomide dithiocarbamates (Zahran *et al.*, 2008) and chromone dithiocarbamates (Huang *et al.*, 2009). As part of our studies in this area, we now describe the structure of the title compound (Kant *et al.*, 2012).

The asymmetric unit is shown in Fig. 1. The 2*H*-chromene ring systems is nearly planar, with a maximum deviation of 0.0804 (22) Å for the atom C7 and the morpholine ring adopts a chair conformation. The coumarin unit makes dihedral angle of 86.34 (9)° with morpholine ring. In the crystal, C—H···O hydrogen bonds (Table 1, Fig. 2) and π–π interactions between fused benzene rings of chromene [shortest centroid–centroid distance = 3.8599 (13) Å] are observed.

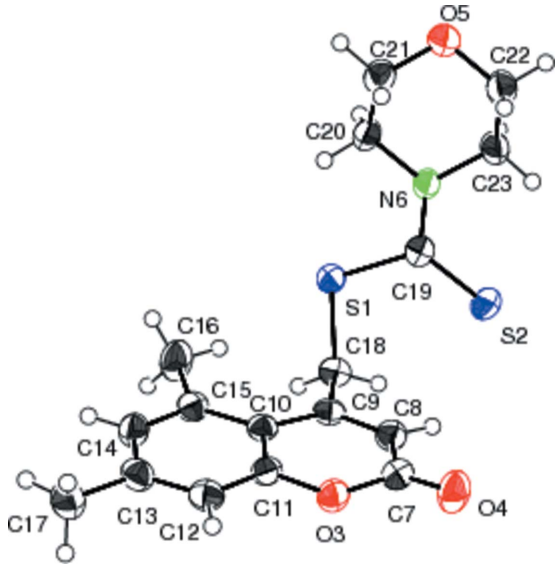


Figure 1
Perspective diagram of the title molecule drawn with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radius.

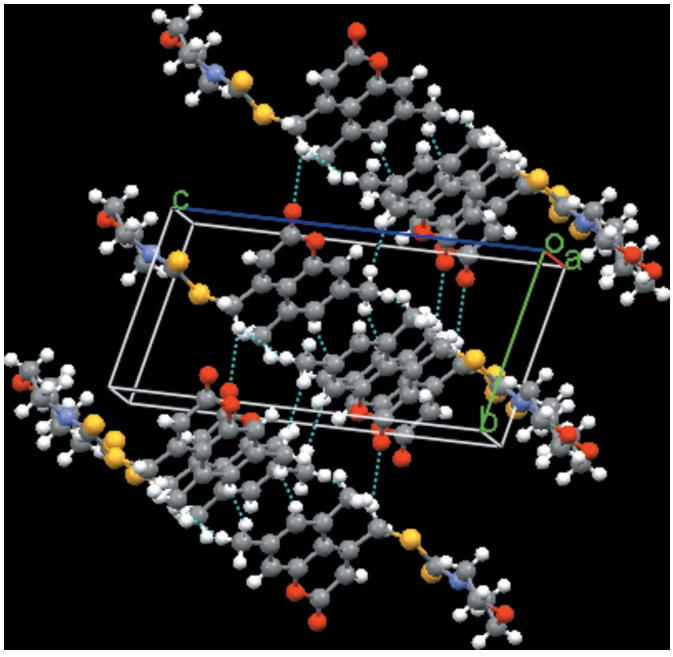


Figure 2
Packing diagram of the molecule viewed parallel to the *b* axis.

Synthesis and crystallization

This compound was prepared according to the reported method (Kant *et al.*, 2012). Colourless needles of the title compound were grown from a mixed solution of EtOH/$CHCl_3$ (*v*/*v* = 1/1) by slow evaporation at room temperature. Yield = 81%, m.p. 445 K. IR (KBr): 645 cm^{-1}(C—S), 1231 cm^{-1} (C═S), 1039 cm^{-1}(C—O), 850 cm^{-1} (C—N),1118 cm^{-1}(C—O—C), 1711 cm^{-1}(C═O). GCMS: *m*/*e*: 349. 1H NMR (400 MHz, $CDCl_3$, δ, p.p.m.) 2.21 (*t*, 3H, –CH_3), 2.61 (*t*, 3H, –CH_3), 3.61 (*s*, 4H, morpholine-CH_2), 3.80 (*s*, 2H, morpholine-CH_2), 4.15(*s*, 2H, morpholine-CH_2), 4.65 (t, 2H, Methylene-CH_2), 6.33 (s, 1H, Ar—H), 6.77 (s, 1H, Ar—H), 6.84 (s, 1H, Ar—H). Elemental analysis for $C_{17}H_{19}NO_3S_2$: C, 58.37; H, 5.42; N, 3.91.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*C*···S1	0.96	2.62	3.358 (2)	134
C17—H17*A*···O4^{i}	0.96	2.58	3.505 (2)	162

Symmetry code: (i) $-x+1, -y+2, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{19}NO_3S_2$
M_r	349.45
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, *b*, *c* (Å)	6.9573 (2), 7.9838 (2), 15.6037 (4)
α, β, γ (°)	75.485 (2), 87.122 (1), 75.763 (1)
V (Å^3)	813.22 (4)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.34
Crystal size (mm)	0.24 × 0.20 × 0.12
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.770, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12588, 2857, 2551
R_{int}	0.036
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.084, 1.08
No. of reflections	2857
No. of parameters	211
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.20

Computer programs: *SMART* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Huang, W., Ding, Y., Miao, Y., Liu, M. Z., Li, Y. & Yang, G. F. (2009). *Eur. J. Med. Chem.* **44**, 3687–3696.
Kant, R., Gupta, V. K., Kapoor, K., Kour, G., Kumar, K. M., Mahabaleshwaraiah, N. M. & Kotresh, O. (2012). *Acta Cryst.* E**68**, o1104–o1105.
Scozzafava, A., Mastrolorenzo, A. & Supuran, C. T. (2000). *Bioorg. Med. Chem. Lett.* **10**, 1887–1891.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Zahran, M. A. H., Salem, T. A.-R., Samaka, R. M., Agwa, H. S. & Awad, A. R. (2008). *Bioorg. Med. Chem.* **16**, 9708–9718.

full crystallographic data

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Crystal data

$C_{17}H_{19}NO_3S_2$
M_r = 349.45
Triclinic, $P\overline{1}$
a = 6.9573 (2) Å
b = 7.9838 (2) Å
c = 15.6037 (4) Å
α = 75.485 (2)°
β = 87.122 (1)°
γ = 75.763 (1)°
V = 813.22 (4) Å^3
Z = 2
$F(000)$ = 368
D_x = 1.427 Mg m^{-3}
Melting point: 445 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2857 reflections
θ = 1.4–25.0°
μ = 0.34 mm^{-1}
T = 296 K
Plate, colourless
0.24 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.770, T_{max} = 1.000
12588 measured reflections
2857 independent reflections
2551 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.0°, θ_{min} = 1.4°
h = −8→8
k = −9→9
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.084
S = 1.08
2857 reflections
211 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.1658P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.041 (3)

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_{iso}*/U_{eq}
S1	0.69951 (6)	0.57313 (5)	0.12898 (2)	0.03649 (15)
S2	1.06731 (6)	0.70892 (6)	0.06881 (3)	0.04197 (15)
O5	0.54406 (19)	0.92765 (17)	−0.19357 (8)	0.0492 (3)
O3	0.65176 (17)	0.93171 (14)	0.37562 (7)	0.0371 (3)
O4	0.8819 (2)	1.05956 (16)	0.30663 (9)	0.0512 (3)
N6	0.74909 (19)	0.75809 (17)	−0.03019 (8)	0.0328 (3)
C7	0.8041 (3)	0.9362 (2)	0.31725 (10)	0.0367 (4)
C8	0.8592 (2)	0.7900 (2)	0.27620 (10)	0.0352 (4)
H8	0.9736	0.7805	0.2425	0.042*
C9	0.7553 (2)	0.66529 (19)	0.28349 (9)	0.0307 (3)
C10	0.5788 (2)	0.67346 (19)	0.33885 (9)	0.0303 (3)
C11	0.5375 (2)	0.80899 (19)	0.38456 (9)	0.0320 (3)
C12	0.3827 (3)	0.8326 (2)	0.44271 (10)	0.0379 (4)
H12	0.3637	0.9241	0.4716	0.045*
C13	0.2570 (3)	0.7202 (2)	0.45765 (10)	0.0385 (4)
C17	0.0869 (3)	0.7390 (3)	0.52080 (12)	0.0503 (5)
H17A	0.1041	0.8149	0.5573	0.076*
H17B	0.0833	0.6237	0.5575	0.076*
H17C	−0.0353	0.7904	0.4879	0.076*
C14	0.2918 (3)	0.5867 (2)	0.41183 (11)	0.0393 (4)
H14	0.2060	0.5112	0.4210	0.047*
C15	0.4458 (2)	0.5596 (2)	0.35363 (10)	0.0354 (4)
C16	0.4565 (3)	0.4090 (2)	0.30953 (13)	0.0523 (5)
H16A	0.3469	0.3558	0.3282	0.078*
H16B	0.5787	0.3208	0.3260	0.078*
H16C	0.4507	0.4549	0.2464	0.078*
C18	0.8329 (2)	0.5257 (2)	0.23235 (10)	0.0347 (4)
H18A	0.8219	0.4104	0.2684	0.042*
H18B	0.9723	0.5194	0.2201	0.042*
C19	0.8421 (2)	0.69039 (19)	0.04831 (10)	0.0306 (3)
C20	0.5643 (2)	0.7179 (2)	−0.05154 (11)	0.0390 (4)
H20A	0.4905	0.6889	0.0023	0.047*
H20B	0.5961	0.6148	−0.0765	0.047*
C21	0.4390 (3)	0.8729 (2)	−0.11608 (11)	0.0432 (4)
H21A	0.3226	0.8400	−0.1318	0.052*
H21B	0.3945	0.9717	−0.0884	0.052*
C22	0.7086 (3)	0.9846 (2)	−0.17124 (12)	0.0459 (4)
H22A	0.6613	1.0835	−0.1439	0.055*
H22B	0.7775	1.0267	−0.2249	0.055*
C23	0.8509 (3)	0.8381 (2)	−0.10910 (11)	0.0403 (4)
H23A	0.9138	0.7468	−0.1394	0.048*
H23B	0.9537	0.8855	−0.0911	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0415 (3)	0.0421 (2)	0.0314 (2)	−0.0195 (2)	0.00148 (17)	−0.00998 (16)
S2	0.0293 (2)	0.0542 (3)	0.0440 (3)	−0.0129 (2)	−0.00102 (18)	−0.01193 (19)
O5	0.0426 (7)	0.0605 (8)	0.0402 (6)	−0.0188 (6)	−0.0063 (5)	0.0033 (5)
O3	0.0413 (7)	0.0378 (6)	0.0383 (6)	−0.0148 (5)	0.0040 (5)	−0.0160 (5)
O4	0.0559 (8)	0.0475 (7)	0.0639 (8)	−0.0285 (7)	0.0133 (6)	−0.0251 (6)
N6	0.0277 (7)	0.0347 (7)	0.0355 (7)	−0.0102 (6)	0.0002 (5)	−0.0055 (5)
C7	0.0368 (9)	0.0392 (9)	0.0369 (8)	−0.0124 (8)	−0.0012 (7)	−0.0110 (7)
C8	0.0344 (9)	0.0395 (9)	0.0342 (8)	−0.0105 (7)	0.0020 (7)	−0.0123 (6)
C9	0.0335 (8)	0.0290 (7)	0.0267 (7)	−0.0031 (7)	−0.0051 (6)	−0.0050 (6)
C10	0.0327 (8)	0.0293 (7)	0.0271 (7)	−0.0064 (7)	−0.0046 (6)	−0.0034 (6)
C11	0.0341 (9)	0.0305 (8)	0.0315 (8)	−0.0089 (7)	−0.0040 (6)	−0.0060 (6)
C12	0.0408 (10)	0.0385 (9)	0.0349 (8)	−0.0074 (8)	0.0010 (7)	−0.0120 (7)
C13	0.0348 (9)	0.0421 (9)	0.0340 (8)	−0.0062 (8)	−0.0001 (7)	−0.0037 (7)
C17	0.0442 (11)	0.0601 (11)	0.0456 (10)	−0.0145 (9)	0.0088 (8)	−0.0109 (8)
C14	0.0377 (9)	0.0397 (9)	0.0410 (9)	−0.0157 (8)	−0.0009 (7)	−0.0041 (7)
C15	0.0395 (9)	0.0317 (8)	0.0342 (8)	−0.0092 (7)	−0.0039 (7)	−0.0052 (6)
C16	0.0590 (13)	0.0466 (10)	0.0644 (12)	−0.0286 (10)	0.0127 (10)	−0.0243 (9)
C18	0.0379 (9)	0.0315 (8)	0.0336 (8)	−0.0053 (7)	−0.0017 (7)	−0.0087 (6)
C19	0.0305 (8)	0.0266 (7)	0.0356 (8)	−0.0046 (6)	0.0019 (6)	−0.0116 (6)
C20	0.0355 (9)	0.0408 (9)	0.0418 (9)	−0.0164 (8)	−0.0035 (7)	−0.0042 (7)
C21	0.0319 (9)	0.0474 (10)	0.0468 (9)	−0.0107 (8)	−0.0033 (7)	−0.0035 (8)
C22	0.0417 (10)	0.0463 (10)	0.0464 (10)	−0.0170 (8)	−0.0005 (8)	0.0010 (8)
C23	0.0327 (9)	0.0468 (9)	0.0384 (9)	−0.0114 (8)	0.0042 (7)	−0.0039 (7)

Geometric parameters (Å, º)

S1—C19	1.7850 (15)	C13—C17	1.505 (2)
S1—C18	1.8104 (16)	C17—H17A	0.9600
S2—C19	1.6634 (16)	C17—H17B	0.9600
O5—C21	1.411 (2)	C17—H17C	0.9600
O5—C22	1.419 (2)	C14—C15	1.381 (2)
O3—C7	1.3636 (19)	C14—H14	0.9300
O3—C11	1.3837 (18)	C15—C16	1.513 (2)
O4—C7	1.2088 (19)	C16—H16A	0.9600
N6—C19	1.337 (2)	C16—H16B	0.9600
N6—C23	1.472 (2)	C16—H16C	0.9600
N6—C20	1.472 (2)	C18—H18A	0.9700
C7—C8	1.432 (2)	C18—H18B	0.9700
C8—C9	1.347 (2)	C20—C21	1.497 (2)
C8—H8	0.9300	C20—H20A	0.9700
C9—C10	1.463 (2)	C20—H20B	0.9700
C9—C18	1.509 (2)	C21—H21A	0.9700
C10—C11	1.406 (2)	C21—H21B	0.9700
C10—C15	1.422 (2)	C22—C23	1.499 (2)
C11—C12	1.381 (2)	C22—H22A	0.9700

C12—C13	1.373 (2)	C22—H22B	0.9700
C12—H12	0.9300	C23—H23A	0.9700
C13—C14	1.394 (2)	C23—H23B	0.9700

C19—S1—C18	104.75 (7)	C15—C16—H16A	109.5
C21—O5—C22	109.33 (13)	C15—C16—H16B	109.5
C7—O3—C11	121.95 (12)	H16A—C16—H16B	109.5
C19—N6—C23	121.25 (13)	C15—C16—H16C	109.5
C19—N6—C20	123.64 (13)	H16A—C16—H16C	109.5
C23—N6—C20	113.10 (13)	H16B—C16—H16C	109.5
O4—C7—O3	117.53 (14)	C9—C18—S1	112.31 (10)
O4—C7—C8	126.46 (16)	C9—C18—H18A	109.1
O3—C7—C8	115.98 (14)	S1—C18—H18A	109.1
C9—C8—C7	123.98 (15)	C9—C18—H18B	109.1
C9—C8—H8	118.0	S1—C18—H18B	109.1
C7—C8—H8	118.0	H18A—C18—H18B	107.9
C8—C9—C10	119.08 (14)	N6—C19—S2	124.20 (12)
C8—C9—C18	116.07 (14)	N6—C19—S1	112.43 (11)
C10—C9—C18	124.85 (13)	S2—C19—S1	123.36 (9)
C11—C10—C15	115.86 (14)	N6—C20—C21	111.12 (13)
C11—C10—C9	115.87 (13)	N6—C20—H20A	109.4
C15—C10—C9	128.26 (14)	C21—C20—H20A	109.4
C12—C11—O3	113.45 (13)	N6—C20—H20B	109.4
C12—C11—C10	124.13 (14)	C21—C20—H20B	109.4
O3—C11—C10	122.42 (14)	H20A—C20—H20B	108.0
C13—C12—C11	119.55 (15)	O5—C21—C20	111.68 (14)
C13—C12—H12	120.2	O5—C21—H21A	109.3
C11—C12—H12	120.2	C20—C21—H21A	109.3
C12—C13—C14	117.62 (15)	O5—C21—H21B	109.3
C12—C13—C17	121.79 (16)	C20—C21—H21B	109.3
C14—C13—C17	120.59 (16)	H21A—C21—H21B	107.9
C13—C17—H17A	109.5	O5—C22—C23	112.16 (14)
C13—C17—H17B	109.5	O5—C22—H22A	109.2
H17A—C17—H17B	109.5	C23—C22—H22A	109.2
C13—C17—H17C	109.5	O5—C22—H22B	109.2
H17A—C17—H17C	109.5	C23—C22—H22B	109.2
H17B—C17—H17C	109.5	H22A—C22—H22B	107.9
C15—C14—C13	124.03 (15)	N6—C23—C22	111.21 (14)
C15—C14—H14	118.0	N6—C23—H23A	109.4
C13—C14—H14	118.0	C22—C23—H23A	109.4
C14—C15—C10	118.78 (15)	N6—C23—H23B	109.4
C14—C15—C16	115.96 (15)	C22—C23—H23B	109.4
C10—C15—C16	125.25 (15)	H23A—C23—H23B	108.0

C11—O3—C7—O4	172.02 (14)	C13—C14—C15—C16	−179.20 (16)
C11—O3—C7—C8	−9.6 (2)	C11—C10—C15—C14	−1.4 (2)
O4—C7—C8—C9	−173.11 (16)	C9—C10—C15—C14	177.29 (14)
O3—C7—C8—C9	8.7 (2)	C11—C10—C15—C16	177.88 (15)

C7—C8—C9—C10	−2.2 (2)	C9—C10—C15—C16	−3.5 (3)
C7—C8—C9—C18	177.64 (14)	C8—C9—C18—S1	−99.37 (15)
C8—C9—C10—C11	−3.3 (2)	C10—C9—C18—S1	80.51 (16)
C18—C9—C10—C11	176.86 (13)	C19—S1—C18—C9	94.28 (12)
C8—C9—C10—C15	178.07 (14)	C23—N6—C19—S2	7.4 (2)
C18—C9—C10—C15	−1.8 (2)	C20—N6—C19—S2	170.20 (12)
C7—O3—C11—C12	−176.06 (13)	C23—N6—C19—S1	−171.43 (11)
C7—O3—C11—C10	4.5 (2)	C20—N6—C19—S1	−8.65 (19)
C15—C10—C11—C12	1.7 (2)	C18—S1—C19—N6	−171.04 (11)
C9—C10—C11—C12	−177.11 (14)	C18—S1—C19—S2	10.10 (12)
C15—C10—C11—O3	−178.87 (13)	C19—N6—C20—C21	148.50 (15)
C9—C10—C11—O3	2.3 (2)	C23—N6—C20—C21	−47.48 (19)
O3—C11—C12—C13	179.83 (14)	C22—O5—C21—C20	−61.97 (19)
C10—C11—C12—C13	−0.7 (2)	N6—C20—C21—O5	55.36 (19)
C11—C12—C13—C14	−0.6 (2)	C21—O5—C22—C23	61.16 (19)
C11—C12—C13—C17	179.55 (15)	C19—N6—C23—C22	−148.99 (15)
C12—C13—C14—C15	0.9 (3)	C20—N6—C23—C22	46.56 (19)
C17—C13—C14—C15	−179.25 (15)	O5—C22—C23—N6	−53.5 (2)
C13—C14—C15—C10	0.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*C*···S1	0.96	2.62	3.358 (2)	134
C17—H17*A*···O4^{i}	0.96	2.58	3.505 (2)	162

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.