



Crystal structure of (7-chloro-2-oxo-2H-chromen-4-yl)methyl *N,N*-dimethylcarbamodithioate

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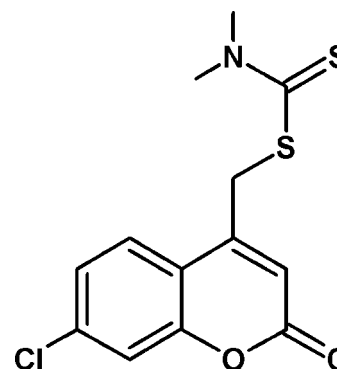
In the title compound, C₁₃H₁₂Cl N O₂S₂, the 2*H*-chromene ring system is almost planar, with a maximum deviation of 0.005 (2) Å. The packing features C—H···S hydrogen bonds and π–π interactions between fused benzene rings of chromene [shortest centroid–centroid distances = 3.6553 (13) and 3.5551 (13) Å].

Keywords: crystal structure; 2*H*-chromene; C—H···S hydrogen bonds; π–π interactions.

CCDC reference: 1055112

1. Related literature

For biological applications of coumarins and dithiocarbamates, see: Boas *et al.* (2004); D'hooghe & De Kimpe (2006); Fernández *et al.* (1995); Rao *et al.* (1981); Trkovnik *et al.* (1983). For a related structure and the synthesis, see: Mahabaleshwaraiyah *et al.* (2012).



2. Experimental

2.1. Crystal data

C₁₃H₁₂ClNO₂S₂
M_r = 313.81
Monoclinic, *P*2₁/*c*
a = 9.7244 (4) Å
b = 7.1157 (3) Å
c = 20.0896 (9) Å
β = 94.404 (3)°

V = 1386.01 (10) Å³
Z = 4
Mo Kα radiation
μ = 0.57 mm⁻¹
T = 296 K
0.24 × 0.20 × 0.12 mm

2.2. Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: ψ scan (*SADABS*; Sheldrick, 2007)
*T*_{min} = 0.770, *T*_{max} = 1.000

16144 measured reflections
4752 independent reflections
2805 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.053
wR(*F*²) = 0.147
S = 1.03
4752 reflections

174 parameters
H-atom parameters constrained
Δρ_{max} = 0.32 e Å⁻³
Δρ_{min} = -0.35 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C16—H16A···S3 ⁱ	0.97	2.84	3.707 (2)	150

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: BG2550).

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supporting information

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Crystal structure of (7-chloro-2-oxo-2*H*-chromen-4-yl)methyl *N,N*-dimethylcarbamodithioate

H. D. Kavitha, M. Vinduvahini, N. M. Mahabaleshwaraiah, O. Kotresh and H. C. Devarajegowda

S1. Comment

Synthetic coumarins are widely used as aroma chemicals because of their odour strength, tenacity, stability to alkali and relatively cheap price; applications include their use as a sweetener and fixative (in perfume); fragrance enhancers (for natural essential oils); blenders (in soaps and detergents); aroma enhancers (in tobacco); and for imparting pleasant odours to industrial products. The coumarins have been the subject of extensive studies because of their interesting biological activities and have, in fact, been used as therapeutic agents for the treatment of various diseases. Coumarins show quite diverse biological activities, including anticoagulant, anti-allergic, anthelmintic, diuretic, insecticidal and antibiotic properties (Trkovnik *et al.*, 1983); Rao *et al.*, 1981). The great electrophilicity of the nitrogen atom as compared to that of sulfur makes the latter more acidic and an active centre in the nucleophilic attack. The fact is that the sulfur anion formed is more stabilized by negative charge distribution. Furthermore, functionalized carbamates are an important class of compounds and their medicinal and biological properties warrant study (D'hooghe *et al.*, 2006). Organic dithiocarbamates are valuable synthetic intermediates (Boas *et al.*, 2004), which are ubiquitously found in a variety of biologically active compounds. Functionalization of the carbamate moiety offers an attractive method for the generation of derivatives, which may constitute interesting medicinal and biological properties (Fernández *et al.*, 1995).

The compound herein reported, (7-chloro-2-oxo-2*H*-chromen-4-yl)methyl dimethylcarbamodithioate (Fig. 1) presents a planar 2*H*-chromene ring system [maximum deviation: 0.005 (2) Å for atom C13]. The crystal structure shows intermolecular C—H···S bonds (C16-H16A···S3, H···S = 2.84 Å; C-H···S: 150°) and π – π interactions between fused benzene rings of chromene [shortest centroid–centroid distances = 3.6553 (13) Å and 3.5551 (13) Å]. A packing view is shown in Fig. 2.

S2. Experimental

All the chemicals used were of analytical reagent grade and were used directly without further purification. The title compound was synthesized according to the reported method (Mahabaleshwaraiah *et al.*, 2012). The compound is recrystallized by ethanol–chloroform mixture. Colourless needles of the title compound were grown from a mixed solution of Ethanol/Chloroform (V/V = 2/1) by slow evaporation at room temperature. Yield = 72%; m.p.: 405–407 K.

S3. Refinement

All H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H, C—H = 0.97 Å for methylene H and C—H = 0.96 Å for methyl H, and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for all other H.

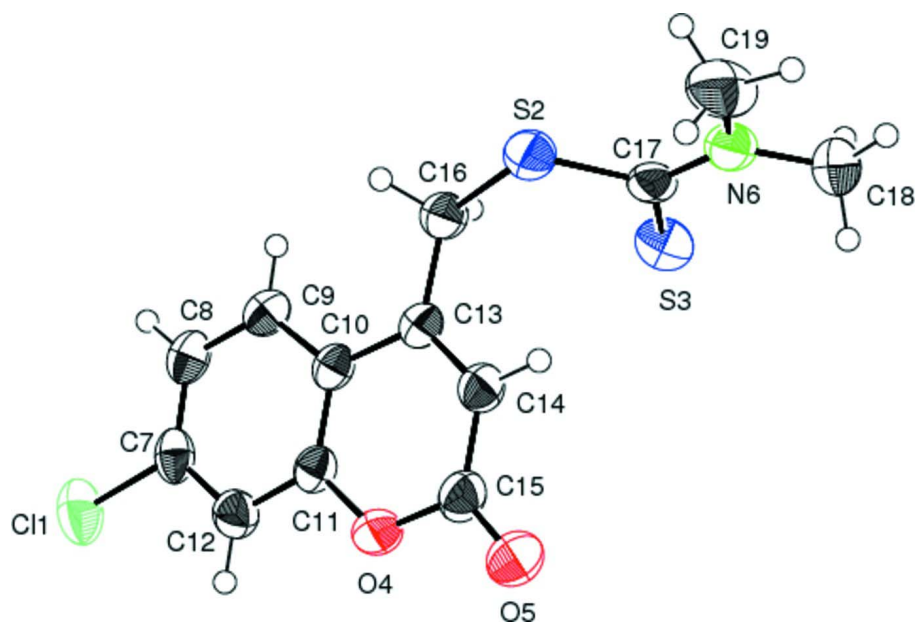


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

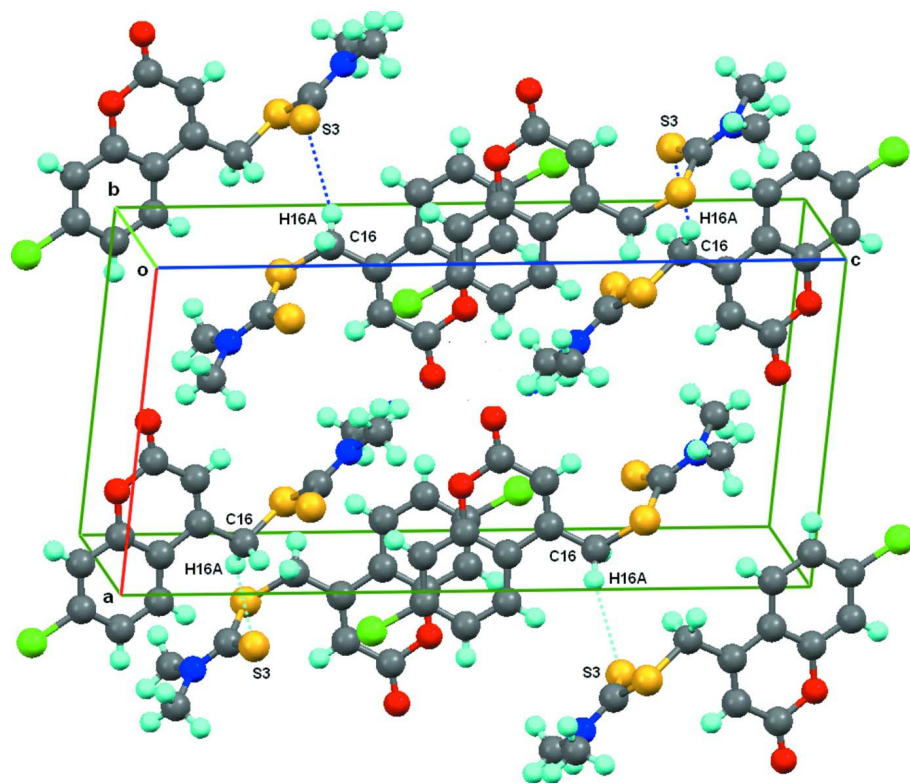


Figure 2

A packing view of the title compound. Dashed lines represent intermolecular interactions.

(7-Chloro-2-oxo-2H-chromen-4-yl)methyl *N,N*-dimethylcarbamdithioate

Crystal data

C₁₃H₁₂ClNO₂S₂
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 β = 94.404 (3)°
V = 1386.01 (10) Å³
Z = 4
F(000) = 648

D_x = 1.504 Mg m⁻³
 Melting point: 407 K
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 2446 reflections
 θ = 2.0–25.0°
 μ = 0.57 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: ψ scan
 (SADABS; Sheldrick, 2007)
T_{min} = 0.770, *T_{max}* = 1.000

16144 measured reflections
 4752 independent reflections
 2805 reflections with *I* > 2σ(*I*)
R_{int} = 0.029
 θ_{\max} = 32.2°, θ_{\min} = 2.0°
h = -14→14
k = -10→10
l = -27→30

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.053
 $wR(F^2)$ = 0.147
S = 1.03
 4752 reflections
 174 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
 $w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.4178P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max}$ = 0.043
 $\Delta\rho_{\max}$ = 0.32 e Å⁻³
 $\Delta\rho_{\min}$ = -0.35 e Å⁻³

Special details

Experimental. IR (KBr, cm⁻¹): 1722 (C=O), 1381 (C=S), 894(C—N). GCMS: m/e: 313; 1H NMR (400 MHz, CDCl₃, δ , p.p.m): 3.38 (s, 3H, N—CH₃), 3.47 (s, 3H, N—CH₃), 4.80 (s, 2H, C4—CH₂), 6.56 (s, 1H, C3—H), 7.45–7.92 (m, 3H, Ar—H). Mol. Formula: C₁₃H₁₂Cl N O₂S₂2; Elemental analysis: C, 49.75; H, 3.85; N, 4.46 (calculated); C, 49.67; H, 3.76; N, 4.39 (found).

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 > 2σ(*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)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
Cl1	-0.17680 (7)	0.68940 (10)	0.60871 (3)	0.0643 (2)

S2	0.19845 (6)	0.93877 (9)	0.24696 (3)	0.05245 (18)
S3	0.25794 (7)	0.52236 (9)	0.23740 (3)	0.05581 (19)
O4	0.27371 (14)	0.7395 (2)	0.50559 (7)	0.0489 (4)
O5	0.48199 (17)	0.7569 (3)	0.47037 (9)	0.0673 (5)
N6	0.37617 (18)	0.7922 (3)	0.17126 (9)	0.0522 (5)
C7	-0.0832 (2)	0.7267 (3)	0.53965 (11)	0.0416 (5)
C8	-0.1507 (2)	0.7599 (3)	0.47806 (12)	0.0442 (5)
H8	-0.2465	0.7639	0.4730	0.053*
C9	-0.0740 (2)	0.7870 (3)	0.42398 (11)	0.0413 (5)
H9	-0.1192	0.8099	0.3823	0.050*
C10	0.07040 (19)	0.7808 (3)	0.43027 (10)	0.0349 (4)
C11	0.1331 (2)	0.7472 (3)	0.49375 (10)	0.0369 (4)
C12	0.0577 (2)	0.7200 (3)	0.54875 (11)	0.0442 (5)
H12	0.1017	0.6977	0.5908	0.053*
C13	0.15923 (19)	0.8083 (3)	0.37605 (10)	0.0368 (4)
C14	0.2966 (2)	0.8017 (3)	0.38965 (11)	0.0419 (5)
H14	0.3529	0.8210	0.3549	0.050*
C15	0.3606 (2)	0.7662 (3)	0.45538 (11)	0.0455 (5)
C16	0.0936 (2)	0.8373 (4)	0.30683 (11)	0.0501 (6)
H16A	0.0133	0.9169	0.3099	0.060*
H16B	0.0609	0.7164	0.2898	0.060*
C17	0.2867 (2)	0.7429 (3)	0.21486 (10)	0.0414 (5)
C18	0.4622 (3)	0.6497 (5)	0.14199 (14)	0.0774 (9)
H18A	0.5282	0.6018	0.1758	0.116*
H18B	0.5098	0.7053	0.1068	0.116*
H18C	0.4050	0.5488	0.1243	0.116*
C19	0.4015 (3)	0.9852 (5)	0.15168 (14)	0.0722 (8)
H19A	0.3167	1.0548	0.1500	0.108*
H19B	0.4372	0.9864	0.1084	0.108*
H19C	0.4673	1.0418	0.1837	0.108*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0719 (4)	0.0596 (4)	0.0660 (4)	0.0019 (3)	0.0351 (3)	-0.0003 (3)
S2	0.0520 (4)	0.0574 (4)	0.0487 (3)	0.0071 (3)	0.0093 (2)	0.0123 (3)
S3	0.0611 (4)	0.0543 (4)	0.0515 (4)	-0.0088 (3)	0.0010 (3)	0.0002 (3)
O4	0.0347 (8)	0.0685 (11)	0.0424 (8)	0.0031 (7)	-0.0036 (6)	-0.0018 (7)
O5	0.0337 (9)	0.1053 (16)	0.0615 (11)	0.0061 (9)	-0.0057 (8)	-0.0083 (10)
N6	0.0336 (10)	0.0785 (15)	0.0446 (10)	0.0000 (9)	0.0038 (8)	0.0131 (10)
C7	0.0477 (12)	0.0289 (10)	0.0503 (12)	-0.0002 (8)	0.0180 (9)	-0.0030 (8)
C8	0.0338 (11)	0.0402 (12)	0.0597 (13)	0.0004 (8)	0.0101 (9)	-0.0016 (9)
C9	0.0339 (10)	0.0405 (12)	0.0492 (12)	0.0014 (8)	0.0012 (8)	0.0022 (9)
C10	0.0329 (10)	0.0290 (9)	0.0428 (10)	0.0004 (7)	0.0030 (8)	-0.0025 (8)
C11	0.0337 (10)	0.0329 (10)	0.0439 (11)	0.0015 (7)	0.0029 (8)	-0.0039 (8)
C12	0.0517 (13)	0.0398 (12)	0.0414 (11)	0.0030 (9)	0.0053 (9)	-0.0024 (9)
C13	0.0317 (10)	0.0375 (11)	0.0410 (10)	0.0018 (8)	0.0016 (8)	-0.0001 (8)
C14	0.0342 (10)	0.0485 (12)	0.0432 (11)	-0.0004 (9)	0.0040 (8)	-0.0017 (9)

C15	0.0340 (11)	0.0521 (13)	0.0503 (12)	0.0019 (9)	0.0017 (9)	-0.0057 (10)
C16	0.0333 (11)	0.0751 (17)	0.0423 (12)	0.0060 (10)	0.0052 (9)	0.0067 (11)
C17	0.0291 (10)	0.0612 (14)	0.0328 (10)	-0.0022 (9)	-0.0047 (7)	0.0045 (9)
C18	0.0583 (17)	0.120 (3)	0.0564 (16)	0.0281 (17)	0.0192 (13)	0.0130 (16)
C19	0.0536 (16)	0.098 (2)	0.0651 (17)	-0.0159 (15)	0.0067 (13)	0.0305 (16)

Geometric parameters (Å, °)

C11—C7	1.737 (2)	C10—C11	1.392 (3)
S2—C17	1.783 (2)	C10—C13	1.454 (3)
S2—C16	1.788 (2)	C11—C12	1.386 (3)
S3—C17	1.663 (2)	C12—H12	0.9300
O4—C11	1.371 (2)	C13—C14	1.343 (3)
O4—C15	1.378 (3)	C13—C16	1.499 (3)
O5—C15	1.198 (3)	C14—C15	1.438 (3)
N6—C17	1.329 (3)	C14—H14	0.9300
N6—C19	1.455 (4)	C16—H16A	0.9700
N6—C18	1.466 (3)	C16—H16B	0.9700
C7—C12	1.369 (3)	C18—H18A	0.9600
C7—C8	1.376 (3)	C18—H18B	0.9600
C8—C9	1.378 (3)	C18—H18C	0.9600
C8—H8	0.9300	C19—H19A	0.9600
C9—C10	1.401 (3)	C19—H19B	0.9600
C9—H9	0.9300	C19—H19C	0.9600
C17—S2—C16	104.05 (11)	C13—C14—H14	118.4
C11—O4—C15	121.80 (16)	C15—C14—H14	118.4
C17—N6—C19	124.1 (2)	O5—C15—O4	117.2 (2)
C17—N6—C18	120.3 (2)	O5—C15—C14	126.1 (2)
C19—N6—C18	115.5 (2)	O4—C15—C14	116.74 (18)
C12—C7—C8	121.98 (19)	C13—C16—S2	117.08 (16)
C12—C7—C11	117.93 (18)	C13—C16—H16A	108.0
C8—C7—C11	120.08 (17)	S2—C16—H16A	108.0
C7—C8—C9	118.91 (19)	C13—C16—H16B	108.0
C7—C8—H8	120.5	S2—C16—H16B	108.0
C9—C8—H8	120.5	H16A—C16—H16B	107.3
C8—C9—C10	121.6 (2)	N6—C17—S3	124.10 (19)
C8—C9—H9	119.2	N6—C17—S2	112.96 (17)
C10—C9—H9	119.2	S3—C17—S2	122.94 (12)
C11—C10—C9	116.96 (19)	N6—C18—H18A	109.5
C11—C10—C13	117.78 (17)	N6—C18—H18B	109.5
C9—C10—C13	125.25 (18)	H18A—C18—H18B	109.5
O4—C11—C12	115.97 (18)	N6—C18—H18C	109.5
O4—C11—C10	121.78 (18)	H18A—C18—H18C	109.5
C12—C11—C10	122.25 (19)	H18B—C18—H18C	109.5
C7—C12—C11	118.3 (2)	N6—C19—H19A	109.5
C7—C12—H12	120.9	N6—C19—H19B	109.5
C11—C12—H12	120.9	H19A—C19—H19B	109.5

C14—C13—C10	118.78 (18)	N6—C19—H19C	109.5
C14—C13—C16	122.65 (18)	H19A—C19—H19C	109.5
C10—C13—C16	118.55 (17)	H19B—C19—H19C	109.5
C13—C14—C15	123.11 (19)		
C12—C7—C8—C9	0.0 (3)	C11—C10—C13—C16	177.7 (2)
C11—C7—C8—C9	-179.30 (16)	C9—C10—C13—C16	-2.9 (3)
C7—C8—C9—C10	0.3 (3)	C10—C13—C14—C15	0.9 (3)
C8—C9—C10—C11	-0.4 (3)	C16—C13—C14—C15	-177.3 (2)
C8—C9—C10—C13	-179.84 (19)	C11—O4—C15—O5	-180.0 (2)
C15—O4—C11—C12	-179.28 (19)	C11—O4—C15—C14	-0.3 (3)
C15—O4—C11—C10	0.5 (3)	C13—C14—C15—O5	179.2 (2)
C9—C10—C11—O4	-179.57 (18)	C13—C14—C15—O4	-0.4 (3)
C13—C10—C11—O4	-0.1 (3)	C14—C13—C16—S2	-20.1 (3)
C9—C10—C11—C12	0.2 (3)	C10—C13—C16—S2	161.75 (16)
C13—C10—C11—C12	179.74 (18)	C17—S2—C16—C13	85.7 (2)
C8—C7—C12—C11	-0.1 (3)	C19—N6—C17—S3	-179.84 (18)
C11—C7—C12—C11	179.17 (15)	C18—N6—C17—S3	-3.0 (3)
O4—C11—C12—C7	179.83 (18)	C19—N6—C17—S2	0.5 (3)
C10—C11—C12—C7	0.0 (3)	C18—N6—C17—S2	177.35 (18)
C11—C10—C13—C14	-0.6 (3)	C16—S2—C17—N6	-176.86 (15)
C9—C10—C13—C14	178.8 (2)	C16—S2—C17—S3	3.46 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C16—H16 <i>A</i> \cdots S3 ⁱ	0.97	2.84	3.707 (2)	150

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