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ISSN 2414-3146

Methyl 2-[(Z)-5-bromo-2-oxoindolin-3-ylidene]-hydrazinecarbodithioate

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Received 5 August 2024

Accepted 9 August 2024

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

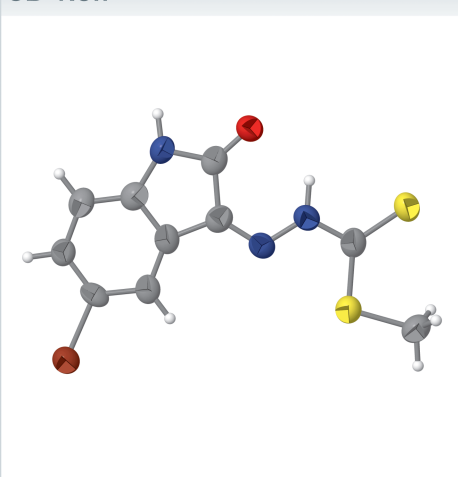
Keywords: crystal structure; dithiocarbazate; 5-bromoisatin; Z configuration; hydrogen bonding; halogen bond.

CCDC reference: 2376721

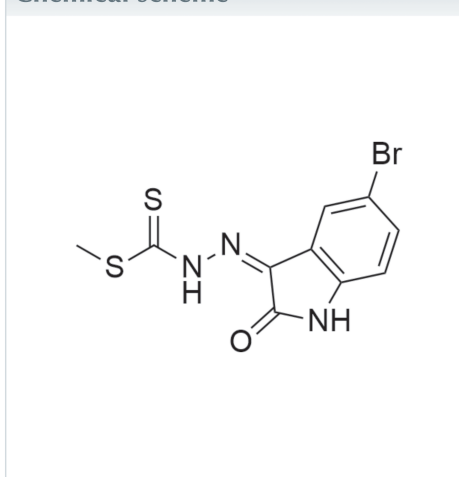
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₁₀H₈BrN₃OS₂, a brominated dithiocarbazate imine derivative, was obtained from the condensation reaction of *S*-methylthiocarbazate (SMDTC) and 5-bromoisatin. The essentially planar molecule exhibits a *Z* configuration, with the dithiocarbazate and 5-bromoisatin fragments located on the same sides of the C=N azomethine bond, which allows for the formation of an intramolecular N–H···O_b (b = bromoisatin) hydrogen bond generating an *S*(6) ring motif. In the crystal, adjacent molecules are linked by pairs of N–H···O hydrogen bonds, forming dimers characterized by an *R*²₂(8) loop motif. In the extended structure, molecules are linked into a three-dimensional network by C–H···S and C–H···Br hydrogen bonds, C–Br···S halogen bonds and aromatic π – π stacking.

3D view



Chemical scheme



Structure description

Isatin-derived dithiocarbazate imines have been reported to exhibit a broad spectrum of physiological properties (Yekke-ghasemi *et al.*, 2020; Ramilo-Gomes *et al.*, 2021). In particular, the *S*-methyl-substituted derivatives have received considerable attention in the field of organic transformations for the preparation of carbothiohydrazones, carbothiohydrazides and various aza-heterocyclic compounds such as pyrazoles, 1,2,4-triazoles and 1,3,4-thiadiazoles (Lin *et al.*, 2013; Moustafa *et al.*, 2021; Bekircan *et al.*, 2022; Malakar *et al.*, 2023; Geoghegan *et al.*, 2024). Recent study has revealed that the imine obtained from the condensation reaction of isatin and *S*-methylthiocarbazate can be directly transformed into the spiro-fused 1,3,4-thiadiazole compound in a straightforward synthetic protocol (Moustafa *et al.*, 2021). This approach opens a new avenue in accessing isatin-based spirocycle molecules. We are concerned with developing new dithiocarbazate imines containing isatin derivatives and continue research work to explore their potential applications (Abdul Manan *et al.*, 2024). Therefore, as part of our ongoing

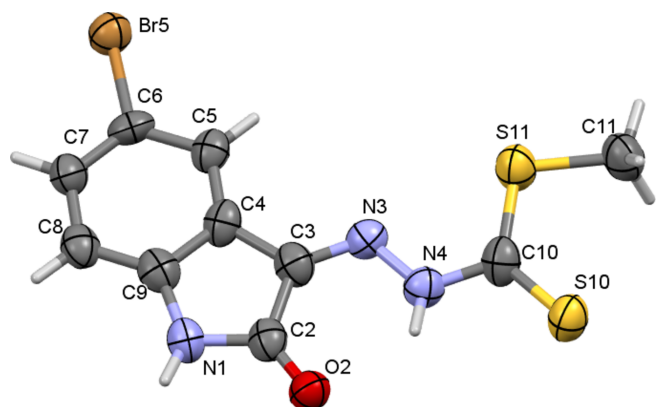


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

research and structural studies on such molecules, we now report the synthesis and crystal structure of the title compound.

The asymmetric unit of the title compound, $C_{10}H_8BrN_3OS_2$ contains one molecule and crystallizes in the $P2_1/n$ monoclinic space group with the *S*-methyl and thione groups being *syn* (Fig. 1). The non-hydrogen atoms in the molecule are close to planar, indicating electron delocalization within the molecule: the dihedral angle between the dithiocarbazate group and the 5-bromoisatin ring is $7.9(3)^\circ$. The imine exists in its thione tautomeric form with the dithiocarbazate unit adopting a *Z* conformation about the $C=N$ bond [$C4-C3=N3-N4 = 177.9(9)^\circ$] with respect to the 5-bromoisatin moiety, while the S10 thioketo sulfur atom is positioned *anti* to the N3 azomethine nitrogen atom [$N3-N4-C10-S10 = 173.8(7)^\circ$]. The presence of an $N-H \cdots O_b$ ($b = \text{bromoisatin}$) intramolecular hydrogen helps to consolidate the planar conformation of the title molecule (Table 1). Otherwise, the bond lengths and angles are comparable to those reported for methyl 2-(5-chloro-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)hydrazine-carbodithioate (Abdul Manan *et al.*, 2011), methyl 2-(1-

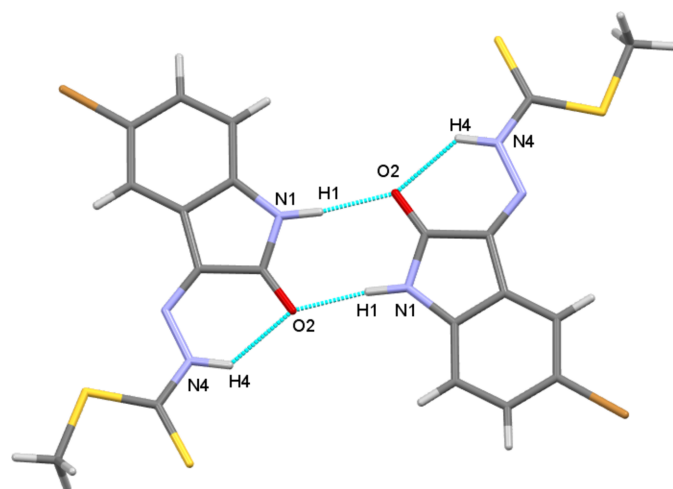


Figure 2
View of the dimers formed by $N-H \cdots O$ hydrogen-bonding giving $R_2^2(8)$ motifs.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N4-H4 \cdots O2$	0.98 (2)	2.04 (8)	2.715 (11)	124 (7)
$N1-H1 \cdots O2^i$	0.97 (2)	1.86 (4)	2.801 (11)	163 (10)
$C5-H5 \cdots Br5^{ii}$	0.95	3.00	3.941 (10)	172
$C7-H7 \cdots S10^{iii}$	0.95	2.83	3.775 (10)	171

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

methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)hydrazine-carbodithioate (Abdul Manan *et al.*, 2012) and methyl (*Z*)-2-(5-fluoro-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)hydrazine-1-carbodithioate (Li *et al.*, 2018).

In the crystal of the title compound, molecules are linked into dimers through pairwise $N1-H1 \cdots O2$ hydrogen bonds in a common $R_2^2(8)$ motif (Fig. 2). These dimers further pack into chains propagating along $[2\bar{1}0]$ through a combination of weak $C5-H5 \cdots Br5$ hydrogen bonds and $Br5 \cdots S11$ [$Br \cdots S = 3.521(3) \text{\AA}$, $C-S \cdots Br = 135.1(3)^\circ$, $C-Br \cdots S = 155.2(3)^\circ$] halogen bonds, forming an extended $R_2^1(9)R_2^2(8)R_2^1(9)$ motif. These chains are connected into the third dimension by further weak $C7-H7 \cdots S10$ hydrogen bonds (Table 1, Fig. 3). These hydrogen bonded arrays have parallel molecules separated such that an equivalent interpenetrating molecular framework exists, interacting with the other *via* aromatic $\pi-\pi$ stacking [$N1/C2-C4/C9$, centroid \cdots centroid separation = $3.307(9) \text{\AA}$].

Synthesis and crystallization

The dithiocarbazate precursor, SMDTC was prepared by the literature method (Das & Livingstone, 1976). The title compound was prepared by adding 5-bromoisatin (2.26 g, 10.0 mmol, 1.0 eq) dissolved in hot ethanol (20 ml) to a solution of the precursor, SMDTC (1.22 g, 10.0 mmol, 1.0 eq) in hot ethanol (35 ml). The mixture was heated (80°C) with continuous stirring for 15 min and later allowed to stand about 20 min at room temperature until a precipitate was formed, which was then filtered and dried over silica gel, yielding orange crystals on recrystallization from ethanol solution (yield: 2.74 g, 83%). m.p. $259-260^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, d_6 -DMSO) δ : (p.p.m.): 2.63 (*s*, 3H), 6.92 (*d*, $J = 8.28 \text{ Hz}$, 1H), 7.59 (*dd*, $J = 8.32, 2.0 \text{ Hz}$, 1H), 7.63 (*d*, $J = 1.92 \text{ Hz}$, 1H), 11.48 (*s*, 1H), 13.90 (*s*, 1H); HRMS m/z (ESI⁺), found: $[M + H]^+$ 329.9335, $C_{10}H_8N_3OS_2^{79}\text{Br}$ requires $[M + H]^+$ 329.9370.

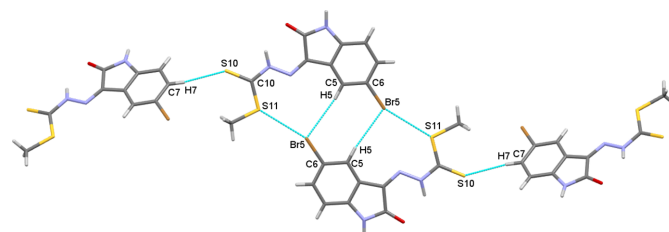


Figure 3
View showing both the weak hydrogen bonds and halogen bonds connecting the hydrogen-bonded dimers in three-dimensions.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as a two-component twin with component 2 rotated by -176.99° around $[0.92\ 0.02\ -0.38]$ (reciprocal) or $[1.00\ 0.02\ 0.00]$ (direct), and a refined twin fraction of 0.056 (3).

Acknowledgements

The authors acknowledge Universiti Teknologi MARA for financial support.

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₈ BrN ₃ OS ₂
<i>M_r</i>	330.22
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	125
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.6331 (3), 7.5726 (3), 24.6985 (10)
β (°)	97.141 (4)
<i>V</i> (Å ³)	1230.98 (9)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	7.63
Crystal size (mm)	0.11 × 0.01 × 0.01 × 0.40 (radius)
Data collection	
Diffractometer	Rigaku XtaLAB P200K
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T</i> _{min} , <i>T</i> _{max}	0.025, 0.114
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	11989, 2513, 1869
<i>R</i> _{int}	0.1931
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.630
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.093, 0.293, 1.14
No. of reflections	2513
No. of parameters	164
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.37, -1.06

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

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full crystallographic data

IUCrData (2024). **9**, x240787 [https://doi.org/10.1107/S2414314624007879]

Methyl 2-[(Z)-5-bromo-2-oxoindolin-3-ylidene]hydrazinecarbodithioate

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Methyl 2-[(Z)-5-bromo-2-oxoindolin-3-ylidene]hydrazinecarbodithioate

Crystal data

$C_{10}H_8BrN_3OS_2$	$F(000) = 656$
$M_r = 330.22$	$D_x = 1.782 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 6.6331 (3) \text{ \AA}$	Cell parameters from 3279 reflections
$b = 7.5726 (3) \text{ \AA}$	$\theta = 3.6\text{--}75.3^\circ$
$c = 24.6985 (10) \text{ \AA}$	$\mu = 7.63 \text{ mm}^{-1}$
$\beta = 97.141 (4)^\circ$	$T = 125 \text{ K}$
$V = 1230.98 (9) \text{ \AA}^3$	Needle, orange
$Z = 4$	$0.11 \times 0.01 \times 0.01 \times 0.40$ (radius) mm

Data collection

Rigaku XtaLAB P200K diffractometer	$T_{\min} = 0.025$, $T_{\max} = 0.114$
Radiation source: Rotating Anode, Rigaku MM-007HF	11959 measured reflections
Rigaku Osmic Confocal Optical System monochromator	2513 independent reflections
Detector resolution: $5.8140 \text{ pixels mm}^{-1}$ shutterless scans	1869 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (CrysAlisPr; Rigaku OD, 2023)	$R_{\text{int}} = 0.193$
	$\theta_{\max} = 76.3^\circ$, $\theta_{\min} = 6.1^\circ$
	$h = -7 \rightarrow 7$
	$k = -9 \rightarrow 9$
	$l = -5 \rightarrow 30$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.093$	$w = 1/[\sigma^2(F_o^2) + (0.145P)^2 + 4.1265P]$
$wR(F^2) = 0.293$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{\max} < 0.001$
2513 reflections	$\Delta\rho_{\max} = 1.37 \text{ e \AA}^{-3}$
164 parameters	$\Delta\rho_{\min} = -1.06 \text{ e \AA}^{-3}$
2 restraints	
Primary atom site location: dual	

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.

Refinement. Refined as a 2-component twin with HKLF5 generated by TWINROT/MAT running in PLATON. NH hydrogen atoms were identified from F_{map} and refined with N-H restrained to 0.98 \AA .

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br5	−0.00632 (16)	0.49654 (14)	0.40002 (4)	0.0565 (4)
S11	0.3366 (4)	0.2379 (4)	0.68815 (10)	0.0606 (7)
S10	0.7209 (4)	0.0479 (4)	0.73636 (10)	0.0602 (7)
O2	0.9075 (10)	0.0482 (9)	0.5665 (3)	0.0519 (15)
N1	0.7784 (13)	0.1254 (11)	0.4779 (3)	0.0497 (17)
N4	0.6432 (12)	0.1539 (11)	0.6357 (3)	0.0500 (17)
N3	0.5194 (11)	0.2188 (10)	0.5925 (3)	0.0471 (17)
C2	0.7769 (15)	0.1156 (13)	0.5335 (4)	0.051 (2)
C6	0.2344 (13)	0.3758 (12)	0.4224 (4)	0.048 (2)
C9	0.5992 (16)	0.2052 (13)	0.4534 (4)	0.052 (2)
C4	0.4781 (16)	0.2581 (12)	0.4928 (4)	0.050 (2)
C5	0.2935 (15)	0.3440 (12)	0.4784 (4)	0.0483 (19)
H5	0.210762	0.379717	0.505144	0.058*
C10	0.5760 (17)	0.1466 (13)	0.6859 (4)	0.054 (2)
C7	0.3544 (14)	0.3217 (13)	0.3840 (4)	0.051 (2)
H7	0.309938	0.343966	0.346543	0.061*
C11	0.3089 (19)	0.2206 (17)	0.7602 (5)	0.065 (3)
H11A	0.175584	0.266410	0.766485	0.098*
H11B	0.415852	0.289473	0.781506	0.098*
H11C	0.320165	0.096497	0.771421	0.098*
C8	0.5376 (16)	0.2359 (13)	0.3979 (4)	0.053 (2)
H8	0.618622	0.199134	0.370855	0.064*
C3	0.5842 (16)	0.2045 (13)	0.5453 (4)	0.052 (2)
H4	0.753 (10)	0.069 (10)	0.633 (4)	0.04 (2)*
H1	0.881 (13)	0.046 (12)	0.467 (4)	0.05 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br5	0.0560 (7)	0.0579 (7)	0.0547 (7)	0.0055 (4)	0.0036 (5)	0.0015 (4)
S11	0.0661 (15)	0.0663 (15)	0.0499 (13)	0.0133 (12)	0.0089 (11)	0.0043 (11)
S10	0.0692 (16)	0.0626 (15)	0.0472 (13)	0.0112 (12)	0.0007 (11)	0.0017 (11)
O2	0.049 (4)	0.055 (4)	0.051 (3)	0.004 (3)	0.002 (3)	−0.001 (3)
N1	0.060 (5)	0.048 (4)	0.043 (4)	0.000 (3)	0.012 (3)	−0.001 (3)
N4	0.052 (4)	0.047 (4)	0.050 (4)	0.007 (3)	0.004 (3)	0.002 (3)
N3	0.049 (4)	0.042 (4)	0.050 (4)	0.002 (3)	0.002 (3)	0.000 (3)
C2	0.058 (5)	0.047 (5)	0.047 (5)	−0.009 (4)	0.008 (4)	−0.006 (4)
C6	0.034 (4)	0.046 (4)	0.061 (5)	0.000 (3)	−0.008 (4)	0.001 (4)
C9	0.060 (6)	0.043 (5)	0.056 (5)	−0.005 (4)	0.013 (4)	−0.001 (4)
C4	0.067 (6)	0.038 (4)	0.043 (4)	−0.003 (4)	0.002 (4)	−0.003 (3)
C5	0.058 (5)	0.042 (4)	0.044 (5)	−0.007 (4)	0.002 (4)	−0.002 (3)
C10	0.074 (6)	0.043 (5)	0.046 (5)	0.004 (4)	0.007 (4)	−0.002 (4)
C7	0.052 (5)	0.055 (5)	0.046 (5)	−0.002 (4)	0.009 (4)	0.006 (4)
C11	0.070 (7)	0.070 (7)	0.058 (6)	0.009 (5)	0.019 (5)	−0.004 (5)
C8	0.060 (6)	0.052 (5)	0.049 (5)	−0.011 (4)	0.013 (4)	0.000 (4)

C3	0.059 (5)	0.046 (5)	0.052 (5)	-0.001 (4)	0.012 (4)	-0.004 (4)
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Geometric parameters (Å, °)

Br5—C6	1.863 (8)	C6—C5	1.410 (13)
S11—C10	1.739 (11)	C6—C7	1.375 (14)
S11—C11	1.816 (11)	C9—C4	1.395 (14)
S10—C10	1.654 (10)	C9—C8	1.399 (14)
O2—C2	1.224 (12)	C4—C5	1.394 (14)
N1—C2	1.378 (12)	C4—C3	1.455 (13)
N1—C9	1.402 (13)	C5—H5	0.9500
N1—H1	0.97 (2)	C7—H7	0.9500
N4—N3	1.355 (11)	C7—C8	1.383 (15)
N4—C10	1.371 (13)	C11—H11A	0.9800
N4—H4	0.98 (2)	C11—H11B	0.9800
N3—C3	1.294 (12)	C11—H11C	0.9800
C2—C3	1.505 (14)	C8—H8	0.9500
C10—S11—C11	101.9 (5)	C4—C5—C6	117.3 (9)
C2—N1—C9	110.1 (8)	C4—C5—H5	121.3
C2—N1—H1	110 (7)	S10—C10—S11	127.1 (6)
C9—N1—H1	137 (7)	N4—C10—S11	114.4 (7)
N3—N4—C10	119.6 (8)	N4—C10—S10	118.4 (8)
N3—N4—H4	124 (5)	C6—C7—H7	118.9
C10—N4—H4	111 (5)	C6—C7—C8	122.3 (9)
C3—N3—N4	116.2 (8)	C8—C7—H7	118.9
O2—C2—N1	126.5 (9)	S11—C11—H11A	109.5
O2—C2—C3	127.3 (9)	S11—C11—H11B	109.5
N1—C2—C3	106.3 (8)	S11—C11—H11C	109.5
C5—C6—Br5	119.9 (7)	H11A—C11—H11B	109.5
C7—C6—Br5	119.3 (7)	H11A—C11—H11C	109.5
C7—C6—C5	120.8 (8)	H11B—C11—H11C	109.5
C4—C9—N1	110.7 (9)	C9—C8—H8	121.2
C4—C9—C8	120.8 (10)	C7—C8—C9	117.5 (9)
C8—C9—N1	128.5 (9)	C7—C8—H8	121.2
C9—C4—C3	106.6 (9)	N3—C3—C2	126.6 (9)
C5—C4—C9	121.3 (9)	N3—C3—C4	126.9 (9)
C5—C4—C3	132.1 (9)	C4—C3—C2	106.3 (8)
C6—C5—H5	121.3		
Br5—C6—C5—C4	-178.0 (7)	C9—N1—C2—O2	177.5 (9)
Br5—C6—C7—C8	178.1 (8)	C9—N1—C2—C3	-2.8 (10)
O2—C2—C3—N3	-3.0 (17)	C9—C4—C5—C6	-0.2 (14)
O2—C2—C3—C4	-178.5 (9)	C9—C4—C3—N3	-175.6 (10)
N1—C2—C3—N3	177.3 (9)	C9—C4—C3—C2	-0.2 (10)
N1—C2—C3—C4	1.8 (10)	C4—C9—C8—C7	0.6 (14)
N1—C9—C4—C5	178.7 (8)	C5—C6—C7—C8	-0.6 (15)
N1—C9—C4—C3	-1.6 (11)	C5—C4—C3—N3	4.0 (17)

N1—C9—C8—C7	-178.4 (9)	C5—C4—C3—C2	179.5 (10)
N4—N3—C3—C2	3.3 (14)	C10—N4—N3—C3	-172.9 (9)
N4—N3—C3—C4	177.9 (9)	C7—C6—C5—C4	0.7 (13)
N3—N4—C10—S11	-3.9 (12)	C11—S11—C10—S10	6.9 (9)
N3—N4—C10—S10	173.8 (7)	C11—S11—C10—N4	-175.7 (8)
C2—N1—C9—C4	2.9 (11)	C8—C9—C4—C5	-0.5 (14)
C2—N1—C9—C8	-178.0 (10)	C8—C9—C4—C3	179.2 (9)
C6—C7—C8—C9	-0.1 (15)	C3—C4—C5—C6	-179.8 (10)

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>
N4—H4 \cdots O2	0.98 (2)	2.04 (8)	2.715 (11)	124 (7)
N1—H1 \cdots O2 ⁱ	0.97 (2)	1.86 (4)	2.801 (11)	163 (10)
C5—H5 \cdots Br5 ⁱⁱ	0.95	3.00	3.941 (10)	172
C7—H7 \cdots S10 ⁱⁱⁱ	0.95	2.83	3.775 (10)	171

Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x-1/2, -y+1/2, z-1/2$.