# organic compounds

# (E)-6-Bromo-3-{2-[2-(4-chlorobenzyl-idene)hydrazinyl]thiazol-5-yl}-2H-chromen-2-one

Afsheen Arshad,[a] Hasnah Osman,[a]‡ Chan Kit Lam,[b] Madhukar Hemamalini[c] and Hoong-Kun Fun[c]*§

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, [b]School of Pharmaceutical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

In the title compound, $C_{19}H_{11}N_3O_2SClBr$, the chromene ring system and the thiazole ring are each approximately planar, with maximum deviations of 0.033 (3) Å and 0.006 (3) Å, respectively. The molecule adopts an $E$ configuration about the central C=N double bond. The central thiazole ring makes dihedral angles of 9.06 (14)° and 12.07 (11)° with the chloro-substituted phenyl ring and the chromene ring, respectively. The molecular structure features a short C—H···O contact, which generates an $S(6)$ ring motif. The crystal structure is stabilized by intermolecular N—H···O hydrogen bonds, which link the molecules into chains along the $b$ axis. $\pi$–$\pi$ stacking interactions [centroid-centroid distance = 3.4813 (15) Å] are also present.

## Related literature

For the biological activity and applications of thiazolyl coumarin derivatives, see: Samsonova et al. (2007); Bullock et al. (2009); Siddiqui et al. (2009); Kalkhambkar et al. (2007); Kamal et al. (2009); Desai et al. (2008). For the synthesis of the title compound, see: Bakkar et al. (2003); Vijesh et al. (2010). For graph-set notation, see: Bernstein et al. (1995).
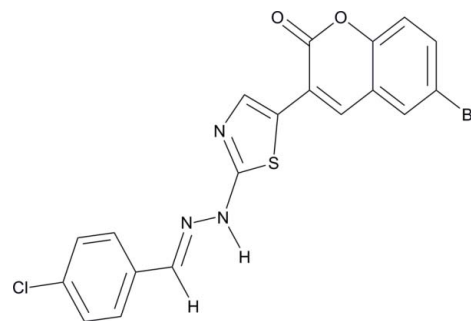
## Experimental

### Crystal data

| | |
|---|---|
| $C_{19}H_{11}BrClN_3O_2S$ | $V$ = 3781.18 (13) Å³ |
| $M_r$ = 460.73 | $Z$ = 8 |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a$ = 30.5837 (7) Å | $\mu$ = 2.45 mm⁻¹ |
| $b$ = 13.6682 (3) Å | $T$ = 296 K |
| $c$ = 9.0454 (1) Å | $0.21 \times 0.16 \times 0.07$ mm |
| $\beta$ = 90.161 (2)° | |

### Data collection

| | |
|---|---|
| Bruker SMART APEXII CCD area-detector diffractometer | 29664 measured reflections |
| | 5499 independent reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2009) | 2216 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.628, $T_{max}$ = 0.842 | $R_{int}$ = 0.058 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.049 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.138 | |
| $S$ = 0.97 | |
| 5499 reflections | $\Delta\rho_{max}$ = 0.31 e Å⁻³ |
| 248 parameters | $\Delta\rho_{min}$ = −0.34 e Å⁻³ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H1N2···O2[i] | 0.81 (4) | 2.16 (4) | 2.957 (4) | 169 (4) |
| C11—H11A···O2 | 0.93 | 2.35 | 2.878 (4) | 115 |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

‡ Additional correspondence author, e-mail: ohasnah@usm.my.
§ Thomson Reuters ResearcherID: A-3561-2009.

# organic compounds

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# supporting information

## (*E*)-6-Bromo-3-{2-[2-(4-chlorobenzylidene)hydrazinyl]thiazol-5-yl}-2*H*-chromen-2-one

## Afsheen Arshad, Hasnah Osman, Chan Kit Lam, Madhukar Hemamalini and Hoong-Kun Fun

### S1. Comment

Thiazolyl coumarin derivatives are reported to be associated with diverse applications. They have industrial applications as fluorescent probes, laser dyes (Samsonova *et al.*, 2007) and luminescents (Bullock *et al.*, 2009). They also exhibit a variety of biological activities as anticonvulsants (Siddiqui *et al.*, 2009), analgesics, anti-inflammatory (Kalkhambkar *et al.*, 2007) and antimicrobial agents (Kamal *et al.*, 2009; Desai *et al.*, 2008). The title compound is a new derivative of thiazolylcoumarin. We present here its crystal structure.

The molecular structure of the compound, (I), displays a trans configuration with respect to the C13═N3 double bond. The chromene (O1/C1–C9) ring system and thiazole (S1/N1/C10–C12) ring are approximately planar, with the maximum deviation of 0.033 (3) Å for atom C2 and 0.006 (3)Å for atom C12, respectively. The central thiazole (S1/N1/C10–C12) ring makes dihedral angles of 9.06 (14)° and 12.07 (11)° with the chloro-substituted phenyl (C14–C19) ring and the chromene (O1/C1–C9) ring, respectively.

In the crystal packing (Fig. 2), the molecular structure is stabilized by an intramolecular C—H···O (Table 1) hydrogen bond which generates an *S*(6) (Bernstein *et al.*, 1995) ring motif. Furthermore, the crystal structure is stabilized by intermolecular N—H···O hydrogen bonds which link the molecules into chains parallel to the *b*-axis. π···π [centroid-centroid distance = 3.4813 (15) Å; 1/2-X, 1/2-Y, 2-Z] stacking interactions between the thiazole (S1/N1/C10–C12) and pyran (O1/C3–C7) rings are also observed.

### S2. Experimental

4-chlorobenzylidene thiosemicarbazone (Bakkar *et al.*, 2003) and 6-bromo-3-(2-bromoacetyl)-2*H*-chromen-2-one (Vijesh *et al.*, 2010) were synthesized as reported in the literature. The title compound (I) was obtained by the cyclocondensation of 4-chlorobenzylidene thiosemicarbazone with 6-bromo-3-(2-bromoacetyl)- 2*H*-chromen-2-one. A solution of 6-bromo-3-(2-bromoacetyl)-2*H*- chromen-2-one (2.5 mmol) and 4-chlorobenzylidene thiosemicarbazone (2.5 mmol) in chloroform-ethanol (2:1) was refluxed for 2 hours at 60°C to yield a dense yellow precipitate. The reaction mixture was cooled in ice bath and basified with ammonia to pH 7–8. The title compound (I) was recrystallized from ethanol-chloroform (1:2) to give yellow block like crystals.

### S3. Refinement

Atom H1N2 was located from a difference Fourier map and refined freely [N–H = 0.81 (4) Å]. The remaining H atoms were positioned geometrically [C–H = 0.93 Å] and were refined using a riding model, with $U_{iso}$(H) = 1.2 $U_{eq}$(C). The highest residual electron density peak is located at 1.20 Å from Br1 and the deepest hole 0.91 located at from Br1.
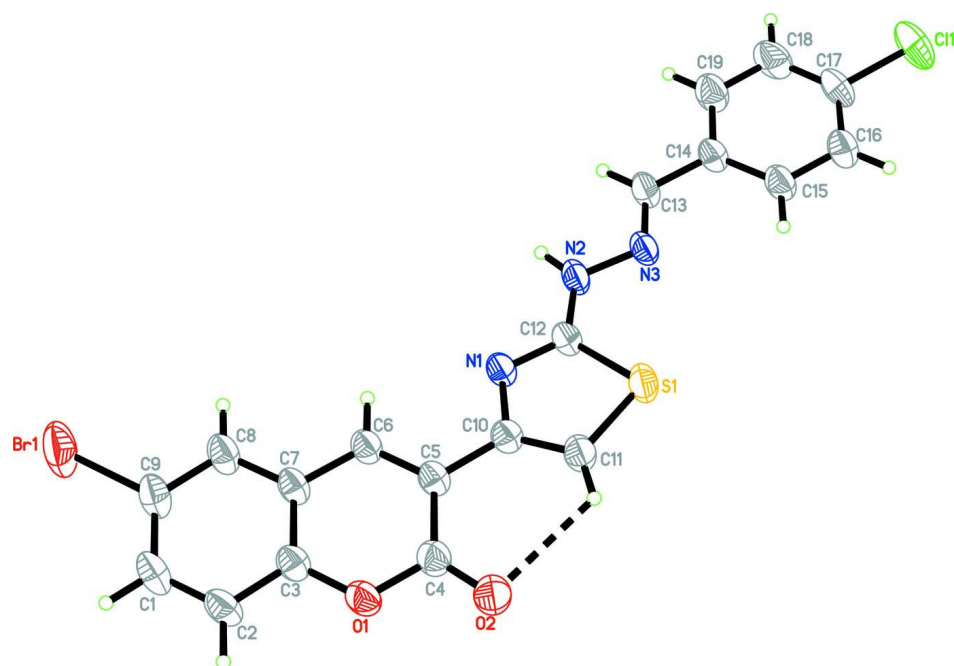
**Figure 1**

The asymmetric unit of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. The intramolecular hydrogen bond is shown as a dashed line.
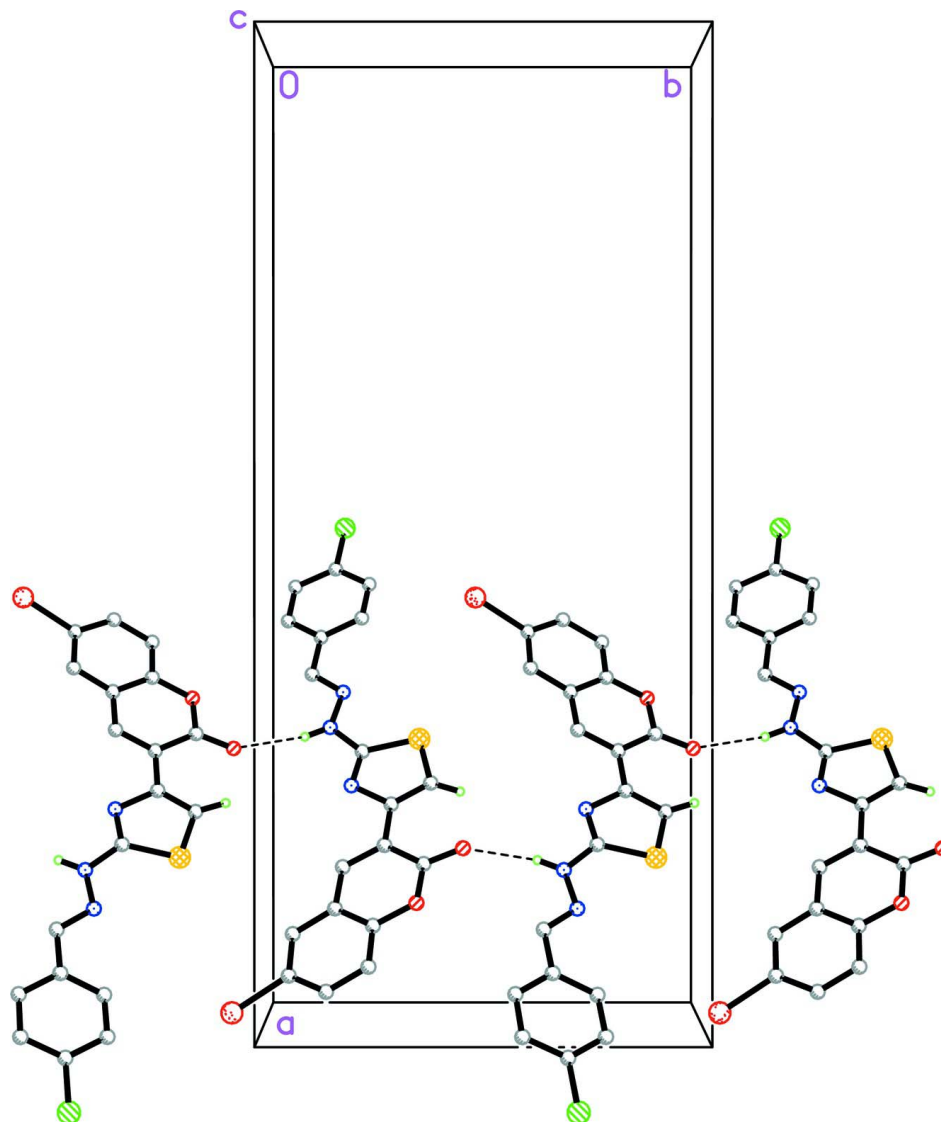
**Figure 2**

The crystal packing of the title compound (I).

## (*E*)-6-Bromo-3-{2-[2-(4-chlorobenzylidene)hydrazinyl]thiazol-5-yl}- 2*H*-chromen-2-one

*Crystal data*

| | |
|---|---|
| $C_{19}H_{11}BrClN_3O_2S$ | $F(000) = 1840$ |
| $M_r = 460.73$ | $D_x = 1.619$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 3684 reflections |
| $a = 30.5837$ (7) Å | $\theta = 2.5–23.1°$ |
| $b = 13.6682$ (3) Å | $\mu = 2.45$ mm$^{-1}$ |
| $c = 9.0454$ (1) Å | $T = 296$ K |
| $\beta = 90.161$ (2)° | Block, yellow |
| $V = 3781.18$ (13) Å$^3$ | $0.21 \times 0.16 \times 0.07$ mm |
| $Z = 8$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEXII CCD area-detector diffractometer | 29664 measured reflections |
| Radiation source: fine-focus sealed tube | 5499 independent reflections |
| Graphite monochromator | 2216 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.058$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2009) | $\theta_{max} = 30.0°$, $\theta_{min} = 2.5°$ |
| | $h = -40 \rightarrow 42$ |
| $T_{min} = 0.628$, $T_{max} = 0.842$ | $k = -19 \rightarrow 19$ |
| | $l = -12 \rightarrow 12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.049$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.138$ | |
| $S = 0.97$ | H atoms treated by a mixture of independent and constrained refinement |
| 5499 reflections | |
| 248 parameters | $w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.960P]$ |
| 0 restraints | where $P = (F_o^2 + 2F_c^2)/3$ |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} = 0.001$ |
| | $\Delta\rho_{max} = 0.31$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.34$ e Å$^{-3}$ |

*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.

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.437955 (16) | 0.51731 (4) | 1.13651 (6) | 0.1287 (3) |
| Cl1 | −0.00680 (3) | 0.31602 (10) | −0.05275 (11) | 0.1132 (4) |
| S1 | 0.19723 (3) | 0.13873 (7) | 0.60268 (9) | 0.0712 (3) |
| O1 | 0.33937 (7) | 0.13971 (15) | 1.0762 (2) | 0.0679 (6) |
| O2 | 0.29214 (8) | 0.04381 (19) | 0.9684 (3) | 0.0902 (7) |
| N1 | 0.23951 (7) | 0.28268 (18) | 0.7199 (2) | 0.0575 (6) |
| N2 | 0.18701 (9) | 0.3330 (2) | 0.5513 (3) | 0.0698 (8) |
| N3 | 0.15428 (8) | 0.3072 (2) | 0.4558 (2) | 0.0629 (7) |
| C1 | 0.41549 (11) | 0.3221 (3) | 1.2104 (4) | 0.0778 (10) |
| H1A | 0.4381 | 0.3273 | 1.2790 | 0.093* |
| C2 | 0.39334 (10) | 0.2362 (3) | 1.1954 (3) | 0.0738 (9) |
| H2A | 0.4009 | 0.1825 | 1.2533 | 0.089* |
| C3 | 0.35967 (9) | 0.2291 (2) | 1.0938 (3) | 0.0609 (8) |
| C4 | 0.30642 (10) | 0.1259 (3) | 0.9763 (3) | 0.0652 (8) |
| C5 | 0.29156 (9) | 0.2090 (2) | 0.8891 (3) | 0.0556 (7) |

| | | | |
|---|---|---|---|
| C6 | 0.31145 (9) | 0.2961 (2) | 0.9077 (3) | 0.0591 (8) |
| H6A | 0.3018 | 0.3493 | 0.8524 | 0.071* |
| C7 | 0.34686 (9) | 0.3096 (2) | 1.0094 (3) | 0.0601 (8) |
| C8 | 0.36987 (9) | 0.3966 (3) | 1.0262 (4) | 0.0715 (9) |
| H8A | 0.3620 | 0.4515 | 0.9716 | 0.086* |
| C9 | 0.40440 (10) | 0.4013 (3) | 1.1240 (4) | 0.0766 (10) |
| C10 | 0.25573 (9) | 0.1967 (2) | 0.7827 (3) | 0.0569 (7) |
| C11 | 0.23679 (10) | 0.1131 (2) | 0.7328 (3) | 0.0662 (8) |
| H11A | 0.2442 | 0.0505 | 0.7645 | 0.079* |
| C12 | 0.20879 (9) | 0.2616 (2) | 0.6261 (3) | 0.0583 (8) |
| C13 | 0.13768 (10) | 0.3778 (3) | 0.3809 (3) | 0.0666 (8) |
| H13A | 0.1486 | 0.4408 | 0.3935 | 0.080* |
| C14 | 0.10205 (10) | 0.3614 (2) | 0.2765 (3) | 0.0609 (8) |
| C15 | 0.08312 (10) | 0.2710 (3) | 0.2569 (3) | 0.0713 (9) |
| H15A | 0.0931 | 0.2183 | 0.3128 | 0.086* |
| C16 | 0.04983 (10) | 0.2566 (3) | 0.1567 (3) | 0.0763 (10) |
| H16A | 0.0377 | 0.1948 | 0.1440 | 0.092* |
| C17 | 0.03487 (10) | 0.3341 (3) | 0.0762 (3) | 0.0767 (10) |
| C18 | 0.05284 (12) | 0.4249 (3) | 0.0907 (4) | 0.0925 (12) |
| H18A | 0.0426 | 0.4771 | 0.0344 | 0.111* |
| C19 | 0.08655 (11) | 0.4378 (3) | 0.1909 (4) | 0.0846 (10) |
| H19A | 0.0991 | 0.4994 | 0.2010 | 0.102* |
| H1N2 | 0.1963 (12) | 0.388 (3) | 0.547 (4) | 0.092 (14)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.1122 (4) | 0.0915 (4) | 0.1821 (5) | −0.0164 (3) | −0.0729 (4) | −0.0212 (3) |
| Cl1 | 0.0812 (6) | 0.1664 (12) | 0.0917 (6) | 0.0210 (7) | −0.0463 (5) | −0.0255 (7) |
| S1 | 0.0712 (5) | 0.0676 (6) | 0.0748 (5) | −0.0092 (4) | −0.0221 (4) | −0.0101 (4) |
| O1 | 0.0663 (13) | 0.0633 (15) | 0.0739 (13) | 0.0083 (11) | −0.0199 (11) | 0.0053 (11) |
| O2 | 0.0935 (17) | 0.0603 (16) | 0.1165 (19) | −0.0022 (14) | −0.0368 (14) | 0.0108 (15) |
| N1 | 0.0574 (14) | 0.0579 (16) | 0.0572 (13) | 0.0024 (12) | −0.0134 (12) | −0.0054 (12) |
| N2 | 0.0731 (18) | 0.065 (2) | 0.0715 (17) | −0.0067 (16) | −0.0335 (14) | −0.0020 (16) |
| N3 | 0.0618 (15) | 0.0675 (18) | 0.0593 (14) | −0.0034 (13) | −0.0222 (12) | −0.0035 (13) |
| C1 | 0.062 (2) | 0.092 (3) | 0.079 (2) | 0.012 (2) | −0.0280 (17) | −0.015 (2) |
| C2 | 0.071 (2) | 0.078 (2) | 0.073 (2) | 0.0179 (19) | −0.0248 (17) | 0.0020 (19) |
| C3 | 0.0561 (17) | 0.064 (2) | 0.0623 (18) | 0.0080 (16) | −0.0080 (15) | −0.0052 (16) |
| C4 | 0.0615 (19) | 0.059 (2) | 0.075 (2) | 0.0033 (17) | −0.0123 (16) | 0.0000 (18) |
| C5 | 0.0544 (16) | 0.057 (2) | 0.0556 (16) | 0.0079 (15) | −0.0070 (13) | −0.0087 (15) |
| C6 | 0.0574 (17) | 0.0558 (19) | 0.0639 (17) | 0.0043 (15) | −0.0139 (14) | −0.0037 (15) |
| C7 | 0.0523 (16) | 0.064 (2) | 0.0638 (18) | 0.0106 (15) | −0.0140 (14) | −0.0096 (16) |
| C8 | 0.0622 (19) | 0.063 (2) | 0.089 (2) | 0.0099 (17) | −0.0253 (17) | −0.0119 (19) |
| C9 | 0.066 (2) | 0.073 (2) | 0.091 (2) | 0.0052 (18) | −0.0242 (18) | −0.022 (2) |
| C10 | 0.0553 (17) | 0.058 (2) | 0.0577 (17) | 0.0031 (15) | −0.0051 (14) | −0.0033 (15) |
| C11 | 0.0664 (19) | 0.058 (2) | 0.074 (2) | 0.0010 (16) | −0.0174 (16) | −0.0036 (17) |
| C12 | 0.0579 (17) | 0.064 (2) | 0.0535 (16) | 0.0003 (15) | −0.0114 (14) | −0.0064 (15) |
| C13 | 0.0686 (19) | 0.068 (2) | 0.0634 (18) | −0.0012 (17) | −0.0199 (16) | −0.0117 (17) |

| C14 | 0.0605 (18) | 0.063 (2) | 0.0592 (17) | 0.0073 (16) | −0.0150 (15) | −0.0078 (16) |
| C15 | 0.0673 (19) | 0.078 (2) | 0.0688 (19) | 0.0023 (18) | −0.0228 (16) | −0.0028 (18) |
| C16 | 0.066 (2) | 0.085 (3) | 0.078 (2) | −0.0002 (19) | −0.0202 (17) | −0.011 (2) |
| C17 | 0.061 (2) | 0.106 (3) | 0.0624 (19) | 0.017 (2) | −0.0232 (16) | −0.015 (2) |
| C18 | 0.095 (3) | 0.095 (3) | 0.088 (3) | 0.025 (2) | −0.037 (2) | 0.005 (2) |
| C19 | 0.089 (2) | 0.074 (2) | 0.090 (2) | 0.009 (2) | −0.032 (2) | −0.004 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C9 | 1.892 (3) | C5—C10 | 1.466 (4) |
| Cl1—C17 | 1.743 (3) | C6—C7 | 1.431 (4) |
| S1—C11 | 1.721 (3) | C6—H6A | 0.9300 |
| S1—C12 | 1.728 (3) | C7—C8 | 1.390 (4) |
| O1—C4 | 1.365 (4) | C8—C9 | 1.377 (4) |
| O1—C3 | 1.379 (4) | C8—H8A | 0.9300 |
| O2—C4 | 1.206 (4) | C10—C11 | 1.359 (4) |
| N1—C12 | 1.297 (3) | C11—H11A | 0.9300 |
| N1—C10 | 1.395 (4) | C13—C14 | 1.458 (4) |
| N2—C12 | 1.361 (4) | C13—H13A | 0.9300 |
| N2—N3 | 1.366 (3) | C14—C15 | 1.376 (4) |
| N2—H1N2 | 0.81 (4) | C14—C19 | 1.383 (4) |
| N3—C13 | 1.283 (4) | C15—C16 | 1.376 (4) |
| C1—C2 | 1.363 (5) | C15—H15A | 0.9300 |
| C1—C9 | 1.377 (5) | C16—C17 | 1.364 (5) |
| C1—H1A | 0.9300 | C16—H16A | 0.9300 |
| C2—C3 | 1.382 (4) | C17—C18 | 1.363 (5) |
| C2—H2A | 0.9300 | C18—C19 | 1.382 (5) |
| C3—C7 | 1.395 (4) | C18—H18A | 0.9300 |
| C4—C5 | 1.455 (4) | C19—H19A | 0.9300 |
| C5—C6 | 1.347 (4) | | |
| | | | |
| C11—S1—C12 | 88.34 (15) | C1—C9—Br1 | 119.5 (2) |
| C4—O1—C3 | 122.0 (2) | C8—C9—Br1 | 119.5 (3) |
| C12—N1—C10 | 109.6 (2) | C11—C10—N1 | 115.0 (2) |
| C12—N2—N3 | 119.1 (3) | C11—C10—C5 | 129.2 (3) |
| C12—N2—H1N2 | 122 (3) | N1—C10—C5 | 115.8 (3) |
| N3—N2—H1N2 | 118 (3) | C10—C11—S1 | 110.7 (2) |
| C13—N3—N2 | 115.4 (3) | C10—C11—H11A | 124.6 |
| C2—C1—C9 | 120.0 (3) | S1—C11—H11A | 124.6 |
| C2—C1—H1A | 120.0 | N1—C12—N2 | 121.2 (3) |
| C9—C1—H1A | 120.0 | N1—C12—S1 | 116.4 (2) |
| C1—C2—C3 | 119.7 (3) | N2—C12—S1 | 122.4 (2) |
| C1—C2—H2A | 120.1 | N3—C13—C14 | 121.3 (3) |
| C3—C2—H2A | 120.1 | N3—C13—H13A | 119.3 |
| O1—C3—C2 | 118.3 (3) | C14—C13—H13A | 119.3 |
| O1—C3—C7 | 120.6 (2) | C15—C14—C19 | 117.6 (3) |
| C2—C3—C7 | 121.1 (3) | C15—C14—C13 | 122.4 (3) |
| O2—C4—O1 | 115.7 (3) | C19—C14—C13 | 120.0 (3) |

| | | | |
|---|---|---|---|
| O2—C4—C5 | 125.6 (3) | C16—C15—C14 | 121.6 (3) |
| O1—C4—C5 | 118.7 (3) | C16—C15—H15A | 119.2 |
| C6—C5—C4 | 118.8 (3) | C14—C15—H15A | 119.2 |
| C6—C5—C10 | 121.3 (3) | C17—C16—C15 | 119.2 (3) |
| C4—C5—C10 | 119.9 (3) | C17—C16—H16A | 120.4 |
| C5—C6—C7 | 122.3 (3) | C15—C16—H16A | 120.4 |
| C5—C6—H6A | 118.8 | C18—C17—C16 | 121.4 (3) |
| C7—C6—H6A | 118.8 | C18—C17—Cl1 | 119.2 (3) |
| C8—C7—C3 | 118.3 (3) | C16—C17—Cl1 | 119.4 (3) |
| C8—C7—C6 | 124.2 (3) | C17—C18—C19 | 118.6 (4) |
| C3—C7—C6 | 117.5 (3) | C17—C18—H18A | 120.7 |
| C9—C8—C7 | 119.8 (3) | C19—C18—H18A | 120.7 |
| C9—C8—H8A | 120.1 | C18—C19—C14 | 121.6 (4) |
| C7—C8—H8A | 120.1 | C18—C19—H19A | 119.2 |
| C1—C9—C8 | 121.0 (3) | C14—C19—H19A | 119.2 |
| | | | |
| C12—N2—N3—C13 | −174.7 (3) | C12—N1—C10—C5 | 178.7 (2) |
| C9—C1—C2—C3 | −0.3 (5) | C6—C5—C10—C11 | 168.5 (3) |
| C4—O1—C3—C2 | −178.7 (3) | C4—C5—C10—C11 | −11.1 (5) |
| C4—O1—C3—C7 | 0.3 (4) | C6—C5—C10—N1 | −9.3 (4) |
| C1—C2—C3—O1 | 176.8 (3) | C4—C5—C10—N1 | 171.1 (3) |
| C1—C2—C3—C7 | −2.2 (5) | N1—C10—C11—S1 | 0.1 (3) |
| C3—O1—C4—O2 | 178.1 (3) | C5—C10—C11—S1 | −177.7 (2) |
| C3—O1—C4—C5 | −1.8 (4) | C12—S1—C11—C10 | −0.5 (2) |
| O2—C4—C5—C6 | −178.4 (3) | C10—N1—C12—N2 | 178.9 (3) |
| O1—C4—C5—C6 | 1.4 (4) | C10—N1—C12—S1 | −1.0 (3) |
| O2—C4—C5—C10 | 1.2 (5) | N3—N2—C12—N1 | −178.7 (3) |
| O1—C4—C5—C10 | −179.0 (3) | N3—N2—C12—S1 | 1.2 (4) |
| C4—C5—C6—C7 | 0.4 (4) | C11—S1—C12—N1 | 0.9 (2) |
| C10—C5—C6—C7 | −179.2 (3) | C11—S1—C12—N2 | −179.0 (3) |
| O1—C3—C7—C8 | −176.8 (3) | N2—N3—C13—C14 | −179.1 (3) |
| C2—C3—C7—C8 | 2.2 (4) | N3—C13—C14—C15 | 2.8 (5) |
| O1—C3—C7—C6 | 1.5 (4) | N3—C13—C14—C19 | −176.2 (3) |
| C2—C3—C7—C6 | −179.5 (3) | C19—C14—C15—C16 | −0.3 (5) |
| C5—C6—C7—C8 | 176.3 (3) | C13—C14—C15—C16 | −179.3 (3) |
| C5—C6—C7—C3 | −1.9 (4) | C14—C15—C16—C17 | −0.8 (5) |
| C3—C7—C8—C9 | 0.3 (5) | C15—C16—C17—C18 | 1.4 (5) |
| C6—C7—C8—C9 | −177.9 (3) | C15—C16—C17—Cl1 | 179.1 (2) |
| C2—C1—C9—C8 | 2.8 (5) | C16—C17—C18—C19 | −0.8 (6) |
| C2—C1—C9—Br1 | −175.8 (3) | Cl1—C17—C18—C19 | −178.5 (3) |
| C7—C8—C9—C1 | −2.8 (5) | C17—C18—C19—C14 | −0.4 (6) |
| C7—C8—C9—Br1 | 175.8 (2) | C15—C14—C19—C18 | 1.0 (5) |
| C12—N1—C10—C11 | 0.6 (4) | C13—C14—C19—C18 | 180.0 (3) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N2—H1N2···O2[i] | 0.81 (4) | 2.16 (4) | 2.957 (4) | 169 (4) |

| C11—H11*A*···O2 | 0.93 | 2.35 | 2.878 (4) | 115 |

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