# Crystal structure of methyl 7-phenyl-6a,7,7a,8,9,10-hexahydro-6*H*,11a*H*-thio-chromeno[3,4-*b*]pyrrolizine-6a-carbox-ylate

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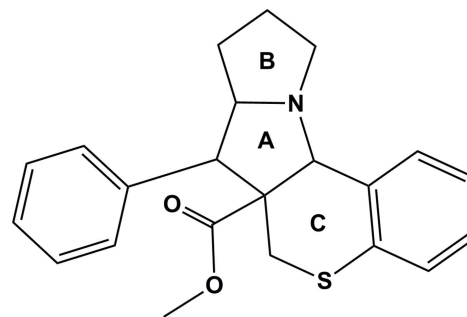
In the title compound, $C_{22}H_{23}NO_2S$, the inner pyrrolidine ring (*A*) adopts an envelope conformation with the methine C atom opposite the fused C—N bond as the flap. The thiopyran ring (*C*) has a half-chair conformation and its mean plane is inclined to the fused benzene ring by 1.74 (11)°, and by 60.52 (11)° to the mean plane of pyrrolidine ring *A*. In the outer pyrrolidine ring (*B*), the C atom opposite the fused C—N bond is disordered [site-occupancy ratio = 0.427 (13): 0.573 (13)] and both rings have envelope conformations, with the disordered C atom as the flap. The planes of the phenyl ring and the benzene ring of the thiochromane unit are inclined to one another by 65.52 (14)°. In the crystal, molecules are linked by a pair of C—H···O hydrogen bonds forming inversion dimers.

## 1. Related literature

For the biological activity of pyrrolizine derivatives, see: Raj *et al.* (2003); Atal (1978); Denny (2001); Suzuki *et al.* (1994). For a related structure, see: Ramesh *et al.* (2007).

## 2. Experimental

### 2.1. Crystal data

| | |
|---|---|
| $C_{22}H_{23}NO_2S$ | $\gamma = 74.385\ (2)°$ |
| $M_r = 365.47$ | $V = 934.88\ (7)$ Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 9.5184\ (4)$ Å | Mo $K\alpha$ radiation |
| $b = 10.4041\ (5)$ Å | $\mu = 0.19$ mm$^{-1}$ |
| $c = 10.6923\ (4)$ Å | $T = 293$ K |
| $\alpha = 81.270\ (2)°$ | $0.30 \times 0.30 \times 0.25$ mm |
| $\beta = 66.626\ (2)°$ | |

### 2.2. Data collection

| | |
|---|---|
| Bruker Kappa APEXII CCD diffractometer | 18019 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2004) | 3265 independent reflections |
| $T_{min} = 0.945$, $T_{max} = 0.954$ | 2504 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.030$ |

### 2.3. Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | 10 restraints |
| $wR(F^2) = 0.112$ | H-atom parameters constrained |
| $S = 1.03$ | $\Delta\rho_{max} = 0.21$ e Å$^{-3}$ |
| 3265 reflections | $\Delta\rho_{min} = -0.21$ e Å$^{-3}$ |
| 246 parameters | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C11—H11$C$···O1$^i$ | 0.97 | 2.48 | 3.365 (3) | 151 |

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

## Acknowledgements

# data reports

## References

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# supporting information

# Crystal structure of methyl 7-phenyl-6a,7,7a,8,9,10-hexahydro-6*H*,11a*H*-thio-chromeno[3,4-*b*]pyrrolizine-6a-carboxylate

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## S1. Structural commentary

Pyrrolizidine alkaloids occur in more than 40 genera, and are responsible for heavy losses of livestock and poisoning in man due to their hepatotoxity. These alkaloids are also reported to possess a number of other biological activities (Atal, 1978) and are used as DNA minor groove alkylating agents (Denny, 2001). Substituted pyrrolidines have gained much importance because they are the structural elements of many alkaloids. It has been found that they exhibit antifungal activity against various pathogens (Amal Raj *et al.*, 2003). Optically active pyrrolidine derivatives have been used as intermediates in controlled asymmetric synthesis (Suzuki *et al.*, 1994). In view of its biological importance, the crystal structure determination of the title compound was undertaken.

The molecular structure of the title compound is shown in Fig. 1. The pyrrolizine ring system is folded about the bridging N1—C8 bond, as observed in a related structure (Ramesh *et al.*, 2007). The five membered substituted pyrrolidine ring (A = N1/C7—C8/C12/C20) exhibits an envelope conformation with C20 as the flap atom [asymmetry parameter $\Delta Cs(C20) = 1.72 \, (2)°$ and puckering parameters $q_2 = 0.463 \, (2)$Å and $\varphi_2 = 288.3 \, (3)°$]. The unsubstituted five-membered ring has a C atom disordered over two positions [site occupancies of C10 and C10′ are 0.427 (13) and 0.573 (13), respectively]. The sum of bond angles around atom N1 (330°) is in accordance with sp$^3$ hybridization.

In the crystal, molecules are linked by a pair of C—H⋯O hydrogen bonds forming inversion dimers (Table 1 and Fig. 2).

## S2. Synthesis and crystallization

A solution of methyl (*Z*)-2-(((2-formylphenyl)thio)methyl)-3-phenyl acrylate (1 mmol) and L-proline(1.2 mmol) in aceto-nitrile (10ml) was refluxed until the completion of the reaction as evidenced by TLC. The solvent was r removed under vacuum. The crude product was subjected to column chromatography on silica gel (100-200 mesh) using petroleum ether-ethyl acetate (9:1) as eluent, which successfully provided the pure product as colorless solid. The product was dissolved in chloroform and heated for two minutes. The resulting solution was subjected to crystallization by slow evaporation of the solvent for 48 hours resulting in the formation of single crystals.

## S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were fixed geometrically and allowed to ride on their parent C atoms: C—H = 0.93-0.98 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms.
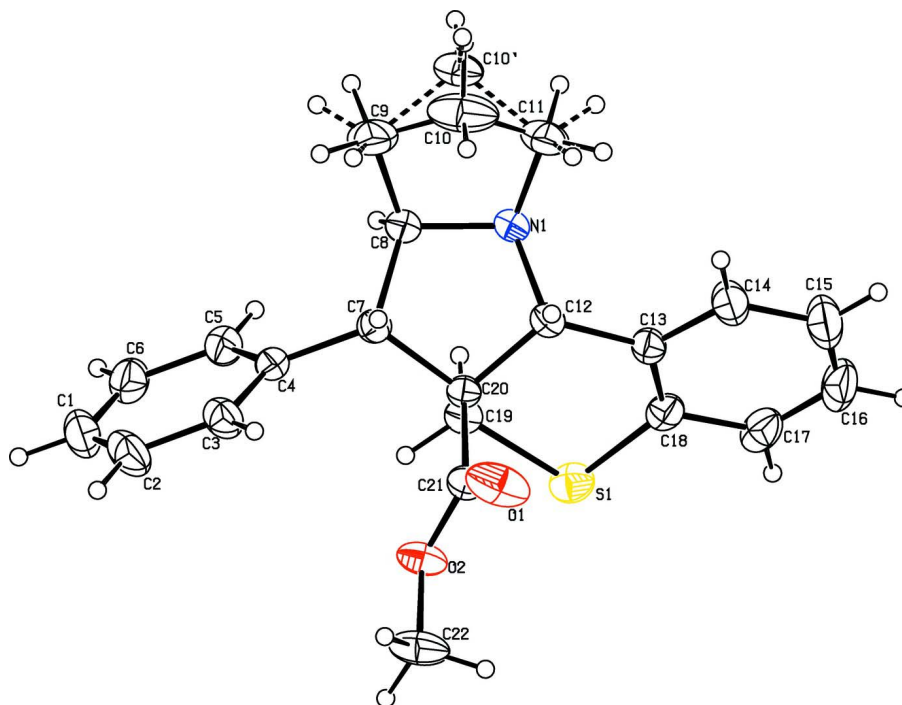
**Figure 1**

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.
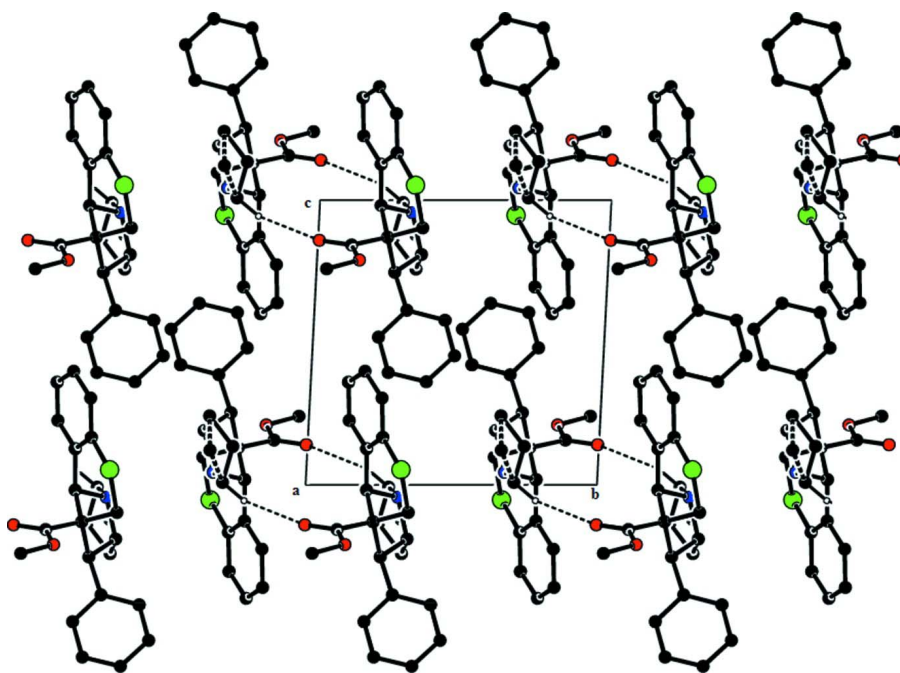


**Figure 2**

The crystal packing of the title compound, viewed along the *a* axis. Dashed lines shows the intermolecular C-H···O hydrogen bonds (see Table 1). H atoms not involved in hydrogen bonding have been omitted for clarity.

**Methyl 7-phenyl-6a,7,7a,8,9,10-hexahydro-6H,11aH-thiochromeno[3,4-b]pyrrolizine-6a-carboxylate**

*Crystal data*

| | |
|---|---|
| $C_{22}H_{23}NO_2S$ | $Z = 2$ |
| $M_r = 365.47$ | $F(000) = 388$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.298$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 9.5184$ (4) Å | Cell parameters from 3265 reflections |
| $b = 10.4041$ (5) Å | $\theta = 2.1–25.0°$ |
| $c = 10.6923$ (4) Å | $\mu = 0.19$ mm$^{-1}$ |
| $\alpha = 81.270$ (2)° | $T = 293$ K |
| $\beta = 66.626$ (2)° | Block, colourless |
| $\gamma = 74.385$ (2)° | $0.30 \times 0.30 \times 0.25$ mm |
| $V = 934.88$ (7) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker Kappa APEXII CCD diffractometer | 18019 measured reflections |
| Radiation source: fine-focus sealed tube | 3265 independent reflections |
| Graphite monochromator | 2504 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scans | $R_{int} = 0.030$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2004) | $\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$ |
| | $h = -11\rightarrow11$ |
| | $k = -12\rightarrow12$ |
| $T_{min} = 0.945$, $T_{max} = 0.954$ | $l = -12\rightarrow12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | $w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.4695P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.112$ | |
| $S = 1.03$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 3265 reflections | $\Delta\rho_{max} = 0.21$ e Å$^{-3}$ |
| 246 parameters | $\Delta\rho_{min} = -0.21$ e Å$^{-3}$ |
| 10 restraints | Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.025 (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 $F^2 > 2$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 | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 0.9603 (3) | 0.3962 (4) | 0.3621 (3) | 0.0705 (8) | |
| H1 | 1.0279 | 0.4231 | 0.2778 | 0.085* | |

| C2 | 0.9631 (3) | 0.2640 (3) | 0.3945 (3) | 0.0702 (8) | |
| H2 | 1.0334 | 0.2005 | 0.3328 | 0.084* | |
| C3 | 0.8613 (3) | 0.2244 (3) | 0.5191 (2) | 0.0541 (6) | |
| H3 | 0.8631 | 0.1341 | 0.5402 | 0.065* | |
| C4 | 0.7568 (2) | 0.3172 (2) | 0.6132 (2) | 0.0417 (5) | |
| C5 | 0.7572 (3) | 0.4499 (2) | 0.5783 (2) | 0.0535 (6) | |
| H5 | 0.6883 | 0.5142 | 0.6397 | 0.064* | |
| C6 | 0.8587 (3) | 0.4888 (3) | 0.4532 (3) | 0.0655 (7) | |
| H6 | 0.8574 | 0.5790 | 0.4312 | 0.079* | |
| C7 | 0.6470 (2) | 0.2688 (2) | 0.74667 (19) | 0.0383 (5) | |
| H7 | 0.6321 | 0.1845 | 0.7293 | 0.046* | |
| C8 | 0.4827 (2) | 0.3576 (2) | 0.8094 (2) | 0.0488 (6) | |
| H8 | 0.4892 | 0.4514 | 0.7964 | 0.059* | |
| C9 | 0.3619 (3) | 0.3412 (4) | 0.7578 (3) | 0.0890 (11) | |
| H9A | 0.3418 | 0.4164 | 0.6965 | 0.107* | 0.427 (13) |
| H9B | 0.4002 | 0.2600 | 0.7085 | 0.107* | 0.427 (13) |
| H9C | 0.2928 | 0.4264 | 0.7482 | 0.107* | 0.573 (13) |
| H9D | 0.4119 | 0.2990 | 0.6710 | 0.107* | 0.573 (13) |
| C10 | 0.2151 (9) | 0.3342 (11) | 0.8782 (7) | 0.057 (2) | 0.427 (13) |
| H10A | 0.1624 | 0.2720 | 0.8659 | 0.069* | 0.427 (13) |
| H10B | 0.1432 | 0.4214 | 0.8954 | 0.069* | 0.427 (13) |
| C10′ | 0.2769 (10) | 0.2563 (10) | 0.8649 (7) | 0.091 (2) | 0.573 (13) |
| H10C | 0.1701 | 0.2721 | 0.8687 | 0.109* | 0.573 (13) |
| H10D | 0.3275 | 0.1631 | 0.8465 | 0.109* | 0.573 (13) |
| C11 | 0.2750 (3) | 0.2854 (3) | 0.9919 (3) | 0.0691 (8) | |
| H11A | 0.2000 | 0.3268 | 1.0756 | 0.083* | 0.427 (13) |
| H11B | 0.2873 | 0.1894 | 1.0068 | 0.083* | 0.427 (13) |
| H11C | 0.2653 | 0.2084 | 1.0558 | 0.083* | 0.573 (13) |
| H11D | 0.1886 | 0.3601 | 1.0319 | 0.083* | 0.573 (13) |
| C12 | 0.5497 (2) | 0.21009 (19) | 0.98166 (19) | 0.0364 (5) | |
| H12 | 0.5360 | 0.1253 | 0.9643 | 0.044* | |
| C13 | 0.5386 (2) | 0.2033 (2) | 1.1270 (2) | 0.0407 (5) | |
| C14 | 0.4304 (3) | 0.1386 (3) | 1.2261 (2) | 0.0595 (6) | |
| H14 | 0.3685 | 0.1005 | 1.2005 | 0.071* | |
| C15 | 0.4123 (4) | 0.1294 (3) | 1.3608 (3) | 0.0781 (8) | |
| H15 | 0.3387 | 0.0858 | 1.4254 | 0.094* | |
| C16 | 0.5026 (4) | 0.1842 (3) | 1.3991 (3) | 0.0767 (9) | |
| H16 | 0.4899 | 0.1786 | 1.4905 | 0.092* | |
| C17 | 0.6118 (3) | 0.2473 (3) | 1.3047 (2) | 0.0611 (7) | |
| H17 | 0.6728 | 0.2845 | 1.3323 | 0.073* | |
| C18 | 0.6326 (3) | 0.2566 (2) | 1.1671 (2) | 0.0450 (5) | |
| C19 | 0.7422 (2) | 0.35732 (19) | 0.9027 (2) | 0.0398 (5) | |
| H19A | 0.6539 | 0.4339 | 0.9156 | 0.048* | |
| H19B | 0.8314 | 0.3793 | 0.8260 | 0.048* | |
| C20 | 0.7012 (2) | 0.23802 (18) | 0.87029 (19) | 0.0339 (4) | |
| C21 | 0.8360 (2) | 0.1159 (2) | 0.8429 (2) | 0.0395 (5) | |
| C22 | 1.1091 (3) | 0.0345 (3) | 0.7589 (3) | 0.0748 (8) | |
| H22A | 1.2034 | 0.0674 | 0.7209 | 0.112* | |

| H22B | 1.1072 | −0.0189 | 0.6941 | 0.112* |
|---|---|---|---|---|
| H22C | 1.1068 | −0.0189 | 0.8409 | 0.112* |
| N1 | 0.42652 (18) | 0.31903 (18) | 0.95607 (17) | 0.0428 (4) |
| O1 | 0.8198 (2) | 0.00459 (16) | 0.8592 (2) | 0.0818 (6) |
| O2 | 0.97460 (16) | 0.14517 (15) | 0.78985 (17) | 0.0542 (4) |
| S1 | 0.78888 (7) | 0.32480 (6) | 1.05291 (6) | 0.0536 (2) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0631 (17) | 0.108 (2) | 0.0412 (14) | −0.0378 (17) | −0.0105 (12) | 0.0030 (15) |
| C2 | 0.0528 (15) | 0.103 (2) | 0.0478 (15) | −0.0215 (15) | −0.0017 (12) | −0.0246 (15) |
| C3 | 0.0475 (13) | 0.0635 (15) | 0.0458 (13) | −0.0114 (11) | −0.0091 (11) | −0.0121 (11) |
| C4 | 0.0354 (11) | 0.0533 (13) | 0.0355 (11) | −0.0070 (10) | −0.0147 (9) | −0.0018 (10) |
| C5 | 0.0506 (13) | 0.0552 (15) | 0.0470 (13) | −0.0061 (11) | −0.0162 (11) | 0.0030 (11) |
| C6 | 0.0671 (17) | 0.0736 (18) | 0.0585 (16) | −0.0253 (15) | −0.0279 (14) | 0.0176 (14) |
| C7 | 0.0363 (10) | 0.0405 (11) | 0.0365 (11) | −0.0051 (9) | −0.0130 (9) | −0.0056 (9) |
| C8 | 0.0350 (11) | 0.0623 (15) | 0.0406 (12) | −0.0016 (10) | −0.0121 (9) | −0.0007 (10) |
| C9 | 0.0467 (15) | 0.157 (3) | 0.0638 (18) | 0.0036 (19) | −0.0299 (14) | −0.028 (2) |
| C10 | 0.035 (4) | 0.066 (5) | 0.074 (4) | −0.010 (3) | −0.021 (3) | −0.015 (4) |
| C10′ | 0.054 (4) | 0.097 (6) | 0.143 (6) | −0.006 (4) | −0.047 (4) | −0.057 (5) |
| C11 | 0.0339 (12) | 0.0849 (19) | 0.0797 (19) | −0.0148 (13) | −0.0153 (12) | 0.0063 (15) |
| C12 | 0.0365 (10) | 0.0324 (10) | 0.0383 (11) | −0.0071 (8) | −0.0112 (9) | −0.0050 (8) |
| C13 | 0.0413 (11) | 0.0363 (11) | 0.0361 (11) | 0.0000 (9) | −0.0103 (9) | −0.0053 (9) |
| C14 | 0.0585 (15) | 0.0644 (16) | 0.0444 (14) | −0.0149 (13) | −0.0089 (11) | 0.0015 (12) |
| C15 | 0.083 (2) | 0.087 (2) | 0.0419 (15) | −0.0166 (17) | −0.0062 (14) | 0.0051 (14) |
| C16 | 0.093 (2) | 0.081 (2) | 0.0349 (14) | 0.0101 (17) | −0.0200 (15) | −0.0067 (13) |
| C17 | 0.0727 (17) | 0.0586 (15) | 0.0491 (15) | 0.0103 (13) | −0.0314 (13) | −0.0163 (12) |
| C18 | 0.0486 (12) | 0.0380 (12) | 0.0425 (12) | 0.0068 (10) | −0.0190 (10) | −0.0105 (9) |
| C19 | 0.0394 (11) | 0.0328 (11) | 0.0467 (12) | −0.0076 (9) | −0.0149 (9) | −0.0048 (9) |
| C20 | 0.0328 (10) | 0.0310 (10) | 0.0367 (10) | −0.0049 (8) | −0.0123 (8) | −0.0047 (8) |
| C21 | 0.0376 (11) | 0.0351 (12) | 0.0432 (12) | −0.0045 (9) | −0.0131 (9) | −0.0070 (9) |
| C22 | 0.0391 (13) | 0.0678 (18) | 0.108 (2) | 0.0126 (12) | −0.0237 (14) | −0.0337 (16) |
| N1 | 0.0315 (9) | 0.0497 (11) | 0.0400 (10) | −0.0050 (8) | −0.0089 (7) | −0.0015 (8) |
| O1 | 0.0528 (10) | 0.0327 (10) | 0.1383 (19) | −0.0052 (8) | −0.0149 (11) | −0.0088 (10) |
| O2 | 0.0325 (8) | 0.0463 (9) | 0.0772 (11) | −0.0004 (7) | −0.0141 (7) | −0.0175 (8) |
| S1 | 0.0555 (4) | 0.0559 (4) | 0.0602 (4) | −0.0130 (3) | −0.0294 (3) | −0.0123 (3) |

*Geometric parameters (Å, º)*

| C1—C6 | 1.360 (4) | C11—H11A | 0.9700 |
|---|---|---|---|
| C1—C2 | 1.362 (4) | C11—H11B | 0.9700 |
| C1—H1 | 0.9300 | C11—H11C | 0.9700 |
| C2—C3 | 1.381 (3) | C11—H11D | 0.9700 |
| C2—H2 | 0.9300 | C12—N1 | 1.476 (3) |
| C3—C4 | 1.384 (3) | C12—C13 | 1.507 (3) |
| C3—H3 | 0.9300 | C12—C20 | 1.530 (3) |
| C4—C5 | 1.375 (3) | C12—H12 | 0.9800 |

| | | | |
|---|---|---|---|
| C4—C7 | 1.505 (3) | C13—C14 | 1.388 (3) |
| C5—C6 | 1.381 (3) | C13—C18 | 1.392 (3) |
| C5—H5 | 0.9300 | C14—C15 | 1.373 (4) |
| C6—H6 | 0.9300 | C14—H14 | 0.9300 |
| C7—C8 | 1.526 (3) | C15—C16 | 1.359 (4) |
| C7—C20 | 1.562 (3) | C15—H15 | 0.9300 |
| C7—H7 | 0.9800 | C16—C17 | 1.366 (4) |
| C8—N1 | 1.472 (3) | C16—H16 | 0.9300 |
| C8—C9 | 1.514 (3) | C17—C18 | 1.396 (3) |
| C8—H8 | 0.9800 | C17—H17 | 0.9300 |
| C9—C10′ | 1.445 (8) | C18—S1 | 1.752 (2) |
| C9—C10 | 1.488 (7) | C19—C20 | 1.520 (3) |
| C9—H9A | 0.9700 | C19—S1 | 1.793 (2) |
| C9—H9B | 0.9700 | C19—H19A | 0.9700 |
| C9—H9C | 0.9700 | C19—H19B | 0.9700 |
| C9—H9D | 0.9700 | C20—C21 | 1.511 (3) |
| C10—C11 | 1.506 (7) | C21—O1 | 1.187 (2) |
| C10—H10A | 0.9700 | C21—O2 | 1.313 (2) |
| C10—H10B | 0.9700 | C22—O2 | 1.435 (3) |
| C10′—C11 | 1.428 (6) | C22—H22A | 0.9600 |
| C10′—H10C | 0.9700 | C22—H22B | 0.9600 |
| C10′—H10D | 0.9700 | C22—H22C | 0.9600 |
| C11—N1 | 1.463 (3) | | |
| | | | |
| C6—C1—C2 | 119.9 (2) | N1—C11—H11A | 109.7 |
| C6—C1—H1 | 120.1 | C10—C11—H11A | 109.7 |
| C2—C1—H1 | 120.1 | C10′—C11—H11B | 81.2 |
| C1—C2—C3 | 120.0 (3) | N1—C11—H11B | 109.7 |
| C1—C2—H2 | 120.0 | C10—C11—H11B | 109.7 |
| C3—C2—H2 | 120.0 | H11A—C11—H11B | 108.2 |
| C2—C3—C4 | 121.0 (2) | C10′—C11—H11C | 110.9 |
| C2—C3—H3 | 119.5 | N1—C11—H11C | 110.9 |
| C4—C3—H3 | 119.5 | C10—C11—H11C | 132.3 |
| C5—C4—C3 | 117.9 (2) | H11A—C11—H11C | 78.6 |
| C5—C4—C7 | 123.32 (19) | H11B—C11—H11C | 31.7 |
| C3—C4—C7 | 118.8 (2) | C10′—C11—H11D | 110.9 |
| C4—C5—C6 | 120.9 (2) | N1—C11—H11D | 110.9 |
| C4—C5—H5 | 119.6 | C10—C11—H11D | 78.1 |
| C6—C5—H5 | 119.6 | H11A—C11—H11D | 33.9 |
| C1—C6—C5 | 120.4 (3) | H11B—C11—H11D | 132.5 |
| C1—C6—H6 | 119.8 | H11C—C11—H11D | 108.9 |
| C5—C6—H6 | 119.8 | N1—C12—C13 | 111.97 (15) |
| C4—C7—C8 | 117.60 (17) | N1—C12—C20 | 102.97 (15) |
| C4—C7—C20 | 117.97 (16) | C13—C12—C20 | 116.79 (16) |
| C8—C7—C20 | 101.70 (15) | N1—C12—H12 | 108.2 |
| C4—C7—H7 | 106.2 | C13—C12—H12 | 108.2 |
| C8—C7—H7 | 106.2 | C20—C12—H12 | 108.2 |
| C20—C7—H7 | 106.2 | C14—C13—C18 | 118.1 (2) |

| | | | |
|---|---|---|---|
| N1—C8—C9 | 106.7 (2) | C14—C13—C12 | 118.3 (2) |
| N1—C8—C7 | 105.94 (16) | C18—C13—C12 | 123.55 (19) |
| C9—C8—C7 | 115.6 (2) | C15—C14—C13 | 121.7 (3) |
| N1—C8—H8 | 109.5 | C15—C14—H14 | 119.1 |
| C9—C8—H8 | 109.5 | C13—C14—H14 | 119.1 |
| C7—C8—H8 | 109.5 | C16—C15—C14 | 119.6 (3) |
| C10′—C9—C10 | 34.0 (3) | C16—C15—H15 | 120.2 |
| C10′—C9—C8 | 102.1 (3) | C14—C15—H15 | 120.2 |
| C10—C9—C8 | 107.7 (3) | C15—C16—C17 | 120.6 (2) |
| C10′—C9—H9A | 139.4 | C15—C16—H16 | 119.7 |
| C10—C9—H9A | 110.2 | C17—C16—H16 | 119.7 |
| C8—C9—H9A | 110.2 | C16—C17—C18 | 120.6 (3) |
| C10′—C9—H9B | 81.7 | C16—C17—H17 | 119.7 |
| C10—C9—H9B | 110.2 | C18—C17—H17 | 119.7 |
| C8—C9—H9B | 110.2 | C13—C18—C17 | 119.4 (2) |
| H9A—C9—H9B | 108.5 | C13—C18—S1 | 123.83 (16) |
| C10′—C9—H9C | 111.0 | C17—C18—S1 | 116.60 (19) |
| C10—C9—H9C | 78.1 | C20—C19—S1 | 111.91 (14) |
| C8—C9—H9C | 111.4 | C20—C19—H19A | 109.2 |
| H9A—C9—H9C | 33.9 | S1—C19—H19A | 109.2 |
| H9B—C9—H9C | 132.2 | C20—C19—H19B | 109.2 |
| C10′—C9—H9D | 111.6 | S1—C19—H19B | 109.2 |
| C10—C9—H9D | 133.3 | H19A—C19—H19B | 107.9 |
| C8—C9—H9D | 111.3 | C21—C20—C19 | 112.36 (16) |
| H9A—C9—H9D | 79.2 | C21—C20—C12 | 112.39 (16) |
| H9B—C9—H9D | 31.5 | C19—C20—C12 | 110.86 (16) |
| H9C—C9—H9D | 109.2 | C21—C20—C7 | 108.94 (15) |
| C9—C10—C11 | 102.6 (5) | C19—C20—C7 | 112.48 (16) |
| C9—C10—H10A | 111.2 | C12—C20—C7 | 99.11 (14) |
| C11—C10—H10A | 111.2 | O1—C21—O2 | 122.81 (19) |
| C9—C10—H10B | 111.2 | O1—C21—C20 | 123.89 (19) |
| C11—C10—H10B | 111.2 | O2—C21—C20 | 113.15 (17) |
| H10A—C10—H10B | 109.2 | O2—C22—H22A | 109.5 |
| C11—C10′—C9 | 108.8 (4) | O2—C22—H22B | 109.5 |
| C11—C10′—H10C | 109.9 | H22A—C22—H22B | 109.5 |
| C9—C10′—H10C | 109.9 | O2—C22—H22C | 109.5 |
| C11—C10′—H10D | 109.9 | H22A—C22—H22C | 109.5 |
| C9—C10′—H10D | 109.9 | H22B—C22—H22C | 109.5 |
| H10C—C10′—H10D | 108.3 | C11—N1—C8 | 107.08 (18) |
| C10′—C11—N1 | 104.2 (3) | C11—N1—C12 | 115.18 (18) |
| C10′—C11—C10 | 33.9 (3) | C8—N1—C12 | 108.21 (15) |
| N1—C11—C10 | 109.6 (3) | C21—O2—C22 | 116.65 (18) |
| C10′—C11—H11A | 138.5 | C18—S1—C19 | 101.43 (10) |
| | | | |
| C6—C1—C2—C3 | 0.8 (4) | C16—C17—C18—C13 | 1.4 (3) |
| C1—C2—C3—C4 | −0.7 (4) | C16—C17—C18—S1 | −173.83 (19) |
| C2—C3—C4—C5 | 0.2 (3) | S1—C19—C20—C21 | −61.3 (2) |
| C2—C3—C4—C7 | 179.2 (2) | S1—C19—C20—C12 | 65.39 (18) |

| | | | |
|---|---|---|---|
| C3—C4—C5—C6 | 0.1 (3) | S1—C19—C20—C7 | 175.32 (13) |
| C7—C4—C5—C6 | −178.8 (2) | N1—C12—C20—C21 | −159.41 (15) |
| C2—C1—C6—C5 | −0.4 (4) | C13—C12—C20—C21 | 77.5 (2) |
| C4—C5—C6—C1 | 0.0 (4) | N1—C12—C20—C19 | 73.91 (18) |
| C5—C4—C7—C8 | 33.6 (3) | C13—C12—C20—C19 | −49.2 (2) |
| C3—C4—C7—C8 | −145.3 (2) | N1—C12—C20—C7 | −44.48 (17) |
| C5—C4—C7—C20 | −88.8 (2) | C13—C12—C20—C7 | −167.61 (16) |
| C3—C4—C7—C20 | 92.3 (2) | C4—C7—C20—C21 | −68.8 (2) |
| C4—C7—C8—N1 | −157.46 (17) | C8—C7—C20—C21 | 160.99 (17) |
| C20—C7—C8—N1 | −27.0 (2) | C4—C7—C20—C19 | 56.5 (2) |
| C4—C7—C8—C9 | 84.7 (3) | C8—C7—C20—C19 | −73.7 (2) |
| C20—C7—C8—C9 | −144.9 (2) | C4—C7—C20—C12 | 173.63 (17) |
| N1—C8—C9—C10′ | −17.6 (5) | C8—C7—C20—C12 | 43.42 (19) |
| C7—C8—C9—C10′ | 99.9 (5) | C19—C20—C21—O1 | 154.4 (2) |
| N1—C8—C9—C10 | 17.1 (6) | C12—C20—C21—O1 | 28.6 (3) |
| C7—C8—C9—C10 | 134.6 (5) | C7—C20—C21—O1 | −80.2 (3) |
| C10′—C9—C10—C11 | 60.9 (6) | C19—C20—C21—O2 | −30.0 (2) |
| C8—C9—C10—C11 | −24.5 (7) | C12—C20—C21—O2 | −155.88 (17) |
| C10—C9—C10′—C11 | −71.8 (7) | C7—C20—C21—O2 | 95.31 (19) |
| C8—C9—C10′—C11 | 32.0 (7) | C10′—C11—N1—C8 | 21.1 (5) |
| C9—C10′—C11—N1 | −33.9 (7) | C10—C11—N1—C8 | −13.9 (5) |
| C9—C10′—C11—C10 | 70.2 (8) | C10′—C11—N1—C12 | −99.3 (5) |
| C9—C10—C11—C10′ | −62.4 (7) | C10—C11—N1—C12 | −134.3 (5) |
| C9—C10—C11—N1 | 23.8 (7) | C9—C8—N1—C11 | −1.9 (3) |
| N1—C12—C13—C14 | 81.6 (2) | C7—C8—N1—C11 | −125.6 (2) |
| C20—C12—C13—C14 | −160.09 (19) | C9—C8—N1—C12 | 122.8 (2) |
| N1—C12—C13—C18 | −99.5 (2) | C7—C8—N1—C12 | −0.9 (2) |
| C20—C12—C13—C18 | 18.9 (3) | C13—C12—N1—C11 | −84.8 (2) |
| C18—C13—C14—C15 | 1.6 (3) | C20—C12—N1—C11 | 148.95 (19) |
| C12—C13—C14—C15 | −179.4 (2) | C13—C12—N1—C8 | 155.49 (18) |
| C13—C14—C15—C16 | −0.3 (4) | C20—C12—N1—C8 | 29.2 (2) |
| C14—C15—C16—C17 | −0.5 (4) | O1—C21—O2—C22 | −3.5 (3) |
| C15—C16—C17—C18 | 0.0 (4) | C20—C21—O2—C22 | −179.14 (19) |
| C14—C13—C18—C17 | −2.1 (3) | C13—C18—S1—C19 | 19.2 (2) |
| C12—C13—C18—C17 | 178.92 (18) | C17—C18—S1—C19 | −165.83 (16) |
| C14—C13—C18—S1 | 172.73 (16) | C20—C19—S1—C18 | −47.73 (16) |
| C12—C13—C18—S1 | −6.3 (3) | | |

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C11—H11C···O1[i] | 0.97 | 2.48 | 3.365 (3) | 151 |

Symmetry code: (i) −x+1, −y, −z+2.