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1-[(4S)-4-Benzyl-2-thioxo-1,3-thiazolidin-3-yl]propan-1-one¹

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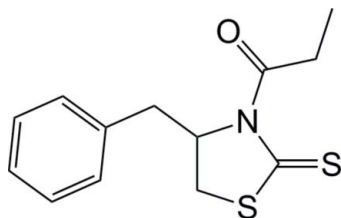
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.041; wR factor = 0.048; data-to-parameter ratio = 16.1.

The analysis of the title chiral auxiliary compound, $\text{C}_{13}\text{H}_{15}\text{NOS}_2$, has enabled the determination of the absolute configuration at the benzyl-bearing ring C atom as *S*. In the crystal structure, molecules aggregate into helical chains along the *b* axis via $\text{C}-\text{H}\cdots\text{O}$ contacts.

Related literature

For background to the use of *N*-acyl thiazolidinethiones as versatile chiral auxiliaries for asymmetric aldol reactions, see: Crimmins & Chaudhary (2000); Crimmins *et al.* (2005); Crimmins & Haley (2006); Crimmins & Dechert (2009). For the synthesis, see: McKennon & Meyer (1993); Delaunay *et al.* (1995); Lu *et al.* (2009).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{15}\text{NOS}_2$
 $M_r = 265.39$
Monoclinic, $P2_1$
 $a = 8.850$ (6) Å
 $b = 7.189$ (5) Å

$c = 10.595$ (7) Å
 $\beta = 95.537$ (6) $^\circ$
 $V = 670.9$ (8) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.38$ mm⁻¹
 $T = 298$ K

0.50 × 0.40 × 0.20 mm

Data collection

Rigaku Mercury diffractometer
Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.831$, $T_{\max} = 0.925$

7301 measured reflections
2734 independent reflections
2361 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.048$
 $S = 0.86$
2734 reflections
170 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³
Absolute structure: Flack (1983),
1138 Friedel pairs
Flack parameter: -0.05 (6)

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C9}-\text{H9}\cdots\text{O1}^{\text{i}}$ | 0.95 | 2.55 | 3.408 (4) | 150 |

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

Data collection: *CrystalClear* (Pflugrath, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2006); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *X-SEED* (Barbour *et al.*, 2001); software used to prepare material for publication: *CrystalStructure*.

NRG thanks the Institute of Life Sciences for allowing him to pursue this work as part of his PhD thesis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2514).

References

- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Crimmins, M. T. & Chaudhary, K. (2000). *Org. Lett.* **2**, 775–777.
Crimmins, M. T., Christie, H. S., Chaudhary, K. & Long, A. (2005). *J. Am. Chem. Soc.* **127**, 13810–13812.
Crimmins, M. T. & Dechert, A.-M. R. (2009). *Org. Lett.* **11**, 1635–1638.
Crimmins, M. T. & Haley, M. W. (2006). *Org. Lett.* **8**, 4223–4225.
Delaunay, D., Toupet, L. & Le Corre, M. J. (1995). *Org. Chem.* **60**, 6604–6607.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Jacobson, R. (1998). Private communication to the Rigaku Corporation, Tokyo, Japan.
Lu, C., Nie, J., Yang, G. & Chen, Z. (2009). *Can. J. Chem.* **87**, 30–32.
McKennon, M. J. & Meyer, A. I. (1993). *J. Org. Chem.* **58**, 3568–3571.
Molecular Structure Corporation & Rigaku (2006). *CrystalStructure*. MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Pflugrath, J. W. (1999). *Acta Cryst.* **D55**, 1718–1725.

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supporting information

Acta Cryst. (2009). E65, o2159 [doi:10.1107/S1600536809030104]

1-[(4S)-4-Benzyl-2-thioxo-1,3-thiazolidin-3-yl]propan-1-one

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S1. Comment

N-Acyl thiazolidinethiones, e.g. (I), are versatile chiral auxiliaries for asymmetric aldol reactions Crimmins & Chaudhary (2000). Many complex natural products have been synthesized using these auxiliaries (Crimmins *et al.* 2005; Crimmins & Haley, 2006; Crimmins & Dechert, 2009). The synthesis of (I) starts from amino alcohol **2** which was converted to thiazolidinethione **3** by reacting with carbon disulfide followed by treatment with propionyl chloride (Fig. 3) (Crimmins & Chaudhary, 2000).

The single crystal analysis of (I), Fig. 1, allowed the determination of the absolute configuration of C1 as S. The crystal structure shows the molecules to aggregate into helical chains along the screw axis via C₉—H₉···O₁ contacts (Fig. 2, Table 1).

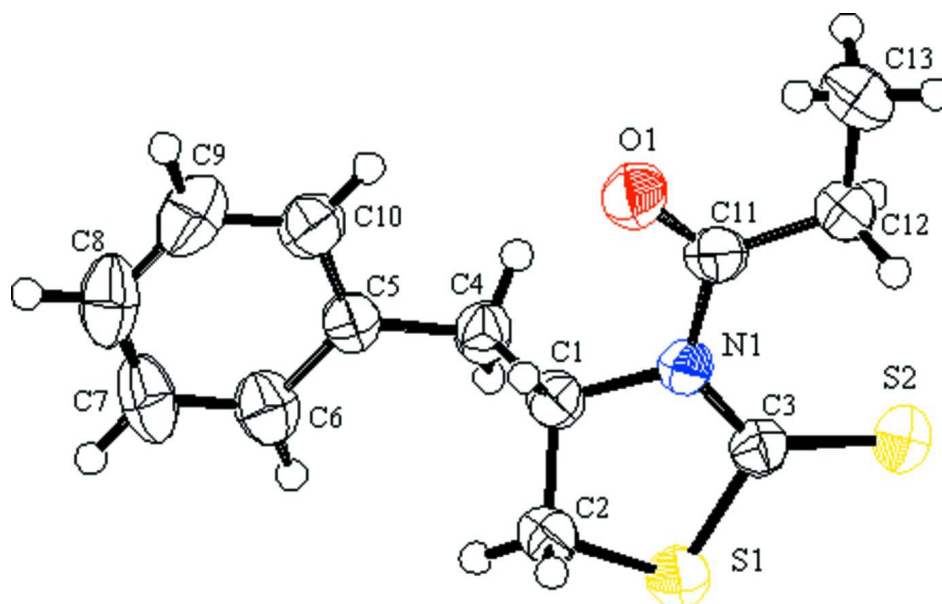
S2. Experimental

To a solution of β -amino alcohol **2** (10 mmol) (McKennon & Meyer, 1993) in aqueous 1.0 N potassium hydroxide (50 ml) was added carbon disulfide (50 mmol, 3.0 ml) slowly. The reaction mixture was refluxed at 110 °C for 12 h to give the desired thiazolidinethione **3** (Delaunay *et al.* 1995). To a solution of compound **3** (0.478 mmol) in dichloromethane (DCM, 3 ml) was added triethylamine (0.956 mmol) and the temperature was maintained at -40 to -78 °C. To that mixture was added propionyl chloride (0.574 mmol) drop wise. The mixture was stirred for 1–2 h, diluted with DCM (10 ml), washed with water (2 x 10 ml), dried over anhydrous Na₂SO₄ and concentrated low vacuum to give (I) as a light-yellow solid; mp. 374–376 K (lit. mp. 374.1 K (Lu *et al.* 2009)).

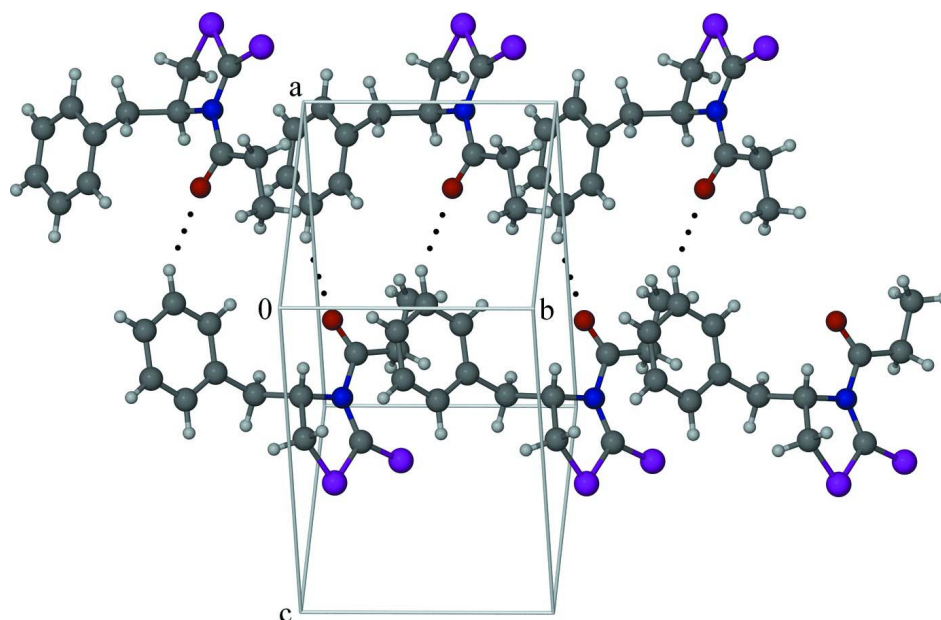
Compound (I) (50 mg) was dissolved in 2:1 DCM/EtOAc (1.0 ml) and left in freezer (10 °C) until fine crystals appeared. Crystals were separated from solution and washed with hexane and dried under vacuum.

S3. Refinement

The H atoms were positioned geometrically and refined in the riding model approximation with C—H = 0.95 Å, and with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

Molecular structure of (I) showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radii.

**Figure 2**

Crystal packing of (I) showing the formation of helical chains. The C-H...O contacts are shown as dashed lines.

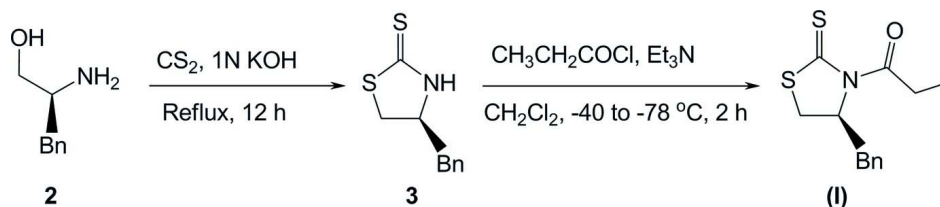


Figure 3

Synthesis of (I).

1-[(4S)-4-Benzyl-2-thioxo-1,3-thiazolidin-3-yl]propan-1-one

Crystal data $\text{C}_{13}\text{H}_{15}\text{NOS}_2$ $M_r = 265.39$ Monoclinic, $P2_1$

Hall symbol: P 2yb

 $a = 8.850$ (6) Å $b = 7.189$ (5) Å $c = 10.595$ (7) Å $\beta = 95.537$ (6)° $V = 670.9$ (8) Å³ $Z = 2$ $F(000) = 280$ $D_x = 1.314$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å

Cell parameters from 3674 reflections

 $\theta = 2.3\text{--}27.4^\circ$ $\mu = 0.38$ mm⁻¹ $T = 298$ K

Prism, yellow

 $0.50 \times 0.40 \times 0.20$ mm*Data collection*

Rigaku Mercury

diffractometer

Detector resolution: 7.31 pixels mm⁻¹ ω scans

Absorption correction: multi-scan

(Jacobson, 1998)

 $T_{\min} = 0.831$, $T_{\max} = 0.925$

7301 measured reflections

2734 independent reflections

2361 reflections with $F^2 > 2\sigma(F^2)$ $R_{\text{int}} = 0.038$ $\theta_{\max} = 27.4^\circ$ $h = -11 \rightarrow 11$ $k = -6 \rightarrow 9$ $l = -13 \rightarrow 13$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.041$ $wR(F^2) = 0.048$ $S = 0.86$

2734 reflections

170 parameters

H-atom parameters constrained

Chebychev polynomial with 3 parameters

(Carruthers & Watkin, 1979) 10359.0000

14093.9000 3595.6900

 $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.32$ e Å⁻³ $\Delta\rho_{\min} = -0.35$ e Å⁻³

Absolute structure: Flack (1983), 1138 Friedel

pairs

Absolute structure parameter: -0.05 (6)*Special details*

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement was performed using all reflections. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| S1 | 0.55104 (6) | 1.08609 (10) | 0.94969 (5) | 0.0574 (2) |
| S2 | 0.80540 (7) | 1.31770 (10) | 1.04864 (6) | 0.0630 (2) |
| O1 | 0.96079 (17) | 1.0605 (2) | 0.69074 (15) | 0.0720 (6) |
| N1 | 0.79082 (15) | 1.1039 (2) | 0.83154 (13) | 0.0410 (4) |
| C1 | 0.6994 (2) | 0.9543 (2) | 0.76431 (19) | 0.0436 (6) |
| C2 | 0.5366 (2) | 0.9806 (2) | 0.79429 (19) | 0.0498 (7) |
| C3 | 0.7324 (2) | 1.1748 (2) | 0.93706 (19) | 0.0462 (6) |
| C4 | 0.7616 (2) | 0.7610 (2) | 0.80159 (19) | 0.0469 (6) |
| C5 | 0.7183 (2) | 0.6180 (2) | 0.70140 (17) | 0.0441 (6) |
| C6 | 0.5872 (2) | 0.5119 (2) | 0.7014 (2) | 0.0561 (7) |
| C7 | 0.5469 (3) | 0.3871 (3) | 0.6051 (2) | 0.0673 (9) |
| C8 | 0.6379 (3) | 0.3610 (3) | 0.5087 (2) | 0.0704 (9) |
| C9 | 0.7667 (3) | 0.4651 (3) | 0.5063 (2) | 0.0719 (9) |
| C10 | 0.8074 (2) | 0.5935 (3) | 0.60097 (19) | 0.0569 (7) |
| C11 | 0.9289 (2) | 1.1496 (2) | 0.7801 (2) | 0.0501 (7) |
| C12 | 1.0320 (2) | 1.3001 (3) | 0.8384 (2) | 0.0545 (7) |
| C13 | 1.1629 (2) | 1.3369 (4) | 0.7610 (2) | 0.0861 (10) |
| H1 | 0.70330 | 0.96970 | 0.67560 | 0.0520* |
| H6 | 0.52430 | 0.52600 | 0.76860 | 0.0670* |
| H7 | 0.45570 | 0.31750 | 0.60530 | 0.0790* |
| H8 | 0.61000 | 0.27260 | 0.44400 | 0.0830* |
| H9 | 0.83030 | 0.44600 | 0.44020 | 0.0870* |
| H10 | 0.89540 | 0.66810 | 0.59680 | 0.0690* |
| H21 | 0.48380 | 1.06070 | 0.73390 | 0.0600* |
| H22 | 0.48550 | 0.86440 | 0.79480 | 0.0590* |
| H41 | 0.72130 | 0.72350 | 0.87750 | 0.0550* |
| H42 | 0.86910 | 0.76750 | 0.81570 | 0.0560* |
| H121 | 1.07080 | 1.26210 | 0.92110 | 0.0650* |
| H122 | 0.97480 | 1.41110 | 0.84380 | 0.0650* |
| H131 | 1.19300 | 1.46340 | 0.77050 | 0.1050* |
| H132 | 1.24580 | 1.25860 | 0.78930 | 0.1050* |
| H133 | 1.13230 | 1.31200 | 0.67430 | 0.1050* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|-------------|-------------|--------------|
| S1 | 0.0512 (2) | 0.0621 (3) | 0.0611 (3) | −0.0066 (3) | 0.0167 (2) | −0.0116 (3) |
| S2 | 0.0587 (3) | 0.0640 (4) | 0.0664 (3) | −0.0025 (3) | 0.0059 (2) | −0.0247 (3) |
| O1 | 0.0664 (9) | 0.0751 (11) | 0.0796 (10) | −0.0150 (9) | 0.0330 (8) | −0.0265 (10) |
| N1 | 0.0401 (7) | 0.0364 (8) | 0.0470 (8) | −0.0001 (7) | 0.0062 (6) | −0.0019 (7) |
| C1 | 0.0419 (10) | 0.0430 (11) | 0.0458 (10) | −0.0008 (8) | 0.0035 (8) | 0.0002 (8) |
| C2 | 0.0417 (10) | 0.0508 (13) | 0.0561 (12) | −0.0027 (9) | 0.0011 (8) | −0.0019 (9) |
| C3 | 0.0427 (10) | 0.0438 (11) | 0.0513 (11) | 0.0037 (8) | 0.0008 (8) | −0.0042 (9) |
| C4 | 0.0510 (11) | 0.0393 (11) | 0.0487 (11) | 0.0028 (8) | −0.0031 (8) | −0.0011 (8) |
| C5 | 0.0453 (10) | 0.0389 (12) | 0.0467 (10) | 0.0008 (8) | −0.0027 (8) | 0.0025 (8) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C6 | 0.0647 (13) | 0.0460 (13) | 0.0569 (12) | -0.0083 (10) | 0.0017 (10) | 0.0087 (9) |
| C7 | 0.0828 (17) | 0.0465 (14) | 0.0678 (15) | -0.0207 (11) | -0.0179 (13) | 0.0093 (11) |
| C8 | 0.104 (2) | 0.0511 (15) | 0.0517 (13) | -0.0052 (13) | -0.0146 (13) | -0.0034 (11) |
| C9 | 0.0992 (19) | 0.0603 (15) | 0.0580 (14) | 0.0079 (15) | 0.0176 (13) | -0.0055 (12) |
| C10 | 0.0579 (11) | 0.0527 (12) | 0.0617 (12) | 0.0015 (12) | 0.0134 (9) | -0.0026 (12) |
| C11 | 0.0415 (11) | 0.0480 (13) | 0.0617 (12) | 0.0026 (8) | 0.0095 (9) | -0.0011 (9) |
| C12 | 0.0430 (10) | 0.0488 (12) | 0.0711 (13) | -0.0016 (10) | 0.0032 (9) | -0.0073 (11) |
| C13 | 0.0543 (13) | 0.086 (2) | 0.121 (2) | -0.0223 (15) | 0.0242 (13) | -0.0216 (19) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|--------------|-----------|
| S1—C2 | 1.806 (2) | C12—C13 | 1.506 (3) |
| S1—C3 | 1.744 (2) | C1—H1 | 0.9500 |
| S2—C3 | 1.650 (2) | C2—H21 | 0.9500 |
| O1—C11 | 1.199 (3) | C2—H22 | 0.9500 |
| N1—C1 | 1.486 (2) | C4—H41 | 0.9500 |
| N1—C3 | 1.374 (3) | C4—H42 | 0.9500 |
| N1—C11 | 1.424 (2) | C6—H6 | 0.9500 |
| C1—C2 | 1.517 (3) | C7—H7 | 0.9500 |
| C1—C4 | 1.532 (2) | C8—H8 | 0.9500 |
| C4—C5 | 1.501 (3) | C9—H9 | 0.9500 |
| C5—C6 | 1.389 (3) | C10—H10 | 0.9500 |
| C5—C10 | 1.395 (3) | C12—H121 | 0.9500 |
| C6—C7 | 1.380 (3) | C12—H122 | 0.9500 |
| C7—C8 | 1.373 (3) | C13—H131 | 0.9500 |
| C8—C9 | 1.366 (4) | C13—H132 | 0.9500 |
| C9—C10 | 1.385 (3) | C13—H133 | 0.9500 |
| C11—C12 | 1.509 (3) | | |
| C2—S1—C3 | 93.92 (9) | C1—C2—H21 | 110.00 |
| C1—N1—C3 | 115.36 (14) | C1—C2—H22 | 111.00 |
| C1—N1—C11 | 115.55 (14) | H21—C2—H22 | 109.00 |
| C3—N1—C11 | 129.05 (14) | C1—C4—H41 | 109.00 |
| N1—C1—C2 | 107.08 (13) | C1—C4—H42 | 109.00 |
| N1—C1—C4 | 111.56 (15) | C5—C4—H41 | 108.00 |
| C2—C1—C4 | 112.58 (14) | C5—C4—H42 | 109.00 |
| S1—C2—C1 | 104.96 (13) | H41—C4—H42 | 109.00 |
| S1—C3—S2 | 118.18 (11) | C5—C6—H6 | 119.00 |
| S1—C3—N1 | 110.37 (12) | C7—C6—H6 | 120.00 |
| S2—C3—N1 | 131.43 (14) | C6—C7—H7 | 120.00 |
| C1—C4—C5 | 112.21 (15) | C8—C7—H7 | 119.00 |
| C4—C5—C6 | 122.19 (16) | C7—C8—H8 | 120.00 |
| C4—C5—C10 | 120.09 (16) | C9—C8—H8 | 121.00 |
| C6—C5—C10 | 117.67 (16) | C8—C9—H9 | 119.00 |
| C5—C6—C7 | 120.91 (19) | C10—C9—H9 | 120.00 |
| C6—C7—C8 | 120.7 (2) | C5—C10—H10 | 119.00 |
| C7—C8—C9 | 119.3 (2) | C9—C10—H10 | 120.00 |
| C8—C9—C10 | 120.7 (2) | C11—C12—H121 | 109.00 |

| | | | |
|---------------|--------------|----------------|--------------|
| C5—C10—C9 | 120.65 (18) | C11—C12—H122 | 109.00 |
| O1—C11—N1 | 117.07 (15) | C13—C12—H121 | 109.00 |
| O1—C11—C12 | 121.82 (17) | C13—C12—H122 | 109.00 |
| N1—C11—C12 | 121.09 (16) | H121—C12—H122 | 109.00 |
| C11—C12—C13 | 111.70 (18) | C12—C13—H131 | 109.00 |
| N1—C1—H1 | 109.00 | C12—C13—H132 | 110.00 |
| C2—C1—H1 | 109.00 | C12—C13—H133 | 109.00 |
| C4—C1—H1 | 108.00 | H131—C13—H132 | 109.00 |
| S1—C2—H21 | 110.00 | H131—C13—H133 | 110.00 |
| S1—C2—H22 | 111.00 | H132—C13—H133 | 109.00 |
| | | | |
| C3—S1—C2—C1 | 22.91 (12) | C4—C1—C2—S1 | 93.51 (15) |
| C2—S1—C3—S2 | 171.92 (11) | N1—C1—C4—C5 | -155.93 (15) |
| C2—S1—C3—N1 | -9.64 (13) | C2—C1—C4—C5 | 83.7 (2) |
| C3—N1—C1—C2 | 25.15 (19) | C1—C4—C5—C6 | -91.3 (2) |
| C3—N1—C1—C4 | -98.44 (17) | C1—C4—C5—C10 | 86.0 (2) |
| C11—N1—C1—C2 | -156.77 (15) | C4—C5—C6—C7 | 177.20 (17) |
| C11—N1—C1—C4 | 79.65 (19) | C10—C5—C6—C7 | -0.1 (3) |
| C1—N1—C3—S1 | -7.69 (18) | C4—C5—C10—C9 | -178.46 (18) |
| C1—N1—C3—S2 | 170.47 (14) | C6—C5—C10—C9 | -1.1 (3) |
| C11—N1—C3—S1 | 174.53 (14) | C5—C6—C7—C8 | 1.9 (3) |
| C11—N1—C3—S2 | -7.3 (3) | C6—C7—C8—C9 | -2.4 (3) |
| C1—N1—C11—O1 | -2.2 (2) | C7—C8—C9—C10 | 1.2 (3) |
| C1—N1—C11—C12 | 179.47 (16) | C8—C9—C10—C5 | 0.6 (3) |
| C3—N1—C11—O1 | 175.56 (17) | O1—C11—C12—C13 | 7.3 (3) |
| C3—N1—C11—C12 | -2.8 (3) | N1—C11—C12—C13 | -174.42 (17) |
| N1—C1—C2—S1 | -29.44 (15) | | |

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> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| C9—H9...O1 ⁱ | 0.95 | 2.55 | 3.408 (4) | 150 |

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