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# 1-[2-(4-Isobutylphenyl)propanoyl]-thiosemicarbazide

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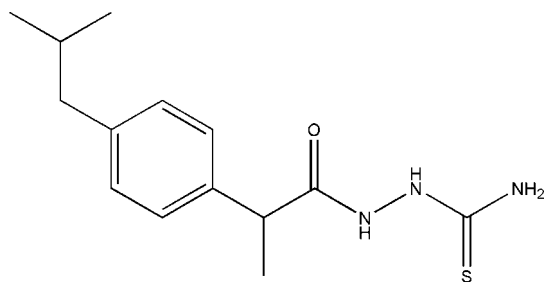
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 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.096; data-to-parameter ratio = 34.2.

In the title compound,  $\text{C}_{14}\text{H}_{21}\text{N}_3\text{OS}$ , intermolecular  $\text{N}-\text{H}\cdots\text{O}$  interactions generate ten-membered rings with  $R_2^2(10)$  ring motifs, whereas  $\text{N}-\text{H}\cdots\text{S}$  interactions generate eight, 14- and 16-membered rings with  $R_2^2(8)$ ,  $R_4^4(14)$  and  $R_4^4(16)$  ring motifs, respectively. There are weak intramolecular  $\text{N}-\text{H}\cdots\pi$  interactions which might influence the conformation of the molecule. The compound has a stereogenic center but the space group is centrosymmetric so the molecule exists as a racemate.

## Related literature

For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For biomedical applications of non-steroidal anti-inflammatory drugs, see, for example; Kawail *et al.* (2005); Klasser & Epstein (2005); Kean & Buchanan (2005); Nielsen & Bundgaard (1988); Khan & Akhter (2005); Zhao *et al.* (2006). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



## Experimental

### Crystal data

$\text{C}_{14}\text{H}_{21}\text{N}_3\text{OS}$   
 $M_r = 279.40$   
Triclinic,  $P\bar{1}$

$a = 5.5347$  (1) Å  
 $b = 10.6209$  (3) Å  
 $c = 13.1435$  (3) Å

$\alpha = 97.935$  (1)°  
 $\beta = 98.418$  (1)°  
 $\gamma = 96.293$  (1)°  
 $V = 750.30$  (3) Å<sup>3</sup>  
 $Z = 2$

Mo  $K\alpha$  radiation  
 $\mu = 0.21$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.54 \times 0.32 \times 0.15$  mm

### Data collection

Bruker SMART APEXII CCD  
area-detector diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Bruker, 2005)  
 $T_{\min} = 0.894$ ,  $T_{\max} = 0.969$

18596 measured reflections  
6524 independent reflections  
5896 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.096$   
 $S = 1.05$   
6524 reflections  
191 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.68$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.32$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                                       | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N}2-\text{H}1\text{N}2\cdots\text{O}1^{\text{i}}$   | 0.857 (15)   | 2.029 (15)         | 2.8745 (9)  | 169.0 (14)           |
| $\text{N}1-\text{H}1\text{N}1\cdots\text{S}1^{\text{ii}}$  | 0.886 (12)   | 2.495 (13)         | 3.3324 (7)  | 157.8 (11)           |
| $\text{N}3-\text{H}1\text{N}3\cdots\text{S}1^{\text{iii}}$ | 0.842 (15)   | 2.577 (15)         | 3.3945 (7)  | 164.1 (14)           |
| $\text{C}7-\text{H}7\text{A}\cdots\text{O}1^{\text{ii}}$   | 1.00         | 2.44               | 3.3501 (9)  | 151                  |
| $\text{N}3-\text{H}2\text{N}3\cdots\text{Cg}1$             | 0.850 (16)   | 2.870 (14)         | 3.5083 (7)  | 133.4 (12)           |

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x + 1, -y + 2, -z + 1$ . Cg1 is the centroid of the C1-C6 benzene ring.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); 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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2428).

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Zhao, X., Tao, X., Wei, D. & Song, Q. (2006). *Eur. J. Med. Chem.* **41**, 1352–1358.

## supporting information

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## 1-[2-(4-Isobutylphenyl)propanoyl]thiosemicarbazide

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### S1. Comment

Non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen are widely used in the treatment of pain and inflammation (Kawai *et al.*, 2005; Klasser & Epstein, 2005). In fact, prolonged use of NSAIDs, for example ibuprofen, has been associated with gastrointestinal complications (Kean & Buchanan, 2005). Therefore, synthetic approaches based upon NSAIDs chemical modification have been undertaken with the aim of improving the NSAID safety profile. The utilization of prodrugs to temporarily mask the acidic group of NSAIDs has been proposed as an approach to reduce or suppress the GI toxicity due to the direct contact effect and also to increase their absorption values (Nielsen & Bundgaard, 1988). Ester prodrugs of ibuprofen have been synthesized with this aim (Khan & Akhter, 2005). Ester prodrugs of ibuprofen were synthesized and found to have anti-inflammatory, analgesic and ulcerogenic activities (Zhao *et al.*, 2006). Due to these reasons, we have synthesized the thiosemicarbazide analogue of ibuprofen and report its crystal structure.

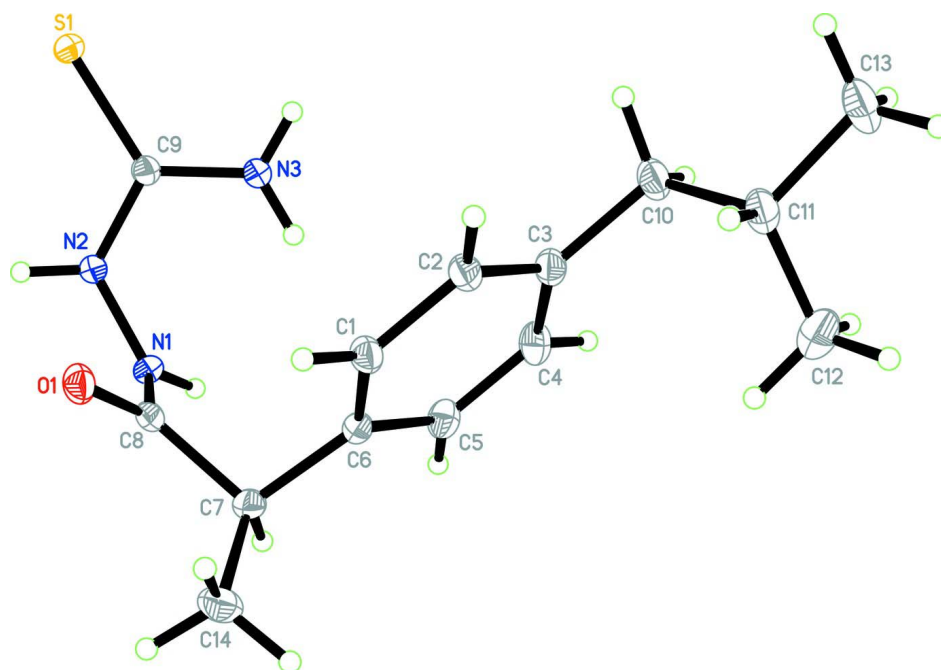
The title compound, I, Fig. 1, comprises a single molecule in the asymmetric unit. Intermolecular N—H $\cdots$ O interactions generate ten-membered rings producing  $R_2^2(10)$  ring motifs, whereas N—H $\cdots$ S interactions generate eight, fourteen, sixteen rings producing  $R_2^2(8)$ ,  $R_4^4(14)$  and  $R_4^4(16)$  ring motifs, respectively. (Fig.2) (Bernstein *et al.*, 1995). There is a weak intramolecular N—H $\cdots$  $\pi$  interaction (Table 1,  $Cg1$  is the centroid of the C1–C6 benzene ring). The compound has a stereogenic center at C7 but the space group is centrosymmetric so the molecule exists as a racemate.

### S2. Experimental

A mixture of 2-[2-(4-isobutylphenyl)propanoyl]hydrazine (0.01 mole), potassium thiocyanate (1.9 g, 0.02 mole), conc. HCl (1 ml) and water (20 ml) was refluxed for 3 h. On cooling the solid obtained was collected by filtration, washed with water and dried. Crystals suitable for X-ray analysis were obtained from ethanol by slow evaporation (Yield 62%; m.p. 447 K).

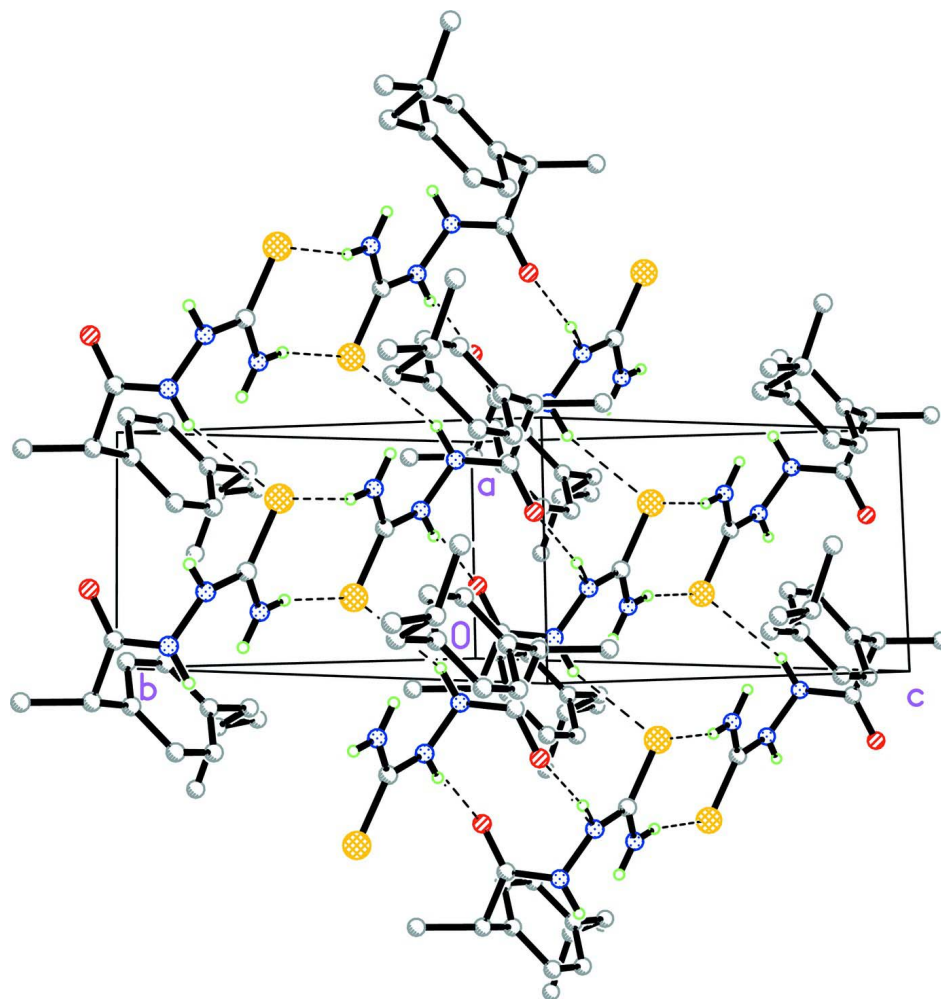
### S3. Refinement

N-bound hydrogen atoms were located from the difference Fourier map and refined freely; see Table 1. The rest of the hydrogen atoms were positioned geometrically and constrained to refine with the parent atoms with C—H = 0.93–1.00 Å and  $U_{iso}(H) = 1.2$  or  $1.5 U_{eq}(C)$ . A rotating group model was used for the methyl groups.



**Figure 1**

Molecular structure of (I) with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small sphere of arbitrary radii. The enantiomer represented has R configuration at C7.



**Figure 2**

The crystal packing of (I) showing the graph set motifs. Intermolecular interactions are shown as dashed lines. H atoms not involved in hydrogen bondings have been removed for clarity.

### 1-[2-(4-Isobutylphenyl)propanoyl]thiosemicarbazide

#### Crystal data

$C_{14}H_{21}N_3OS$

$M_r = 279.40$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 5.5347$  (1) Å

$b = 10.6209$  (3) Å

$c = 13.1435$  (3) Å

$\alpha = 97.935$  (1)°

$\beta = 98.418$  (1)°

$\gamma = 96.293$  (1)°

$V = 750.30$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 300$

$D_x = 1.237$  Mg m<sup>-3</sup>

Melting point: 335 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9906 reflections

$\theta = 2.3$ – $38.2$ °

$\mu = 0.21$  mm<sup>-1</sup>

$T = 100$  K

Block, colourless

$0.54 \times 0.32 \times 0.15$  mm

Data collection

Bruker SMART APEXII CCD area-detector  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan  
(SADABS; Bruker, 2005)  
 $T_{\min} = 0.894$ ,  $T_{\max} = 0.969$

18596 measured reflections  
6524 independent reflections  
5896 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$   
 $\theta_{\max} = 35.0^\circ$ ,  $\theta_{\min} = 1.6^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -16 \rightarrow 17$   
 $l = -20 \rightarrow 21$

Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.096$   
 $S = 1.05$   
6524 reflections  
191 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 atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.1966P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

**Experimental.** The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

|     | <i>x</i>     | <i>y</i>      | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|----------------------------------|
| S1  | 0.30182 (3)  | 0.806105 (17) | 0.407445 (14) | 0.01523 (5)                      |
| O1  | 0.65430 (10) | 0.57112 (5)   | 0.62717 (5)   | 0.01802 (10)                     |
| N1  | 0.87208 (11) | 0.64109 (6)   | 0.50767 (5)   | 0.01429 (10)                     |
| N2  | 0.66238 (12) | 0.66716 (6)   | 0.44588 (5)   | 0.01530 (11)                     |
| N3  | 0.74599 (12) | 0.87876 (6)   | 0.52340 (5)   | 0.01701 (11)                     |
| C1  | 0.95446 (14) | 0.81565 (7)   | 0.78524 (6)   | 0.01651 (12)                     |
| H1A | 0.8281       | 0.7578        | 0.8019        | 0.020*                           |
| C2  | 0.96885 (14) | 0.94657 (7)   | 0.82013 (6)   | 0.01724 (12)                     |
| H2A | 0.8519       | 0.9769        | 0.8604        | 0.021*                           |
| C3  | 1.15276 (14) | 1.03429 (7)   | 0.79679 (6)   | 0.01707 (12)                     |
| C4  | 1.32484 (15) | 0.98630 (8)   | 0.73933 (6)   | 0.01981 (14)                     |
| H4A | 1.4534       | 1.0439        | 0.7239        | 0.024*                           |
| C5  | 1.31130 (14) | 0.85529 (8)   | 0.70412 (6)   | 0.01828 (13)                     |
| H5A | 1.4303       | 0.8249        | 0.6650        | 0.022*                           |

|      |              |              |              |              |
|------|--------------|--------------|--------------|--------------|
| C6   | 1.12491 (13) | 0.76844 (7)  | 0.72571 (5)  | 0.01440 (11) |
| C7   | 1.09656 (13) | 0.62723 (7)  | 0.67782 (6)  | 0.01577 (12) |
| H7A  | 1.2328       | 0.6134       | 0.6369       | 0.019*       |
| C8   | 0.85365 (13) | 0.60673 (6)  | 0.60322 (6)  | 0.01385 (11) |
| C9   | 0.58753 (12) | 0.78460 (6)  | 0.46377 (5)  | 0.01334 (11) |
| C10  | 1.16404 (17) | 1.17610 (7)  | 0.83421 (6)  | 0.02134 (14) |
| H10A | 0.9976       | 1.2013       | 0.8173       | 0.026*       |
| H10B | 1.2750       | 1.2240       | 0.7960       | 0.026*       |
| C11  | 1.25548 (16) | 1.21505 (8)  | 0.95183 (6)  | 0.02091 (14) |
| H11A | 1.1465       | 1.1631       | 0.9893       | 0.025*       |
| C12  | 1.5176 (2)   | 1.18766 (13) | 0.98222 (10) | 0.0422 (3)   |
| H12A | 1.5659       | 1.2084       | 1.0580       | 0.063*       |
| H12B | 1.6290       | 1.2402       | 0.9485       | 0.063*       |
| H12C | 1.5271       | 1.0967       | 0.9598       | 0.063*       |
| C13  | 1.2345 (2)   | 1.35641 (8)  | 0.98524 (8)  | 0.02918 (18) |
| H13A | 1.2943       | 1.3802       | 1.0601       | 0.044*       |
| H13B | 1.0617       | 1.3706       | 0.9700       | 0.044*       |
| H13C | 1.3339       | 1.4091       | 0.9470       | 0.044*       |
| C14  | 1.09915 (18) | 0.53538 (8)  | 0.75758 (7)  | 0.02360 (15) |
| H14A | 1.2581       | 0.5521       | 0.8044       | 0.035*       |
| H14B | 1.0747       | 0.4467       | 0.7214       | 0.035*       |
| H14C | 0.9664       | 0.5484       | 0.7982       | 0.035*       |
| H1N2 | 0.556 (3)    | 0.6019 (14)  | 0.4190 (11)  | 0.027 (3)*   |
| H1N1 | 1.013 (2)    | 0.6698 (13)  | 0.4891 (10)  | 0.024 (3)*   |
| H2N3 | 0.888 (3)    | 0.8658 (13)  | 0.5509 (11)  | 0.029 (3)*   |
| H1N3 | 0.703 (3)    | 0.9524 (14)  | 0.5348 (11)  | 0.027 (3)*   |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$      | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|---------------|--------------|--------------|
| S1  | 0.01232 (8) | 0.01386 (8) | 0.01930 (9) | 0.00173 (5)   | 0.00039 (6)  | 0.00418 (6)  |
| O1  | 0.0155 (2)  | 0.0151 (2)  | 0.0225 (3)  | -0.00111 (18) | 0.00474 (19) | 0.00054 (19) |
| N1  | 0.0111 (2)  | 0.0143 (2)  | 0.0172 (2)  | 0.00244 (18)  | 0.00100 (19) | 0.00253 (19) |
| N2  | 0.0134 (2)  | 0.0117 (2)  | 0.0190 (3)  | 0.00211 (19)  | -0.0017 (2)  | 0.00032 (19) |
| N3  | 0.0137 (2)  | 0.0116 (2)  | 0.0239 (3)  | 0.00168 (19)  | -0.0009 (2)  | 0.0003 (2)   |
| C1  | 0.0146 (3)  | 0.0140 (3)  | 0.0202 (3)  | 0.0002 (2)    | 0.0040 (2)   | 0.0003 (2)   |
| C2  | 0.0164 (3)  | 0.0145 (3)  | 0.0197 (3)  | 0.0017 (2)    | 0.0028 (2)   | -0.0006 (2)  |
| C3  | 0.0196 (3)  | 0.0145 (3)  | 0.0151 (3)  | -0.0006 (2)   | -0.0012 (2)  | 0.0020 (2)   |
| C4  | 0.0206 (3)  | 0.0196 (3)  | 0.0175 (3)  | -0.0040 (3)   | 0.0034 (2)   | 0.0018 (2)   |
| C5  | 0.0153 (3)  | 0.0213 (3)  | 0.0169 (3)  | -0.0004 (2)   | 0.0033 (2)   | -0.0002 (2)  |
| C6  | 0.0127 (3)  | 0.0145 (3)  | 0.0149 (3)  | 0.0020 (2)    | 0.0002 (2)   | 0.0005 (2)   |
| C7  | 0.0147 (3)  | 0.0148 (3)  | 0.0173 (3)  | 0.0043 (2)    | 0.0008 (2)   | 0.0007 (2)   |
| C8  | 0.0141 (3)  | 0.0098 (2)  | 0.0168 (3)  | 0.0020 (2)    | 0.0019 (2)   | -0.0004 (2)  |
| C9  | 0.0128 (3)  | 0.0121 (2)  | 0.0152 (3)  | 0.0012 (2)    | 0.0025 (2)   | 0.0026 (2)   |
| C10 | 0.0288 (4)  | 0.0131 (3)  | 0.0194 (3)  | -0.0001 (3)   | -0.0021 (3)  | 0.0019 (2)   |
| C11 | 0.0263 (4)  | 0.0156 (3)  | 0.0185 (3)  | -0.0009 (3)   | 0.0011 (3)   | 0.0004 (2)   |
| C12 | 0.0356 (5)  | 0.0422 (6)  | 0.0389 (6)  | 0.0109 (5)    | -0.0156 (4)  | -0.0103 (5)  |
| C13 | 0.0385 (5)  | 0.0165 (3)  | 0.0286 (4)  | -0.0021 (3)   | 0.0034 (4)   | -0.0032 (3)  |

|     |            |            |            |            |            |            |
|-----|------------|------------|------------|------------|------------|------------|
| C14 | 0.0315 (4) | 0.0181 (3) | 0.0212 (3) | 0.0078 (3) | 0.0000 (3) | 0.0044 (3) |
|-----|------------|------------|------------|------------|------------|------------|

*Geometric parameters (Å, °)*

|              |             |               |             |
|--------------|-------------|---------------|-------------|
| S1—C9        | 1.6982 (7)  | C5—H5A        | 0.9500      |
| O1—C8        | 1.2259 (9)  | C6—C7         | 1.5261 (10) |
| N1—C8        | 1.3699 (10) | C7—C8         | 1.5190 (10) |
| N1—N2        | 1.3927 (9)  | C7—C14        | 1.5270 (11) |
| N1—H1N1      | 0.884 (14)  | C7—H7A        | 1.0000      |
| N2—C9        | 1.3578 (9)  | C10—C11       | 1.5381 (12) |
| N2—H1N2      | 0.855 (15)  | C10—H10A      | 0.9900      |
| N3—C9        | 1.3318 (9)  | C10—H10B      | 0.9900      |
| N3—H2N3      | 0.851 (14)  | C11—C12       | 1.5178 (14) |
| N3—H1N3      | 0.843 (14)  | C11—C13       | 1.5269 (12) |
| C1—C2        | 1.3925 (10) | C11—H11A      | 1.0000      |
| C1—C6        | 1.4019 (10) | C12—H12A      | 0.9800      |
| C1—H1A       | 0.9500      | C12—H12B      | 0.9800      |
| C2—C3        | 1.4002 (11) | C12—H12C      | 0.9800      |
| C2—H2A       | 0.9500      | C13—H13A      | 0.9800      |
| C3—C4        | 1.3957 (12) | C13—H13B      | 0.9800      |
| C3—C10       | 1.5100 (11) | C13—H13C      | 0.9800      |
| C4—C5        | 1.3947 (11) | C14—H14A      | 0.9800      |
| C4—H4A       | 0.9500      | C14—H14B      | 0.9800      |
| C5—C6        | 1.3946 (11) | C14—H14C      | 0.9800      |
|              |             |               |             |
| C8—N1—N2     | 119.30 (6)  | N1—C8—C7      | 114.12 (6)  |
| C8—N1—H1N1   | 123.8 (9)   | N3—C9—N2      | 117.81 (6)  |
| N2—N1—H1N1   | 114.5 (8)   | N3—C9—S1      | 123.05 (5)  |
| C9—N2—N1     | 119.39 (6)  | N2—C9—S1      | 119.12 (5)  |
| C9—N2—H1N2   | 119.6 (9)   | C3—C10—C11    | 113.56 (6)  |
| N1—N2—H1N2   | 115.4 (9)   | C3—C10—H10A   | 108.9       |
| C9—N3—H2N3   | 121.5 (10)  | C11—C10—H10A  | 108.9       |
| C9—N3—H1N3   | 118.9 (10)  | C3—C10—H10B   | 108.9       |
| H2N3—N3—H1N3 | 119.6 (13)  | C11—C10—H10B  | 108.9       |
| C2—C1—C6     | 120.56 (7)  | H10A—C10—H10B | 107.7       |
| C2—C1—H1A    | 119.7       | C12—C11—C13   | 110.83 (8)  |
| C6—C1—H1A    | 119.7       | C12—C11—C10   | 111.70 (8)  |
| C1—C2—C3     | 121.12 (7)  | C13—C11—C10   | 110.21 (7)  |
| C1—C2—H2A    | 119.4       | C12—C11—H11A  | 108.0       |
| C3—C2—H2A    | 119.4       | C13—C11—H11A  | 108.0       |
| C4—C3—C2     | 117.97 (7)  | C10—C11—H11A  | 108.0       |
| C4—C3—C10    | 121.57 (7)  | C11—C12—H12A  | 109.5       |
| C2—C3—C10    | 120.45 (7)  | C11—C12—H12B  | 109.5       |
| C5—C4—C3     | 121.16 (7)  | H12A—C12—H12B | 109.5       |
| C5—C4—H4A    | 119.4       | C11—C12—H12C  | 109.5       |
| C3—C4—H4A    | 119.4       | H12A—C12—H12C | 109.5       |
| C6—C5—C4     | 120.71 (7)  | H12B—C12—H12C | 109.5       |
| C6—C5—H5A    | 119.6       | C11—C13—H13A  | 109.5       |

|              |             |                |             |
|--------------|-------------|----------------|-------------|
| C4—C5—H5A    | 119.6       | C11—C13—H13B   | 109.5       |
| C5—C6—C1     | 118.45 (7)  | H13A—C13—H13B  | 109.5       |
| C5—C6—C7     | 120.22 (6)  | C11—C13—H13C   | 109.5       |
| C1—C6—C7     | 121.14 (6)  | H13A—C13—H13C  | 109.5       |
| C8—C7—C6     | 104.02 (5)  | H13B—C13—H13C  | 109.5       |
| C8—C7—C14    | 112.04 (7)  | C7—C14—H14A    | 109.5       |
| C6—C7—C14    | 113.91 (6)  | C7—C14—H14B    | 109.5       |
| C8—C7—H7A    | 108.9       | H14A—C14—H14B  | 109.5       |
| C6—C7—H7A    | 108.9       | C7—C14—H14C    | 109.5       |
| C14—C7—H7A   | 108.9       | H14A—C14—H14C  | 109.5       |
| O1—C8—N1     | 121.87 (7)  | H14B—C14—H14C  | 109.5       |
| O1—C8—C7     | 123.83 (7)  |                |             |
|              |             |                |             |
| C8—N1—N2—C9  | 81.80 (8)   | C1—C6—C7—C14   | -59.88 (9)  |
| C6—C1—C2—C3  | 0.06 (12)   | N2—N1—C8—O1    | 16.17 (10)  |
| C1—C2—C3—C4  | -1.36 (11)  | N2—N1—C8—C7    | -159.10 (6) |
| C1—C2—C3—C10 | 179.31 (7)  | C6—C7—C8—O1    | -91.51 (8)  |
| C2—C3—C4—C5  | 1.40 (12)   | C14—C7—C8—O1   | 31.97 (10)  |
| C10—C3—C4—C5 | -179.28 (7) | C6—C7—C8—N1    | 83.65 (7)   |
| C3—C4—C5—C6  | -0.13 (12)  | C14—C7—C8—N1   | -152.87 (6) |
| C4—C5—C6—C1  | -1.19 (11)  | N1—N2—C9—N3    | 14.79 (10)  |
| C4—C5—C6—C7  | 173.91 (7)  | N1—N2—C9—S1    | -166.70 (5) |
| C2—C1—C6—C5  | 1.22 (11)   | C4—C3—C10—C11  | -106.27 (9) |
| C2—C1—C6—C7  | -173.83 (7) | C2—C3—C10—C11  | 73.03 (10)  |
| C5—C6—C7—C8  | -112.59 (7) | C3—C10—C11—C12 | 62.58 (11)  |
| C1—C6—C7—C8  | 62.37 (8)   | C3—C10—C11—C13 | -173.75 (8) |
| C5—C6—C7—C14 | 125.16 (8)  |                |             |

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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N2—H1N2...O1 <sup>i</sup>   | 0.857 (15)  | 2.029 (15)    | 2.8745 (9)            | 169.0 (14)              |
| N1—H1N1...S1 <sup>ii</sup>  | 0.886 (12)  | 2.495 (13)    | 3.3324 (7)            | 157.8 (11)              |
| N3—H1N3...S1 <sup>iii</sup> | 0.842 (15)  | 2.577 (15)    | 3.3945 (7)            | 164.1 (14)              |
| C7—H7A...O1 <sup>ii</sup>   | 1.00        | 2.44          | 3.3501 (9)            | 151                     |
| N3—H2N3...Cg1               | 0.850 (16)  | 2.870 (14)    | 3.5083 (7)            | 133.4 (12)              |

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