

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1-(*o*-Tolyl)thioureaRodrigo S. Corrêa,^a Leandro Ribeiro,^a Javier Ellena,^a
Oswaldo Estévez-Hernández^b and Julio Duque^{b*}^aGrupo de Cristalografía, Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, Brazil, and ^bDepartment of Structure Analysis, Institute of Materials, Zapata & G, University of Havana, Cuba

Correspondence e-mail: duque@imre.co.uh.cu

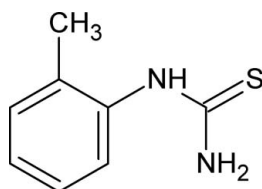
Received 10 July 2008; accepted 29 July 2008

Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.046; wR factor = 0.141; data-to-parameter ratio = 19.0.

In the title compound, $\text{C}_8\text{H}_{10}\text{N}_2\text{S}$, the *o*-tolyl group and the thiourea core are planar. The mean planes of the two groups are almost perpendicular [82.19 (8°)]. The thiourea group is in the thioamide form, in which resonance is present. In the crystal structure, molecules are linked by intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, forming two infinite chains parallel to the (110) and (1 $\bar{1}$ 0) planes.

Related literature

For general background, see: Koketsu & Ishihara (2006); Struga *et al.* (2007). For related structures, see: Corrêa *et al.* (2006); Corrêa *et al.* (2008); Estévez-Hernández *et al.* (2008); Duque *et al.* (2008). For the synthesis, see: Otazo-Sánchez *et al.* (2001). For related literature, see: Otazo *et al.* (2001); Ramadas *et al.* (1998).



Experimental

Crystal data

$\text{C}_8\text{H}_{10}\text{N}_2\text{S}$
 $M_r = 166.25$
 Monoclinic, $C2/c$
 $a = 15.1323$ (3) Å
 $b = 7.7965$ (2) Å
 $c = 15.3222$ (4) Å
 $\beta = 90.828$ (2)°

$V = 1807.61$ (8) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 294$ K
 $0.31 \times 0.22 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer

Absorption correction: gaussian
 (Coppens *et al.*, 1965)
 $T_{\min} = 0.973$, $T_{\max} = 0.991$

6748 measured reflections
 1914 independent reflections

1438 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.140$
 $S = 1.03$
 1914 reflections

101 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1—N2	1.321 (2)	C1—S1	1.6868 (18)
C1—N1	1.329 (2)	C2—N1	1.435 (2)
N2—C1—N1	117.34 (16)	N1—C1—S1	121.03 (13)
N2—C1—S1	121.63 (14)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots S1 ⁱ	0.86	2.53	3.368 (2)	165
N2—H2B \cdots S1 ⁱⁱ	0.86	2.52	3.362 (2)	166

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; 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, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are grateful for financial support from the Brazilian agencies CNPq, FAPESP and CAPES. RSC acknowledges the CNPq for a fellowship (Project 134576/2007-1).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2105).

References

- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- Corrêa, R. S., Estévez-Hernández, O., Ellena, J. & Duque, J. (2008). *Acta Cryst.* **E64**, o1414.
- Corrêa, R. S., Santana, S. A., Salloum, R., Silva, R. M. & Doriguetto, A. C. (2006). *Acta Cryst.* **C62**, o115–o117.
- Duque, J., Estevez-Hernandez, O., Reguera, E., Corrêa, R. S. & Gutierrez Maria, P. *Acta Cryst.* **E64**, o1068.
- Estévez-Hernández, O., Duque, J., Ellena, J. & Corrêa, R. S. (2008). *Acta Cryst.* **E64**, o1157.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Koketsu, M. & Ishihara, H. (2006). *Curr. Org. Synth.* **3**, 439–455.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otazo, E., Pérez, L., Estévez, O., Rojas, S. & Alonso, J. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 2211–2218.

- Otazo-Sánchez, E., Pérez-Marín, L., Estévez-Hernández, O., Rojas-Lima, S. & Alonso-Chamorro, J. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 2211–2218.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Ramadas, K., Suresh, G., Janarthanan, N. & Masilamani, S. (1998). *Pestic. Sci.* **52**, 145–151.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Struga, M., Kossakowski, J., Kedzierska, E., Fidecka, S. & Stefanska, J. (2007). *Chem. Pharm. Bull.* **55**, 796–799.

supporting information

Acta Cryst. (2008). E64, o1670–o1671 [doi:10.1107/S1600536808024161]

1-(*o*-Tolyl)thiourea

Rodrigo S. Corrêa, Leandro Ribeiro, Javier Ellena, Osvaldo Estévez-Hernández and Julio Duque

S1. Comment

Thiourea itself as well as its derivatives are known to be biologically active (Koketsu & Ishihara, 2006). Their antimicrobial, cytotoxic and anti-HIV activities have been recently tested (Struga *et al.*, 2007). Also, *ortho*-substituted aromatic thiourea derivatives have received special attention because of their fungicidal activity (Ramadas *et al.*, 1998). The reaction of the furoyl isothiocyanate with *o*-toluidine in dry acetone yielded the title compound, *N*-(*o*-tolyl) thiourea, as a secondary product (Fig. 1).

The title molecule is present in the thioamide form and it is a typical N-monosubstituted thiourea derivative with usual geometric parameters. The C—S bond [1.687 (2) Å] shows the expected double-bond character. The short bond-lengths of the C1—N1 [1.329 (2) Å] and C1—N2 [1.321 (2) Å] indicate partial double bond character, similarly to other thiourea derivatives where electron delocalization in the N—C—S moiety is present (Corrêa *et al.*, 2008; Estévez-Hernández *et al.*, 2008, Duque *et al.*, 2008). In addition, the values of the bond angles that are close to 120° also suggest the resonance effect.

As might be expected both the central thiourea fragment as well as the *o*-tolyl group are planar. The largest deviation from the least square plane through the seven atoms of the *o*-tolyl group occurs for the atom C2 [displacement = 0.0038 (15) Å], with a r.m.s. deviation of 0.0022 Å for all the carbons in the *o*-tolyl group. In the thiourea fragment, the largest displacement is for the atom C1 [0.001 (1) Å], with a r.m.s. deviation of 0.003 Å. The *o*-tolyl group is almost perpendicular to the plane formed by the thiourea molecule (82.19 (8)°).

Fig. 2 shows the arrangement of the molecules in the unit cell. In the crystal structure, the molecules are linked by N—H···S hydrogen bonds that stabilize the packing (Table 1). In the previous studies (Corrêa *et al.*, 2006; Corrêa *et al.*, 2008) have been reported the N—H···S interactions with the formation of the centrosymmetric dimers. In contrast to these structures, in the present structure these intermolecular interactions form two independent chains parallel to the (110) and (1–10) planes (Figure 3).

S2. Experimental

The title compound was obtained as a secondary product during the synthesis of 1-(2-furoyl)-3-(*o*-tolyl) thiourea according to procedure described by Otazo-Sánchez *et al.* (2001) by converting furoyl chloride into furoyl isothiocyanate and then condensing with the appropriate *o*-toluidine. The colourless prism-shaped single crystals were formed by slow evaporation from a methanol/acetonitrile (1:1) solution.

S3. Refinement

All the hydrogen atoms were located in the difference Fourier maps. Nevertheless, they were situated in the idealized positions and refined using the riding-hydrogen model. N—H = 0.86 Å, C_{aryl}—H = 0.93 Å, C_{methyl} = 0.96 Å. $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C}_{\text{aryl}})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

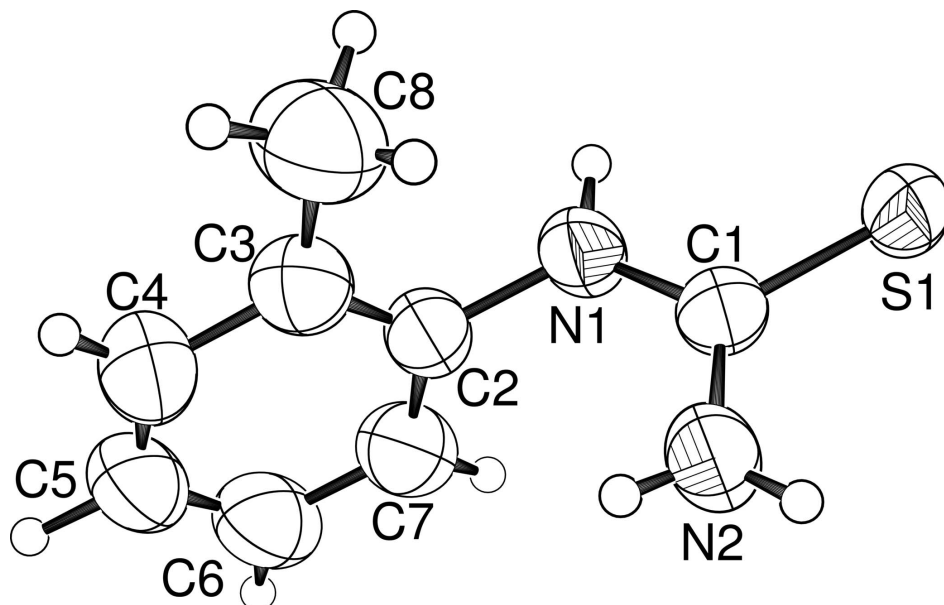


Figure 1

The title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and the H atoms are shown as small spheres of arbitrary radii.

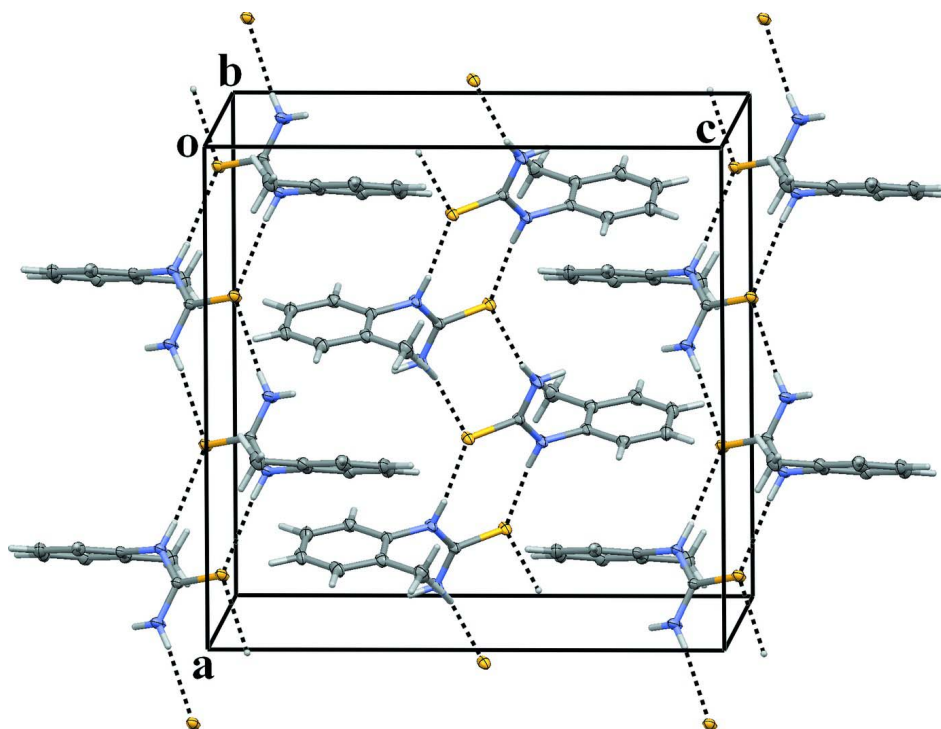
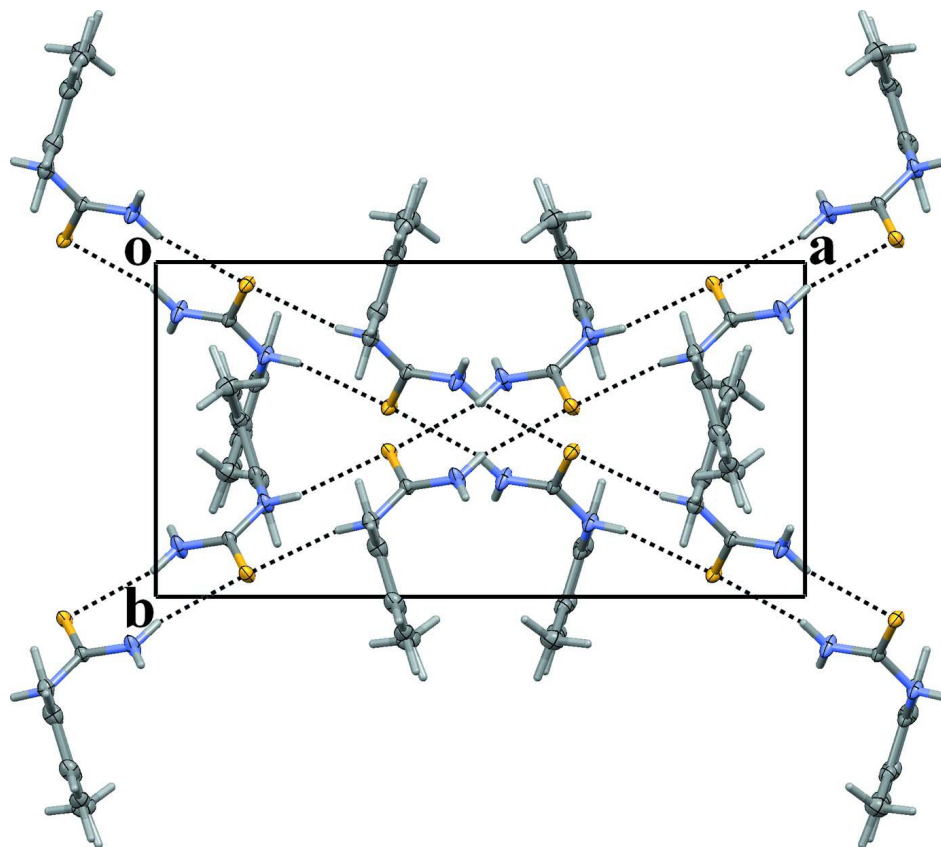


Figure 2

Representation of the chains linked by N—H...S hydrogen bonds.

**Figure 3**

Crystal packing view along *c* axis showing the two independent chains.

1-(*o*-Tolyl)thiourea

Crystal data

$C_8H_{10}N_2S$

$M_r = 166.25$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 15.1323 (3) \text{ \AA}$

$b = 7.7965 (2) \text{ \AA}$

$c = 15.3222 (4) \text{ \AA}$

$\beta = 90.828 (2)^\circ$

$V = 1807.61 (8) \text{ \AA}^3$

$Z = 8$

$F(000) = 704$

$D_x = 1.222 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 15611 reflections

$\theta = 2.9\text{--}26.7^\circ$

$\mu = 0.30 \text{ mm}^{-1}$

$T = 294 \text{ K}$

Prism, colourless

$0.31 \times 0.22 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube Enraf

Nonius FR590

Horizontally mounted graphite crystal

monochromator

φ scans and ω scans with κ offsets

Absorption correction: gaussian

(Coppens *et al.*, 1965)

$T_{\min} = 0.973$, $T_{\max} = 0.991$

6748 measured reflections

1914 independent reflections

1438 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 26.8^\circ$, $\theta_{\min} = 3.8^\circ$

$h = -19 \rightarrow 18$

$k = -9 \rightarrow 9$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.140$
 $S = 1.03$
 1914 reflections
 101 parameters
 0 restraints
 40 constraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0896P)^2 + 0.2205P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Special details

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.11314 (11)	0.8287 (2)	0.06714 (12)	0.0577 (5)
C2	0.15409 (11)	0.6359 (3)	0.18736 (12)	0.0611 (5)
C3	0.12742 (14)	0.4692 (3)	0.18788 (14)	0.0740 (6)
C4	0.11722 (18)	0.3923 (3)	0.27051 (17)	0.0886 (7)
H4	0.0995	0.2783	0.2737	0.106*
C5	0.13277 (17)	0.4810 (4)	0.34545 (15)	0.0887 (7)
H5	0.1256	0.4269	0.399	0.106*
C6	0.15879 (16)	0.6486 (4)	0.34321 (15)	0.0884 (7)
H6	0.1691	0.7089	0.3947	0.106*
C7	0.16938 (15)	0.7262 (3)	0.26419 (14)	0.0769 (6)
H7	0.187	0.8404	0.2618	0.092*
C8	0.1108 (2)	0.3713 (4)	0.10584 (18)	0.1082 (9)
H8A	0.0882	0.2598	0.1197	0.162*
H8B	0.1651	0.3594	0.0748	0.162*
H8C	0.0685	0.4317	0.0701	0.162*
N1	0.16917 (10)	0.7203 (2)	0.10564 (10)	0.0665 (5)
H1	0.218	0.6992	0.0797	0.08*
N2	0.03568 (11)	0.8514 (3)	0.10408 (12)	0.0897 (7)
H2A	0.0232	0.797	0.1512	0.108*
H2B	-0.0023	0.9205	0.081	0.108*
S1	0.14045 (3)	0.93276 (6)	-0.02514 (3)	0.0663 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0496 (9)	0.0631 (10)	0.0607 (10)	0.0091 (8)	0.0069 (8)	0.0058 (8)
C2	0.0486 (9)	0.0738 (12)	0.0610 (11)	0.0136 (8)	0.0074 (8)	0.0143 (9)
C3	0.0718 (13)	0.0793 (14)	0.0711 (13)	0.0099 (11)	0.0082 (10)	0.0043 (10)

C4	0.0938 (16)	0.0817 (14)	0.0906 (17)	0.0062 (12)	0.0181 (14)	0.0225 (13)
C5	0.0963 (16)	0.1078 (18)	0.0624 (13)	0.0242 (15)	0.0148 (11)	0.0210 (13)
C6	0.0920 (16)	0.1113 (19)	0.0619 (13)	0.0199 (14)	0.0023 (11)	0.0010 (13)
C7	0.0741 (13)	0.0871 (14)	0.0696 (13)	0.0052 (11)	0.0053 (10)	0.0012 (11)
C8	0.130 (2)	0.1022 (18)	0.0930 (18)	-0.0140 (18)	0.0182 (17)	-0.0160 (16)
N1	0.0539 (8)	0.0834 (11)	0.0626 (9)	0.0202 (7)	0.0146 (7)	0.0205 (8)
N2	0.0616 (10)	0.1243 (16)	0.0838 (12)	0.0374 (10)	0.0250 (9)	0.0451 (12)
S1	0.0622 (4)	0.0697 (4)	0.0673 (4)	0.0189 (2)	0.0158 (2)	0.0183 (2)

Geometric parameters (Å, °)

C1—N2	1.321 (2)	C5—H5	0.93
C1—N1	1.329 (2)	C6—C7	1.365 (3)
C1—S1	1.6868 (18)	C6—H6	0.93
C2—C3	1.361 (3)	C7—H7	0.93
C2—C7	1.388 (3)	C8—H8A	0.96
C2—N1	1.435 (2)	C8—H8B	0.96
C3—C4	1.411 (3)	C8—H8C	0.96
C3—C8	1.489 (3)	N1—H1	0.86
C4—C5	1.358 (4)	N2—H2A	0.86
C4—H4	0.93	N2—H2B	0.86
C5—C6	1.365 (4)		
N2—C1—N1	117.34 (16)	C5—C6—H6	120.5
N2—C1—S1	121.63 (14)	C6—C7—C2	120.5 (2)
N1—C1—S1	121.03 (13)	C6—C7—H7	119.8
C3—C2—C7	121.68 (19)	C2—C7—H7	119.8
C3—C2—N1	119.57 (19)	C3—C8—H8A	109.5
C7—C2—N1	118.73 (19)	C3—C8—H8B	109.5
C2—C3—C4	116.6 (2)	H8A—C8—H8B	109.5
C2—C3—C8	122.1 (2)	C3—C8—H8C	109.5
C4—C3—C8	121.4 (2)	H8A—C8—H8C	109.5
C5—C4—C3	121.5 (2)	H8B—C8—H8C	109.5
C5—C4—H4	119.3	C1—N1—C2	124.75 (15)
C3—C4—H4	119.3	C1—N1—H1	117.6
C4—C5—C6	120.9 (2)	C2—N1—H1	117.6
C4—C5—H5	119.6	C1—N2—H2A	120
C6—C5—H5	119.6	C1—N2—H2B	120
C7—C6—C5	119.0 (2)	H2A—N2—H2B	120
C7—C6—H6	120.5		
C7—C2—C3—C4	-0.8 (3)	C5—C6—C7—C2	-0.1 (3)
N1—C2—C3—C4	177.56 (18)	C3—C2—C7—C6	0.7 (3)
C7—C2—C3—C8	180.0 (2)	N1—C2—C7—C6	-177.68 (18)
N1—C2—C3—C8	-1.7 (3)	N2—C1—N1—C2	-4.6 (3)
C2—C3—C4—C5	0.4 (3)	S1—C1—N1—C2	175.28 (16)
C8—C3—C4—C5	179.6 (3)	C3—C2—N1—C1	101.4 (2)
C3—C4—C5—C6	0.1 (4)	C7—C2—N1—C1	-80.2 (3)

C4—C5—C6—C7 -0.2 (4)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...S1 ⁱ	0.86	2.53	3.368 (2)	165
N2—H2B...S1 ⁱⁱ	0.86	2.52	3.362 (2)	166

Symmetry codes: (i) $-x+1/2, -y+3/2, -z$; (ii) $-x, -y+2, -z$.