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1-(2,6-Dichlorobenzoyl)-3-(3,5-dichlorophenyl)thiourea

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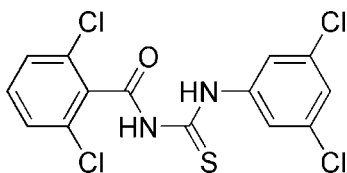
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.032; wR factor = 0.087; data-to-parameter ratio = 17.9.

The crystal structure of the title compound, $\text{C}_{14}\text{H}_8\text{Cl}_4\text{N}_2\text{OS}$, is composed of discrete molecules with bond lengths and angles quite typical for thiourea compounds of this class. The plane containing the central SONNCC atom set subtends a dihedral angle of $31.47(3)^\circ$ with the benzene ring. An intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond stabilizes the molecular conformation and the molecules form centrosymmetric dimers *via* intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds.

Related literature

For general background, see: Upadlgaya & Srivastava (1982); Wegner *et al.* (1986); Krishnamurthy *et al.* (1999). For related structures, see: Khawar Rauf *et al.* (2006a, 2007). For a description of the Cambridge Structural Database, see: Allen (2002). For bond lengths and angles in N,N' -disubstituted thiourea compounds, see: Arslan *et al.* (2004); Khawar Rauf *et al.* (2006b); Yamin & Yusof, (2003).



Experimental

Crystal data

 $\text{C}_{14}\text{H}_8\text{Cl}_4\text{N}_2\text{OS}$
 $M_r = 394.08$

 Monoclinic, $P2_1/c$
 $a = 14.7737(13)$ Å

 $b = 10.3744(6)$ Å

 $c = 10.6935(11)$ Å

 $\beta = 97.250(7)^\circ$
 $V = 1625.9(2)$ Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.86$ mm⁻¹
 $T = 173(2)$ K

 $0.42 \times 0.38 \times 0.21$ mm

Data collection

Stoe IPDSII two-circle diffractometer

Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)

 $T_{\min} = 0.715$, $T_{\max} = 0.841$

12823 measured reflections

3724 independent reflections

 3306 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.05$

3724 reflections

208 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}$	0.91 (2)	1.89 (2)	2.6581 (17)	141 (2)
$\text{N1}-\text{H1}\cdots\text{S1}^{\dagger}$	0.82 (2)	2.57 (2)	3.3653 (14)	163 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2225).

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supporting information

Acta Cryst. (2009). E65, o177 [doi:10.1107/S1600536808042736]

1-(2,6-Dichlorobenzoyl)-3-(3,5-dichlorophenyl)thiourea

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S1. Comment

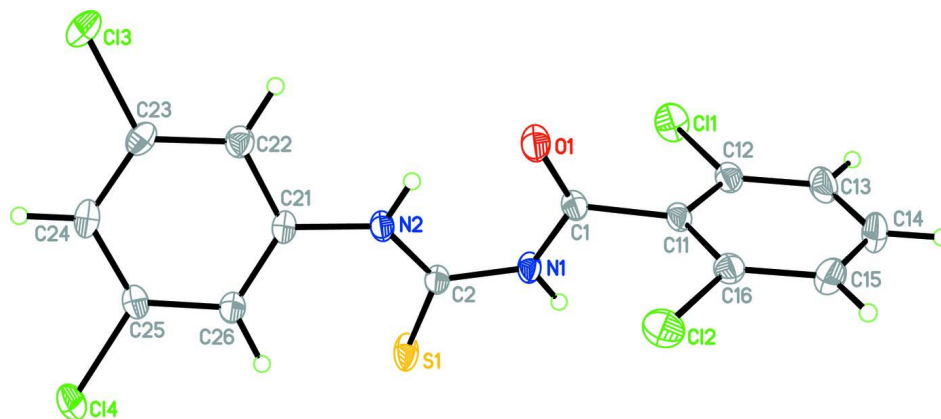
Aliphatic and acylthioureas are well known for their fungicidal, antiviral, pesticidal and plant-growth regulating activities (Upadlgaya & Srivastava, 1982; Wegner *et al.*, 1986). Symmetrical and unsymmetrical thioureas have shown antifungal activity against the plant pathogens *Pyricularia oryzae* and *Drechslera oryzae* (Krishnamurthy *et al.*, 1999). The background to this study has been set out in our previous work on the structural and biological chemistry of chloro substituted *N,N'*-disubstituted thioureas (Khawar Rauf *et al.*, 2006a; 2007). The biological studies of these thiourea derivatives are under investigation. Herein, as a continuation of these studies, the structure of the title compound (I) is described (Fig. 1). Bond lengths and angles, can be regarded as typical for *N,N'*-disubstituted thiourea compounds as found in the Cambridge Structural Database v5.28 (Allen, 2002; Khawar Rauf *et al.*, 2006b; Arslan *et al.*, 2004; Yamin & Yusof, 2003). The molecule exists in the thione form with typical thiourea C—S and C—O bonds, as well as shortened C—N bond lengths. The thiocarbonyl and carbonyl groups are almost coplanar. The molecule features an intramolecular N—H···O hydrogen bond and in the crystal structure, molecules associate *via* N—H···S intermolecular hydrogen bonds to form centrosymmetric dimers (Table 1; Fig 2). In addition to the intramolecular hydrogen bond, O1 is involved in a short O···Cl contact [O1···Cl2ⁱ: 3.0936 (14) Å, symmetry operator *i*: 1 - *x*, 1 - *y*, 1 - *z*].

S2. Experimental

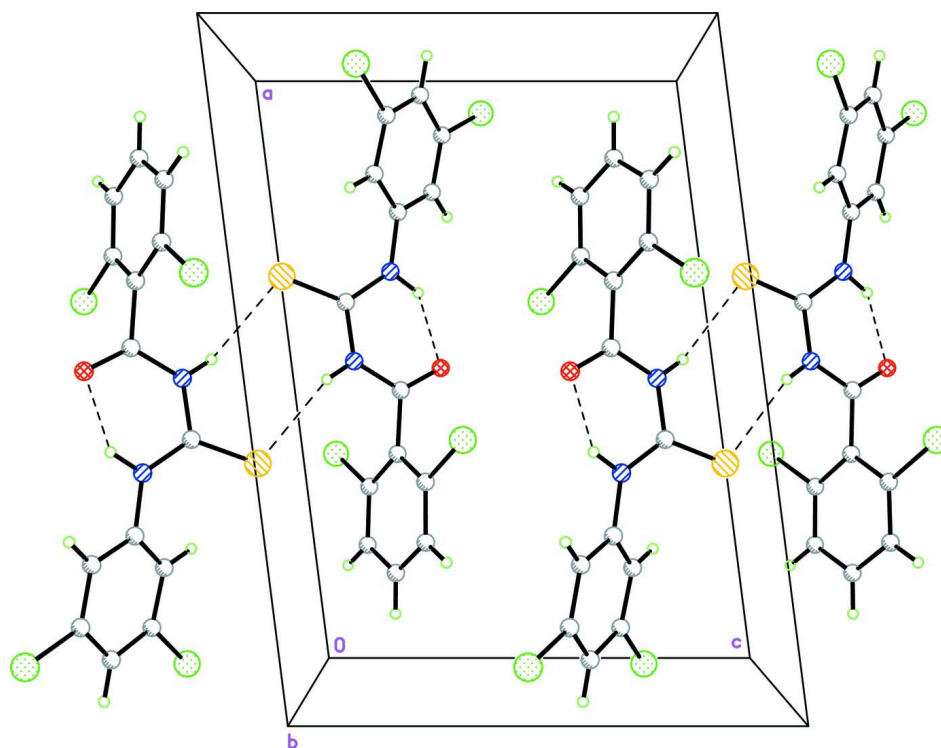
Freshly prepared 2,6-dichlorobenzoyl isothiocyanate (2.32 g, 10 mmol) was stirred in acetone (40 ml) for 20 minutes. Neat 3,5-dichloroaniline (1.62 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified (pH 4) water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from methanol/ 1,1-dichloromethane (1:10 *v/v*) to give fine crystals of (I), with an overall yield of 80%.

S3. Refinement

Hydrogen atoms bonded to C were included in calculated positions and refined as riding on their parent C atom with C—H = 0.95 Å $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms bonded to N were freely refined.

**Figure 1**

Molecular structure of (I) showing atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Partial packing diagram of (I) with view onto the *ac* plane. Hydrogen bonds shown as dashed lines.

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Crystal data

$C_{14}H_8Cl_4N_2OS$

$M_r = 394.08$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 14.7737$ (13) Å

$b = 10.3744$ (6) Å

$c = 10.6935$ (11) Å

$\beta = 97.250$ (7)°

$V = 1625.9$ (2) Å³

$Z = 4$

$F(000) = 792$

$D_x = 1.610$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 13230 reflections
 $\theta = 3.8\text{--}27.8^\circ$
 $\mu = 0.86 \text{ mm}^{-1}$

$T = 173 \text{ K}$
 Plate, colourless
 $0.42 \times 0.38 \times 0.21 \text{ mm}$

Data collection

Stoe IPDPSII two-circle
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (MULABS; Spek, 2003; Blessing, 1995)
 $T_{\min} = 0.715$, $T_{\max} = 0.841$

12823 measured reflections
 3724 independent reflections
 3306 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.7^\circ$
 $h = -19 \rightarrow 19$
 $k = -13 \rightarrow 13$
 $l = -10 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.05$
 3724 reflections
 208 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
 $w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.486P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0246 (15)

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.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.35875 (3)	0.16745 (4)	0.09234 (4)	0.02939 (13)
Cl2	0.39163 (3)	0.58457 (4)	0.39696 (4)	0.02796 (12)
Cl3	0.93189 (3)	0.14605 (4)	0.52460 (4)	0.03065 (13)
Cl4	0.97033 (3)	0.59117 (4)	0.27286 (4)	0.02639 (12)
C1	0.46669 (10)	0.35599 (15)	0.26849 (14)	0.0171 (3)
O1	0.50255 (7)	0.29825 (13)	0.36158 (11)	0.0257 (3)
N1	0.51344 (8)	0.40910 (14)	0.17722 (13)	0.0185 (3)
H1	0.4844 (15)	0.443 (2)	0.115 (2)	0.028 (5)*
S1	0.64669 (2)	0.48065 (5)	0.04928 (4)	0.02559 (13)
C2	0.60770 (10)	0.41647 (15)	0.17586 (15)	0.0168 (3)
N2	0.65773 (8)	0.36848 (14)	0.27949 (13)	0.0178 (3)

H2	0.6248 (15)	0.327 (2)	0.333 (2)	0.033 (6)*
C11	0.36443 (10)	0.37608 (15)	0.24447 (14)	0.0170 (3)
C12	0.30851 (10)	0.29239 (16)	0.16745 (15)	0.0196 (3)
C13	0.21408 (11)	0.30756 (19)	0.14814 (18)	0.0265 (4)
H13	0.1771	0.2506	0.0941	0.032*
C14	0.17491 (11)	0.40754 (19)	0.2093 (2)	0.0300 (4)
H14	0.1105	0.4177	0.1978	0.036*
C15	0.22860 (12)	0.49305 (18)	0.28705 (18)	0.0270 (4)
H15	0.2014	0.5610	0.3288	0.032*
C16	0.32308 (10)	0.47701 (16)	0.30247 (15)	0.0195 (3)
C21	0.75373 (10)	0.37152 (16)	0.31296 (14)	0.0170 (3)
C22	0.79148 (10)	0.27196 (16)	0.39134 (15)	0.0196 (3)
H22	0.7539	0.2054	0.4175	0.024*
C23	0.88510 (10)	0.27226 (16)	0.43034 (15)	0.0208 (3)
C24	0.94227 (10)	0.36829 (17)	0.39447 (15)	0.0217 (3)
H24	1.0062	0.3666	0.4205	0.026*
C25	0.90178 (10)	0.46720 (16)	0.31857 (15)	0.0189 (3)
C26	0.80870 (10)	0.47105 (16)	0.27637 (15)	0.0184 (3)
H26	0.7832	0.5394	0.2242	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0285 (2)	0.0291 (2)	0.0314 (2)	-0.00172 (16)	0.00678 (17)	-0.00990 (17)
C12	0.0319 (2)	0.0247 (2)	0.0269 (2)	-0.00439 (15)	0.00228 (17)	-0.00444 (16)
C13	0.0275 (2)	0.0330 (2)	0.0291 (2)	0.00629 (16)	-0.00562 (16)	0.01025 (18)
C14	0.01753 (19)	0.0297 (2)	0.0324 (2)	-0.00597 (14)	0.00488 (15)	0.00171 (16)
C1	0.0145 (6)	0.0204 (8)	0.0165 (7)	-0.0021 (5)	0.0017 (5)	0.0004 (6)
O1	0.0169 (5)	0.0394 (7)	0.0207 (6)	-0.0008 (5)	0.0015 (4)	0.0116 (5)
N1	0.0121 (6)	0.0269 (7)	0.0160 (6)	0.0004 (5)	0.0005 (5)	0.0066 (5)
S1	0.01402 (18)	0.0436 (3)	0.0194 (2)	0.00106 (16)	0.00325 (14)	0.01158 (17)
C2	0.0135 (6)	0.0201 (8)	0.0168 (7)	0.0008 (5)	0.0018 (5)	0.0010 (6)
N2	0.0120 (6)	0.0237 (7)	0.0177 (6)	-0.0012 (5)	0.0014 (5)	0.0037 (5)
C11	0.0138 (6)	0.0216 (8)	0.0158 (7)	-0.0009 (5)	0.0032 (5)	0.0048 (6)
C12	0.0172 (7)	0.0226 (8)	0.0192 (8)	-0.0013 (6)	0.0035 (5)	0.0014 (6)
C13	0.0169 (7)	0.0316 (9)	0.0298 (9)	-0.0065 (6)	-0.0021 (6)	0.0016 (7)
C14	0.0135 (7)	0.0371 (10)	0.0391 (10)	0.0025 (7)	0.0016 (7)	0.0051 (8)
C15	0.0222 (8)	0.0267 (9)	0.0330 (10)	0.0065 (6)	0.0065 (7)	0.0029 (7)
C16	0.0191 (7)	0.0205 (8)	0.0186 (7)	-0.0009 (6)	0.0015 (6)	0.0028 (6)
C21	0.0126 (6)	0.0226 (8)	0.0157 (7)	0.0014 (5)	0.0009 (5)	-0.0016 (6)
C22	0.0178 (7)	0.0232 (8)	0.0178 (7)	-0.0002 (6)	0.0016 (5)	0.0013 (6)
C23	0.0213 (7)	0.0244 (8)	0.0157 (7)	0.0050 (6)	-0.0010 (6)	0.0017 (6)
C24	0.0142 (6)	0.0298 (9)	0.0204 (8)	0.0020 (6)	-0.0009 (5)	-0.0026 (7)
C25	0.0150 (7)	0.0242 (8)	0.0178 (7)	-0.0024 (6)	0.0027 (5)	-0.0019 (6)
C26	0.0147 (6)	0.0213 (8)	0.0188 (7)	0.0007 (5)	0.0011 (5)	0.0005 (6)

Geometric parameters (Å, °)

C11—C12	1.7397 (17)	C13—C14	1.390 (3)
C12—C16	1.7417 (17)	C13—H13	0.9500
C13—C23	1.7414 (17)	C14—C15	1.393 (3)
C14—C25	1.7445 (16)	C14—H14	0.9500
C1—O1	1.224 (2)	C15—C16	1.395 (2)
C1—N1	1.3796 (19)	C15—H15	0.9500
C1—C11	1.5146 (19)	C21—C26	1.400 (2)
N1—C2	1.3967 (18)	C21—C22	1.401 (2)
N1—H1	0.82 (2)	C22—C23	1.393 (2)
S1—C2	1.6745 (16)	C22—H22	0.9500
C2—N2	1.347 (2)	C23—C24	1.391 (2)
N2—C21	1.4186 (18)	C24—C25	1.395 (2)
N2—H2	0.91 (2)	C24—H24	0.9500
C11—C12	1.394 (2)	C25—C26	1.393 (2)
C11—C16	1.396 (2)	C26—H26	0.9500
C12—C13	1.393 (2)		
O1—C1—N1	124.54 (14)	C14—C15—C16	118.71 (16)
O1—C1—C11	121.70 (13)	C14—C15—H15	120.6
N1—C1—C11	113.75 (13)	C16—C15—H15	120.6
C1—N1—C2	128.18 (14)	C15—C16—C11	121.63 (15)
C1—N1—H1	118.9 (15)	C15—C16—C12	119.48 (13)
C2—N1—H1	112.9 (15)	C11—C16—C12	118.89 (12)
N2—C2—N1	114.54 (13)	C26—C21—C22	120.66 (14)
N2—C2—S1	127.07 (11)	C26—C21—N2	122.87 (14)
N1—C2—S1	118.38 (11)	C22—C21—N2	116.38 (14)
C2—N2—C21	128.79 (13)	C23—C22—C21	118.86 (15)
C2—N2—H2	114.5 (15)	C23—C22—H22	120.6
C21—N2—H2	116.7 (15)	C21—C22—H22	120.6
C12—C11—C16	118.01 (13)	C24—C23—C22	122.24 (15)
C12—C11—C1	121.24 (14)	C24—C23—C13	119.19 (12)
C16—C11—C1	120.72 (14)	C22—C23—C13	118.57 (13)
C13—C12—C11	121.66 (15)	C23—C24—C25	117.16 (14)
C13—C12—C1	119.56 (13)	C23—C24—H24	121.4
C11—C12—C1	118.78 (11)	C25—C24—H24	121.4
C14—C13—C12	118.88 (16)	C26—C25—C24	122.87 (15)
C14—C13—H13	120.6	C26—C25—C14	118.19 (13)
C12—C13—H13	120.6	C24—C25—C14	118.93 (12)
C13—C14—C15	121.08 (15)	C25—C26—C21	118.19 (14)
C13—C14—H14	119.5	C25—C26—H26	120.9
C15—C14—H14	119.5	C21—C26—H26	120.9
O1—C1—N1—C2	-4.9 (3)	C14—C15—C16—C12	178.83 (14)
C11—C1—N1—C2	174.63 (15)	C12—C11—C16—C15	1.5 (2)
C1—N1—C2—N2	-2.2 (2)	C1—C11—C16—C15	-176.47 (15)
C1—N1—C2—S1	177.27 (14)	C12—C11—C16—C12	-178.89 (12)

N1—C2—N2—C21	-173.75 (15)	C1—C11—C16—C12	3.2 (2)
S1—C2—N2—C21	6.9 (3)	C2—N2—C21—C26	30.3 (3)
O1—C1—C11—C12	-95.3 (2)	C2—N2—C21—C22	-152.93 (16)
N1—C1—C11—C12	85.17 (19)	C26—C21—C22—C23	-1.2 (2)
O1—C1—C11—C16	82.6 (2)	N2—C21—C22—C23	-178.08 (14)
N1—C1—C11—C16	-96.94 (18)	C21—C22—C23—C24	0.2 (2)
C16—C11—C12—C13	-0.1 (2)	C21—C22—C23—C13	-178.45 (12)
C1—C11—C12—C13	177.83 (15)	C22—C23—C24—C25	1.1 (2)
C16—C11—C12—C11	179.03 (12)	C13—C23—C24—C25	179.77 (12)
C1—C11—C12—C11	-3.0 (2)	C23—C24—C25—C26	-1.5 (2)
C11—C12—C13—C14	-1.1 (3)	C23—C24—C25—C14	179.11 (12)
C11—C12—C13—C14	179.72 (14)	C24—C25—C26—C21	0.5 (2)
C12—C13—C14—C15	1.1 (3)	C14—C25—C26—C21	179.94 (12)
C13—C14—C15—C16	0.2 (3)	C22—C21—C26—C25	0.9 (2)
C14—C15—C16—C11	-1.5 (3)	N2—C21—C26—C25	177.49 (14)

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—H2...O1	0.91 (2)	1.89 (2)	2.6581 (17)	141 (2)
N1—H1...S1 ⁱ	0.82 (2)	2.57 (2)	3.3653 (14)	163 (2)

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