Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-(2-Chlorophenyl)-4-(4-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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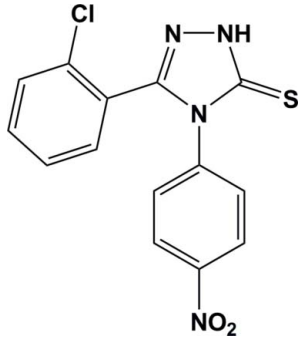
Received 15 May 2011; accepted 28 May 2011

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.072; wR factor = 0.174; data-to-parameter ratio = 19.9.

In the crystal structure of the title triazole compound, $C_{14}H_9ClN_4O_2S$, molecules are connected into centrosymmetric dimers by pairs of N—H···S hydrogen bonds. In addition, there are weak C—H···N hydrogen bonds stabilizing the crystal structure. The dihedral angles between the triazole ring and the two benzene rings are 73.0 (4) and 72.9 (4)°.

Related literature

For related structures, see: Genç *et al.* (2004); Kumaran *et al.* (1999). For the synthesis of triazoles, see: Zamani *et al.* (2003).



Experimental

Crystal data

$C_{14}H_9ClN_4O_2S$
M_r = 332.77
Monoclinic, $P2_1/n$
a = 6.7262 (13) Å
b = 17.109 (3) Å
c = 13.101 (3) Å
β = 95.89 (3)°
V = 1499.7 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 298 K
0.35 × 0.3 × 0.3 mm

Data collection

Stoe IPDS 2T diffractometer
16462 measured reflections
4038 independent reflections
2850 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.072
$wR(F^2)$ = 0.174
S = 1.18
4038 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1···S1^{i}	0.86 (3)	2.48 (3)	3.328 (3)	172 (3)
C2—H2···N1^{ii}	0.93	2.54	3.454 (5)	170

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

Data collection: *X-AREA* (Stoe & Cie, 2005); 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: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are grateful to Urmia University for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5548).

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supporting information

Acta Cryst. (2011). E**67**, o1612 [doi:10.1107/S1600536811020459]

3-(2-Chlorophenyl)-4-(4-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Abbas Nikoo, Karim Akbari Dilmaghani, Ali Hassanzadeh and Behrouz Notash

S1. Comment

In the medicinal chemistry, 1,2,4-triazoles are widely used. Cyclization of 1,4-disubstituted thiosemicarbazides produced 4,5-disubstituted 1,2,4-triazoles (Zamani *et al.*, 2003). 4-nitro phenylisothiocyanate reacted with 2-chlorophenylcarboxylic acid hydrazide to yield the corresponding 1-(2-chlorobenzoyl)-4-(4-nitrophenyl)thiosemicarbazide (**1**), whereas cyclization of (**1**) with $NaHCO_3$ 10% solution gave the 3-(2-Chlorophenyl)-4-(4-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (**2**) (Fig. 1).The structures of the compounds were assigned on the basis of IR, ^{1}H-NMR and ^{13}C-NMR spectra.

The molecular structure of the title compound is shown in Fig. 2. In the crystal structure of the title compound, there are intermolecular N—H···S and weak C—H···N hydrogen bonding which play important role in the stabilization of the crystal structure (Table 1 and Fig. 3).

S2. Experimental

Starting materials were obtained from Merck. For the synthesis of 1-(2-chlorobenzoyl)-4-(4-nitrophenyl)thiosemicarbazide (**1**), a mixture of 2-chlorophenylcarboxylic acid hydrazide (0.01 mol, 1.7 g) and 4-nitrophenyl isothiocynate (0.01 mol, 1.8 g) in absolute ethanol was refluxed for 6 h. The solid material obtained on cooling was filtered, washed with diethyl ether, dried and crystallized from ethanol (yield 82%; m.p. 170–172°C). IR (KBr, cm^{-1}): 3315, 3184 (N—H), 1643 (C═O), 1457, 1330 (NO_2), 1273 (C═S); ^{1}H NMR (300 MHz, DMSO-d_6): 7.42–7.53 (3*H*, m, 2-chlorophenyl), 7.74 (1*H*, s, 2-chlorophenyl), 7.90 (2*H*, d, J = 8.7, Ar—H), 8.21 (2*H*, d, J = 8.7, Ar—H), 9.99 (1*H*, br, –NH—Ar), 10.30 (1*H*, s, –CS—NH–), 10.56 (1*H*, br, –CO—NH–); ^{13}C NMR (75 MHz, DMSO-d_6): 121.59, 124.66, 125.11, 127.43, 130.39, 131.22, 132.19, 146.25, 165.93 and 181.58. For the synthesis of (**2**), a stirred mixture of (**1**) (1 mmol, 0.35 g) and $NaHCO_3$ 10% (10 ml) was refluxed for 6 h. After cooling, the solution was acidified with hydrochloric acid and the precipitate was filtered. The precipitate was then crystallized from ethanol (yield 57%; m.p. 223–225°C). IR (KBr, cm^{-1}): 3286 (N—H), 1608 (C═N), 1465, 1336 (NO_2), 1529, 1177, 1071, 963 (N—═S, amide I, II, III and IV bands); ^{1}H NMR (300 MHz, $CDCl_3$): 7.37–7.53 (6*H*, m, Ar—H), 7.91 (1*H*, s, 2-chlorophenyl), 8.23 (2*H*, d, J = 8.7, Ar—H), 12.24 (1*H*, s, SH); ^{13}C NMR (75 MHz, $CDCl_3$): 124.43, 127.26, 127.48, 128.74, 130.30, 130.50, 131.58, 132.23, 133, 133.07.

S3. Refinement

The H atom attached to amine group was found in a difference Fourier map and refined isotropically without restraint. The C—H protons were positioned geometrically and refined as riding atoms with C—H = 0.93 Å and *U*iso(H) = 1.2 *U*eq(C).

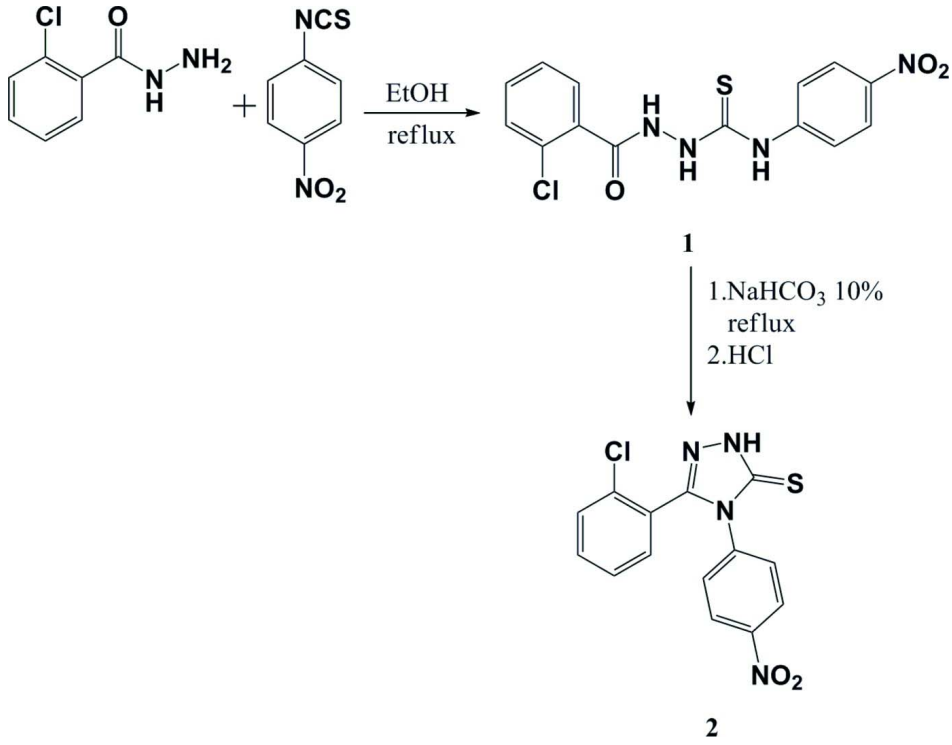

Figure 1

The reaction scheme for synthesis of the title compound.

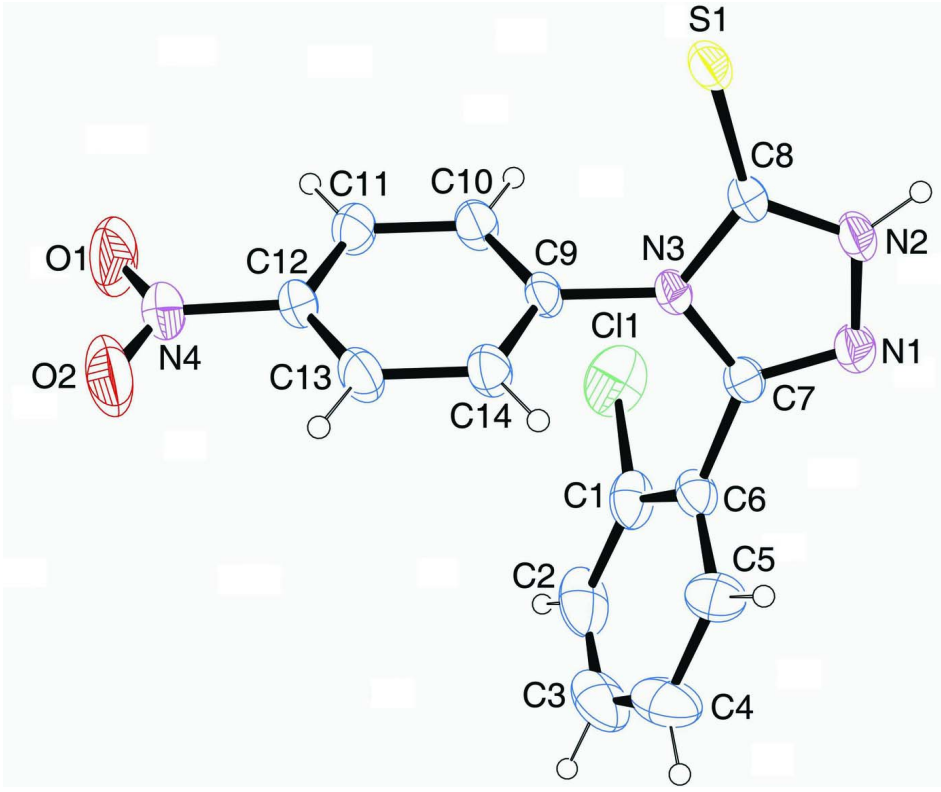

Figure 2

The molecular structure of the title compound with displacement ellipsoids drawn at 30% probability level.

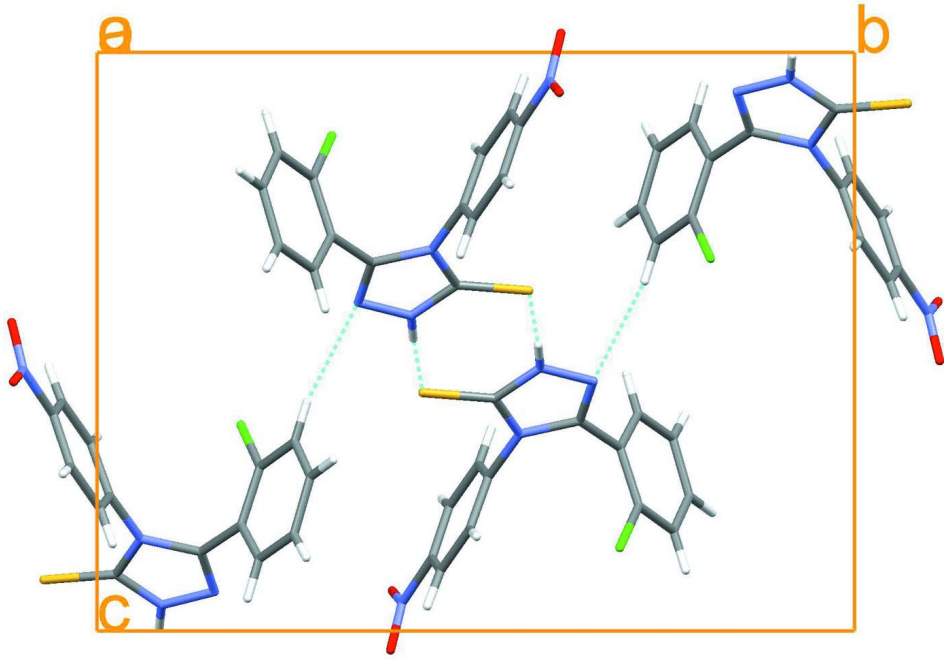

Figure 3

The packing diagram of the title compound down the *a* axis. The intermolecular N—H···S, C—H···N hydrogen bonds are shown as blue dashed lines.

3-(2-Chlorophenyl)-4-(4-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)- thione

Crystal data

$C_{14}H_9ClN_4O_2S$
$M_r = 332.77$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 6.7262$ (13) Å
$b = 17.109$ (3) Å
$c = 13.101$ (3) Å
$\beta = 95.89$ (3)°
$V = 1499.7$ (5) Å^3
$Z = 4$
$F(000) = 680.0$
$D_x = 1.474$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4038 reflections
$\theta = 2.4$–$29.2°$
$\mu = 0.41$ mm^{-1}
$T = 298$ K
Block, brown
0.35 × 0.3 × 0.3 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.15 pixels mm^{-1}
rotation method scans
16462 measured reflections
4038 independent reflections
2850 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 29.2°$, $\theta_{min} = 2.4°$
$h = -9 \rightarrow 9$
$k = -23 \rightarrow 22$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.174$
$S = 1.18$
4038 reflections
203 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
$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.4737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-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.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.23357 (11)	1.07003 (4)	0.08833 (6)	0.0535 (2)
Cl1	0.4224 (2)	0.80997 (7)	0.35611 (8)	0.0955 (4)
N3	0.4499 (3)	0.94203 (12)	0.15936 (15)	0.0400 (5)
C8	0.2956 (4)	0.97505 (15)	0.09792 (19)	0.0417 (6)
C7	0.4517 (4)	0.86289 (16)	0.13680 (19)	0.0433 (6)

C9	0.5843 (4)	0.98312 (15)	0.23334 (19)	0.0403 (5)
N2	0.2132 (4)	0.91476 (14)	0.04511 (19)	0.0512 (6)
C14	0.7779 (4)	0.99626 (19)	0.2123 (2)	0.0538 (7)
H14	0.8207	0.9795	0.1506	0.065*
C12	0.8404 (4)	1.05784 (17)	0.3744 (2)	0.0512 (7)
N1	0.3080 (4)	0.84485 (14)	0.06799 (19)	0.0523 (6)
C6	0.6088 (4)	0.80956 (16)	0.1831 (2)	0.0479 (6)
C11	0.6475 (5)	1.04638 (19)	0.3956 (2)	0.0555 (7)
H11	0.6049	1.0640	0.4569	0.067*
C5	0.7588 (5)	0.78584 (19)	0.1248 (3)	0.0644 (9)
H5	0.7544	0.8011	0.0565	0.077*
N4	0.9821 (5)	1.09731 (19)	0.4514 (2)	0.0732 (8)
C1	0.6151 (5)	0.78478 (19)	0.2838 (2)	0.0612 (8)
C13	0.9084 (4)	1.0349 (2)	0.2844 (2)	0.0598 (8)
H13	1.0395	1.0449	0.2716	0.072*
C10	0.5174 (4)	1.00804 (19)	0.3240 (2)	0.0508 (7)
H10	0.3858	0.9991	0.3367	0.061*
O2	1.1498 (5)	1.1103 (2)	0.4306 (3)	0.1210 (13)
C2	0.7732 (8)	0.7390 (2)	0.3270 (3)	0.0859 (13)
H2	0.7789	0.7230	0.3951	0.103*
O1	0.9257 (5)	1.1125 (2)	0.5332 (2)	0.1153 (12)
C3	0.9209 (7)	0.7181 (2)	0.2669 (5)	0.0946 (15)
H3	1.0281	0.6883	0.2954	0.114*
C4	0.9137 (6)	0.7400 (2)	0.1668 (4)	0.0852 (13)
H4	1.0131	0.7240	0.1270	0.102*
H1	0.104 (5)	0.9176 (17)	0.006 (2)	0.048 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0494 (4)	0.0469 (4)	0.0592 (4)	0.0006 (3)	−0.0187 (3)	0.0028 (3)
Cl1	0.1317 (10)	0.1029 (8)	0.0554 (5)	−0.0121 (7)	0.0263 (6)	0.0092 (5)
N3	0.0405 (11)	0.0458 (12)	0.0315 (10)	0.0015 (9)	−0.0071 (8)	0.0005 (8)
C8	0.0380 (12)	0.0494 (14)	0.0360 (12)	−0.0011 (10)	−0.0041 (10)	0.0027 (10)
C7	0.0465 (14)	0.0479 (14)	0.0341 (12)	0.0028 (11)	−0.0024 (10)	0.0026 (10)
C9	0.0384 (12)	0.0472 (14)	0.0328 (12)	0.0008 (10)	−0.0081 (10)	0.0017 (10)
N2	0.0500 (13)	0.0513 (14)	0.0476 (13)	0.0014 (10)	−0.0187 (11)	−0.0010 (10)
C14	0.0428 (15)	0.077 (2)	0.0415 (15)	0.0000 (13)	0.0016 (12)	−0.0100 (13)
C12	0.0479 (15)	0.0567 (17)	0.0453 (15)	0.0043 (12)	−0.0134 (12)	−0.0085 (12)
N1	0.0579 (14)	0.0506 (13)	0.0450 (13)	0.0029 (11)	−0.0112 (11)	−0.0022 (10)
C6	0.0503 (15)	0.0420 (14)	0.0485 (15)	−0.0010 (11)	−0.0094 (12)	0.0050 (11)
C11	0.0558 (17)	0.0692 (19)	0.0408 (15)	0.0009 (14)	0.0015 (13)	−0.0119 (13)
C5	0.065 (2)	0.0530 (18)	0.075 (2)	0.0103 (15)	0.0080 (17)	0.0146 (15)
N4	0.0633 (18)	0.085 (2)	0.0659 (19)	0.0037 (15)	−0.0195 (15)	−0.0246 (15)
C1	0.082 (2)	0.0535 (17)	0.0446 (16)	−0.0095 (15)	−0.0103 (15)	0.0079 (13)
C13	0.0355 (14)	0.084 (2)	0.0592 (18)	−0.0052 (14)	−0.0003 (12)	−0.0125 (16)
C10	0.0401 (14)	0.0705 (19)	0.0415 (14)	−0.0031 (12)	0.0038 (11)	−0.0056 (13)
O2	0.0646 (18)	0.172 (3)	0.122 (3)	−0.030 (2)	−0.0108 (17)	−0.065 (2)

C2	0.116 (3)	0.063 (2)	0.069 (2)	−0.007 (2)	−0.039 (2)	0.0228 (18)
O1	0.100 (2)	0.168 (3)	0.074 (2)	−0.015 (2)	−0.0115 (17)	−0.061 (2)
C3	0.082 (3)	0.057 (2)	0.134 (4)	0.0075 (19)	−0.043 (3)	0.018 (2)
C4	0.064 (2)	0.056 (2)	0.135 (4)	0.0139 (17)	0.008 (2)	0.018 (2)

Geometric parameters (Å, º)

S1—C8	1.679 (3)	C6—C1	1.382 (4)
Cl1—C1	1.736 (4)	C6—C5	1.387 (5)
N3—C8	1.369 (3)	C11—C10	1.382 (4)
N3—C7	1.386 (3)	C11—H11	0.9300
N3—C9	1.439 (3)	C5—C4	1.373 (5)
C8—N2	1.331 (3)	C5—H5	0.9300
C7—N1	1.290 (3)	N4—O1	1.203 (4)
C7—C6	1.479 (4)	N4—O2	1.208 (4)
C9—C14	1.377 (4)	C1—C2	1.393 (5)
C9—C10	1.380 (4)	C13—H13	0.9300
N2—N1	1.374 (3)	C10—H10	0.9300
N2—H1	0.86 (3)	C2—C3	1.377 (7)
C14—C13	1.389 (4)	C2—H2	0.9300
C14—H14	0.9300	C3—C4	1.360 (7)
C12—C13	1.366 (4)	C3—H3	0.9300
C12—C11	1.369 (4)	C4—H4	0.9300
C12—N4	1.478 (4)		
C8—N3—C7	107.5 (2)	C12—C11—H11	120.7
C8—N3—C9	125.5 (2)	C10—C11—H11	120.7
C7—N3—C9	127.0 (2)	C4—C5—C6	120.7 (4)
N2—C8—N3	103.6 (2)	C4—C5—H5	119.7
N2—C8—S1	128.6 (2)	C6—C5—H5	119.7
N3—C8—S1	127.68 (19)	O1—N4—O2	123.3 (3)
N1—C7—N3	111.1 (2)	O1—N4—C12	117.8 (3)
N1—C7—C6	126.3 (2)	O2—N4—C12	118.9 (3)
N3—C7—C6	122.4 (2)	C6—C1—C2	120.5 (4)
C14—C9—C10	121.4 (2)	C6—C1—Cl1	119.5 (3)
C14—C9—N3	119.1 (2)	C2—C1—Cl1	120.0 (3)
C10—C9—N3	119.5 (2)	C12—C13—C14	118.7 (3)
C8—N2—N1	113.7 (2)	C12—C13—H13	120.6
C8—N2—H1	124 (2)	C14—C13—H13	120.6
N1—N2—H1	122 (2)	C9—C10—C11	119.4 (3)
C9—C14—C13	119.1 (3)	C9—C10—H10	120.3
C9—C14—H14	120.5	C11—C10—H10	120.3
C13—C14—H14	120.5	C3—C2—C1	118.6 (4)
C13—C12—C11	122.8 (3)	C3—C2—H2	120.7
C13—C12—N4	118.1 (3)	C1—C2—H2	120.7
C11—C12—N4	119.1 (3)	C4—C3—C2	121.6 (4)
C7—N1—N2	104.0 (2)	C4—C3—H3	119.2
C1—C6—C5	118.9 (3)	C2—C3—H3	119.2

C1—C6—C7	122.1 (3)	C3—C4—C5	119.7 (4)
C5—C6—C7	118.9 (3)	C3—C4—H4	120.2
C12—C11—C10	118.6 (3)	C5—C4—H4	120.2
C7—N3—C8—N2	1.3 (3)	C13—C12—C11—C10	1.8 (5)
C9—N3—C8—N2	−178.7 (2)	N4—C12—C11—C10	−178.7 (3)
C7—N3—C8—S1	−176.1 (2)	C1—C6—C5—C4	−1.5 (5)
C9—N3—C8—S1	3.8 (4)	C7—C6—C5—C4	176.2 (3)
C8—N3—C7—N1	−1.3 (3)	C13—C12—N4—O1	−174.9 (4)
C9—N3—C7—N1	178.7 (3)	C11—C12—N4—O1	5.6 (5)
C8—N3—C7—C6	175.2 (2)	C13—C12—N4—O2	2.6 (5)
C9—N3—C7—C6	−4.8 (4)	C11—C12—N4—O2	−176.9 (4)
C8—N3—C9—C14	−107.0 (3)	C5—C6—C1—C2	2.2 (5)
C7—N3—C9—C14	72.9 (4)	C7—C6—C1—C2	−175.4 (3)
C8—N3—C9—C10	73.4 (3)	C5—C6—C1—Cl1	−176.9 (2)
C7—N3—C9—C10	−106.6 (3)	C7—C6—C1—Cl1	5.4 (4)
N3—C8—N2—N1	−1.0 (3)	C11—C12—C13—C14	−1.9 (5)
S1—C8—N2—N1	176.4 (2)	N4—C12—C13—C14	178.7 (3)
C10—C9—C14—C13	0.5 (5)	C9—C14—C13—C12	0.7 (5)
N3—C9—C14—C13	−179.0 (3)	C14—C9—C10—C11	−0.6 (5)
N3—C7—N1—N2	0.7 (3)	N3—C9—C10—C11	179.0 (3)
C6—C7—N1—N2	−175.6 (3)	C12—C11—C10—C9	−0.6 (5)
C8—N2—N1—C7	0.2 (3)	C6—C1—C2—C3	−1.0 (5)
N1—C7—C6—C1	−109.4 (4)	Cl1—C1—C2—C3	178.1 (3)
N3—C7—C6—C1	74.7 (4)	C1—C2—C3—C4	−1.0 (6)
N1—C7—C6—C5	73.0 (4)	C2—C3—C4—C5	1.8 (6)
N3—C7—C6—C5	−103.0 (3)	C6—C5—C4—C3	−0.5 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···S1^{i}	0.86 (3)	2.48 (3)	3.328 (3)	172 (3)
C2—H2···N1^{ii}	0.93	2.54	3.454 (5)	170

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