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Crystal structure of 2-{[2-(3-phenylallylidene)hydrazin-1-yl]thiocarbonylsulfanylmethyl}pyridinium chloride

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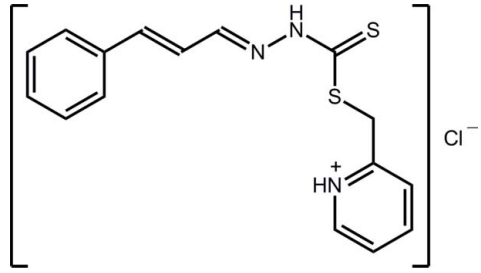
In the title salt of an *S*-substituted dithiocarbazate, $C_{16}H_{16}N_3S_2^+\cdot Cl^-$, the dihedral angles between the almost planar (r.m.s deviation = 0.005 Å) central CN_2S_2 residue and the terminal pyridinium and phenyl rings are 80.09 (11) and 3.82 (11)°, respectively, indicating the cation has an L-shape; the amine H and thione S atoms are *syn*. The conformation about each of the imine [1.376 (3) Å] and ethene [1.333 (4) Å] bonds is *E*. The shortened C—C bond [1.444 (4) Å] linking the double bonds is consistent with conjugation in this part of the molecule. In the crystal, supramolecular layers with a jagged topology are formed by charged-assisted amine-H···Cl^- and pyridinium-N^+—H···Cl^- hydrogen bonds. The layers stack along the *a* axis with no specific directional interactions between them.

Keywords: crystal structure; hydrogen bonding; *S*-substituted dithiocarbazates; salt.

CCDC reference: 1030368

1. Related literature

For general background to related Schiff bases formed between *S*-substituted dithiocarbazates and cinnamaldehyde, see: Low *et al.* (2013). For the biological activity of similar sulfur/nitrogen-containing Schiff base derivatives, see: Khoo *et al.* (2014). For the synthetic procedure, see: Crouse *et al.* (2004).



2. Experimental

2.1. Crystal data

$C_{16}H_{16}N_3S_2^+\cdot Cl^-$
M_r = 349.89
Orthorhombic, $Pna2_1$
a = 24.2206 (8) Å
b = 8.2838 (2) Å
c = 8.3206 (4) Å
V = 1669.43 (11) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 4.35 mm^{-1}
T = 150 K
0.12 × 0.05 × 0.01 mm

2.2. Data collection

Agilent Xcaliber Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.80, T_{max} = 0.96
5463 measured reflections
2460 independent reflections
2327 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.04
2460 reflections
205 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 971 Friedel pairs
Absolute structure parameter: −0.009 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···Cl1^{i}	0.88 (2)	2.29 (2)	3.104 (3)	153 (3)
N3—H3*N*···Cl1	0.88 (2)	2.13 (2)	2.9833 (19)	163 (3)

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7295).

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supporting information

Acta Cryst. (2014). E**70**, o1207–o1208 [doi:10.1107/S1600536814023228]

Crystal structure of 2-{[2-(3-phenylallylidene)hydrazin-1-yl]thiocarbonylsulfanylmethyl}pyridinium chloride

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S1. Synthesis and crystallization

An equimolar amount of *trans*-cinnamaldehyde (1.26 ml) was added to a solution of *S*-2-picolyldithiocarbazate hydrochloride (2.36 g, 0.01 mol), prepared by literature methods (Crouse *et al.*, 2004), dissolved in hot absolute ethanol (100 ml). The mixture was heated while being stirred to reduce it to half the original volume and then cooled. The yellow compound was filtered, washed with absolute ethanol then dried over silica gel. Single crystals of diffraction quality were obtained after recrystallisation from its methanolic solution. % yield = 90%. *M*.pt = 465-466 K. HR—MS: *m*/*z* = [M—Cl+H]$^+$ Calcd. 314.07802, Found 314.07826. RP-HPLC retention time, RT = 15 min. FT—IR: ν (cm^{-1}) = 3048 (w), 1621 (m), 1033 (m), 978 (s) and 951 (m). UV-Vis in DMSO: λ_{max} nm (log ε) = 360 (4.65), 377 (4.52, sh), 344 (4.53, sh). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ = 13.53 (*s*, 1H), 8.78 (*d*, J = 5.2, 1H), 8.37 (*t*, J = 7.8, 1H), 8.14 (*d*, J = 9.4, 1H), 7.98 (*d*, J = 8.0, 1H), 7.86 - 7.78 (*m*, 1H), 7.66 (*d*, J = 6.7, 2H), 7.38 (*q*, J = 6.3, 3H), 7.21 (*d*, J = 16.0, 1H), 6.97 (*dd*, J = 16.0, 9.4, 1H), 4.87 (*s*, 2H); the N-bound H was not observed. ^{13}C NMR (75 MHz, DMSO-d$_6$) δ = 193.66, 153.87, 150.12, 144.22, 142.97, 142.77, 135.54, 129.49, 128.90, 127.53, 126.39, 124.86, 124.04, 34.92. GC—MS (fragmentation pattern) *m*/*z* = 313, 187,130, 125, 103, 92, 77, 65, 51.

S2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) = 1.2U_{eq}(C). The N—H H atoms were refined with N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N).

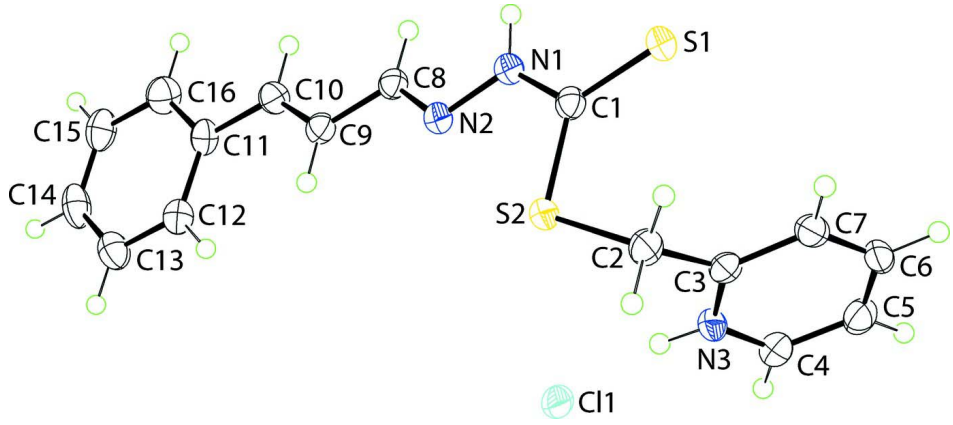

Figure 1

The molecular structure of the title compound showing displacement ellipsoids at the 50% probability level.

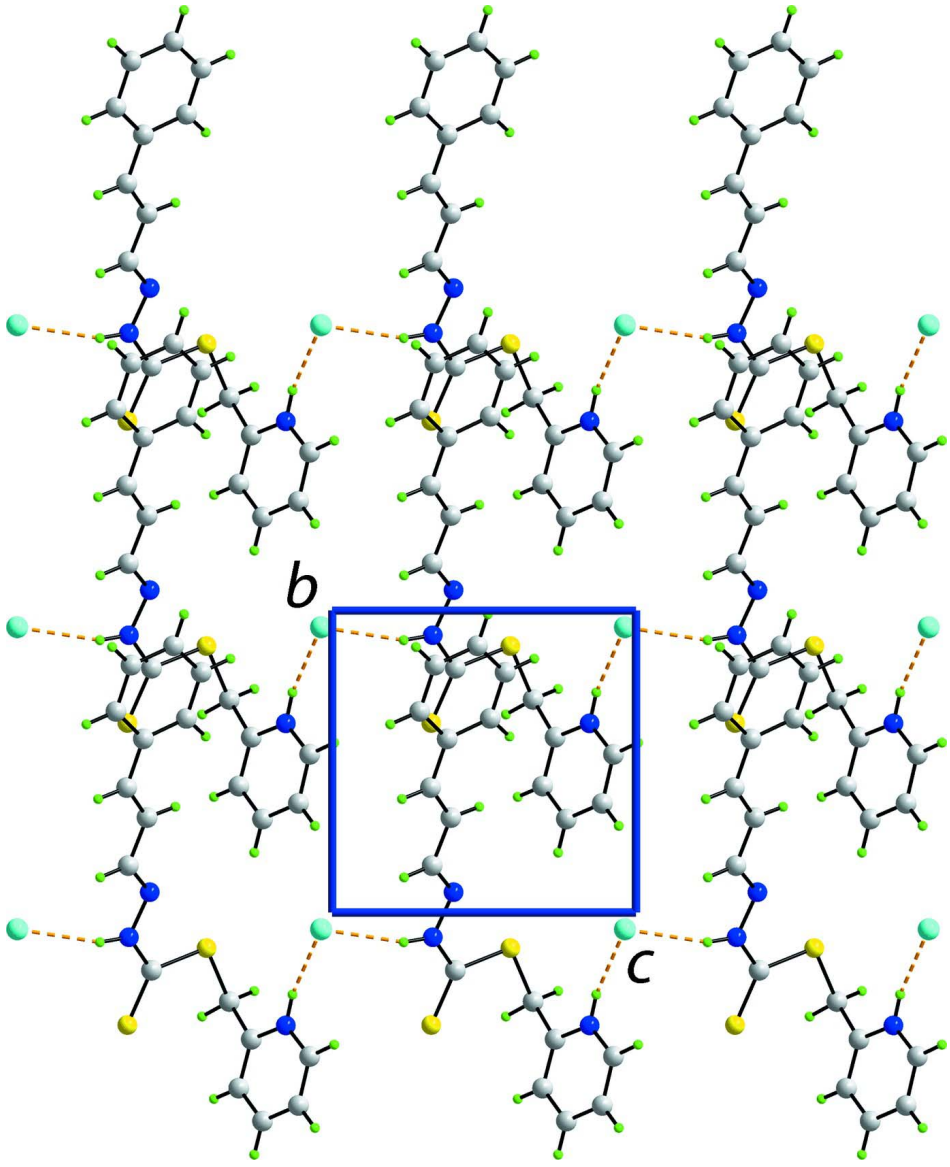

Figure 2

A view of the supramolecular layer in the *bc* plane mediated by charge-assisted N—H···Cl hydrogen bonds (orange dashed lines).

2-{[2-(3-Phenylallylidene)hydrazin-1-yl]thiocarbonylsulfanylmethyl}pyridinium chloride

Crystal data

$C_{16}H_{16}N_3S_2^+\cdot Cl^-$
M_r = 349.89
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
a = 24.2206 (8) Å
b = 8.2838 (2) Å
c = 8.3206 (4) Å
V = 1669.43 (11) Å^3
Z = 4
$F(000)$ = 728
D_x = 1.392 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54180 Å

Cell parameters from 3280 reflections
θ = 4–71°
μ = 4.35 mm^{-1}
T = 150 K
Plate, yellow
0.12 × 0.05 × 0.01 mm

Data collection

Agilent Xcaliber Eos Gemini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.1952 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.80, T_{max} = 0.96
5463 measured reflections
2460 independent reflections
2327 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 67.7°, θ_{min} = 3.7°
h = −29→28
k = −7→9
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.04
2460 reflections
205 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.1085P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 971 Friedel pairs
Absolute structure parameter: −0.009 (16)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
Cl1	0.63222 (3)	−0.05537 (7)	0.96332 (11)	0.03476 (18)
S1	0.69437 (3)	−0.37225 (7)	0.32589 (10)	0.02657 (17)
S2	0.71117 (3)	−0.11756 (6)	0.58644 (10)	0.02635 (17)
N1	0.65178 (9)	−0.0817 (2)	0.3311 (4)	0.0252 (5)
H1N	0.6375 (13)	−0.098 (4)	0.235 (2)	0.030*
N2	0.64340 (9)	0.0675 (2)	0.3995 (3)	0.0259 (5)
N3	0.67390 (9)	−0.3736 (2)	0.8473 (3)	0.0268 (5)
H3N	0.6674 (12)	−0.2714 (16)	0.869 (4)	0.032*
C1	0.68354 (9)	−0.1909 (3)	0.4053 (4)	0.0238 (6)
C2	0.74713 (11)	−0.2944 (3)	0.6613 (4)	0.0297 (7)
H2A	0.7679	−0.3442	0.5717	0.036*

H2B	0.7742	−0.2598	0.7434	0.036*
C3	0.70984 (10)	−0.4195 (3)	0.7339 (4)	0.0264 (6)
C4	0.64075 (12)	−0.4762 (3)	0.9260 (4)	0.0306 (7)
H4	0.6164	−0.4375	1.0068	0.037*
C5	0.64217 (12)	−0.6385 (3)	0.8889 (4)	0.0339 (7)
H5	0.6189	−0.7130	0.9432	0.041*
C6	0.67820 (12)	−0.6902 (3)	0.7709 (4)	0.0327 (7)
H6	0.6798	−0.8014	0.7435	0.039*
C7	0.71189 (12)	−0.5813 (3)	0.6926 (4)	0.0301 (7)
H7	0.7364	−0.6171	0.6108	0.036*
C8	0.60714 (9)	0.1556 (3)	0.3289 (4)	0.0241 (6)
H8	0.5884	0.1164	0.2365	0.029*
C9	0.59502 (10)	0.3146 (3)	0.3905 (4)	0.0257 (6)
H9	0.6141	0.3502	0.4837	0.031*
C10	0.55839 (10)	0.4140 (3)	0.3235 (4)	0.0272 (6)
H10	0.5403	0.3757	0.2297	0.033*
C11	0.54303 (10)	0.5752 (3)	0.3785 (4)	0.0276 (7)
C12	0.56395 (11)	0.6430 (3)	0.5201 (4)	0.0287 (7)
H12	0.5893	0.5831	0.5834	0.034*
C13	0.54828 (11)	0.7955 (3)	0.5692 (5)	0.0346 (7)
H13	0.5632	0.8404	0.6648	0.042*
C14	0.51043 (12)	0.8835 (3)	0.4779 (5)	0.0381 (8)
H14	0.4990	0.9877	0.5123	0.046*
C15	0.48967 (11)	0.8192 (3)	0.3381 (5)	0.0376 (8)
H15	0.4641	0.8793	0.2755	0.045*
C16	0.50597 (11)	0.6662 (4)	0.2882 (5)	0.0365 (8)
H16	0.4916	0.6231	0.1910	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0546 (4)	0.0238 (3)	0.0258 (4)	0.0111 (3)	0.0018 (4)	0.0001 (3)
S1	0.0320 (3)	0.0197 (3)	0.0279 (4)	0.0013 (2)	0.0003 (3)	−0.0026 (3)
S2	0.0362 (3)	0.0192 (3)	0.0237 (4)	0.0015 (2)	−0.0028 (3)	−0.0013 (3)
N1	0.0312 (10)	0.0209 (10)	0.0235 (15)	0.0022 (8)	0.0006 (12)	−0.0007 (10)
N2	0.0335 (11)	0.0199 (10)	0.0244 (15)	0.0009 (8)	0.0008 (11)	−0.0005 (9)
N3	0.0347 (10)	0.0189 (9)	0.0268 (16)	0.0051 (8)	−0.0042 (12)	−0.0023 (10)
C1	0.0244 (11)	0.0221 (11)	0.0250 (18)	−0.0015 (9)	0.0025 (12)	0.0017 (11)
C2	0.0318 (13)	0.0256 (13)	0.0316 (19)	0.0058 (10)	−0.0097 (14)	0.0018 (13)
C3	0.0304 (13)	0.0244 (12)	0.0244 (19)	0.0081 (10)	−0.0126 (13)	0.0018 (11)
C4	0.0357 (13)	0.0283 (12)	0.028 (2)	0.0021 (10)	−0.0020 (14)	0.0028 (12)
C5	0.0392 (14)	0.0296 (13)	0.033 (2)	−0.0011 (11)	−0.0098 (15)	0.0069 (13)
C6	0.0476 (15)	0.0196 (12)	0.031 (2)	0.0055 (11)	−0.0154 (16)	−0.0036 (11)
C7	0.0373 (14)	0.0263 (13)	0.027 (2)	0.0100 (10)	−0.0094 (14)	−0.0034 (12)
C8	0.0251 (10)	0.0237 (11)	0.0236 (16)	−0.0030 (9)	−0.0008 (14)	0.0022 (12)
C9	0.0282 (11)	0.0241 (12)	0.0247 (17)	−0.0007 (10)	0.0026 (13)	0.0017 (11)
C10	0.0261 (11)	0.0264 (12)	0.0291 (18)	−0.0005 (9)	−0.0006 (14)	−0.0011 (13)
C11	0.0240 (11)	0.0227 (12)	0.036 (2)	−0.0019 (9)	0.0002 (13)	0.0032 (11)

C12	0.0269 (12)	0.0258 (12)	0.033 (2)	0.0008 (10)	0.0037 (13)	0.0015 (12)
C13	0.0347 (13)	0.0286 (13)	0.041 (2)	−0.0020 (10)	0.0072 (16)	−0.0055 (14)
C14	0.0352 (14)	0.0214 (12)	0.058 (3)	0.0018 (10)	0.0138 (17)	−0.0036 (14)
C15	0.0345 (13)	0.0272 (13)	0.051 (2)	0.0053 (10)	0.0036 (16)	0.0082 (15)
C16	0.0339 (13)	0.0346 (15)	0.041 (2)	0.0037 (11)	−0.0025 (15)	0.0019 (13)

Geometric parameters (Å, º)

S1—C1	1.662 (3)	C6—H6	0.9500
S2—C1	1.757 (3)	C7—H7	0.9500
S2—C2	1.815 (3)	C8—C9	1.444 (4)
N1—C1	1.339 (3)	C8—H8	0.9500
N1—N2	1.376 (3)	C9—C10	1.333 (4)
N1—H1N	0.880 (10)	C9—H9	0.9500
N2—C8	1.284 (4)	C10—C11	1.460 (3)
N3—C3	1.339 (4)	C10—H10	0.9500
N3—C4	1.340 (4)	C11—C16	1.392 (4)
N3—H3N	0.880 (10)	C11—C12	1.400 (4)
C2—C3	1.502 (4)	C12—C13	1.381 (4)
C2—H2A	0.9900	C12—H12	0.9500
C2—H2B	0.9900	C13—C14	1.396 (5)
C3—C7	1.384 (4)	C13—H13	0.9500
C4—C5	1.380 (4)	C14—C15	1.375 (5)
C4—H4	0.9500	C14—H14	0.9500
C5—C6	1.381 (4)	C15—C16	1.391 (4)
C5—H5	0.9500	C15—H15	0.9500
C6—C7	1.380 (4)	C16—H16	0.9500
C1—S2—C2	101.42 (13)	C6—C7—H7	120.2
C1—N1—N2	120.1 (3)	C3—C7—H7	120.2
C1—N1—H1N	123 (2)	N2—C8—C9	119.7 (3)
N2—N1—H1N	117 (2)	N2—C8—H8	120.2
C8—N2—N1	114.9 (3)	C9—C8—H8	120.2
C3—N3—C4	123.6 (2)	C10—C9—C8	123.4 (3)
C3—N3—H3N	122 (2)	C10—C9—H9	118.3
C4—N3—H3N	114 (2)	C8—C9—H9	118.3
N1—C1—S1	121.2 (2)	C9—C10—C11	127.1 (3)
N1—C1—S2	112.4 (2)	C9—C10—H10	116.4
S1—C1—S2	126.41 (16)	C11—C10—H10	116.4
C3—C2—S2	113.99 (18)	C16—C11—C12	118.1 (3)
C3—C2—H2A	108.8	C16—C11—C10	119.4 (3)
S2—C2—H2A	108.8	C12—C11—C10	122.6 (3)
C3—C2—H2B	108.8	C13—C12—C11	121.1 (3)
S2—C2—H2B	108.8	C13—C12—H12	119.5
H2A—C2—H2B	107.6	C11—C12—H12	119.5
N3—C3—C7	118.3 (3)	C12—C13—C14	119.8 (3)
N3—C3—C2	118.5 (2)	C12—C13—H13	120.1
C7—C3—C2	123.2 (3)	C14—C13—H13	120.1

N3—C4—C5	119.6 (3)	C15—C14—C13	119.9 (2)
N3—C4—H4	120.2	C15—C14—H14	120.1
C5—C4—H4	120.2	C13—C14—H14	120.1
C4—C5—C6	118.5 (3)	C14—C15—C16	120.1 (3)
C4—C5—H5	120.8	C14—C15—H15	119.9
C6—C5—H5	120.8	C16—C15—H15	119.9
C7—C6—C5	120.4 (3)	C15—C16—C11	121.0 (3)
C7—C6—H6	119.8	C15—C16—H16	119.5
C5—C6—H6	119.8	C11—C16—H16	119.5
C6—C7—C3	119.6 (3)		

C1—N1—N2—C8	−171.9 (2)	C2—C3—C7—C6	176.6 (3)
N2—N1—C1—S1	179.90 (19)	N1—N2—C8—C9	180.0 (2)
N2—N1—C1—S2	−1.0 (3)	N2—C8—C9—C10	179.4 (3)
C2—S2—C1—N1	176.37 (19)	C8—C9—C10—C11	179.2 (3)
C2—S2—C1—S1	−4.5 (2)	C9—C10—C11—C16	176.5 (3)
C1—S2—C2—C3	−76.9 (2)	C9—C10—C11—C12	−3.8 (5)
C4—N3—C3—C7	1.7 (4)	C16—C11—C12—C13	0.1 (4)
C4—N3—C3—C2	−176.4 (3)	C10—C11—C12—C13	−179.6 (3)
S2—C2—C3—N3	−52.0 (3)	C11—C12—C13—C14	0.8 (4)
S2—C2—C3—C7	129.9 (3)	C12—C13—C14—C15	−1.1 (5)
C3—N3—C4—C5	−1.1 (4)	C13—C14—C15—C16	0.5 (5)
N3—C4—C5—C6	0.1 (4)	C14—C15—C16—C11	0.5 (5)
C4—C5—C6—C7	0.1 (4)	C12—C11—C16—C15	−0.8 (4)
C5—C6—C7—C3	0.6 (4)	C10—C11—C16—C15	178.9 (3)
N3—C3—C7—C6	−1.5 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···Cl1^{i}	0.88 (2)	2.29 (2)	3.104 (3)	153 (3)
N3—H3*N*···Cl1	0.88 (2)	2.13 (2)	2.9833 (19)	163 (3)

Symmetry code: (i) *x*, *y*, *z*−1.