Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of 1-{(*Z*)-[(2*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-ylidene]amino}-3-ethylthiourea

Ming Yueh Tan,[a] Karen A. Crouse,[a] Thahira Begum S. A. Ravoof[a]* and Edward R. T. Tiekink[b]*

[a]Department of Chemistry, Universiti Putra Malaysia, 43400 Serdang, Malaysia, and [b]Centre for Crystalline Materials, Faculty of Science and Technology, Sunway University, No. 5 Jalan Universiti, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia. *Correspondence e-mail: thahira@upm.edu.my, edwardt@sunway.edu.my

Received 2 December 2015; accepted 8 December 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

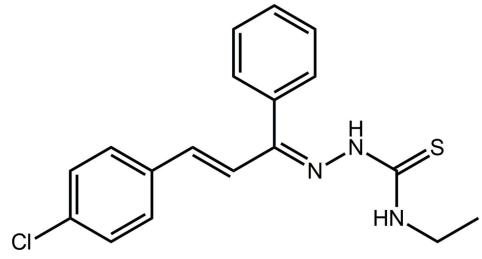
In the title thiosemicarbazone compound, $C_{18}H_{18}ClN_3S$, the CN_3S residue is almost planar (r.m.s. deviation = 0.0031 Å) and forms dihedral angles of 65.99 (7) and 34.60 (10)° with the phenyl and chlorobenzene rings, respectively; the dihedral angle between the aromatic rings is 85.13 (8)°. The conformation about the C=N bond is *Z*, and that about the C=C bonds is *E*. The imine N and ethyl N atoms are *syn* and are linked by an ethyl–imine N—H···N hydrogen bond. This H atom also forms an intermolecular hydrogen bond to the thione S atom, resulting in a supramolecular helical chain propagating along the *b* axis. The chains are consolidated into a three-dimensional architecture by phenyl-C—H···Cl contacts and weak π–π interactions between centrosymmetrically related chlorobenzene rings [inter-centroid distance = 3.9127 (15) Å].

Keywords: crystal structure; hydrogen bonding; thiosemicarbazone.

CCDC reference: 1441045

1. Related literature

For background to the coordination chemistry and applications of metal thiosemicarbazones, see: Dilworth & Hueting (2012). For the structure of a closely related thiosemicarbazone compound, 1-benzothiophene-2-carbaldehyde 4-ethylthiosemicarbazone, with almost planar semicarbazone units (two molecules comprise the asymmetric unit) and *E* conformations for the C=N bonds, see: Kayed *et al.* (2009).



2. Experimental

2.1. Crystal data

$C_{18}H_{18}ClN_3S$
M_r = 343.86
Monoclinic, $P2_1/c$
a = 10.580 (1) Å
b = 12.0438 (9) Å
c = 13.9561 (10) Å
β = 90.196 (8)°
V = 1778.3 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 293 K
0.20 × 0.15 × 0.10 mm

2.2. Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.800, T_{max} = 1.000
11178 measured reflections
4078 independent reflections
1963 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.120
S = 1.00
4078 reflections
216 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N3	0.88 (2)	2.25 (2)	2.629 (3)	106 (2)
N1—H1*N*···S1^{i}	0.88 (2)	2.84 (2)	3.693 (2)	165 (2)
C43—H43···Cl1^{ii}	0.93	2.82	3.708 (3)	160

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

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

This research was funded by Universiti Putra Malaysia (UPM) under Research University Grant Schemes (RUGS No. 9419400), the Fundamental Research Grant Scheme (FRGS No. 5524425) and the Science Fund (Science Fund No. 06–01-

04-SF810). MYT wishes to thank the UPM for the award of a Graduate Research Fellowship.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7555).

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supporting information

Acta Cryst. (2015). E**71**, o1047–o1048 [https://doi.org/10.1107/S2056989015023531]

Crystal structure of 1-{(*Z*)-[(2*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-ylidene]amino}-3-ethylthiourea

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S1. Refinement

S2. Experimental

An ethanol solution (20 ml) of 4-chlorochalcone (0.243 g, 1 mmol) was slowly added to a solution of 4-ethyl-3-thiosemicarbazide (0.119 g, 1 mmol) in absolute ethanol (20 ml), while stirring and heating for about 20 mins. The yellow precipitate was filtered, washed with cold ethanol and dried in vacuo. Light brown prisms of the title compound were grown at room temperature from the slow evaporation of a solvent mixture of dimethylformamide and acetonitrile; M.pt: 154–156 °C.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.93 to 0.97 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) = 1.2–1.5U_{eq}(C). The N—H atom was refined with N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(N).

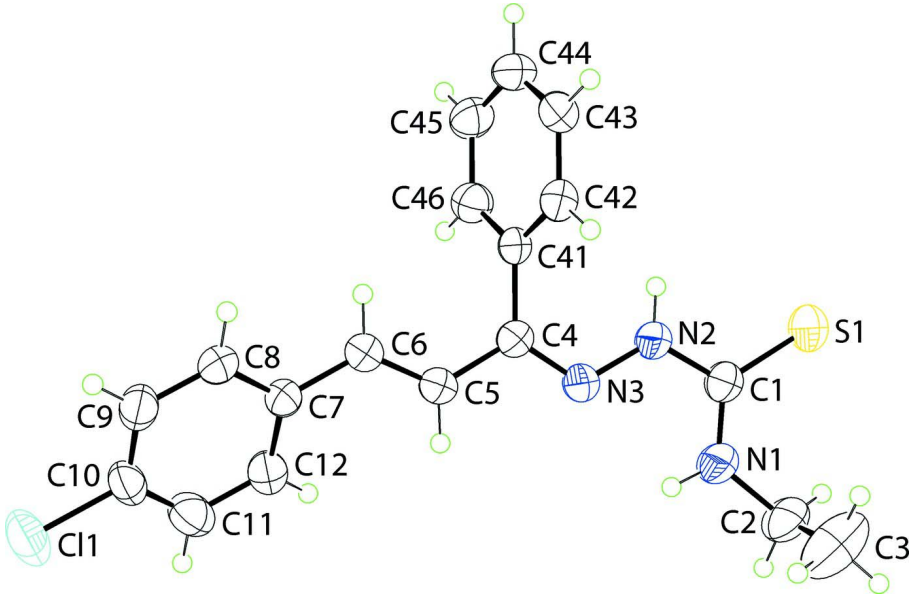

Figure 1

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

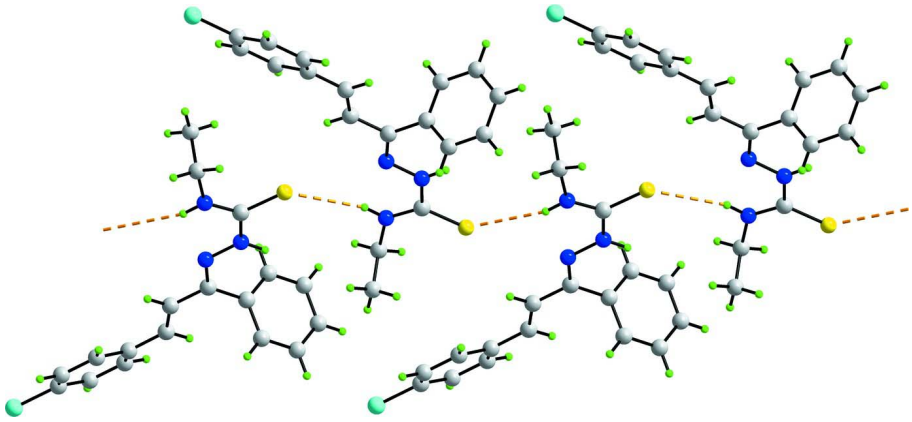

Figure 2

A view of the helical supramolecular chain along the *b* axis and sustained by N—H···S hydrogen bonds shown as orange dashed lines.

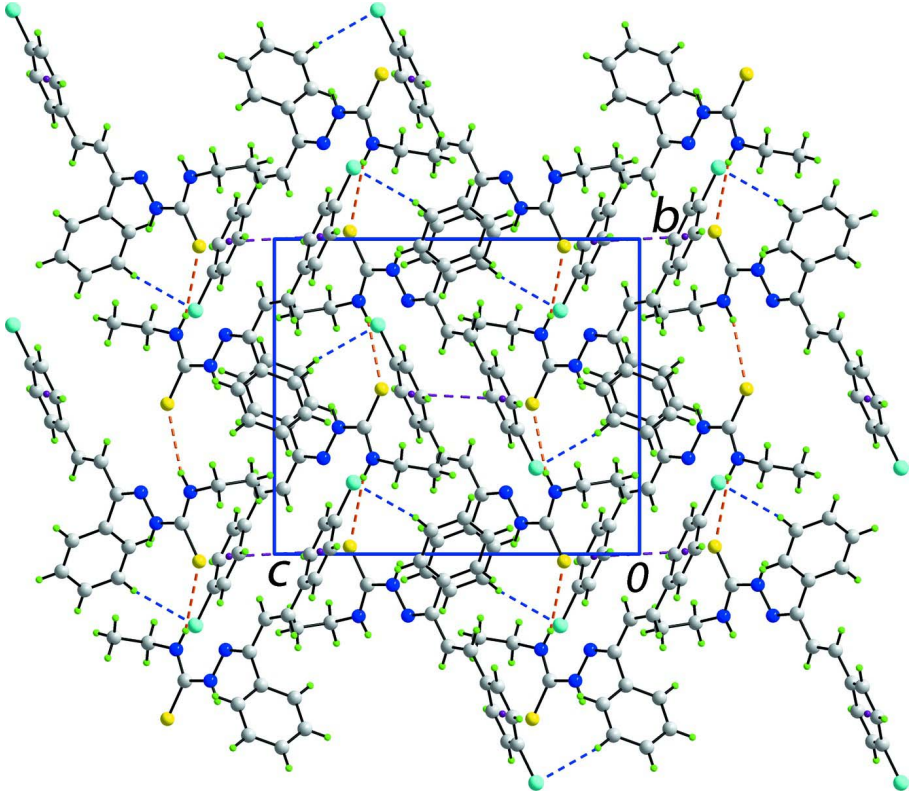

Figure 3

A view of the unit cell contents in projection down the *a* axis. The N—H···S (orange), C—H···Cl (blue) and π—π (purple) interactions are shown as dashed lines.

1-{(*Z*)-[(2*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-ylidene]amino}-3-ethylthiourea

Crystal data

$C_{18}H_{18}ClN_3S$
M_r = 343.86

Monoclinic, $P2_1/c$
a = 10.580 (1) Å

b = 12.0438 (9) Å
c = 13.9561 (10) Å
β = 90.196 (8)°
V = 1778.3 (2) Å^3
Z = 4
$F(000)$ = 720
D_x = 1.284 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2181 reflections
θ = 2.9–27.5°
μ = 0.33 mm^{-1}
T = 293 K
Prism, light-brown
0.20 × 0.15 × 0.10 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4041 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)

T_{min} = 0.800, T_{max} = 1.000
11178 measured reflections
4078 independent reflections
1963 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −13→12
k = −14→15
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.120
S = 1.00
4078 reflections
216 parameters
2 restraints
Hydrogen site location: mixed

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2014), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0044 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
S1	1.05835 (7)	−0.02341 (6)	0.20649 (5)	0.0606 (2)
Cl1	0.48690 (8)	0.72659 (6)	0.71676 (5)	0.0754 (3)
N1	1.0584 (2)	0.19712 (18)	0.23053 (16)	0.0579 (6)
H1N	1.025 (2)	0.2566 (14)	0.2562 (18)	0.070*
N2	0.9246 (2)	0.09776 (16)	0.32430 (15)	0.0543 (6)
H2N	0.900 (2)	0.0320 (11)	0.3439 (17)	0.065*
N3	0.88627 (18)	0.19560 (15)	0.36594 (14)	0.0484 (5)
C1	1.0138 (2)	0.0979 (2)	0.25424 (18)	0.0470 (6)
C2	1.1491 (2)	0.2179 (2)	0.1541 (2)	0.0636 (8)
H2A	1.2065	0.1553	0.1494	0.076*
H2B	1.1986	0.2832	0.1699	0.076*
C3	1.0860 (3)	0.2351 (4)	0.0601 (2)	0.1085 (13)
H3A	1.0393	0.1696	0.0431	0.163*

H3B	1.1485	0.2497	0.0121	0.163*
H3C	1.0292	0.2971	0.0643	0.163*
C4	0.8004 (2)	0.18918 (18)	0.43172 (16)	0.0420 (6)
C5	0.7641 (2)	0.29357 (18)	0.47552 (16)	0.0443 (6)
H5	0.8101	0.3565	0.4592	0.053*
C6	0.6697 (2)	0.30579 (18)	0.53736 (16)	0.0434 (6)
H6	0.6254	0.2419	0.5537	0.052*
C7	0.6281 (2)	0.40943 (18)	0.58244 (16)	0.0409 (6)
C8	0.5030 (2)	0.42061 (19)	0.61122 (16)	0.0463 (6)
H8	0.4477	0.3614	0.6026	0.056*
C9	0.4589 (3)	0.5176 (2)	0.65233 (16)	0.0517 (7)
H9	0.3749	0.5240	0.6708	0.062*
C10	0.5415 (3)	0.60409 (19)	0.66531 (16)	0.0504 (7)
C11	0.6661 (3)	0.5955 (2)	0.63902 (18)	0.0576 (7)
H11	0.7209	0.6548	0.6489	0.069*
C12	0.7099 (3)	0.49840 (19)	0.59786 (18)	0.0529 (7)
H12	0.7943	0.4925	0.5804	0.063*
C41	0.7411 (2)	0.08309 (17)	0.46264 (17)	0.0391 (6)
C42	0.6659 (2)	0.02282 (19)	0.39972 (17)	0.0446 (6)
H42	0.6525	0.0488	0.3377	0.054*
C43	0.6108 (2)	−0.07542 (19)	0.42866 (19)	0.0506 (7)
H43	0.5608	−0.1156	0.3860	0.061*
C44	0.6294 (2)	−0.1139 (2)	0.5200 (2)	0.0550 (7)
H44	0.5916	−0.1799	0.5394	0.066*
C45	0.7037 (2)	−0.0552 (2)	0.58311 (19)	0.0553 (7)
H45	0.7163	−0.0817	0.6450	0.066*
C46	0.7597 (2)	0.0428 (2)	0.55490 (17)	0.0491 (6)
H46	0.8101	0.0821	0.5978	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0614 (5)	0.0544 (4)	0.0661 (5)	0.0084 (3)	0.0204 (4)	−0.0080 (4)
Cl1	0.1222 (7)	0.0502 (4)	0.0539 (4)	0.0289 (4)	0.0068 (4)	−0.0074 (3)
N1	0.0567 (14)	0.0503 (14)	0.0670 (15)	−0.0007 (11)	0.0263 (12)	0.0014 (12)
N2	0.0638 (14)	0.0380 (12)	0.0614 (13)	0.0005 (10)	0.0292 (11)	−0.0016 (11)
N3	0.0531 (12)	0.0375 (11)	0.0548 (12)	0.0017 (9)	0.0176 (11)	−0.0023 (10)
C1	0.0433 (14)	0.0470 (16)	0.0506 (14)	0.0010 (11)	0.0098 (12)	−0.0017 (13)
C2	0.0500 (16)	0.0699 (18)	0.0710 (19)	−0.0065 (13)	0.0207 (15)	0.0061 (16)
C3	0.078 (2)	0.172 (4)	0.076 (2)	−0.021 (2)	0.006 (2)	0.031 (3)
C4	0.0426 (14)	0.0386 (14)	0.0450 (14)	−0.0014 (10)	0.0090 (12)	−0.0001 (12)
C5	0.0482 (15)	0.0349 (13)	0.0500 (14)	−0.0011 (10)	0.0094 (12)	−0.0001 (11)
C6	0.0465 (14)	0.0378 (14)	0.0459 (14)	−0.0015 (10)	0.0062 (12)	−0.0017 (11)
C7	0.0491 (15)	0.0368 (13)	0.0368 (13)	0.0022 (11)	0.0066 (11)	0.0014 (11)
C8	0.0537 (16)	0.0411 (14)	0.0442 (14)	0.0000 (11)	0.0115 (12)	0.0051 (12)
C9	0.0611 (17)	0.0494 (16)	0.0448 (15)	0.0155 (13)	0.0141 (13)	0.0075 (13)
C10	0.079 (2)	0.0373 (14)	0.0348 (13)	0.0122 (13)	0.0034 (13)	−0.0021 (12)
C11	0.0728 (19)	0.0446 (16)	0.0555 (16)	−0.0044 (13)	−0.0035 (15)	−0.0065 (14)

C12	0.0543 (17)	0.0489 (16)	0.0555 (16)	−0.0019 (12)	0.0096 (13)	−0.0080 (13)
C41	0.0404 (13)	0.0342 (13)	0.0427 (14)	0.0028 (10)	0.0110 (11)	−0.0028 (11)
C42	0.0470 (15)	0.0450 (14)	0.0419 (13)	0.0016 (11)	0.0075 (12)	−0.0019 (12)
C43	0.0538 (16)	0.0433 (14)	0.0547 (17)	−0.0066 (12)	0.0098 (13)	−0.0102 (13)
C44	0.0603 (17)	0.0396 (14)	0.0652 (18)	−0.0061 (12)	0.0154 (15)	0.0042 (14)
C45	0.0653 (18)	0.0503 (16)	0.0502 (15)	0.0011 (13)	0.0076 (14)	0.0104 (14)
C46	0.0532 (16)	0.0472 (15)	0.0469 (15)	−0.0046 (12)	0.0003 (12)	−0.0003 (13)

Geometric parameters (Å, º)

S1—C1	1.674 (2)	C7—C8	1.392 (3)
Cl1—C10	1.740 (2)	C7—C12	1.393 (3)
N1—C1	1.327 (3)	C8—C9	1.383 (3)
N1—C2	1.459 (3)	C8—H8	0.9300
N1—H1N	0.874 (10)	C9—C10	1.372 (4)
N2—C1	1.361 (3)	C9—H9	0.9300
N2—N3	1.376 (2)	C10—C11	1.373 (4)
N2—H2N	0.878 (10)	C11—C12	1.384 (3)
N3—C4	1.296 (2)	C11—H11	0.9300
C2—C3	1.484 (4)	C12—H12	0.9300
C2—H2A	0.9700	C41—C42	1.388 (3)
C2—H2B	0.9700	C41—C46	1.389 (3)
C3—H3A	0.9600	C42—C43	1.380 (3)
C3—H3B	0.9600	C42—H42	0.9300
C3—H3C	0.9600	C43—C44	1.370 (3)
C4—C5	1.450 (3)	C43—H43	0.9300
C4—C41	1.488 (3)	C44—C45	1.375 (4)
C5—C6	1.330 (3)	C44—H44	0.9300
C5—H5	0.9300	C45—C46	1.379 (3)
C6—C7	1.466 (3)	C45—H45	0.9300
C6—H6	0.9300	C46—H46	0.9300
C1—N1—C2	124.9 (2)	C9—C8—C7	121.6 (2)
C1—N1—H1N	119.5 (17)	C9—C8—H8	119.2
C2—N1—H1N	115.1 (17)	C7—C8—H8	119.2
C1—N2—N3	120.56 (18)	C10—C9—C8	118.7 (2)
C1—N2—H2N	115.5 (16)	C10—C9—H9	120.6
N3—N2—H2N	123.6 (16)	C8—C9—H9	120.6
C4—N3—N2	117.15 (18)	C9—C10—C11	121.3 (2)
N1—C1—N2	115.3 (2)	C9—C10—Cl1	119.1 (2)
N1—C1—S1	125.86 (17)	C11—C10—Cl1	119.6 (2)
N2—C1—S1	118.80 (17)	C10—C11—C12	119.8 (2)
N1—C2—C3	112.0 (2)	C10—C11—H11	120.1
N1—C2—H2A	109.2	C12—C11—H11	120.1
C3—C2—H2A	109.2	C11—C12—C7	120.4 (2)
N1—C2—H2B	109.2	C11—C12—H12	119.8
C3—C2—H2B	109.2	C7—C12—H12	119.8
H2A—C2—H2B	107.9	C42—C41—C46	118.9 (2)

C2—C3—H3A	109.5	C42—C41—C4	120.5 (2)
C2—C3—H3B	109.5	C46—C41—C4	120.7 (2)
H3A—C3—H3B	109.5	C43—C42—C41	120.3 (2)
C2—C3—H3C	109.5	C43—C42—H42	119.8
H3A—C3—H3C	109.5	C41—C42—H42	119.8
H3B—C3—H3C	109.5	C44—C43—C42	120.2 (2)
N3—C4—C5	115.73 (19)	C44—C43—H43	119.9
N3—C4—C41	123.63 (19)	C42—C43—H43	119.9
C5—C4—C41	120.64 (18)	C43—C44—C45	120.1 (2)
C6—C5—C4	124.7 (2)	C43—C44—H44	119.9
C6—C5—H5	117.6	C45—C44—H44	119.9
C4—C5—H5	117.6	C44—C45—C46	120.2 (2)
C5—C6—C7	126.8 (2)	C44—C45—H45	119.9
C5—C6—H6	116.6	C46—C45—H45	119.9
C7—C6—H6	116.6	C45—C46—C41	120.2 (2)
C8—C7—C12	118.1 (2)	C45—C46—H46	119.9
C8—C7—C6	119.6 (2)	C41—C46—H46	119.9
C12—C7—C6	122.3 (2)		

C1—N2—N3—C4	179.6 (2)	C9—C10—C11—C12	0.5 (4)
C2—N1—C1—N2	−176.5 (2)	Cl1—C10—C11—C12	−179.8 (2)
C2—N1—C1—S1	3.9 (4)	C10—C11—C12—C7	0.3 (4)
N3—N2—C1—N1	−0.2 (4)	C8—C7—C12—C11	−1.2 (4)
N3—N2—C1—S1	179.39 (19)	C6—C7—C12—C11	178.8 (2)
C1—N1—C2—C3	87.9 (4)	N3—C4—C41—C42	−65.7 (3)
N2—N3—C4—C5	178.8 (2)	C5—C4—C41—C42	114.7 (2)
N2—N3—C4—C41	−0.9 (4)	N3—C4—C41—C46	114.5 (3)
N3—C4—C5—C6	173.2 (2)	C5—C4—C41—C46	−65.2 (3)
C41—C4—C5—C6	−7.1 (4)	C46—C41—C42—C43	0.0 (3)
C4—C5—C6—C7	−179.0 (2)	C4—C41—C42—C43	−179.9 (2)
C5—C6—C7—C8	152.8 (2)	C41—C42—C43—C44	0.3 (3)
C5—C6—C7—C12	−27.2 (4)	C42—C43—C44—C45	−0.4 (4)
C12—C7—C8—C9	1.3 (3)	C43—C44—C45—C46	0.1 (4)
C6—C7—C8—C9	−178.7 (2)	C44—C45—C46—C41	0.2 (4)
C7—C8—C9—C10	−0.4 (4)	C42—C41—C46—C45	−0.2 (3)
C8—C9—C10—C11	−0.5 (4)	C4—C41—C46—C45	179.6 (2)
C8—C9—C10—Cl1	179.87 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N3	0.88 (2)	2.25 (2)	2.629 (3)	106 (2)
N1—H1*N*···S1^{i}	0.88 (2)	2.84 (2)	3.693 (2)	165 (2)
C43—H43···Cl1^{ii}	0.93	2.82	3.708 (3)	160

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