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1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-aminium chloride–thiourea (1/1)

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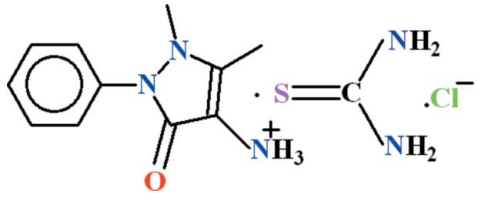
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.111; data-to-parameter ratio = 20.2.

In the title compound, $C_{11}H_{14}N_3O^+\cdot Cl^-\cdot CH_4N_2S$, the components are connected into a two-dimensional polymeric structure parallel to (001) *via* N—H···Cl, N—H···O, N—H···S and C—H···S hydrogen bonds. The dihedral angle between the phenyl and 2,3-dihydro-1*H*-pyrazole rings is 44.96 (7)°.

Related literature

For the structure of 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol- 4-aminium 2-hydroxybenzoate, see: Chitradevi *et al.* (2009).



Experimental

Crystal data

$C_{11}H_{14}N_3O^+\cdot Cl^-\cdot CH_4N_2S$
M_r = 315.82
Monoclinic, $P2_1/c$
a = 9.9733 (11) Å
b = 8.2572 (8) Å
c = 18.859 (2) Å
β = 90.851 (4)°
V = 1552.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 296 K
0.30 × 0.15 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.935, T_{max} = 0.950
14413 measured reflections
3876 independent reflections
2948 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.111
S = 1.02
3876 reflections
192 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···S1^{i}	0.92 (2)	2.28 (2)	3.1619 (17)	159.9 (19)
N3—H3B···O1^{ii}	0.90 (2)	1.87 (2)	2.764 (2)	174 (2)
N3—H3C···Cl1^{iii}	0.952 (19)	2.08 (2)	3.0316 (16)	180 (2)
N4—H4A···Cl1	0.86	2.41	3.2404 (17)	163
N4—H4B···O1^{iv}	0.86	2.12	2.970 (2)	170
N5—H5A···Cl1	0.86	2.74	3.4956 (19)	148
N5—H5A···S1^{v}	0.86	2.87	3.3768 (17)	120
N5—H5B···Cl1^{vi}	0.86	2.56	3.4091 (18)	171
C10—H10B···S1^{vi}	0.96	2.85	3.505 (2)	126

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; 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 *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2395).

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supporting information

Acta Cryst. (2011). E**67**, o2193 [doi:10.1107/S1600536811029989]

1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-aminium chloride–thiourea (1/1)

Shahzad Murtaza, Muhammad Hamza and M. Nawaz Tahir

S1. Comment

The crystal structure of 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol- 4-aminium 2-hydroxybenzoate (Chitradevi *et al.*, 2009) has been published which is related to the title compound (Fig. 1).

The asymmetric unit of title compound consists of three components: 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-aminium cation, chloride ion and thiourea molecule. In cation the phenyl ring A (C1—C6) and 2,3-dihydro-1*H*-pyrazole ring B (N1/N2/C7/C8/C9) are planar with r. m. s. deviations of 0.005 and 0.020 Å. The dihedral angle between A/B is 44.96 (7)°. The attached atoms O1, N3, C10 and C11 are at a distance of -0.122 (3), 0.005 (3), 0.034 (3) and 0.513 (3) Å respectively, from the mean plane of B. The thiourea molecule (S1/C12/N4/N5) is planar with r.m.s. deviations of 0.003 Å. There exist intermolecular hydrogen bonds of N–H···Cl, N–H···O, N–H···S and C–H···S types (Table 1, Fig. 2). The crystal components are connected by hydrogen bonds into infinite two dimensional polymeric network parallel to (0 0 1)

S2. Experimental

4-Aminophenazone (0.203 g, 1.0 mmol) and thiourea (0.076 g, 1.0 mmol) were dissolved in ethanol (15 ml) and the mixture was acidified by 1 N HCl. The mixture was refluxed for one hour and solvent was evaporated on rotary evaporator to almost dryness. The crude product was recrystallized from ethanol yielding light yellow needles of the title compound.

S3. Refinement

The coordinates of of NH_3 group H atoms were refined. Other H atoms were positioned geometrically (N—H = 0.86, C–H = 0.93–0.96 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) = xU_{eq}(C, N), where x = 1.5 for CH_3 and NH_3 and x = 1.2 for other H-atoms.

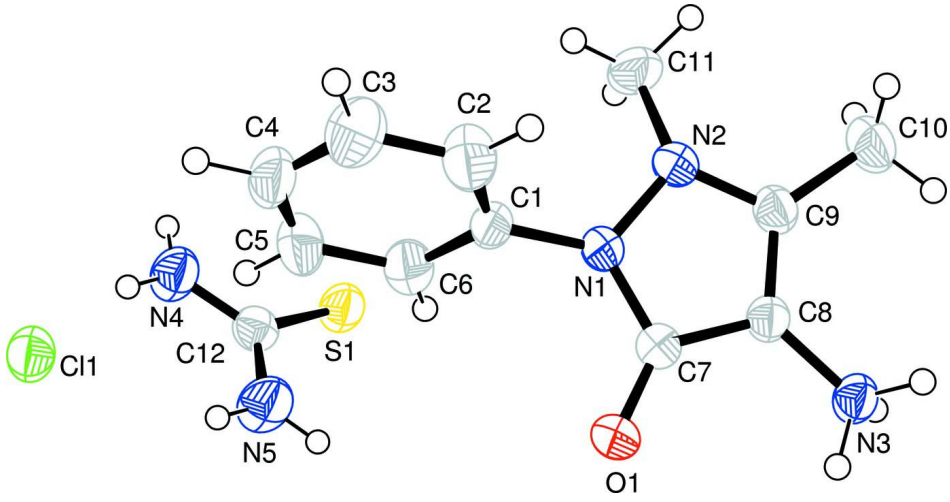

Figure 1

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

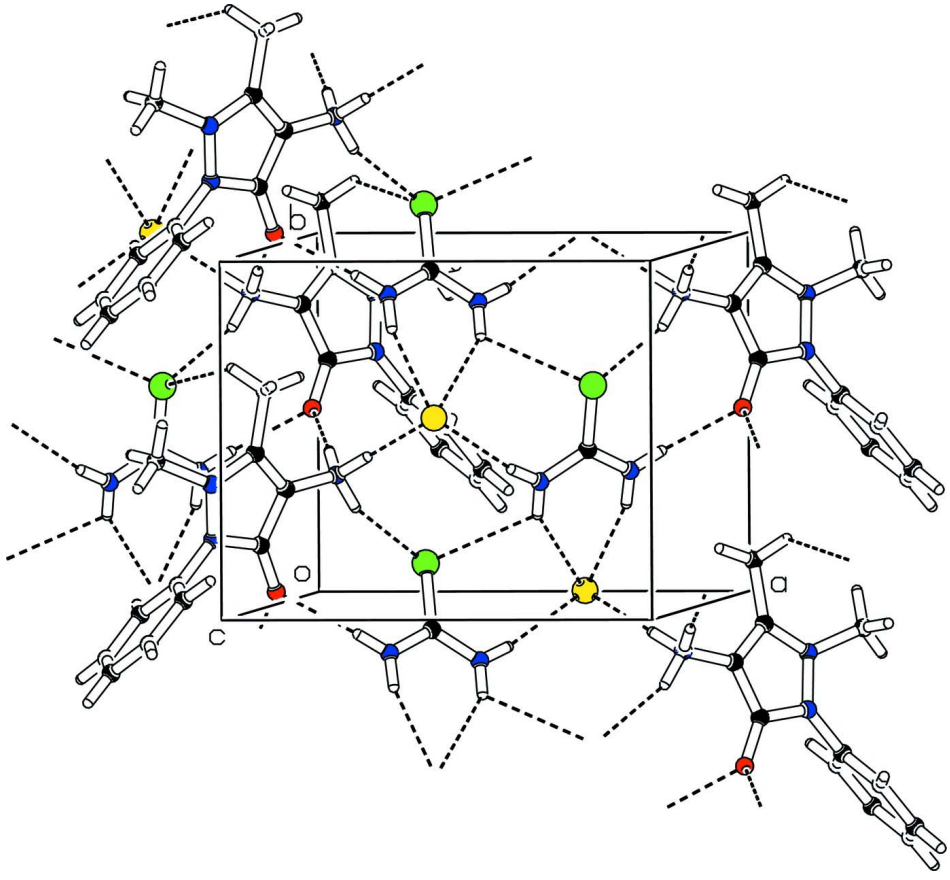

Figure 2

The partial packing (*PLATON*; Spek, 2009) showing hydrogen-bond interactions.

1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-aminium chloride– thiourea (1/1)

Crystal data

$C_{11}H_{14}N_3O^+·Cl^-·CH_4N_2S$
M_r = 315.82
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.9733 (11) Å
b = 8.2572 (8) Å
c = 18.859 (2) Å
β = 90.851 (4)°
V = 1552.9 (3) Å^3
Z = 4
$F(000)$ = 664
D_x = 1.351 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2948 reflections
θ = 2.0–28.4°
μ = 0.38 mm^{-1}
T = 296 K
Needle, light yellow
0.30 × 0.15 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 7.50 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.935, T_{max} = 0.950
14413 measured reflections
3876 independent reflections
2948 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 28.4°, θ_{min} = 2.0°
h = −13→12
k = −10→6
l = −24→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.111
S = 1.02
3876 reflections
192 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
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.4062P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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}
O1	0.02683 (12)	0.52568 (13)	0.17891 (7)	0.0429 (4)
N1	0.15623 (14)	0.67708 (15)	0.10210 (8)	0.0380 (4)
N2	0.15254 (14)	0.83360 (15)	0.07471 (8)	0.0395 (5)
N3	−0.10897 (15)	0.84880 (18)	0.20387 (9)	0.0369 (5)

C1	0.22930 (16)	0.55157 (19)	0.06724 (9)	0.0365 (5)
C2	0.2008 (2)	0.5159 (2)	−0.00289 (11)	0.0539 (7)
C3	0.2738 (2)	0.3964 (3)	−0.03623 (12)	0.0631 (8)
C4	0.3709 (2)	0.3132 (2)	0.00038 (13)	0.0568 (7)
C5	0.3968 (2)	0.3477 (3)	0.07011 (13)	0.0587 (7)
C6	0.3260 (2)	0.4689 (2)	0.10411 (11)	0.0488 (6)
C7	0.05681 (16)	0.65825 (18)	0.15067 (9)	0.0335 (5)
C8	−0.00154 (15)	0.81326 (18)	0.15630 (9)	0.0328 (4)
C9	0.05869 (16)	0.91713 (19)	0.11086 (9)	0.0360 (5)
C10	0.0318 (2)	1.0926 (2)	0.09755 (12)	0.0506 (6)
C11	0.2742 (2)	0.9003 (2)	0.04478 (12)	0.0528 (7)
S1	0.70196 (5)	0.59619 (6)	0.27908 (3)	0.0490 (2)
N4	0.76836 (16)	0.35228 (19)	0.19593 (9)	0.0531 (6)
N5	0.57194 (16)	0.3262 (2)	0.25376 (10)	0.0579 (6)
C12	0.67972 (17)	0.4139 (2)	0.24001 (10)	0.0398 (5)
Cl1	0.64868 (5)	0.01267 (5)	0.13661 (3)	0.0476 (2)
H2	0.13349	0.57146	−0.02737	0.0647*
H3	0.25677	0.37259	−0.08371	0.0758*
H3A	−0.148 (2)	0.757 (3)	0.2222 (10)	0.0554*
H3B	−0.084 (2)	0.913 (3)	0.2403 (12)	0.0554*
H3C	−0.185 (2)	0.900 (2)	0.1825 (11)	0.0554*
H4	0.41951	0.23278	−0.02225	0.0681*
H5	0.46218	0.28957	0.09489	0.0704*
H6	0.34432	0.49342	0.15140	0.0586*
H10A	0.00647	1.10791	0.04870	0.0759*
H10B	0.11123	1.15417	0.10810	0.0759*
H10C	−0.03966	1.12835	0.12730	0.0759*
H11A	0.34012	0.91528	0.08178	0.0791*
H11B	0.25437	1.00266	0.02288	0.0791*
H11C	0.30826	0.82695	0.00990	0.0791*
H4A	0.75487	0.25846	0.17735	0.0637*
H4B	0.83942	0.40608	0.18589	0.0637*
H5A	0.56147	0.23283	0.23429	0.0695*
H5B	0.51243	0.36276	0.28217	0.0695*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0447 (7)	0.0331 (6)	0.0512 (7)	0.0023 (5)	0.0121 (6)	0.0107 (5)
N1	0.0424 (8)	0.0269 (7)	0.0450 (8)	0.0047 (5)	0.0125 (7)	0.0051 (6)
N2	0.0432 (8)	0.0291 (7)	0.0466 (9)	0.0016 (6)	0.0112 (7)	0.0070 (6)
N3	0.0362 (8)	0.0326 (7)	0.0421 (9)	0.0020 (6)	0.0066 (6)	−0.0039 (6)
C1	0.0348 (8)	0.0302 (7)	0.0449 (10)	0.0017 (6)	0.0116 (7)	0.0002 (7)
C2	0.0556 (12)	0.0522 (11)	0.0538 (12)	0.0118 (9)	−0.0051 (10)	−0.0050 (9)
C3	0.0764 (15)	0.0585 (13)	0.0547 (13)	0.0047 (11)	0.0069 (11)	−0.0174 (10)
C4	0.0596 (12)	0.0352 (9)	0.0763 (15)	0.0044 (9)	0.0263 (11)	−0.0066 (9)
C5	0.0512 (12)	0.0495 (11)	0.0755 (15)	0.0192 (9)	0.0085 (11)	0.0085 (10)
C6	0.0506 (11)	0.0476 (10)	0.0483 (11)	0.0100 (8)	0.0030 (9)	0.0026 (8)

C7	0.0335 (8)	0.0326 (8)	0.0343 (8)	0.0014 (6)	0.0021 (7)	0.0020 (6)
C8	0.0318 (8)	0.0305 (7)	0.0362 (8)	0.0016 (6)	0.0025 (7)	−0.0008 (6)
C9	0.0373 (9)	0.0298 (8)	0.0410 (9)	0.0020 (6)	0.0008 (7)	0.0006 (7)
C10	0.0546 (11)	0.0319 (9)	0.0655 (13)	0.0052 (8)	0.0041 (10)	0.0057 (8)
C11	0.0569 (12)	0.0411 (10)	0.0610 (13)	−0.0050 (8)	0.0257 (10)	0.0052 (9)
S1	0.0444 (3)	0.0403 (3)	0.0627 (3)	−0.0045 (2)	0.0134 (2)	−0.0056 (2)
N4	0.0495 (9)	0.0461 (9)	0.0641 (11)	−0.0048 (7)	0.0135 (8)	−0.0113 (8)
N5	0.0479 (9)	0.0522 (10)	0.0740 (12)	−0.0143 (8)	0.0133 (9)	−0.0110 (9)
C12	0.0366 (9)	0.0402 (9)	0.0426 (10)	−0.0004 (7)	−0.0018 (7)	0.0038 (7)
Cl1	0.0445 (3)	0.0443 (3)	0.0542 (3)	0.0060 (2)	0.0050 (2)	−0.0028 (2)

Geometric parameters (Å, º)

S1—C12	1.6891 (18)	C2—C3	1.383 (3)
O1—C7	1.2554 (19)	C3—C4	1.366 (3)
N1—C1	1.432 (2)	C4—C5	1.366 (3)
N1—C7	1.369 (2)	C5—C6	1.387 (3)
N1—N2	1.3921 (18)	C7—C8	1.411 (2)
N2—C9	1.355 (2)	C8—C9	1.359 (2)
N2—C11	1.454 (2)	C9—C10	1.494 (2)
N3—C8	1.438 (2)	C2—H2	0.9300
N3—H3B	0.90 (2)	C3—H3	0.9300
N3—H3A	0.92 (2)	C4—H4	0.9300
N3—H3C	0.952 (19)	C5—H5	0.9300
N4—C12	1.324 (2)	C6—H6	0.9300
N5—C12	1.325 (2)	C10—H10A	0.9600
N4—H4A	0.8600	C10—H10B	0.9600
N4—H4B	0.8600	C10—H10C	0.9600
N5—H5B	0.8600	C11—H11A	0.9600
N5—H5A	0.8600	C11—H11B	0.9600
C1—C2	1.380 (3)	C11—H11C	0.9600
C1—C6	1.364 (3)		
N2—N1—C1	120.81 (14)	C7—C8—C9	109.79 (14)
N2—N1—C7	109.78 (12)	N3—C8—C9	127.24 (14)
C1—N1—C7	127.13 (13)	N2—C9—C8	108.13 (14)
N1—N2—C9	107.49 (13)	C8—C9—C10	129.66 (16)
N1—N2—C11	118.56 (13)	N2—C9—C10	122.19 (15)
C9—N2—C11	126.10 (13)	C1—C2—H2	120.00
H3B—N3—H3C	105.7 (18)	C3—C2—H2	120.00
C8—N3—H3C	115.0 (13)	C2—C3—H3	120.00
C8—N3—H3A	112.9 (14)	C4—C3—H3	120.00
C8—N3—H3B	113.3 (13)	C5—C4—H4	120.00
H3A—N3—H3B	108.2 (19)	C3—C4—H4	120.00
H3A—N3—H3C	100.7 (17)	C4—C5—H5	120.00
H4A—N4—H4B	120.00	C6—C5—H5	120.00
C12—N4—H4A	120.00	C5—C6—H6	120.00
C12—N4—H4B	120.00	C1—C6—H6	120.00

H5A—N5—H5B	120.00	H10B—C10—H10C	109.00
C12—N5—H5A	120.00	C9—C10—H10C	109.00
C12—N5—H5B	120.00	C9—C10—H10A	109.00
N1—C1—C6	119.27 (16)	C9—C10—H10B	109.00
C2—C1—C6	121.05 (16)	H10A—C10—H10B	110.00
N1—C1—C2	119.68 (15)	H10A—C10—H10C	109.00
C1—C2—C3	119.05 (18)	N2—C11—H11B	109.00
C2—C3—C4	120.2 (2)	N2—C11—H11A	109.00
C3—C4—C5	120.3 (2)	H11A—C11—H11C	110.00
C4—C5—C6	120.3 (2)	N2—C11—H11C	109.00
C1—C6—C5	119.10 (19)	H11A—C11—H11B	110.00
N1—C7—C8	104.54 (13)	H11B—C11—H11C	109.00
O1—C7—C8	131.16 (15)	N4—C12—N5	117.65 (16)
O1—C7—N1	124.22 (14)	S1—C12—N4	122.12 (13)
N3—C8—C7	122.97 (14)	S1—C12—N5	120.22 (14)

C1—N1—N2—C9	169.48 (14)	N1—C1—C2—C3	178.85 (17)
C1—N1—N2—C11	−39.5 (2)	C6—C1—C2—C3	−1.3 (3)
C7—N1—N2—C9	5.48 (18)	C2—C1—C6—C5	0.3 (3)
C7—N1—N2—C11	156.51 (16)	N1—C1—C6—C5	−179.83 (17)
N2—N1—C1—C2	−56.2 (2)	C1—C2—C3—C4	1.2 (3)
C7—N1—C1—C2	104.8 (2)	C2—C3—C4—C5	−0.2 (3)
N2—N1—C1—C6	123.92 (17)	C3—C4—C5—C6	−0.9 (3)
C7—N1—C1—C6	−75.1 (2)	C4—C5—C6—C1	0.8 (3)
N2—N1—C7—C8	−4.53 (18)	O1—C7—C8—N3	5.1 (3)
N2—N1—C7—O1	172.53 (15)	O1—C7—C8—C9	−174.75 (18)
C1—N1—C7—O1	9.8 (3)	N1—C7—C8—N3	−178.19 (15)
C1—N1—C7—C8	−167.26 (15)	N1—C7—C8—C9	2.02 (19)
N1—N2—C9—C10	177.29 (16)	N3—C8—C9—C10	0.0 (3)
N1—N2—C9—C8	−4.06 (18)	C7—C8—C9—N2	1.30 (19)
C11—N2—C9—C8	−152.29 (17)	C7—C8—C9—C10	179.82 (18)
C11—N2—C9—C10	29.1 (3)	N3—C8—C9—N2	−178.49 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···S1^{i}	0.92 (2)	2.28 (2)	3.1619 (17)	159.9 (19)
N3—H3*B*···O1^{ii}	0.90 (2)	1.87 (2)	2.764 (2)	174 (2)
N3—H3*C*···Cl1^{iii}	0.952 (19)	2.08 (2)	3.0316 (16)	180 (2)
N4—H4*A*···Cl1	0.86	2.41	3.2404 (17)	163
N4—H4*B*···O1^{iv}	0.86	2.12	2.970 (2)	170
N5—H5*A*···Cl1	0.86	2.74	3.4956 (19)	148
N5—H5*A*···S1^{v}	0.86	2.87	3.3768 (17)	120
N5—H5*B*···Cl1^{vi}	0.86	2.56	3.4091 (18)	171
C10—H10*B*···S1^{vi}	0.96	2.85	3.505 (2)	126

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