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2-(4-Chlorobenzoyl)-1-(diaminomethylene)hydrazinium chloride monohydrate

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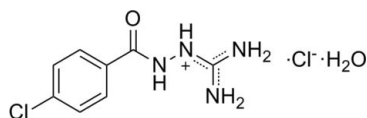
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.063; wR factor = 0.142; data-to-parameter ratio = 16.1.

In the cation of the title compound, $\text{C}_8\text{H}_{10}\text{ClN}_4\text{O}^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$, the guanidinium group is planar (maximum deviation = 0.0001 Å) and nearly perpendicular to carboxamide group, making a dihedral angle of 87.0 (3)°. The N atoms of the guanidine fragment have a planar trigonal configuration and the N atom of the carboxamide group adopts a pyramidal configuration. In the crystal structure, intermolecular N—H...O, N—H...Cl and O—H...Cl hydrogen bonds link the cations, anions and water molecules into layers parallel to the bc plane.

Related literature

For a related structure, see: Kolev & Petrova (2003). For aminoguanidine structures, see: Bharatam *et al.* (2004); Koskinen *et al.* (1997); Hammerl *et al.* (2005); Macháčková *et al.* (2007); Murugavel *et al.* (2009a,b). For the preparation of guanyl hydrazides, see: Grinstein & Chipen (1961). For the application of guanyl hydrazides in the synthesis of 3-substituted 5-amino-1,2,4-triazoles, see: Dolzhenko *et al.* (2009).



Experimental

Crystal data

 $\text{C}_8\text{H}_{10}\text{ClN}_4\text{O}^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$ $M_r = 267.12$ Monoclinic, $P2_1/c$ $a = 19.349$ (4) Å $b = 4.3563$ (9) Å $c = 14.516$ (3) Å $\beta = 102.360$ (3)° $V = 1195.2$ (4) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.54$ mm⁻¹ $T = 100$ K

0.40 × 0.30 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2004)

 $T_{\min} = 0.814$, $T_{\max} = 0.924$

9756 measured reflections

2330 independent reflections

2099 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.063$ $wR(F^2) = 0.142$ $S = 1.17$

2330 reflections

145 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.79$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl2}^i$	0.90	2.36	3.194 (4)	154
$\text{N2}-\text{H2}\cdots\text{O1W}$	0.90	2.24	3.031 (4)	146
$\text{N2}-\text{H2}\cdots\text{Cl2}^{ii}$	0.90	2.71	3.260 (4)	121
$\text{N3}-\text{H3B}\cdots\text{O1}^{iii}$	0.90	1.96	2.848 (3)	167
$\text{N3}-\text{H3A}\cdots\text{Cl2}^{iv}$	0.90	2.43	3.280 (4)	157
$\text{N4}-\text{H4B}\cdots\text{O1W}$	0.90	2.04	2.834 (4)	147
$\text{N4}-\text{H4A}\cdots\text{Cl2}^{iv}$	0.90	2.44	3.286 (4)	156
$\text{O1W}-\text{H1W}\cdots\text{Cl2}^v$	0.85	2.58	3.292 (4)	142
$\text{O1W}-\text{H2W}\cdots\text{Cl2}$	0.85	2.30	3.134 (4)	164

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2005); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL (Sheldrick, 2008), publCIF (Westrip, 2010) and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2710).

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supporting information

Acta Cryst. (2010). E66, o1152–o1153 [https://doi.org/10.1107/S1600536810014108]

2-(4-Chlorobenzoyl)-1-(diaminomethylene)hydrazinium chloride monohydrate

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S1. Comment

Carboxylic acids guanyl hydrazides are important starting compounds for the preparation of 3-substituted 5-amino-1,2,4-triazoles (Dolzhenko *et al.*, 2009). Until the present time, the crystal structure of guanyl hydrazides was investigated only for the zwitterionic 2-guanyl hydrazide of carbonic acid (Kolev & Petrova, 2003), which previously was considered as aminoguanidine hydrogen carbonate. Here we report the crystal structure of the title compound.

Carboxylic acids guanyl hydrazides can be regarded as acylated aminoguanidines. Therefore, by analogy with protonated aminoguanidine, it is possible to assume the existence of tautomeric forms **A–C** (Fig. 1) for the title compound. In addition, the presence of acyl group makes it possible of tautomers **D–G**, the **B–G** forms can exist as *cis*- and *trans*-isomers. Quantum chemical calculations predict the tautomer **A** is to be the more stable for aminoguanidine (Bharatam *et al.*, 2004). This prediction is corroborated by X-ray analyses of aminoguanidine salts (Hammerl *et al.*, 2005; Koskinen *et al.*, 1997; Macháčková *et al.*, 2007; Murugavel *et al.*, 2009a,b).

According to our X-ray investigation, the 4-chlorobenzoic acid 2-guanyl hydrazide hydrochloride monohydrate in the crystal exists as tautomer **A** (Fig. 2), similarly to aminoguanidine salts. Guanidine fragment (N2/N3/N4/C1) of the molecule is planar. The N1 atom has a trigonal-pyramidal configuration (the sum of bond angles centered on the N1 atom is 354.9° and deviates from the guanidine plane by 0.181 (6) Å. In accordance with the structure of carbonic acid 2-guanylhazide (Kolev & Petrova, 2003), carbonyl group is almost perpendicular to the plane of guanidine fragment (dihedral angle between the guanidine and O1/C2/N1 planes amounts 87.0 (3)°). The bonds C1–N3 and C1–N4 have lengths of 1.321 (5) and 1.324 (5) Å, respectively, close to the analogous bonds in aminoguanidine cation, though the C1–N2 bond is somewhat longer – 1.343 (5) Å instead of 1.325–1.341 Å (Hammerl *et al.*, 2005; Koskinen *et al.*, 1997; Macháčková *et al.*, 2007; Murugavel *et al.*, 2009a,b). Apparently, it indicates decrease of π -electron delocalization in the guanidine fragment of the studied molecule in relation to the aminoguanidine and guanidine cations (Bharatam *et al.*, 2004). The N1–N2 bond length of 1.379 (4) Å is essentially equal to the length of analogous bond in the zwitterionic 2-guanyl hydrazide of carbonic acid (1.382 (1) Å, Kolev & Petrova, 2003) and slightly shorter than in aminoguanidine salts (1.396–1.414 Å) (Hammerl *et al.*, 2005; Koskinen *et al.*, 1997; Macháčková *et al.*, 2007; Murugavel *et al.*, 2009a,b). The negative inductive effect of carbonyl group and decrease in π -electron delocalization result in considerable reduction of basicity of the 4-chlorobenzoic acid 2-guanyl hydrazide in comparison with the aminoguanidine. Thus, we obtained the $pK_a = 7.85 \pm 0.04$ by potentiometric titration of the title compound with 0.1 M aqueous potassium hydroxide, whereas the $pK_a = 11.5 \pm 0.1$ was reported for the aminoguanidine (Koskinen *et al.*, 1997).

The crystal packing is shown in Fig. 3. The $C_8H_{10}ClN_4O$ cations form stacks along the *b* axis of the monoclinic cell. In the neighbouring stacks along the *c* axis the cations are related by a glide-reflection plane which is perpendicular to [0, 1, 0] with glide component [0, 0, 1/2]. Along the *a* axis the $C_8H_{10}ClN_4O$ cations of the neighbouring stacks are turned from each other by 180° and displaced on 0.5 of cell parameter in direction of the *b* axis, i.e. they are space related by the 2-fold screw axes with direction [0, 1, 0] at 0, *y*, 1/4 with screw component [0, 1/2, 0]. In the stacks the adjacent cations are

connected with each other by the $N3-H3B \cdots O1^{iii}$ hydrogen bonds. The rows of chloride anions and water molecules are localized between the stacks of $C_8H_{10}ClN_4O$ cations close to the guanidine fragments. Chloride anions additionally stabilize the location of $C_8H_{10}ClN_4O$ cations in the stacks by means of two groups of hydrogen bonds (Table 1): the $N1-H1 \cdots Cl2^i$ and $N2-H2 \cdots Cl2^{ii}$, the $N3-H3A \cdots Cl2^{iv}$ and $N4-H4A \cdots Cl2^{iv}$. As a result, equally oriented stacks of the cations form layers along the c axis with identity period equal to the unit cell parameter c . The rows of water molecules are ordered along the b axis by means of the hydrogen bonds $N2-H2 \cdots O1W$, $N4-H4B \cdots O1W$, $O1W-H1W \cdots Cl2^v$ and $O1W-H2W \cdots Cl2$. Thereby, the $C_8H_{10}ClN_4O$ cations, water molecules and chloride anions form a rigid three-dimensional framework in the crystal.

S2. Experimental

4-Chlorobenzoic acid 2-guanyl hydrazide hydrochloride monohydrate was prepared by fusion of 4-chlorobenzoyl chloride with aminoguanidine hydrochloride according to Grinstein & Chipen (1961). The crystals suitable for crystallographic analysis were grown by recrystallization from water-ethanol 1:1 mixture.

S3. Refinement

C-bound H atoms were positioned geometrically ($C-H$ 0.93 Å), while the rest H atoms were located on difference map and further placed in idealized positions ($N-H$ 0.90 Å, $O-H$ 0.85 Å). All H atoms were refined as riding on their parent atoms, with $U_{iso}(H) = 1.2-1.5 U_{eq}(\text{parent atom})$.

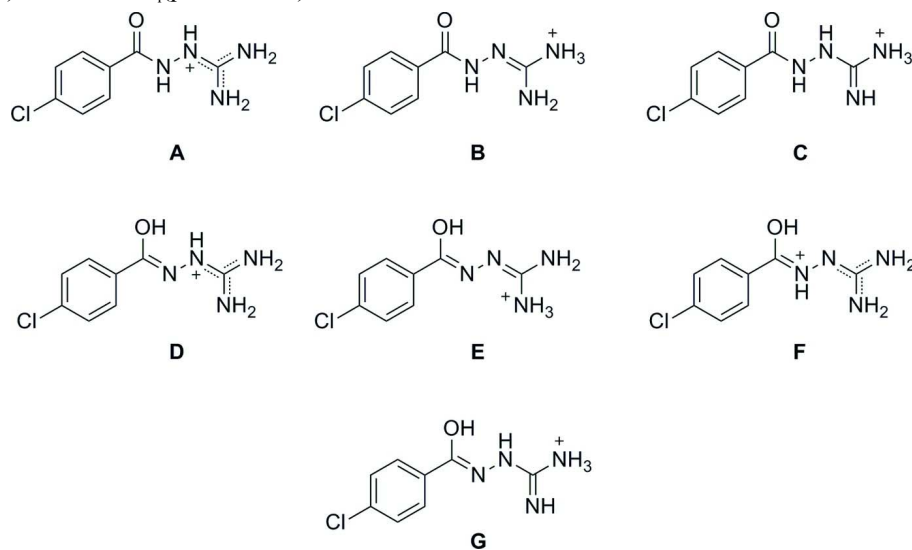


Figure 1

Possible tautomeric forms for 2-guanylhydrazide of 4-chlorobenzoic acid.

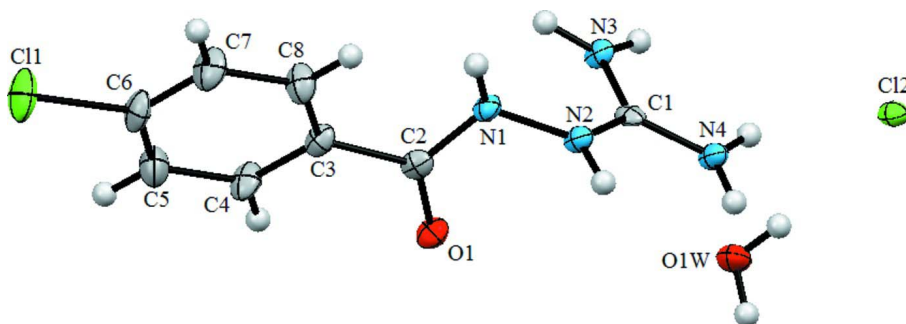


Figure 2

The molecular structure of 4-chlorobenzoyl-1-(diaminomethylene)hydrazinium chloride monohydrate with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

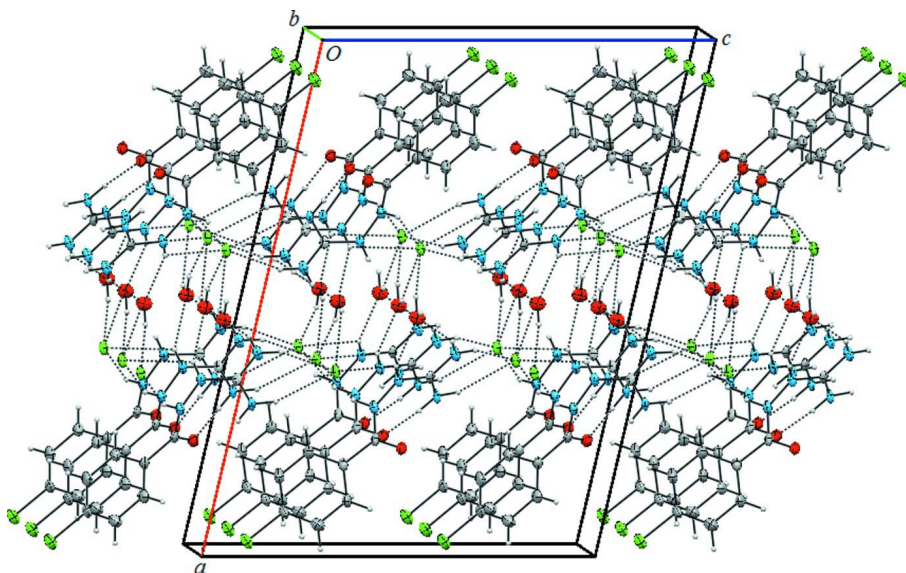


Figure 3

Molecular packing in the crystal, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

2-(4-chlorobenzoyl)-1-(diaminomethylene)hydrazinium chloride monohydrate

Crystal data

$C_8H_{10}ClN_4O^+ \cdot Cl^- \cdot H_2O$

$M_r = 267.12$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 19.349 (4) \text{ \AA}$

$b = 4.3563 (9) \text{ \AA}$

$c = 14.516 (3) \text{ \AA}$

$\beta = 102.360 (3)^\circ$

$V = 1195.2 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 552$

$D_x = 1.484 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 195 reflections

$\theta = 3\text{--}25^\circ$

$\mu = 0.54 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Plate, colourless

$0.40 \times 0.30 \times 0.15 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2004)
 $T_{\min} = 0.814$, $T_{\max} = 0.924$

9756 measured reflections
2330 independent reflections
2099 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -23 \rightarrow 23$
 $k = -5 \rightarrow 5$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.142$
 $S = 1.17$
2330 reflections
145 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 7.6548P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

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.

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.04674 (6)	0.7630 (4)	0.43499 (8)	0.0378 (3)
C12	0.61291 (5)	0.8080 (2)	0.16436 (7)	0.0176 (2)
O1	0.23490 (15)	0.4393 (7)	0.1141 (2)	0.0206 (6)
N1	0.30500 (17)	0.8203 (8)	0.1875 (2)	0.0167 (7)
H1	0.3168	0.9410	0.2387	0.020*
N2	0.36010 (18)	0.7335 (8)	0.1466 (2)	0.0168 (7)
H2	0.3904	0.5813	0.1693	0.020*
N3	0.32072 (18)	1.0675 (8)	0.0221 (2)	0.0170 (7)
H3B	0.2901	1.1579	0.0524	0.020*
H3A	0.3270	1.1318	-0.0344	0.020*
N4	0.41145 (18)	0.7296 (8)	0.0186 (2)	0.0191 (8)
H4B	0.4390	0.5690	0.0416	0.023*
H4A	0.4156	0.8225	-0.0354	0.023*
C1	0.3636 (2)	0.8462 (9)	0.0616 (3)	0.0151 (8)
C2	0.2468 (2)	0.6400 (10)	0.1752 (3)	0.0167 (8)
C3	0.1974 (2)	0.6938 (10)	0.2392 (3)	0.0189 (9)

C4	0.1303 (2)	0.5694 (12)	0.2146 (3)	0.0255 (10)
H4	0.1166	0.4678	0.1573	0.031*
C5	0.0832 (2)	0.5933 (12)	0.2738 (3)	0.0288 (11)
H5	0.0379	0.5112	0.2564	0.035*
C6	0.1048 (2)	0.7415 (12)	0.3591 (3)	0.0248 (10)
C7	0.1710 (2)	0.8685 (12)	0.3853 (3)	0.0294 (11)
H7	0.1843	0.9706	0.4426	0.035*
C8	0.2176 (2)	0.8438 (12)	0.3260 (3)	0.0253 (10)
H8	0.2627	0.9273	0.3437	0.030*
O1W	0.48997 (16)	0.3347 (7)	0.1577 (2)	0.0256 (7)
H1W	0.5036	0.1484	0.1625	0.038*
H2W	0.5283	0.4382	0.1677	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0308 (6)	0.0615 (9)	0.0261 (6)	0.0026 (6)	0.0171 (5)	−0.0009 (6)
C12	0.0268 (5)	0.0130 (4)	0.0146 (5)	0.0001 (4)	0.0079 (4)	0.0004 (4)
O1	0.0231 (15)	0.0225 (16)	0.0159 (14)	0.0020 (13)	0.0038 (11)	−0.0030 (13)
N1	0.0226 (17)	0.0160 (17)	0.0134 (16)	0.0018 (15)	0.0078 (13)	−0.0013 (14)
N2	0.0253 (18)	0.0142 (17)	0.0126 (16)	0.0030 (14)	0.0079 (13)	0.0017 (13)
N3	0.0267 (18)	0.0169 (17)	0.0094 (15)	0.0041 (15)	0.0083 (13)	0.0026 (14)
N4	0.0297 (19)	0.0139 (17)	0.0172 (17)	0.0031 (15)	0.0125 (14)	0.0020 (14)
C1	0.022 (2)	0.0111 (19)	0.0118 (18)	−0.0043 (16)	0.0037 (15)	−0.0046 (15)
C2	0.023 (2)	0.017 (2)	0.0103 (18)	0.0039 (17)	0.0025 (15)	0.0039 (16)
C3	0.023 (2)	0.022 (2)	0.0126 (19)	0.0048 (18)	0.0052 (16)	0.0013 (17)
C4	0.024 (2)	0.035 (3)	0.017 (2)	0.000 (2)	0.0056 (17)	−0.011 (2)
C5	0.022 (2)	0.038 (3)	0.029 (2)	−0.002 (2)	0.0102 (18)	−0.002 (2)
C6	0.024 (2)	0.037 (3)	0.016 (2)	0.007 (2)	0.0109 (17)	0.0046 (19)
C7	0.032 (2)	0.042 (3)	0.016 (2)	0.001 (2)	0.0092 (18)	−0.006 (2)
C8	0.024 (2)	0.037 (3)	0.016 (2)	−0.004 (2)	0.0059 (17)	−0.0025 (19)
O1W	0.0256 (16)	0.0157 (15)	0.0359 (18)	0.0004 (13)	0.0076 (13)	0.0033 (14)

Geometric parameters (Å, °)

C11—C6	1.736 (4)	C2—C3	1.488 (5)
O1—C2	1.232 (5)	C3—C4	1.381 (6)
N1—C2	1.352 (5)	C3—C8	1.398 (6)
N1—N2	1.379 (4)	C4—C5	1.384 (6)
N1—H1	0.8999	C4—H4	0.9300
N2—C1	1.343 (5)	C5—C6	1.380 (7)
N2—H2	0.9001	C5—H5	0.9300
N3—C1	1.321 (5)	C6—C7	1.373 (7)
N3—H3B	0.9002	C7—C8	1.377 (6)
N3—H3A	0.9000	C7—H7	0.9300
N4—C1	1.324 (5)	C8—H8	0.9300
N4—H4B	0.8999	O1W—H1W	0.8517
N4—H4A	0.9002	O1W—H2W	0.8542

C2—N1—N2	118.8 (3)	C4—C3—C2	118.1 (4)
C2—N1—H1	120.3	C8—C3—C2	122.8 (4)
N2—N1—H1	115.6	C3—C4—C5	121.2 (4)
C1—N2—N1	119.4 (3)	C3—C4—H4	119.4
C1—N2—H2	116.6	C5—C4—H4	119.4
N1—N2—H2	123.2	C6—C5—C4	118.6 (4)
C1—N3—H3B	121.8	C6—C5—H5	120.7
C1—N3—H3A	115.4	C4—C5—H5	120.7
H3B—N3—H3A	122.7	C7—C6—C5	121.5 (4)
C1—N4—H4B	122.8	C7—C6—C11	119.7 (3)
C1—N4—H4A	116.1	C5—C6—C11	118.8 (4)
H4B—N4—H4A	121.1	C6—C7—C8	119.5 (4)
N3—C1—N4	120.9 (4)	C6—C7—H7	120.2
N3—C1—N2	121.0 (4)	C8—C7—H7	120.2
N4—C1—N2	118.2 (4)	C7—C8—C3	120.3 (4)
O1—C2—N1	122.0 (4)	C7—C8—H8	119.8
O1—C2—C3	121.0 (4)	C3—C8—H8	119.8
N1—C2—C3	117.1 (4)	H1W—O1W—H2W	104.3
C4—C3—C8	118.9 (4)		
C2—N1—N2—C1	94.5 (4)	C2—C3—C4—C5	175.8 (4)
N1—N2—C1—N3	8.8 (6)	C3—C4—C5—C6	-0.8 (8)
N1—N2—C1—N4	-171.3 (3)	C4—C5—C6—C7	1.1 (8)
N2—N1—C2—O1	-15.4 (6)	C4—C5—C6—C11	-178.3 (4)
N2—N1—C2—C3	164.5 (3)	C5—C6—C7—C8	-1.1 (8)
O1—C2—C3—C4	-15.6 (6)	C11—C6—C7—C8	178.3 (4)
N1—C2—C3—C4	164.5 (4)	C6—C7—C8—C3	0.8 (8)
O1—C2—C3—C8	159.5 (4)	C4—C3—C8—C7	-0.5 (7)
N1—C2—C3—C8	-20.5 (6)	C2—C3—C8—C7	-175.5 (4)
C8—C3—C4—C5	0.5 (7)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots Cl2 ⁱ	0.90	2.36	3.194 (4)	154
N2—H2 \cdots O1W	0.90	2.24	3.031 (4)	146
N2—H2 \cdots Cl2 ⁱⁱ	0.90	2.71	3.260 (4)	121
N3—H3B \cdots O1 ⁱⁱⁱ	0.90	1.96	2.848 (3)	167
N3—H3A \cdots Cl2 ^{iv}	0.90	2.43	3.280 (4)	157
N4—H4B \cdots O1W	0.90	2.04	2.834 (4)	147
N4—H4A \cdots Cl2 ^{iv}	0.90	2.44	3.286 (4)	156
O1W—H1W \cdots Cl2 ^v	0.85	2.58	3.292 (4)	142
O1W—H2W \cdots Cl2	0.85	2.30	3.134 (4)	164

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