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# 2-Amino-6-methylpyridinium 3-chlorobenzoate

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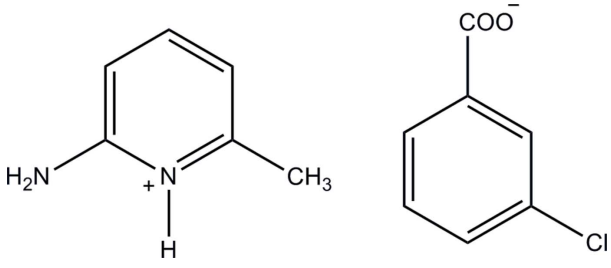
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; disorder in main residue; $R$ factor = 0.045; $wR$ factor = 0.128; data-to-parameter ratio = 13.4.

In the title salt, $C_6H_9N_2^+\cdot C_7H_4ClO_2^-$, the 3-chlorobenzoate anion shows a whole-molecule disorder over two positions with a refined occupancy ratio of 0.505 (4):0.495 (4). In the crystal, the cations and anions are linked *via* N—H···O hydrogen bonds, forming a centrosymmetric 2 + 2 aggregate with $R_2^2(8)$ and $R_4^2(8)$ ring motifs. The crystal structure also features a $\pi$–$\pi$ stacking interaction between the pyridinium rings with a centroid–centroid distance of 3.8339 (9) Å.

## Related literature

For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For related structures, see: Hemamalini & Fun (2010); Thanigaimani *et al.* (2012); Draguta *et al.* (2012). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).




## Experimental

### Crystal data

$C_6H_9N_2^+\cdot C_7H_4ClO_2^-$
$M_r$ = 264.70
Monoclinic, $C2/c$
$a$ = 22.3118 (15) Å
$b$ = 15.2053 (10) Å
$c$ = 7.4166 (5) Å
$\beta$ = 100.924 (1)°
$V$ = 2470.5 (3) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.30 mm$^{-1}$
$T$ = 100 K
0.36 × 0.06 × 0.05 mm

### Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.898, $T_{max}$ = 0.985
24731 measured reflections
3575 independent reflections
2446 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.053

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.128
$S$ = 1.06
3575 reflections
267 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H2*N*2···O1 | 0.94 (2) | 1.69 (2) | 2.614 (7) | 168 (2) |
| N2—H1*N*2···O2 | 0.86 (2) | 1.98 (3) | 2.832 (14) | 170 (2) |
| N2—H1*N*1···O2$^{i}$ | 0.88 (2) | 2.06 (2) | 2.853 (11) | 150 (2) |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5234).

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# supplementary materials

*Acta Cryst.* (2013). E**69**, o318 [doi:10.1107/S1600536813002559]

## 2-Amino-6-methylpyridinium 3-chlorobenzoate

**Kaliyaperumal Thanigaimani, Nuridayanti Che Khalib, Suhana Arshad and Ibrahim Abdul Razak**

### Comment

Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996). Related crystal structures of 2-amino-4-methylpyridinium 3-chlorobenzoate (Hemamalini & Fun, 2010) and 2-amino-5-methylpyridinium 3-chlorobenzoate (Thanigaimani *et al.*, 2012) have been reported. In order to study potential hydrogen bonding interactions the crystal structure determination of the title compound (I) was carried out.

The asymmetric unit (Fig. 1) contains one 2-amino-6-methylpyridinium cation and one 3-chlorobenzoate anion. The proton transfers from the one of the carboxyl group oxygen atom (O1) to atom N1 of 2-amino-5-methylpyrimidine resulted in the widening of C1—N1—C5 angle of the pyridinium ring to 122.93 (13)°, compared to the corresponding angle of 118.43 (9)° in neutral 6-methylpyridin-2-amine (Draguta *et al.*, 2012). The whole 3-chlorobenzoate anion is disordered over two positions with a refined occupancy ratio of 0.505 (4):0.495 (4). The 2-amino-5-methylpyridinium cation is essentially planar, with a maximum deviation of 0.030 (2) Å for atom C4. The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the protonated N1 atom and the 2-amino group (N2) are hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) *via* a pair of intermolecular N1—H2N2···O1 and N2—H1N2···O2 hydrogen bonds, forming an $R_2^2(8)$ (Bernstein *et al.*, 1995) ring motif. The motifs are centrosymmetrically paired *via* intermolecular N2—H1N1···O2$^{i}$ hydrogen bonds between the ions which form $R_4^2(8)$ ring motif, resulting in a DDAA array (where D is a hydrogen-bond donor and A is a hydrogen-bond acceptor) of quadruple hydrogen bonds (symmetry code in Table 1). The crystal structure is further stabilized by a $\pi$–$\pi$ interaction between the pyridinium ring (*Cg*1 = N1/C1–C5) cations [*Cg*1···*Cg*1 = 3.8339 (9) Å; *x*, 1 - *y*, -1/2 - *z*].

### Experimental

Hot methanol solutions (20 ml) of 2-amino-6-methylpyridine (54 mg, Aldrich) and 3-chlorobenzoic acid (39 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound (I) appeared after a few days.

### Refinement

N-bound H atoms were located in a difference Fourier map and refined freely [refined N—H distances: 0.94 (2), 0.88 (2) and 0.86 (2) Å]. The remaining H atoms were positioned geometrically (C—H = 0.95 and 0.98 Å) and were refined using a riding model, with $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(methyl C). A rotating-group model was used for the methyl group. The whole 3-chlorobenzoate anion was disordered over two positions with a refined ratio of 0.505 (4):0.495 (4). For the disordred anion, bond-length restraints [Cl—C = 1.73 (1) Å and O—C = 1.23 (1) Å] and a *SAME* instruction were applied.

### Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

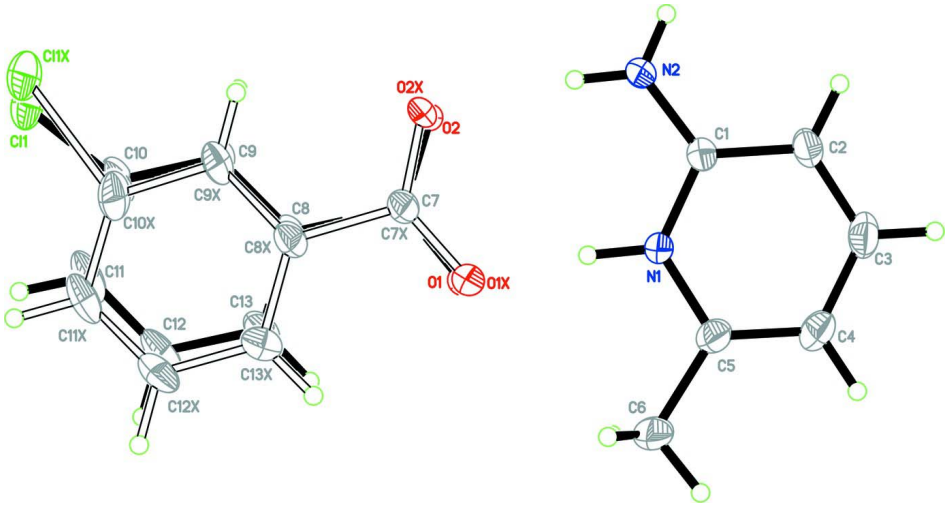


**Figure 1**

The molecular structure of the title compound with atom labels with 50% probability displacement ellipsoids. All disordered components are shown.

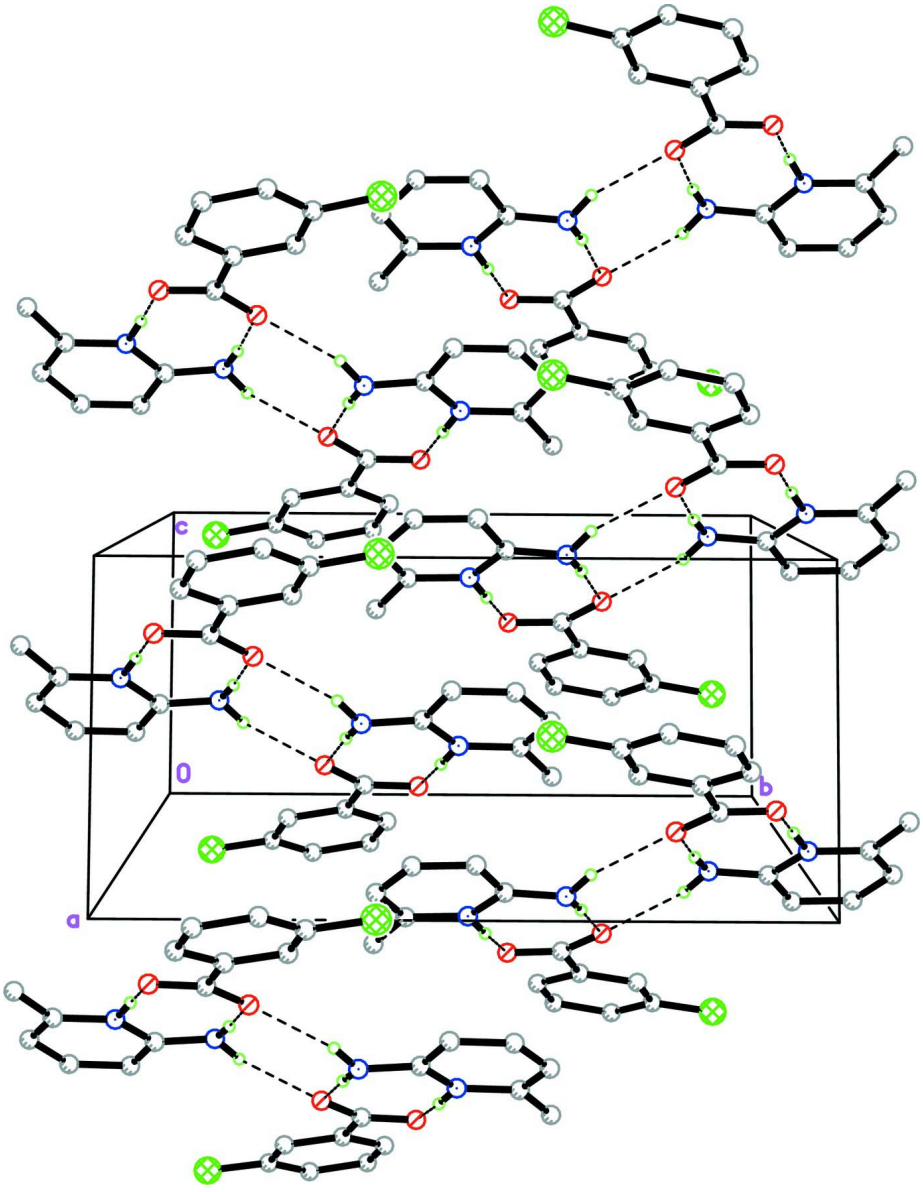


**Figure 2**

The crystal packing of the title compound. Only major disordered component is shown. H atoms not involved in the hydrogen bonds (dashed lines) have been omitted for clarity.

### 2-Amino-6-methylpyridinium 3-chlorobenzoate

*Crystal data*

$C_6H_9N_2^+·C_7H_4ClO_2^-$
$M_r$ = 264.70
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 22.3118 (15) Å
*b* = 15.2053 (10) Å
*c* = 7.4166 (5) Å
*β* = 100.924 (1)°
*V* = 2470.5 (3) Å$^3$
*Z* = 8
*F*(000) = 1104
$D_x$ = 1.423 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4651 reflections
*θ* = 2.7–29.3°
*μ* = 0.30 mm$^{-1}$

$T$ = 100 K
Needle, colourless

0.36 × 0.06 × 0.05 mm

*Data collection*

Bruker SMART APEXII DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.898, $T_{max}$ = 0.985

24731 measured reflections
3575 independent reflections
2446 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.053
$\theta_{max}$ = 30.0°, $\theta_{min}$ = 1.6°
$h$ = −30→31
$k$ = −21→21
$l$ = −10→10

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.128
$S$ = 1.06
3575 reflections
267 parameters
5 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
$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 1.2878P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$

*Special details*

**Experimental**. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cl1 | 0.51442 (12) | 0.09433 (16) | 0.5251 (4) | 0.0377 (5) | 0.505 (4) |
| O1 | 0.3604 (3) | 0.4344 (4) | 0.2546 (10) | 0.0298 (12) | 0.505 (4) |
| O2 | 0.3335 (7) | 0.2966 (7) | 0.1833 (12) | 0.0279 (16) | 0.505 (4) |
| C7 | 0.3716 (3) | 0.3536 (4) | 0.2547 (8) | 0.0223 (11) | 0.505 (4) |
| C8 | 0.43409 (15) | 0.3242 (2) | 0.3507 (6) | 0.0224 (7) | 0.505 (4) |
| C9 | 0.4472 (5) | 0.2368 (8) | 0.3839 (11) | 0.0217 (13) | 0.505 (4) |
| H9A | 0.4166 | 0.1945 | 0.3394 | 0.026* | 0.505 (4) |
| C10 | 0.5042 (5) | 0.2072 (5) | 0.4815 (14) | 0.0368 (18) | 0.505 (4) |
| C11 | 0.54930 (16) | 0.2695 (3) | 0.5297 (6) | 0.0348 (9) | 0.505 (4) |
| H11A | 0.5890 | 0.2515 | 0.5885 | 0.042* | 0.505 (4) |
| C12 | 0.53779 (14) | 0.3580 (3) | 0.4939 (5) | 0.0345 (9) | 0.505 (4) |

| | | | | | |
|---|---|---|---|---|---|
| H12A | 0.5693 | 0.4000 | 0.5301 | 0.041* | 0.505 (4) |
| C13 | 0.48029 (14) | 0.3853 (2) | 0.4052 (5) | 0.0286 (8) | 0.505 (4) |
| H13A | 0.4725 | 0.4460 | 0.3816 | 0.034* | 0.505 (4) |
| Cl1X | 0.52750 (12) | 0.11634 (16) | 0.5138 (4) | 0.0336 (4) | 0.495 (4) |
| O1X | 0.3491 (3) | 0.4332 (4) | 0.3044 (10) | 0.0294 (11) | 0.495 (4) |
| O2X | 0.3302 (7) | 0.2910 (8) | 0.2304 (12) | 0.0273 (15) | 0.495 (4) |
| C7X | 0.3620 (3) | 0.3525 (4) | 0.3103 (9) | 0.0225 (11) | 0.495 (4) |
| C8X | 0.42352 (17) | 0.3289 (2) | 0.4266 (6) | 0.0222 (8) | 0.495 (4) |
| C9X | 0.4418 (5) | 0.2415 (8) | 0.4305 (11) | 0.0223 (14) | 0.495 (4) |
| H9XA | 0.4152 | 0.1963 | 0.3748 | 0.027* | 0.495 (4) |
| C10X | 0.5005 (5) | 0.2239 (4) | 0.5195 (13) | 0.0314 (16) | 0.495 (4) |
| C11X | 0.53950 (16) | 0.2854 (3) | 0.6185 (6) | 0.0319 (9) | 0.495 (4) |
| H11B | 0.5787 | 0.2691 | 0.6844 | 0.038* | 0.495 (4) |
| C12X | 0.51893 (15) | 0.3713 (2) | 0.6175 (5) | 0.0303 (8) | 0.495 (4) |
| H12B | 0.5445 | 0.4155 | 0.6820 | 0.036* | 0.495 (4) |
| C13X | 0.46134 (15) | 0.3931 (2) | 0.5228 (5) | 0.0272 (8) | 0.495 (4) |
| H13B | 0.4474 | 0.4522 | 0.5233 | 0.033* | 0.495 (4) |
| N1 | 0.25283 (5) | 0.49267 (8) | 0.09853 (17) | 0.0197 (3) | |
| N2 | 0.21460 (7) | 0.35423 (9) | 0.0235 (2) | 0.0337 (4) | |
| C1 | 0.20717 (6) | 0.44124 (10) | 0.0094 (2) | 0.0211 (3) | |
| C2 | 0.15454 (7) | 0.48210 (10) | −0.0898 (2) | 0.0238 (3) | |
| H2A | 0.1223 | 0.4479 | −0.1572 | 0.029* | |
| C3 | 0.15048 (7) | 0.57153 (11) | −0.0877 (2) | 0.0307 (4) | |
| H3A | 0.1149 | 0.5996 | −0.1533 | 0.037* | |
| C4 | 0.19795 (8) | 0.62255 (11) | 0.0095 (3) | 0.0363 (4) | |
| H4A | 0.1944 | 0.6848 | 0.0121 | 0.044* | |
| C5 | 0.24940 (7) | 0.58195 (10) | 0.1006 (2) | 0.0257 (3) | |
| C6 | 0.30466 (8) | 0.62859 (11) | 0.2048 (3) | 0.0372 (4) | |
| H6A | 0.2955 | 0.6913 | 0.2136 | 0.056* | |
| H6B | 0.3388 | 0.6213 | 0.1402 | 0.056* | |
| H6C | 0.3157 | 0.6036 | 0.3284 | 0.056* | |
| H1N1 | 0.1883 (11) | 0.3210 (14) | −0.050 (3) | 0.046 (6)* | |
| H2N2 | 0.2887 (10) | 0.4672 (15) | 0.165 (3) | 0.050 (6)* | |
| H1N2 | 0.2487 (11) | 0.3311 (14) | 0.077 (3) | 0.044 (6)* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0260 (10) | 0.0318 (11) | 0.0523 (8) | 0.0162 (6) | 0.0001 (7) | 0.0009 (8) |
| O1 | 0.016 (2) | 0.0172 (13) | 0.051 (4) | −0.0007 (13) | −0.0063 (17) | −0.0018 (18) |
| O2 | 0.020 (2) | 0.0134 (18) | 0.043 (4) | 0.0000 (14) | −0.014 (3) | 0.000 (3) |
| C7 | 0.012 (2) | 0.0175 (16) | 0.035 (3) | −0.0021 (13) | −0.0015 (19) | 0.0004 (19) |
| C8 | 0.0103 (15) | 0.0277 (16) | 0.027 (2) | 0.0008 (11) | −0.0011 (13) | −0.0050 (15) |
| C9 | 0.014 (2) | 0.0240 (19) | 0.028 (4) | 0.0072 (15) | 0.006 (3) | −0.005 (3) |
| C10 | 0.013 (2) | 0.037 (3) | 0.055 (4) | 0.016 (2) | −0.006 (2) | −0.016 (2) |
| C11 | 0.0138 (16) | 0.059 (3) | 0.029 (2) | 0.0094 (15) | −0.0032 (14) | −0.0084 (17) |
| C12 | 0.0134 (15) | 0.054 (2) | 0.0331 (19) | −0.0063 (14) | −0.0032 (12) | −0.0057 (15) |
| C13 | 0.0182 (15) | 0.0351 (17) | 0.0299 (18) | −0.0033 (12) | −0.0019 (12) | −0.0044 (13) |
| Cl1X | 0.0247 (9) | 0.0289 (10) | 0.0442 (7) | 0.0119 (6) | −0.0011 (6) | 0.0025 (7) |
| O1X | 0.021 (3) | 0.0190 (14) | 0.043 (3) | −0.0005 (14) | −0.0066 (16) | −0.0035 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2X | 0.0172 (18) | 0.020 (2) | 0.038 (4) | −0.0025 (14) | −0.011 (3) | 0.002 (2) |
| C7X | 0.013 (2) | 0.0213 (18) | 0.032 (3) | −0.0016 (14) | 0.0023 (18) | 0.002 (2) |
| C8X | 0.0144 (16) | 0.0268 (17) | 0.0247 (19) | −0.0003 (12) | 0.0018 (14) | −0.0018 (15) |
| C9X | 0.010 (2) | 0.035 (3) | 0.023 (3) | 0.0040 (18) | 0.005 (2) | −0.003 (3) |
| C10X | 0.021 (2) | 0.022 (3) | 0.051 (4) | 0.016 (2) | 0.007 (3) | 0.001 (3) |
| C11X | 0.0132 (15) | 0.052 (2) | 0.0276 (19) | 0.0019 (14) | −0.0032 (14) | −0.0008 (17) |
| C12X | 0.0193 (15) | 0.0391 (19) | 0.0294 (18) | −0.0090 (13) | −0.0031 (13) | −0.0029 (14) |
| C13X | 0.0243 (16) | 0.0254 (16) | 0.0302 (18) | −0.0062 (12) | 0.0011 (13) | −0.0025 (12) |
| N1 | 0.0155 (6) | 0.0161 (6) | 0.0264 (6) | 0.0011 (4) | 0.0012 (5) | 0.0000 (4) |
| N2 | 0.0220 (7) | 0.0179 (6) | 0.0526 (9) | 0.0009 (5) | −0.0147 (6) | −0.0074 (6) |
| C1 | 0.0171 (7) | 0.0200 (7) | 0.0251 (7) | 0.0015 (5) | 0.0012 (5) | −0.0020 (5) |
| C2 | 0.0165 (7) | 0.0285 (8) | 0.0253 (7) | 0.0031 (6) | 0.0008 (5) | −0.0008 (6) |
| C3 | 0.0232 (8) | 0.0318 (9) | 0.0356 (9) | 0.0091 (6) | 0.0016 (6) | 0.0068 (7) |
| C4 | 0.0313 (9) | 0.0191 (7) | 0.0563 (11) | 0.0053 (6) | 0.0030 (8) | 0.0057 (7) |
| C5 | 0.0231 (8) | 0.0179 (7) | 0.0366 (8) | −0.0001 (6) | 0.0068 (6) | 0.0006 (6) |
| C6 | 0.0254 (9) | 0.0189 (7) | 0.0652 (12) | −0.0044 (6) | 0.0036 (8) | −0.0039 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C10 | 1.753 (7) | C11X—C12X | 1.385 (5) |
| O1—C7 | 1.253 (6) | C11X—H11B | 0.9500 |
| O2—C7 | 1.258 (14) | C12X—C13X | 1.383 (4) |
| C7—C8 | 1.509 (8) | C12X—H12B | 0.9500 |
| C8—C9 | 1.372 (12) | C13X—H13B | 0.9500 |
| C8—C13 | 1.390 (5) | N1—C1 | 1.3530 (18) |
| C9—C10 | 1.413 (16) | N1—C5 | 1.3599 (19) |
| C9—H9A | 0.9500 | N1—H2N2 | 0.94 (2) |
| C10—C11 | 1.379 (11) | N2—C1 | 1.335 (2) |
| C11—C12 | 1.385 (6) | N2—H1N1 | 0.88 (2) |
| C11—H11A | 0.9500 | N2—H1N2 | 0.86 (2) |
| C12—C13 | 1.390 (4) | C1—C2 | 1.4067 (19) |
| C12—H12A | 0.9500 | C2—C3 | 1.363 (2) |
| C13—H13A | 0.9500 | C2—H2A | 0.9500 |
| Cl1X—C10X | 1.747 (6) | C3—C4 | 1.398 (2) |
| O1X—C7X | 1.259 (7) | C3—H3A | 0.9500 |
| O2X—C7X | 1.253 (14) | C4—C5 | 1.365 (2) |
| C7X—C8X | 1.519 (8) | C4—H4A | 0.9500 |
| C8X—C9X | 1.389 (13) | C5—C6 | 1.503 (2) |
| C8X—C13X | 1.395 (5) | C6—H6A | 0.9800 |
| C9X—C10X | 1.377 (17) | C6—H6B | 0.9800 |
| C9X—H9XA | 0.9500 | C6—H6C | 0.9800 |
| C10X—C11X | 1.388 (12) | | |
| | | | |
| O1—C7—O2 | 123.8 (9) | C10X—C11X—H11B | 121.4 |
| O1—C7—C8 | 117.2 (6) | C13X—C12X—C11X | 120.3 (3) |
| O2—C7—C8 | 118.9 (8) | C13X—C12X—H12B | 119.9 |
| C9—C8—C13 | 118.3 (6) | C11X—C12X—H12B | 119.9 |
| C9—C8—C7 | 121.2 (6) | C12X—C13X—C8X | 120.4 (3) |
| C13—C8—C7 | 120.5 (4) | C12X—C13X—H13B | 119.8 |
| C8—C9—C10 | 122.8 (10) | C8X—C13X—H13B | 119.8 |

| | | | |
|---|---|---|---|
| C8—C9—H9A | 118.6 | C1—N1—C5 | 122.95 (13) |
| C10—C9—H9A | 118.6 | C1—N1—H2N2 | 120.4 (14) |
| C11—C10—C9 | 117.1 (7) | C5—N1—H2N2 | 116.7 (14) |
| C11—C10—Cl1 | 124.2 (7) | C1—N2—H1N1 | 117.5 (14) |
| C9—C10—Cl1 | 118.7 (8) | C1—N2—H1N2 | 121.7 (14) |
| C10—C11—C12 | 121.2 (4) | H1N1—N2—H1N2 | 119 (2) |
| C10—C11—H11A | 119.4 | N2—C1—N1 | 117.63 (13) |
| C12—C11—H11A | 119.4 | N2—C1—C2 | 123.89 (14) |
| C11—C12—C13 | 120.1 (3) | N1—C1—C2 | 118.48 (13) |
| C11—C12—H12A | 119.9 | C3—C2—C1 | 119.04 (14) |
| C13—C12—H12A | 119.9 | C3—C2—H2A | 120.5 |
| C8—C13—C12 | 120.3 (3) | C1—C2—H2A | 120.5 |
| C8—C13—H13A | 119.8 | C2—C3—C4 | 120.93 (14) |
| C12—C13—H13A | 119.8 | C2—C3—H3A | 119.5 |
| O2X—C7X—O1X | 127.3 (10) | C4—C3—H3A | 119.5 |
| O2X—C7X—C8X | 117.5 (8) | C5—C4—C3 | 119.24 (15) |
| O1X—C7X—C8X | 115.2 (7) | C5—C4—H4A | 120.4 |
| C9X—C8X—C13X | 120.8 (6) | C3—C4—H4A | 120.4 |
| C9X—C8X—C7X | 117.9 (6) | N1—C5—C4 | 119.32 (15) |
| C13X—C8X—C7X | 121.3 (4) | N1—C5—C6 | 115.76 (13) |
| C10X—C9X—C8X | 116.4 (9) | C4—C5—C6 | 124.91 (15) |
| C10X—C9X—H9XA | 121.8 | C5—C6—H6A | 109.5 |
| C8X—C9X—H9XA | 121.8 | C5—C6—H6B | 109.5 |
| C9X—C10X—C11X | 124.5 (7) | H6A—C6—H6B | 109.5 |
| C9X—C10X—Cl1X | 118.1 (8) | C5—C6—H6C | 109.5 |
| C11X—C10X—Cl1X | 117.3 (7) | H6A—C6—H6C | 109.5 |
| C12X—C11X—C10X | 117.3 (4) | H6B—C6—H6C | 109.5 |
| C12X—C11X—H11B | 121.4 | | |

| | | | |
|---|---|---|---|
| O1—C7—C8—C9 | 169.3 (5) | C7X—C8X—C9X—C10X | 172.7 (6) |
| O2—C7—C8—C9 | −9.3 (8) | C8X—C9X—C10X—C11X | 6.5 (12) |
| O1—C7—C8—C13 | −11.7 (7) | C8X—C9X—C10X—Cl1X | −175.4 (5) |
| O2—C7—C8—C13 | 169.7 (6) | C9X—C10X—C11X—C12X | −4.3 (11) |
| C13—C8—C9—C10 | 4.3 (9) | Cl1X—C10X—C11X—C12X | 177.7 (4) |
| C7—C8—C9—C10 | −176.7 (6) | C10X—C11X—C12X—C13X | 1.0 (7) |
| C8—C9—C10—C11 | −5.7 (11) | C11X—C12X—C13X—C8X | −0.4 (6) |
| C8—C9—C10—Cl1 | 177.0 (5) | C9X—C8X—C13X—C12X | 2.8 (7) |
| C9—C10—C11—C12 | 3.9 (10) | C7X—C8X—C13X—C12X | −175.5 (3) |
| Cl1—C10—C11—C12 | −178.8 (5) | C5—N1—C1—N2 | −177.15 (15) |
| C10—C11—C12—C13 | −1.1 (7) | C5—N1—C1—C2 | 1.9 (2) |
| C9—C8—C13—C12 | −1.2 (6) | N2—C1—C2—C3 | 176.80 (16) |
| C7—C8—C13—C12 | 179.9 (4) | N1—C1—C2—C3 | −2.2 (2) |
| C11—C12—C13—C8 | −0.4 (6) | C1—C2—C3—C4 | 0.7 (3) |
| O2X—C7X—C8X—C9X | 2.7 (9) | C2—C3—C4—C5 | 1.2 (3) |
| O1X—C7X—C8X—C9X | −176.6 (5) | C1—N1—C5—C4 | 0.0 (2) |
| O2X—C7X—C8X—C13X | −178.9 (6) | C1—N1—C5—C6 | −179.36 (14) |
| O1X—C7X—C8X—C13X | 1.8 (6) | C3—C4—C5—N1 | −1.5 (3) |
| C13X—C8X—C9X—C10X | −5.7 (9) | C3—C4—C5—C6 | 177.75 (17) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H2*N*2···O1 | 0.94 (2) | 1.69 (2) | 2.614 (7) | 168 (2) |
| N2—H1*N*2···O2 | 0.86 (2) | 1.98 (3) | 2.832 (14) | 170 (2) |
| N2—H1*N*1···O2$^{i}$ | 0.88 (2) | 2.06 (2) | 2.853 (11) | 150 (2) |

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