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6-Amino-2-(pivaloylamino)pyridinium benzoate

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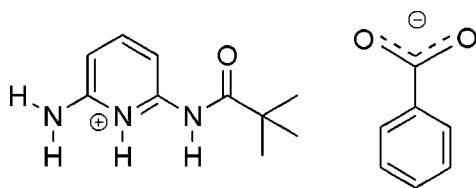
Received 26 July 2013; accepted 23 August 2013

Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.066; wR factor = 0.141; data-to-parameter ratio = 16.9.

In the crystal structure of the title salt, $\text{C}_{10}\text{H}_{16}\text{N}_3\text{O}^+ \cdot \text{C}_7\text{H}_5\text{O}_2^-$, the cations and anions are linked to each other *via* $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming infinite chains running along [010]. The crystal structure also features $\text{C}-\text{H} \cdots \text{O}$ and $\pi-\pi$ stacking interactions, which assemble the chains into supra-molecular layers parallel to (100). The $\pi-\pi$ stacking interactions are observed between the pyridine rings of inversion-related cations with a centroid-centroid distance of 3.867 (2) Å.

Related literature

For co-crystallization of pharmaceuticals, see: Vishweshwar *et al.* (2006); Lemmerer (2012). For the crystal structures of related compounds, see: Ośmiałowski *et al.* (2010*b*); Aakeröy *et al.* (2006, 2010). For the role of steric effects in hydrogen-bonded compounds, see Ośmiałowski *et al.* (2012*a,b*, 2010*a,b*). For the synthesis of 2-pivaloylamino-6-aminopyridine, see: Ośmiałowski *et al.* (2010*a*).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{16}\text{N}_3\text{O}^+ \cdot \text{C}_7\text{H}_5\text{O}_2^-$
 $M_r = 315.37$
Monoclinic, $P2_1/c$
 $a = 15.1438$ (4) Å

$b = 5.7099$ (2) Å
 $c = 18.7388$ (6) Å
 $\beta = 91.967$ (2)°
 $V = 1619.38$ (9) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹

$T = 123$ K
 $0.13 \times 0.10 \times 0.08$ mm

Data collection

Bruker-Nonius KappaCCD diffractometer with APEXII detector
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.988$, $T_{\max} = 0.993$

10993 measured reflections
3724 independent reflections
2054 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.094$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.141$
 $S = 1.00$
3724 reflections
220 parameters

4 restraints
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| $\text{N1}-\text{H1} \cdots \text{O13A}^i$ | 0.91 (2) | 1.67 (2) | 2.571 (2) | 170 (2) |
| $\text{N6}-\text{H6A} \cdots \text{O13B}^i$ | 0.90 (2) | 2.05 (2) | 2.934 (3) | 167 (2) |
| $\text{N6}-\text{H6B} \cdots \text{O13B}^{ii}$ | 0.91 (2) | 2.05 (2) | 2.869 (3) | 149 (2) |
| $\text{N7}-\text{H7} \cdots \text{O13A}^i$ | 0.86 (2) | 2.24 (2) | 2.984 (3) | 146 (2) |
| $\text{C4}-\text{H4} \cdots \text{O8}^{iii}$ | 0.95 | 2.49 | 3.433 (3) | 172 |

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

Data collection: COLLECT (Bruker, 2008); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SIR2004 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL2013 and publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2103).

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supplementary materials

Acta Cryst. (2013). E69, o1483–o1484 [doi:10.1107/S1600536813023787]

6-Amino-2-(pivaloylamino)pyridinium benzoate

Lilianna Chęcińska, Borys Ośmiałowski and Arto Valkonen

1. Comment

Co-crystallization is used in the pharmaceutical industry to improve the shelf life of drugs (Vishweshwar *et al.*, 2006; Lemmerer, 2012). It is also used in many fields of chemistry, including material science. It is known that 2-acylamino-pyridine forms co-crystals with acids, while in 2-aminopyridine acid complexes proton transfer takes place, yielding salts (Aakeröy *et al.*, 2010; 2006). The current report deals with the competition between formation of a salt and co-crystal. It is worth pointing out that the 2-acylamino moiety prefers to form co-crystals, while the 6-amino moiety prefers salt formation. In 2-pivaloylamino pyridine, both groups are present in the same molecule. Moreover, the increased acidity of NH in the —NHCO— group, in general, increases the hydrogen bonding donation ability of the NH proton. On the other hand, we used the sterically demanding pivaloyl group to hinder the efficient $\text{NH}\cdots\text{O}=\text{C}$ interaction of the —NHCO— *t*Bu part of the title molecule. Thus the interacting acid is pushed to transfer the proton to the heterocyclic nitrogen and to form a salt with 2-pivaloylamino-6-aminopyridine. It is worth noting that the NH_2 group attached to C6 of the pyridine ring causes an increase of electron density at the ring nitrogen. More systematic studies on co-crystallization of 2-acylamino-pyridine with benzoic acids are in progress. For the steric effects in hydrogen bonded compounds, refer to our previous publications (Ośmiałowski *et al.*, 2012*a,b*; 2010*a,b*).

As illustrated in Figure 1, the asymmetric unit of the title salt, (I), contains one protonated 2-pivaloylamino-6-aminopyridine cation and one benzoate anion, both located in general positions.

The geometric parameters of the 2-pivaloylamino-6-aminopyridine cation are in good agreement with those found for the related structures (Ośmiałowski *et al.*, 2010*a,b*). In the benzoate anion the C—O distances, 1.268 (3) Å and 1.253 (3) Å, clearly indicate the delocalization of the negative charge within the carboxylate group.

In the crystal of the title salt, cations and anions are connected *via* four N—H \cdots O hydrogen bonds (Table 1 and Figure 2). The protonated N1 atom and two nitrogen atoms (N6 and N7) interact with the carboxylate oxygen atoms (O13A and O13B; symmetry code (i): $x, y + 1, z$) and form hydrogen-bonded aggregates. Such structural motifs are further propagated into infinite chains running along *b* axis by N6—H6B \cdots O13Bⁱⁱ [symmetry code (ii): $-x + 1, y + 1/2, -z + 1/2$] hydrogen bond. The crystal structure of (I) is further stabilized by an almost linear C4—H4 \cdots O8ⁱⁱⁱ interaction (Table 1 and Figure 2) and by $\pi\cdots\pi$ stacking interactions; both of which connect the adjacent one-dimensional-chains to produce (100) supramolecular sheets. The thickness of each separate layer is equal to the *a* unit cell constant. No direction-specific interactions have been found between the supramolecular sheets.

The aforementioned $\pi\cdots\pi$ stacking interactions are observed between the pyridine rings of inversion-related cations, with a $\text{Cg}\cdots\text{Cg}^{\text{iv}}$ distance of 3.867 (2) Å and interplanar distance of 3.455 (1) Å; Cg is the centroid of the N2/C2–C6 ring, symmetry code (iv): $1 - x, 1 - y, 1 - z$.

2. Experimental

For the synthesis of the title compound, equimolar amounts of 2-pivaloylamino-6-aminopyridine and benzoic acid were mixed in methanol. The solution was left for a couple of days for slow evaporation and produced single crystals. The parent 2-pivaloylamino-6-aminopyridine was prepared according to a literature procedure (Ośmiałowski *et al.*, 2010a).

3. Refinement

All non-hydrogen atoms were refined anisotropically. H atoms bonded to N atoms were located in a difference map and refined with distance restraints of N1—H1 (and N7—H7) = 0.88 (2) Å, N6—H6A (and N6—H6B) = 0.91 (2) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. Other H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{methyl C})$.

Computing details

Data collection: *COLLECT* (Bruker, 2008); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

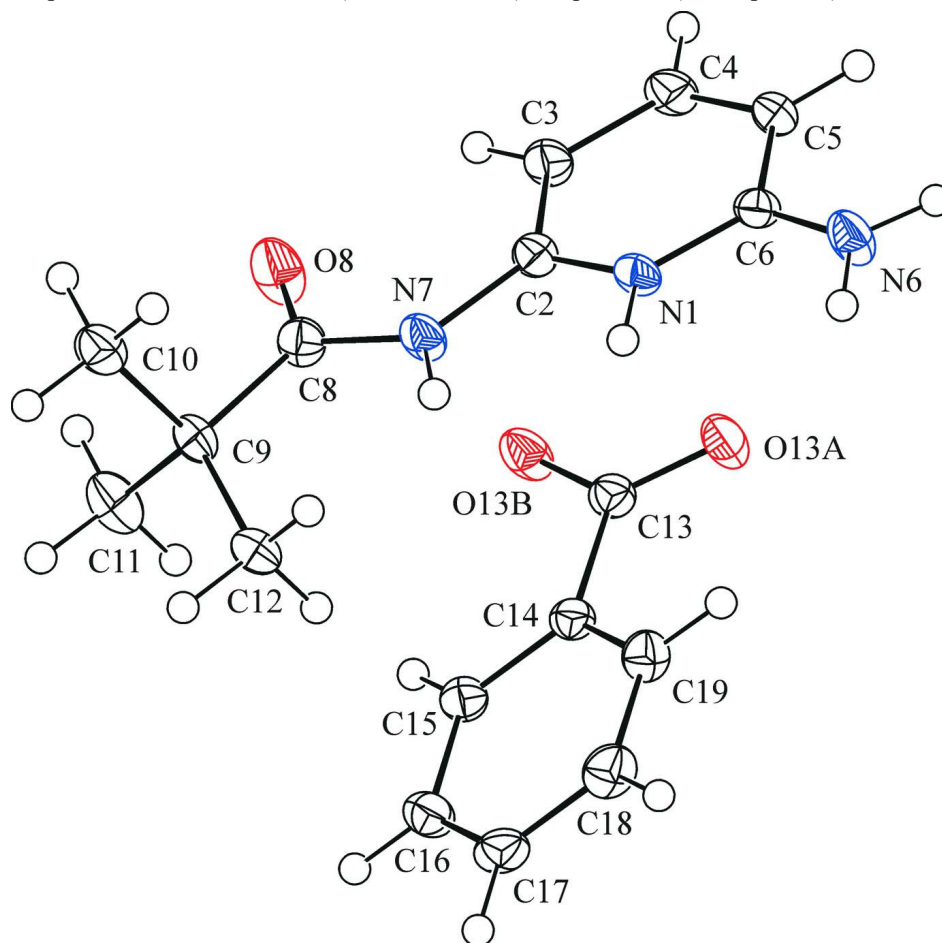
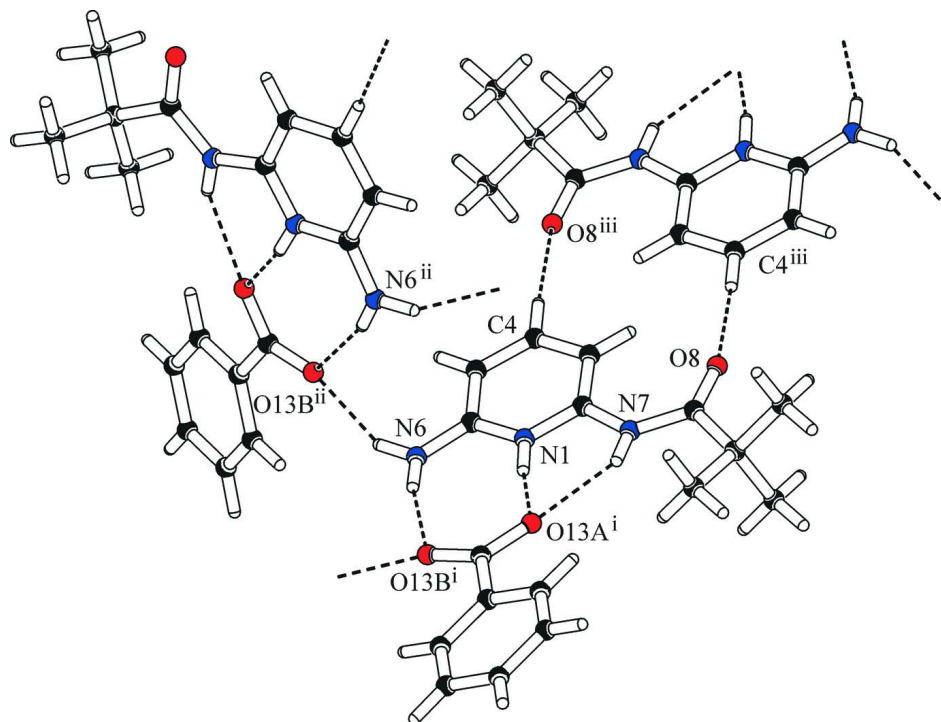


Figure 1

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.


Figure 2

A part of the crystal structure of (I), showing the intermolecular interactions as dashed lines [symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, y + 1/2, -z + 1/2$; (iii) $-x + 1, -y, -z + 1$].

6-Amino-2-(pivaloylamino)pyridinium benzoate

Crystal data

$C_{10}H_{16}N_3O^+ \cdot C_7H_5O_2^-$

$M_r = 315.37$

Monoclinic, $P2_1/c$

$a = 15.1438$ (4) Å

$b = 5.7099$ (2) Å

$c = 18.7388$ (6) Å

$\beta = 91.967$ (2)°

$V = 1619.38$ (9) Å³

$Z = 4$

$F(000) = 672$

$D_x = 1.293$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4257 reflections

$\theta = 0.4$ – 28.3 °

$\mu = 0.09$ mm⁻¹

$T = 123$ K

Block, colourless

$0.13 \times 0.10 \times 0.08$ mm

Data collection

Bruker–Nonius KappaCCD

diffractometer with APEXII detector

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2004)

$T_{\min} = 0.988$, $T_{\max} = 0.993$

10993 measured reflections

3724 independent reflections

2054 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.094$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.5$ °

$h = -19 \rightarrow 18$

$k = -7 \rightarrow 7$

$l = -24 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.141$
 $S = 1.00$
 3724 reflections
 220 parameters
 4 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0496P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Special details

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.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|------------|--------------|----------------------------------|
| O8 | 0.69413 (12) | 0.1535 (3) | 0.54656 (10) | 0.0370 (5) |
| N1 | 0.57982 (12) | 0.6015 (4) | 0.39112 (11) | 0.0205 (5) |
| H1 | 0.6221 (14) | 0.710 (4) | 0.3842 (13) | 0.025* |
| N6 | 0.48943 (14) | 0.7758 (4) | 0.30603 (12) | 0.0278 (5) |
| H6A | 0.5311 (15) | 0.882 (4) | 0.2960 (14) | 0.033* |
| H6B | 0.4404 (14) | 0.774 (4) | 0.2764 (13) | 0.033* |
| N7 | 0.68521 (13) | 0.4637 (4) | 0.47095 (11) | 0.0231 (5) |
| H7 | 0.7141 (15) | 0.580 (4) | 0.4546 (13) | 0.028* |
| C2 | 0.60154 (15) | 0.4307 (4) | 0.43895 (13) | 0.0223 (6) |
| C3 | 0.54405 (15) | 0.2505 (4) | 0.45137 (14) | 0.0249 (6) |
| H3 | 0.5582 | 0.1307 | 0.4850 | 0.030* |
| C4 | 0.46378 (16) | 0.2513 (4) | 0.41222 (14) | 0.0261 (6) |
| H4 | 0.4225 | 0.1295 | 0.4200 | 0.031* |
| C5 | 0.44278 (15) | 0.4204 (4) | 0.36334 (13) | 0.0227 (6) |
| H5 | 0.3881 | 0.4149 | 0.3369 | 0.027* |
| C6 | 0.50276 (15) | 0.6023 (4) | 0.35252 (13) | 0.0209 (6) |
| C8 | 0.72715 (16) | 0.3289 (4) | 0.52242 (14) | 0.0234 (6) |
| C9 | 0.81731 (15) | 0.4228 (4) | 0.54969 (13) | 0.0219 (6) |
| C10 | 0.79992 (16) | 0.5515 (5) | 0.61949 (14) | 0.0293 (6) |
| H10A | 0.7718 | 0.4443 | 0.6526 | 0.044* |
| H10B | 0.7608 | 0.6852 | 0.6096 | 0.044* |
| H10C | 0.8560 | 0.6072 | 0.6409 | 0.044* |
| C11 | 0.87823 (17) | 0.2125 (4) | 0.56515 (16) | 0.0326 (7) |
| H11A | 0.8896 | 0.1308 | 0.5204 | 0.049* |
| H11B | 0.8497 | 0.1049 | 0.5980 | 0.049* |
| H11C | 0.9342 | 0.2675 | 0.5869 | 0.049* |
| C12 | 0.86140 (15) | 0.5877 (5) | 0.49737 (14) | 0.0263 (6) |
| H12A | 0.8723 | 0.5037 | 0.4529 | 0.040* |
| H12B | 0.9176 | 0.6436 | 0.5185 | 0.040* |
| H12C | 0.8225 | 0.7216 | 0.4871 | 0.040* |

| | | | | |
|------|--------------|-------------|--------------|------------|
| O13A | 0.71169 (10) | -0.1201 (3) | 0.37777 (10) | 0.0287 (5) |
| O13B | 0.64016 (11) | 0.0950 (3) | 0.29481 (10) | 0.0289 (5) |
| C13 | 0.70775 (15) | 0.0432 (4) | 0.33191 (13) | 0.0215 (6) |
| C14 | 0.79105 (15) | 0.1829 (4) | 0.32285 (13) | 0.0203 (6) |
| C15 | 0.87128 (15) | 0.0994 (4) | 0.35068 (13) | 0.0220 (6) |
| H15 | 0.8731 | -0.0436 | 0.3766 | 0.026* |
| C16 | 0.94848 (16) | 0.2232 (4) | 0.34092 (14) | 0.0255 (6) |
| H16 | 1.0031 | 0.1649 | 0.3600 | 0.031* |
| C17 | 0.94615 (16) | 0.4311 (4) | 0.30351 (14) | 0.0271 (6) |
| H17 | 0.9992 | 0.5155 | 0.2966 | 0.033* |
| C18 | 0.86638 (16) | 0.5174 (5) | 0.27596 (14) | 0.0279 (6) |
| H18 | 0.8647 | 0.6621 | 0.2509 | 0.033* |
| C19 | 0.78894 (16) | 0.3920 (4) | 0.28499 (13) | 0.0245 (6) |
| H19 | 0.7345 | 0.4494 | 0.2652 | 0.029* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| O8 | 0.0319 (11) | 0.0331 (11) | 0.0450 (13) | -0.0155 (8) | -0.0117 (9) | 0.0167 (10) |
| N1 | 0.0153 (11) | 0.0213 (11) | 0.0248 (12) | -0.0069 (8) | 0.0000 (8) | 0.0002 (9) |
| N6 | 0.0206 (12) | 0.0284 (13) | 0.0339 (14) | -0.0070 (9) | -0.0076 (10) | 0.0059 (11) |
| N7 | 0.0175 (11) | 0.0242 (12) | 0.0275 (13) | -0.0068 (9) | -0.0028 (9) | 0.0046 (10) |
| C2 | 0.0197 (13) | 0.0264 (14) | 0.0208 (14) | -0.0036 (10) | 0.0006 (10) | -0.0012 (11) |
| C3 | 0.0208 (13) | 0.0273 (15) | 0.0266 (15) | -0.0069 (10) | 0.0002 (11) | 0.0067 (11) |
| C4 | 0.0202 (14) | 0.0284 (14) | 0.0297 (16) | -0.0106 (11) | 0.0016 (11) | -0.0020 (12) |
| C5 | 0.0166 (12) | 0.0281 (14) | 0.0234 (14) | -0.0049 (10) | -0.0005 (10) | -0.0004 (11) |
| C6 | 0.0165 (12) | 0.0254 (14) | 0.0210 (14) | -0.0004 (10) | 0.0029 (10) | -0.0029 (11) |
| C8 | 0.0235 (13) | 0.0221 (14) | 0.0246 (15) | -0.0043 (11) | -0.0006 (11) | 0.0012 (11) |
| C9 | 0.0172 (12) | 0.0227 (13) | 0.0255 (14) | -0.0018 (10) | -0.0039 (10) | -0.0019 (11) |
| C10 | 0.0215 (13) | 0.0354 (16) | 0.0309 (15) | -0.0046 (11) | -0.0012 (11) | -0.0032 (13) |
| C11 | 0.0264 (15) | 0.0257 (16) | 0.0449 (19) | 0.0005 (11) | -0.0076 (12) | 0.0017 (13) |
| C12 | 0.0171 (13) | 0.0323 (15) | 0.0295 (15) | -0.0046 (11) | -0.0007 (10) | -0.0001 (12) |
| O13A | 0.0198 (9) | 0.0276 (10) | 0.0384 (12) | -0.0058 (7) | -0.0032 (8) | 0.0102 (9) |
| O13B | 0.0199 (9) | 0.0326 (11) | 0.0335 (11) | -0.0030 (7) | -0.0069 (8) | 0.0078 (9) |
| C13 | 0.0201 (13) | 0.0225 (14) | 0.0220 (14) | -0.0029 (10) | 0.0016 (10) | -0.0010 (12) |
| C14 | 0.0186 (13) | 0.0227 (14) | 0.0197 (14) | -0.0027 (10) | 0.0022 (10) | -0.0021 (11) |
| C15 | 0.0214 (13) | 0.0219 (13) | 0.0227 (14) | -0.0017 (10) | 0.0019 (10) | 0.0010 (11) |
| C16 | 0.0192 (13) | 0.0288 (15) | 0.0287 (15) | -0.0016 (10) | 0.0012 (10) | -0.0017 (12) |
| C17 | 0.0251 (14) | 0.0302 (15) | 0.0264 (15) | -0.0118 (11) | 0.0062 (11) | -0.0010 (12) |
| C18 | 0.0329 (15) | 0.0231 (14) | 0.0278 (15) | -0.0058 (11) | 0.0025 (12) | 0.0051 (12) |
| C19 | 0.0264 (14) | 0.0230 (14) | 0.0242 (14) | -0.0012 (11) | -0.0008 (11) | 0.0010 (12) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|------------|----------|--------|
| O8—C8 | 1.214 (3) | C10—H10B | 0.9800 |
| N1—C6 | 1.352 (3) | C10—H10C | 0.9800 |
| N1—C2 | 1.358 (3) | C11—H11A | 0.9800 |
| N1—H1 | 0.905 (16) | C11—H11B | 0.9800 |
| N6—C6 | 1.330 (3) | C11—H11C | 0.9800 |
| N6—H6A | 0.899 (17) | C12—H12A | 0.9800 |

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|------------|------------|---------------|-----------|
| N6—H6B | 0.913 (16) | C12—H12B | 0.9800 |
| N7—C8 | 1.373 (3) | C12—H12C | 0.9800 |
| N7—C2 | 1.396 (3) | O13A—C13 | 1.268 (3) |
| N7—H7 | 0.859 (17) | O13B—C13 | 1.253 (3) |
| C2—C3 | 1.373 (3) | C13—C14 | 1.507 (3) |
| C3—C4 | 1.398 (3) | C14—C19 | 1.389 (3) |
| C3—H3 | 0.9500 | C14—C15 | 1.390 (3) |
| C4—C5 | 1.361 (3) | C15—C16 | 1.384 (3) |
| C4—H4 | 0.9500 | C15—H15 | 0.9500 |
| C5—C6 | 1.400 (3) | C16—C17 | 1.379 (4) |
| C5—H5 | 0.9500 | C16—H16 | 0.9500 |
| C8—C9 | 1.538 (3) | C17—C18 | 1.388 (4) |
| C9—C12 | 1.529 (3) | C17—H17 | 0.9500 |
| C9—C10 | 1.531 (3) | C18—C19 | 1.389 (3) |
| C9—C11 | 1.536 (3) | C18—H18 | 0.9500 |
| C10—H10A | 0.9800 | C19—H19 | 0.9500 |
| | | | |
| C6—N1—C2 | 122.7 (2) | C9—C10—H10C | 109.5 |
| C6—N1—H1 | 121.5 (16) | H10A—C10—H10C | 109.5 |
| C2—N1—H1 | 115.6 (16) | H10B—C10—H10C | 109.5 |
| C6—N6—H6A | 123.2 (17) | C9—C11—H11A | 109.5 |
| C6—N6—H6B | 119.4 (17) | C9—C11—H11B | 109.5 |
| H6A—N6—H6B | 116 (2) | H11A—C11—H11B | 109.5 |
| C8—N7—C2 | 128.1 (2) | C9—C11—H11C | 109.5 |
| C8—N7—H7 | 117.2 (17) | H11A—C11—H11C | 109.5 |
| C2—N7—H7 | 114.7 (17) | H11B—C11—H11C | 109.5 |
| N1—C2—C3 | 120.7 (2) | C9—C12—H12A | 109.5 |
| N1—C2—N7 | 112.5 (2) | C9—C12—H12B | 109.5 |
| C3—C2—N7 | 126.9 (2) | H12A—C12—H12B | 109.5 |
| C2—C3—C4 | 117.0 (2) | C9—C12—H12C | 109.5 |
| C2—C3—H3 | 121.5 | H12A—C12—H12C | 109.5 |
| C4—C3—H3 | 121.5 | H12B—C12—H12C | 109.5 |
| C5—C4—C3 | 122.3 (2) | O13B—C13—O13A | 124.6 (2) |
| C5—C4—H4 | 118.9 | O13B—C13—C14 | 118.9 (2) |
| C3—C4—H4 | 118.9 | O13A—C13—C14 | 116.5 (2) |
| C4—C5—C6 | 119.1 (2) | C19—C14—C15 | 119.4 (2) |
| C4—C5—H5 | 120.4 | C19—C14—C13 | 120.5 (2) |
| C6—C5—H5 | 120.4 | C15—C14—C13 | 120.0 (2) |
| N6—C6—N1 | 117.5 (2) | C16—C15—C14 | 120.4 (2) |
| N6—C6—C5 | 124.3 (2) | C16—C15—H15 | 119.8 |
| N1—C6—C5 | 118.2 (2) | C14—C15—H15 | 119.8 |
| O8—C8—N7 | 122.5 (2) | C17—C16—C15 | 120.0 (2) |
| O8—C8—C9 | 122.4 (2) | C17—C16—H16 | 120.0 |
| N7—C8—C9 | 115.0 (2) | C15—C16—H16 | 120.0 |
| C12—C9—C10 | 110.1 (2) | C16—C17—C18 | 120.1 (2) |
| C12—C9—C11 | 109.3 (2) | C16—C17—H17 | 119.9 |
| C10—C9—C11 | 109.5 (2) | C18—C17—H17 | 119.9 |
| C12—C9—C8 | 113.8 (2) | C17—C18—C19 | 120.0 (2) |
| C10—C9—C8 | 105.9 (2) | C17—C18—H18 | 120.0 |

| | | | |
|---------------|------------|------------------|------------|
| C11—C9—C8 | 108.1 (2) | C19—C18—H18 | 120.0 |
| C9—C10—H10A | 109.5 | C14—C19—C18 | 120.0 (2) |
| C9—C10—H10B | 109.5 | C14—C19—H19 | 120.0 |
| H10A—C10—H10B | 109.5 | C18—C19—H19 | 120.0 |
| C6—N1—C2—C3 | -1.4 (4) | O8—C8—C9—C10 | -79.0 (3) |
| C6—N1—C2—N7 | 178.4 (2) | N7—C8—C9—C10 | 98.3 (3) |
| C8—N7—C2—N1 | 178.5 (2) | O8—C8—C9—C11 | 38.3 (3) |
| C8—N7—C2—C3 | -1.8 (4) | N7—C8—C9—C11 | -144.3 (2) |
| N1—C2—C3—C4 | 0.7 (4) | O13B—C13—C14—C19 | 12.4 (4) |
| N7—C2—C3—C4 | -179.1 (2) | O13A—C13—C14—C19 | -167.2 (2) |
| C2—C3—C4—C5 | 0.6 (4) | O13B—C13—C14—C15 | -165.7 (2) |
| C3—C4—C5—C6 | -1.1 (4) | O13A—C13—C14—C15 | 14.7 (3) |
| C2—N1—C6—N6 | -178.5 (2) | C19—C14—C15—C16 | 0.1 (4) |
| C2—N1—C6—C5 | 0.8 (4) | C13—C14—C15—C16 | 178.2 (2) |
| C4—C5—C6—N6 | 179.6 (3) | C14—C15—C16—C17 | 0.1 (4) |
| C4—C5—C6—N1 | 0.4 (4) | C15—C16—C17—C18 | 0.4 (4) |
| C2—N7—C8—O8 | 1.0 (4) | C16—C17—C18—C19 | -1.1 (4) |
| C2—N7—C8—C9 | -176.4 (2) | C15—C14—C19—C18 | -0.8 (4) |
| O8—C8—C9—C12 | 159.9 (2) | C13—C14—C19—C18 | -178.9 (2) |
| N7—C8—C9—C12 | -22.8 (3) | C17—C18—C19—C14 | 1.3 (4) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...O13A ⁱ | 0.91 (2) | 1.67 (2) | 2.571 (2) | 170 (2) |
| N6—H6A...O13B ⁱ | 0.90 (2) | 2.05 (2) | 2.934 (3) | 167 (2) |
| N6—H6B...O13B ⁱⁱ | 0.91 (2) | 2.05 (2) | 2.869 (3) | 149 (2) |
| N7—H7...O13A ⁱ | 0.86 (2) | 2.24 (2) | 2.984 (3) | 146 (2) |
| C4—H4...O8 ⁱⁱⁱ | 0.95 | 2.49 | 3.433 (3) | 172 |

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