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# 2-Aminopyridinium 4-hydroxybenzoate

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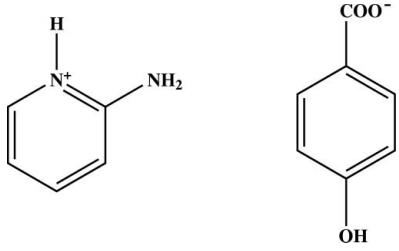
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.001 Å; $R$ factor = 0.049; $wR$ factor = 0.140; data-to-parameter ratio = 32.1.

In the title compound, $C_5H_7N_2^+\cdot C_7H_5O_3^-$, the carboxylate mean plane of the 4-hydroxybenzoate anion is twisted by 8.78 (5)° from the attached ring. The cations and anions are linked *via* O—H···O, N—H···O and C—H···O hydrogen bonds, forming a three-dimensional network. In addition, $\pi$–$\pi$ interactions involving the benzene and pyridinium rings, with centroid–centroid distances of 3.5500 (6) and 3.6594 (6) Å, are observed.

## Related literature

For the applications of 2-aminopyridine, see: Windholz (1976). For related structures, see: Chao *et al.* (1975); Heath *et al.* (1992); Jebas & Balasubramanian (2006); Joanna & Zaworotko (2005); Smith *et al.* (2000).




## Experimental

### Crystal data

$C_5H_7N_2^+\cdot C_7H_5O_3^-$
$M_r$ = 232.24
Monoclinic, $P2_1/n$
$a$ = 10.0647 (2) Å
$b$ = 10.9369 (2) Å
$c$ = 10.7985 (2) Å
$\beta$ = 111.036 (1)°
$V$ = 1109.44 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 100.0 (1) K
0.34 × 0.29 × 0.17 mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.966, $T_{max}$ = 0.983
22398 measured reflections
5078 independent reflections
3835 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.140
$S$ = 1.02
5078 reflections
158 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1*O1*···O2$^{i}$ | 0.82 | 1.86 | 2.6257 (9) | 154 |
| N2—H1*N2*···O2$^{ii}$ | 0.86 | 1.98 | 2.8224 (11) | 167 |
| N2—H2*N2*···O3$^{iii}$ | 0.86 | 1.99 | 2.8396 (11) | 171 |
| N1—H1*N1*···O3$^{ii}$ | 0.88 (1) | 1.81 (1) | 2.6861 (10) | 169 (2) |
| C10—H10*A*···O1 | 0.93 | 2.51 | 3.3482 (14) | 149 |
| C11—H11*A*···O2$^{i}$ | 0.93 | 2.34 | 3.1899 (12) | 152 |

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x-1, y-1, z$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2* and *SAINT* (Bruker, 2005); 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, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2696).

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# supporting information

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## 2-Aminopyridinium 4-hydroxybenzoate

**Ching Kheng Quah, Samuel Robinson Jebas and Hoong-Kun Fun**

### S1. Comment

2-Aminopyridine is used in the manufacture of pharmaceuticals, especially antihistaminic drugs (Windholz, 1976). As an extension of our systematic study of hydrogen bonding patterns of 2-aminopyridine with aromatic carboxylic acids, the title compound was synthesized and its crystal structure determined.

The asymmetric unit contains one 2-aminopyridinium cation and 4-hydroxybenzoate anion. The proton transfer from the carboxyl group to atom N1 of 2-aminopyridine resulted in the widening of C8—N1—C12 angle of the pyridinium ring to 122.35°, compared to the corresponding angle of 117.7 (1)° in neutral 2-aminopyridine (Chao *et al.*, 1975). Similar feature is observed in various 2-aminopyridine acid complexes (Joanna & Zaworotko, 2005; Smith *et al.*, 2000). The bond distances and angles in the title compound are comparable to those in various 2-aminopyridine acid complexes and 4-hydroxybenzoic acid (Joanna & Zaworotko, 2005; Heath *et al.*, 1992).

The 2-aminopyridinium cation is essentially planar, with a maximum deviation of 0.016 (1) Å for atom N1. In the 4-hydroxybenzoate anion, the carboxylate group is twisted slightly from the attached ring; the dihedral angle between C1-C6 and O2/O3/C6/C7 planes is 8.78 (5)°.

The crystal packing is consolidated by intermolecular O—H···O, N—H···O and C—H···O hydrogen bonds (Table 1). These hydrogen bonds link the molecules into a three-dimensional network. The packing is further strengthened by $\pi$-$\pi$ interactions involving the benzene (centroid Cg1) and pyridinium (centroid Cg2) rings, with Cg1···Cg2$^{iv}$ = 3.6594 (6) Å and Cg2···Cg2$^{v}$ = 3.5500 (6) Å [symmetry code: (iv) 1-x, 1-y, 1-z; (v) -x, 1-y, 1-z].

### S2. Experimental

2-Aminopyridine and 4-hydroxybenzoic acid were mixed in methanol in a 1:1 molar ratio. The clear colourless solution obtained was allowed to evaporate slowly. Colourless crystals were obtained after a week.

### S3. Refinement

H atoms were placed in calculated positions, with C-H = 0.93 Å, N-H = 0.86 Å and O-H = 0.82 Å and refined using a riding model with $U_{iso}$(H) = 1.2$U_{eq}$(C,N) and 1.5$U_{eq}$(O). Atom H1N1 was located in a difference map and was refined with an N-H distance restraint of 0.86 Å.

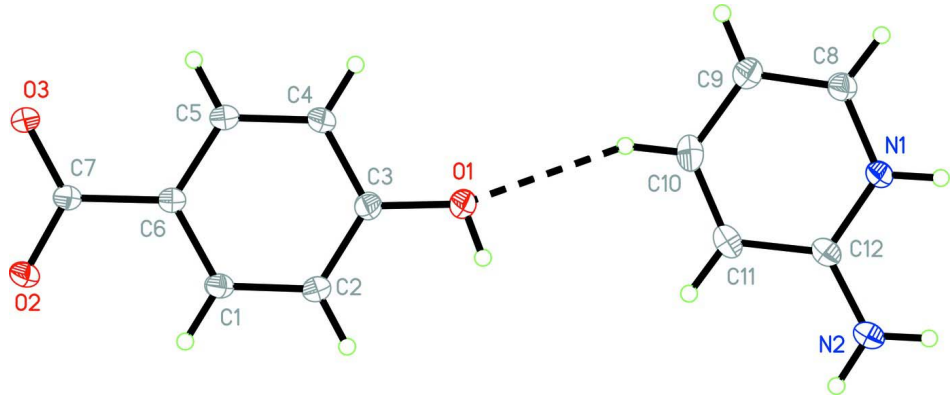


**Figure 1**

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. The dashed line indicates a hydrogen bond.

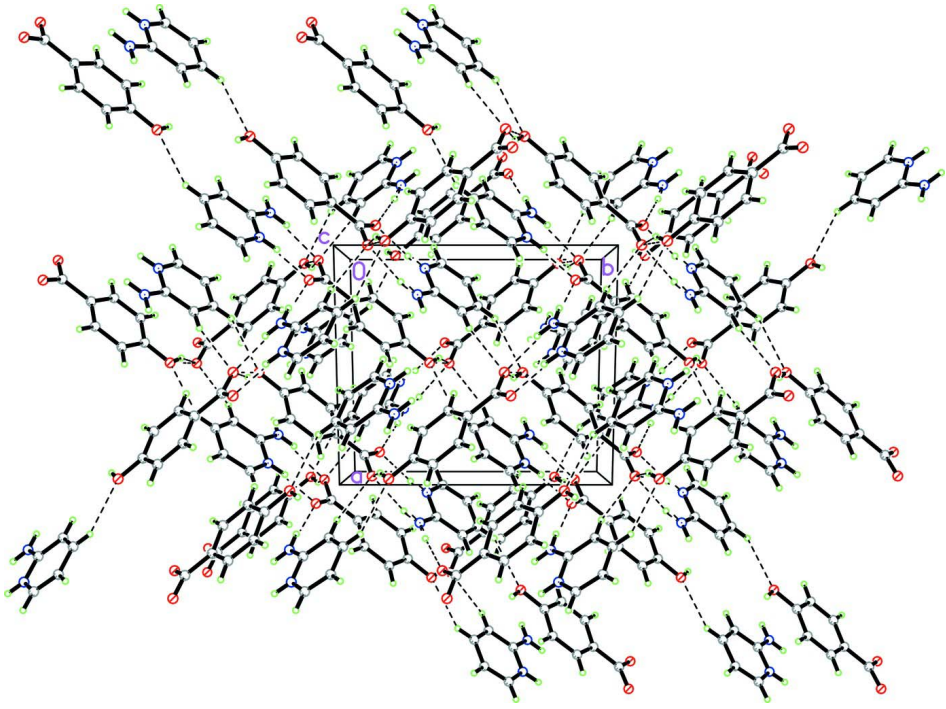


**Figure 2**

The crystal packing of the title compound, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

### 2-Aminopyridinium 4-hydroxybenzoate

*Crystal data*

$C_5H_7N_2^+·C_7H_5O_3^-$
$M_r$ = 232.24
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a$ = 10.0647 (2) Å
$b$ = 10.9369 (2) Å
$c$ = 10.7985 (2) Å
$\beta$ = 111.036 (1)°
$V$ = 1109.44 (4) Å$^3$
$Z$ = 4
$F$(000) = 488
$D_x$ = 1.390 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 6837 reflections
$\theta$ = 2.8–35.6°
$\mu$ = 0.10 mm$^{-1}$

$T$ = 100 K
Block, colourless

0.34 × 0.29 × 0.17 mm

*Data collection*

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.966, $T_{max}$ = 0.983

22398 measured reflections
5078 independent reflections
3835 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030
$\theta_{max}$ = 35.6°, $\theta_{min}$ = 2.4°
$h$ = −16→11
$k$ = −17→17
$l$ = −16→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.140
$S$ = 1.02
5078 reflections
158 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.2186P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

*Special details*

**Experimental**. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.52173 (8) | 0.67777 (7) | 0.56764 (7) | 0.02345 (16) |
| H1O1 | 0.5435 | 0.6430 | 0.6395 | 0.035* |
| O2 | 0.97943 (7) | 1.10528 (6) | 0.70095 (6) | 0.01770 (14) |
| O3 | 0.88217 (8) | 1.12535 (7) | 0.48165 (6) | 0.02051 (14) |
| N1 | 0.06716 (8) | 0.30978 (7) | 0.51061 (7) | 0.01683 (15) |
| N2 | 0.18939 (9) | 0.28645 (8) | 0.73537 (8) | 0.02239 (17) |
| H1N2 | 0.1354 | 0.2254 | 0.7348 | 0.027* |
| H2N2 | 0.2550 | 0.3085 | 0.8082 | 0.027* |
| C1 | 0.81342 (9) | 0.89872 (8) | 0.69825 (8) | 0.01647 (16) |
| H1A | 0.8873 | 0.9180 | 0.7769 | 0.020* |
| C2 | 0.72397 (10) | 0.80096 (9) | 0.69536 (8) | 0.01740 (16) |
| H2A | 0.7387 | 0.7548 | 0.7714 | 0.021* |

| | | | | |
|---|---|---|---|---|
| C3 | 0.61195 (10) | 0.77231 (9) | 0.57782 (9) | 0.01771 (16) |
| C4 | 0.59084 (11) | 0.84236 (10) | 0.46429 (9) | 0.02258 (19) |
| H4A | 0.5157 | 0.8243 | 0.3862 | 0.027* |
| C5 | 0.68141 (10) | 0.93876 (9) | 0.46745 (9) | 0.02087 (18) |
| H5A | 0.6673 | 0.9842 | 0.3910 | 0.025* |
| C6 | 0.79383 (9) | 0.96844 (8) | 0.58454 (8) | 0.01518 (15) |
| C7 | 0.89111 (9) | 1.07305 (8) | 0.58888 (8) | 0.01503 (15) |
| C8 | 0.03894 (10) | 0.36798 (9) | 0.39292 (9) | 0.01886 (17) |
| H8A | −0.0348 | 0.3399 | 0.3183 | 0.023* |
| C9 | 0.11667 (11) | 0.46682 (9) | 0.38189 (10) | 0.02141 (18) |
| H9A | 0.0968 | 0.5068 | 0.3012 | 0.026* |
| C10 | 0.22817 (11) | 0.50629 (9) | 0.49691 (10) | 0.02254 (19) |
| H10A | 0.2836 | 0.5728 | 0.4919 | 0.027* |
| C11 | 0.25595 (10) | 0.44821 (9) | 0.61585 (10) | 0.02098 (18) |
| H11A | 0.3297 | 0.4750 | 0.6911 | 0.025* |
| C12 | 0.17140 (10) | 0.34698 (9) | 0.62328 (9) | 0.01766 (16) |
| H1N1 | 0.0145 (17) | 0.2453 (12) | 0.5101 (19) | 0.051 (5)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0264 (4) | 0.0269 (4) | 0.0164 (3) | −0.0110 (3) | 0.0069 (3) | 0.0002 (3) |
| O2 | 0.0180 (3) | 0.0203 (3) | 0.0128 (3) | −0.0017 (2) | 0.0032 (2) | −0.0020 (2) |
| O3 | 0.0219 (3) | 0.0218 (3) | 0.0143 (3) | −0.0048 (3) | 0.0023 (2) | 0.0040 (2) |
| N1 | 0.0170 (3) | 0.0179 (3) | 0.0144 (3) | −0.0029 (3) | 0.0042 (3) | −0.0020 (3) |
| N2 | 0.0227 (4) | 0.0254 (4) | 0.0147 (3) | −0.0055 (3) | 0.0015 (3) | −0.0015 (3) |
| C1 | 0.0167 (4) | 0.0186 (4) | 0.0127 (3) | −0.0001 (3) | 0.0036 (3) | 0.0001 (3) |
| C2 | 0.0189 (4) | 0.0194 (4) | 0.0136 (3) | −0.0011 (3) | 0.0056 (3) | 0.0016 (3) |
| C3 | 0.0192 (4) | 0.0198 (4) | 0.0151 (3) | −0.0037 (3) | 0.0073 (3) | −0.0011 (3) |
| C4 | 0.0230 (4) | 0.0288 (5) | 0.0126 (3) | −0.0093 (4) | 0.0024 (3) | 0.0002 (3) |
| C5 | 0.0225 (4) | 0.0245 (5) | 0.0133 (3) | −0.0053 (3) | 0.0036 (3) | 0.0023 (3) |
| C6 | 0.0159 (3) | 0.0164 (4) | 0.0127 (3) | 0.0000 (3) | 0.0044 (3) | 0.0002 (3) |
| C7 | 0.0154 (3) | 0.0156 (4) | 0.0129 (3) | 0.0010 (3) | 0.0037 (3) | 0.0001 (3) |
| C8 | 0.0185 (4) | 0.0218 (4) | 0.0159 (4) | −0.0018 (3) | 0.0057 (3) | −0.0008 (3) |
| C9 | 0.0226 (4) | 0.0220 (4) | 0.0206 (4) | −0.0025 (3) | 0.0090 (3) | 0.0011 (3) |
| C10 | 0.0210 (4) | 0.0205 (4) | 0.0276 (4) | −0.0052 (3) | 0.0105 (4) | −0.0025 (3) |
| C11 | 0.0169 (4) | 0.0213 (4) | 0.0229 (4) | −0.0034 (3) | 0.0049 (3) | −0.0046 (3) |
| C12 | 0.0162 (4) | 0.0190 (4) | 0.0163 (4) | −0.0005 (3) | 0.0040 (3) | −0.0032 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C3 | 1.3543 (11) | C3—C4 | 1.3957 (13) |
| O1—H1O1 | 0.8200 | C4—C5 | 1.3861 (13) |
| O2—C7 | 1.2675 (10) | C4—H4A | 0.93 |
| O3—C7 | 1.2654 (10) | C5—C6 | 1.3990 (12) |
| N1—C12 | 1.3528 (11) | C5—H5A | 0.93 |
| N1—C8 | 1.3571 (12) | C6—C7 | 1.4956 (12) |
| N1—H1N1 | 0.881 (9) | C8—C9 | 1.3644 (13) |

| | | | |
|---|---|---|---|
| N2—C12 | 1.3338 (12) | C8—H8A | 0.93 |
| N2—H1N2 | 0.86 | C9—C10 | 1.4099 (14) |
| N2—H2N2 | 0.86 | C9—H9A | 0.93 |
| C1—C2 | 1.3908 (13) | C10—C11 | 1.3687 (14) |
| C1—C6 | 1.3980 (12) | C10—H10A | 0.93 |
| C1—H1A | 0.93 | C11—C12 | 1.4161 (13) |
| C2—C3 | 1.3975 (12) | C11—H11A | 0.93 |
| C2—H2A | 0.93 | | |

| | | | |
|---|---|---|---|
| C3—O1—H1O1 | 109.5 | C1—C6—C5 | 118.72 (8) |
| C12—N1—C8 | 122.35 (8) | C1—C6—C7 | 120.36 (8) |
| C12—N1—H1N1 | 121.1 (13) | C5—C6—C7 | 120.92 (8) |
| C8—N1—H1N1 | 116.5 (13) | O3—C7—O2 | 122.89 (8) |
| C12—N2—H1N2 | 120.0 | O3—C7—C6 | 119.10 (7) |
| C12—N2—H2N2 | 120.0 | O2—C7—C6 | 118.00 (7) |
| H1N2—N2—H2N2 | 120.0 | N1—C8—C9 | 121.30 (9) |
| C2—C1—C6 | 120.90 (8) | N1—C8—H8A | 119.3 |
| C2—C1—H1A | 119.5 | C9—C8—H8A | 119.3 |
| C6—C1—H1A | 119.5 | C8—C9—C10 | 117.75 (9) |
| C1—C2—C3 | 119.83 (8) | C8—C9—H9A | 121.1 |
| C1—C2—H2A | 120.1 | C10—C9—H9A | 121.1 |
| C3—C2—H2A | 120.1 | C11—C10—C9 | 120.96 (9) |
| O1—C3—C4 | 117.49 (8) | C11—C10—H10A | 119.5 |
| O1—C3—C2 | 122.94 (8) | C9—C10—H10A | 119.5 |
| C4—C3—C2 | 119.57 (8) | C10—C11—C12 | 119.44 (9) |
| C5—C4—C3 | 120.30 (8) | C10—C11—H11A | 120.3 |
| C5—C4—H4A | 119.9 | C12—C11—H11A | 120.3 |
| C3—C4—H4A | 119.9 | N2—C12—N1 | 118.41 (8) |
| C4—C5—C6 | 120.67 (8) | N2—C12—C11 | 123.43 (8) |
| C4—C5—H5A | 119.7 | N1—C12—C11 | 118.17 (8) |
| C6—C5—H5A | 119.7 | | |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | −0.63 (14) | C5—C6—C7—O3 | −8.78 (13) |
| C1—C2—C3—O1 | 179.36 (9) | C1—C6—C7—O2 | −8.40 (12) |
| C1—C2—C3—C4 | −0.07 (14) | C5—C6—C7—O2 | 171.26 (9) |
| O1—C3—C4—C5 | −178.61 (9) | C12—N1—C8—C9 | 1.07 (14) |
| C2—C3—C4—C5 | 0.84 (15) | N1—C8—C9—C10 | 0.35 (14) |
| C3—C4—C5—C6 | −0.92 (16) | C8—C9—C10—C11 | −0.87 (15) |
| C2—C1—C6—C5 | 0.55 (13) | C9—C10—C11—C12 | 0.02 (15) |
| C2—C1—C6—C7 | −179.78 (8) | C8—N1—C12—N2 | 178.22 (9) |
| C4—C5—C6—C1 | 0.22 (14) | C8—N1—C12—C11 | −1.90 (14) |
| C4—C5—C6—C7 | −179.44 (9) | C10—C11—C12—N2 | −178.79 (9) |
| C1—C6—C7—O3 | 171.56 (8) | C10—C11—C12—N1 | 1.33 (14) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*O*1···O2$^{i}$ | 0.82 | 1.86 | 2.6257 (9) | 154 |

| | | | | |
|---|---|---|---|---|
| N2—H1*N*2···O2$^{ii}$ | 0.86 | 1.98 | 2.8224 (11) | 167 |
| N2—H2*N*2···O3$^{iii}$ | 0.86 | 1.99 | 2.8396 (11) | 171 |
| N1—H1*N*1···O3$^{ii}$ | 0.88 (1) | 1.81 (1) | 2.6861 (10) | 169 (2) |
| C10—H10*A*···O1 | 0.93 | 2.51 | 3.3482 (14) | 149 |
| C11—H11*A*···O2$^{i}$ | 0.93 | 2.34 | 3.1899 (12) | 152 |

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (ii) $x-1, y-1, z$; (iii) $x-1/2, -y+3/2, z+1/2$.