# 2,3-Diaminopyridinium benzoate

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In the title compound, $C_5H_8N_3^+ \cdot C_7H_5O_2^-$, the pyridine N atom is protonated. The carboxylate group of the benzoate anion is twisted away from the attached ring by 10.91 (9)°. In the crystal structure, N—H···O hydrogen bonds between 2,3-diaminopyridinium cations and benzoate anions, and $\pi$–$\pi$ interactions between the pyridinium rings [centroid–centroid distance = 3.6467 (9) Å] form a two-dimensional network parallel to (001). In the network, N—H···O hydrogen bonds form $R_2^2(8)$ and $R_2^1(7)$ ring motifs.

## Related literature

For general background to pyridine derivatives, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For bond-length data, see: Allen *et al.* (1987). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).
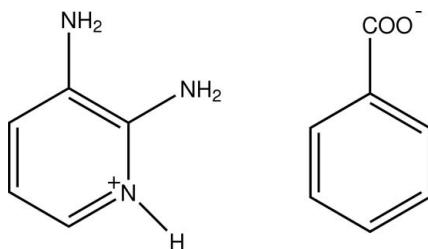
## Experimental

### Crystal data

| | |
|---|---|
| $C_5H_8N_3^+ \cdot C_7H_5O_2^-$ | $V = 2329.03$ (12) Å$^3$ |
| $M_r = 231.25$ | $Z = 8$ |
| Orthorhombic, $Pbca$ | Mo $K\alpha$ radiation |
| $a = 10.1498$ (3) Å | $\mu = 0.09$ mm$^{-1}$ |
| $b = 11.0656$ (3) Å | $T = 100$ K |
| $c = 20.7368$ (7) Å | $0.43 \times 0.40 \times 0.03$ mm |

‡ Thomson Reuters ResearcherID: A-3561-2009.

### Data collection

| | |
|---|---|
| Bruker SMART APEXII CCD area-detector diffractometer | 27109 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2005) | 3443 independent reflections |
| $T_{min} = 0.935$, $T_{max} = 0.998$ | 2559 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.070$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.124$ | |
| $S = 1.09$ | |
| 3443 reflections | $\Delta\rho_{max} = 0.26$ e Å$^{-3}$ |
| 206 parameters | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1N1···O2 | 0.96 (2) | 1.77 (2) | 2.7218 (18) | 176 (2) |
| N2—H1N2···O1 | 0.90 (2) | 1.94 (2) | 2.8377 (18) | 173 (2) |
| N2—H2N2···O2$^i$ | 0.88 (2) | 2.01 (2) | 2.8873 (17) | 170 (2) |
| N3—H1N3···O2$^i$ | 0.91 (2) | 2.02 (2) | 2.9206 (19) | 173 (2) |
| N3—H2N3···O1$^{ii}$ | 0.95 (2) | 2.00 (2) | 2.9382 (19) | 170 (2) |

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *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, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2821).

## References

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# supporting information

## 2,3-Diaminopyridinium benzoate

### Kasthuri Balasubramani and Hoong-Kun Fun

### S1. Comment

Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996). Pyridine and its substituted derivatives are often involved in hydrogen-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). Since our aim is to study some interesting hydrogen-bonding interactions, the crystal structure of the title compound is presented here.

The asymmetric unit (Fig 1), contains a protonated 2,3-diaminopyridinium cation and a benzoate anion. The bond lengths (Allen *et al.*,1987) and angles are normal. In the 2,3-diaminopyridinium cation, the protonated N1 atom has lead to a slight increase in C8—N1—C12 angle to 123.30 (14)°. Moreover, the carboxylate group is twisted slightly out of the attached ring; the dihedral angle between C1—C6 and O1/O2/C7/C6 planes is 10.91 (9)°. The 2,3-diaminopyridinium cation is planar, with a maximum deviation of 0.0089 (17) Å for atom C9.

In the crystal packing, the protonated N1 atom and the 2-amino group (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) *via* a pair of N—H⋯O hydrogen bonds forming an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). The two amino groups (N2 and N3) are involved in N—H⋯O hydrogen bonding interactions to form an $R_2^1(7)$ ring motif. The cationic and anionic units are linked through N—H⋯O hydrogen bonds (Table 1 and Fig 2) to form a two-dimensional network parallel to the (001) plane. The crystal structure is further stabilized by $\pi$-$\pi$ stacking interactions between the pyridinium rings of the cations at (x, y, z) and (-x, 1-y, 1-z), with a centroid to centroid distance of 3.6467 (9) Å.

### S2. Experimental

Hot methanol solutions (20 ml) of 2,3-diaminopyridine (27 mg, Aldrich) and benzoic acid (31 mg, Merck) were mixed and warmed over a heating magnetic stirrer for 5 minutes. The resulting solution was allowed to cool slowly at room temperature. Crystals of the title compound appeared from the mother liquor after a few days.

### S3. Refinement

All H atoms were located in a difference Fourier map and allowed to refine freely [N-H = 0.89 (2)–0.95 (2) Å and C–H = 0.97 (18)–1.02 (2) Å].
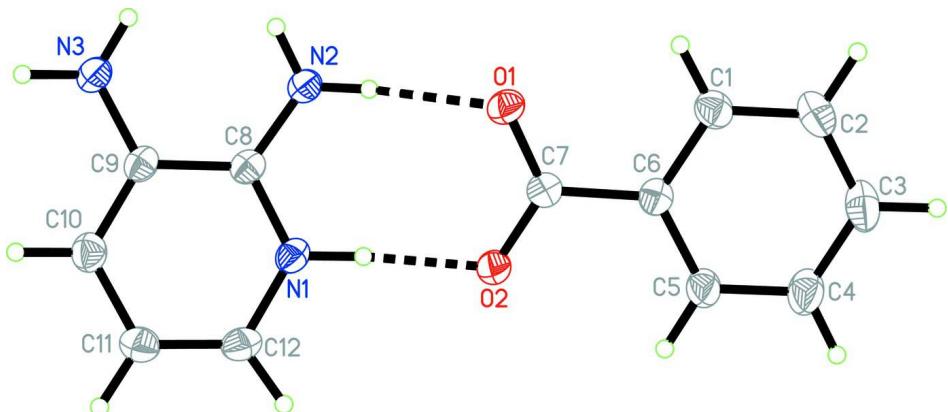
**Figure 1**

The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate hydrogen bonds.
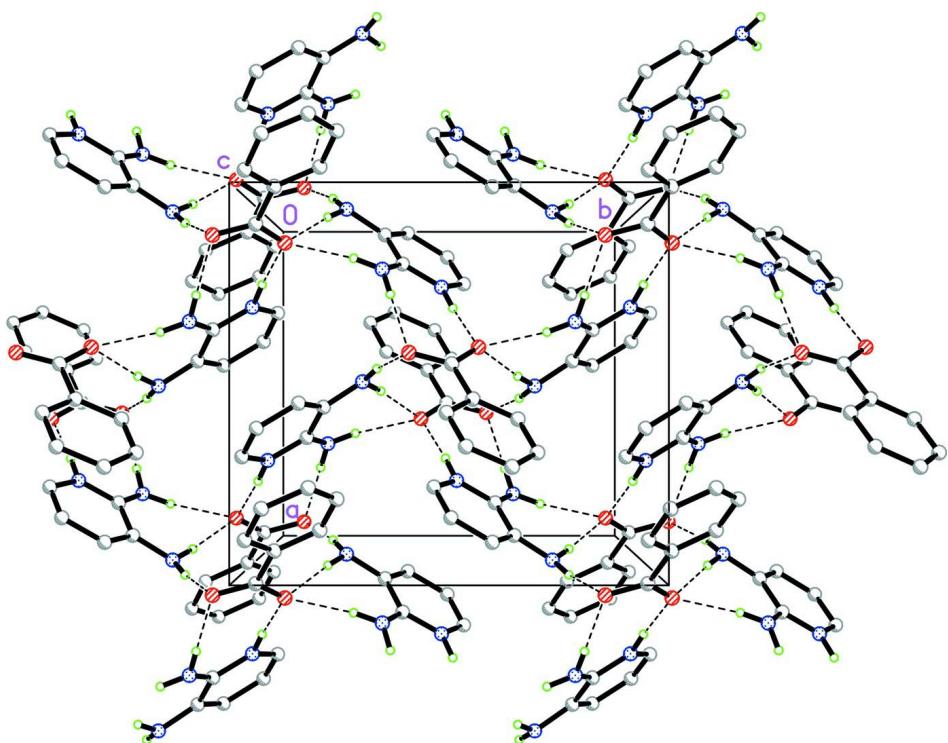


**Figure 2**

Part of the crystal packing of the title compound. Dashed lines indicate hydrogen bonds.

**2,3-Diaminopyridinium benzoate**

*Crystal data*
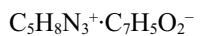
| | |
|---|---|
| $C_5H_8N_3{}^+ \cdot C_7H_5O_2{}^-$ | $c = 20.7368\ (7)$ Å |
| $M_r = 231.25$ | $V = 2329.03\ (12)$ Å$^3$ |
| Orthorhombic, $Pbca$ | $Z = 8$ |
| Hall symbol: -P 2ac 2ab | $F(000) = 976$ |
| $a = 10.1498\ (3)$ Å | $D_x = 1.319$ Mg m$^{-3}$ |
| $b = 11.0656\ (3)$ Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |

| Cell parameters from 3782 reflections | $T = 100$ K |
|---|---|
| $\theta = 2.8–27.9°$ | Plate, brown |
| $\mu = 0.09$ mm$^{-1}$ | $0.43 \times 0.40 \times 0.03$ mm |

*Data collection*

| Bruker SMART APEXII CCD area-detector diffractometer | 27109 measured reflections |
|---|---|
| Radiation source: fine-focus sealed tube | 3443 independent reflections |
| Graphite monochromator | 2559 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.070$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2005) | $\theta_{max} = 30.1°$, $\theta_{min} = 2.9°$ |
| | $h = -14 \rightarrow 14$ |
| | $k = -15 \rightarrow 15$ |
| $T_{min} = 0.935$, $T_{max} = 0.998$ | $l = -26 \rightarrow 29$ |

*Refinement*

| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
|---|---|
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.124$ | |
| $S = 1.09$ | H atoms treated by a mixture of independent and constrained refinement |
| 3443 reflections | |
| 206 parameters | $w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 1.0527P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} = 0.001$ |
| | $\Delta\rho_{max} = 0.26$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

*Special details*

**Experimental**. The crystal was placed in the cold stream of an Oxford Cyrosystems 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.41320 (11) | 0.39789 (9) | 0.63510 (5) | 0.0253 (3) |
| O2 | 0.39681 (11) | 0.57595 (9) | 0.58541 (5) | 0.0257 (3) |
| C6 | 0.54129 (15) | 0.55976 (13) | 0.67572 (8) | 0.0217 (3) |
| C1 | 0.57778 (16) | 0.49395 (15) | 0.73019 (8) | 0.0271 (4) |
| C2 | 0.66687 (18) | 0.54115 (17) | 0.77390 (10) | 0.0347 (4) |
| C3 | 0.72160 (19) | 0.65474 (16) | 0.76378 (10) | 0.0365 (4) |
| C4 | 0.68658 (19) | 0.72004 (16) | 0.70966 (10) | 0.0375 (5) |
| C5 | 0.59687 (17) | 0.67368 (14) | 0.66578 (9) | 0.0296 (4) |
| C7 | 0.44423 (15) | 0.50698 (13) | 0.62917 (7) | 0.0211 (3) |
| C9 | 0.06661 (15) | 0.32936 (13) | 0.46855 (8) | 0.0220 (3) |

| | | | |
|---|---|---|---|
| C8 | 0.15562 (15) | 0.37759 (13) | 0.51515 (8) | 0.0211 (3) |
| N1 | 0.22115 (13) | 0.47997 (11) | 0.50049 (7) | 0.0230 (3) |
| N2 | 0.17608 (14) | 0.32713 (12) | 0.57320 (7) | 0.0239 (3) |
| N3 | −0.00614 (14) | 0.22766 (12) | 0.48334 (8) | 0.0273 (3) |
| C12 | 0.20715 (17) | 0.53936 (14) | 0.44310 (9) | 0.0270 (4) |
| C11 | 0.12491 (17) | 0.49519 (15) | 0.39762 (9) | 0.0288 (4) |
| C10 | 0.05443 (17) | 0.38821 (14) | 0.41056 (9) | 0.0268 (4) |
| H12A | 0.262 (2) | 0.6122 (17) | 0.4384 (9) | 0.039 (5)* |
| H11A | 0.1152 (17) | 0.5333 (16) | 0.3555 (9) | 0.028 (5)* |
| H10A | −0.0033 (18) | 0.3556 (15) | 0.3778 (9) | 0.027 (5)* |
| H1A | 0.5401 (19) | 0.4138 (17) | 0.7363 (9) | 0.037 (5)* |
| H2A | 0.690 (2) | 0.4955 (18) | 0.8134 (10) | 0.045 (6)* |
| H3A | 0.785 (2) | 0.6890 (17) | 0.7969 (10) | 0.043 (6)* |
| H4A | 0.726 (2) | 0.7970 (19) | 0.7013 (10) | 0.051 (6)* |
| H5A | 0.5737 (18) | 0.7200 (17) | 0.6276 (9) | 0.032 (5)* |
| H1N1 | 0.283 (2) | 0.5096 (18) | 0.5312 (9) | 0.039 (5)* |
| H1N2 | 0.248 (2) | 0.3487 (16) | 0.5959 (9) | 0.033 (5)* |
| H2N2 | 0.146 (2) | 0.253 (2) | 0.5800 (10) | 0.047 (6)* |
| H1N3 | 0.021 (2) | 0.1812 (18) | 0.5170 (10) | 0.042 (6)* |
| H2N3 | −0.043 (2) | 0.1882 (17) | 0.4469 (10) | 0.041 (6)* |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0278 (6) | 0.0181 (5) | 0.0298 (6) | −0.0009 (4) | −0.0021 (5) | 0.0002 (4) |
| O2 | 0.0280 (6) | 0.0205 (5) | 0.0285 (6) | −0.0020 (4) | −0.0058 (5) | 0.0020 (4) |
| C6 | 0.0181 (7) | 0.0209 (7) | 0.0261 (8) | 0.0037 (5) | 0.0001 (6) | −0.0025 (6) |
| C1 | 0.0252 (8) | 0.0271 (8) | 0.0291 (9) | 0.0039 (6) | −0.0009 (7) | 0.0015 (7) |
| C2 | 0.0335 (10) | 0.0398 (10) | 0.0308 (10) | 0.0067 (8) | −0.0089 (8) | 0.0007 (8) |
| C3 | 0.0339 (10) | 0.0346 (9) | 0.0410 (11) | 0.0058 (7) | −0.0150 (8) | −0.0104 (8) |
| C4 | 0.0361 (10) | 0.0245 (8) | 0.0520 (12) | −0.0009 (7) | −0.0165 (9) | −0.0026 (8) |
| C5 | 0.0298 (9) | 0.0227 (7) | 0.0364 (10) | 0.0003 (6) | −0.0111 (8) | 0.0019 (7) |
| C7 | 0.0197 (7) | 0.0210 (7) | 0.0226 (8) | 0.0019 (5) | 0.0027 (6) | −0.0013 (6) |
| C9 | 0.0194 (7) | 0.0182 (7) | 0.0285 (9) | 0.0017 (5) | −0.0004 (6) | −0.0027 (6) |
| C8 | 0.0192 (7) | 0.0175 (6) | 0.0265 (8) | 0.0028 (5) | 0.0011 (6) | −0.0016 (6) |
| N1 | 0.0223 (7) | 0.0186 (6) | 0.0281 (7) | −0.0011 (5) | −0.0013 (6) | −0.0012 (5) |
| N2 | 0.0237 (7) | 0.0213 (6) | 0.0269 (8) | −0.0029 (5) | −0.0020 (6) | 0.0014 (5) |
| N3 | 0.0288 (7) | 0.0217 (6) | 0.0314 (8) | −0.0048 (5) | −0.0055 (7) | 0.0010 (6) |
| C12 | 0.0286 (9) | 0.0204 (7) | 0.0320 (9) | −0.0014 (6) | 0.0008 (7) | 0.0038 (6) |
| C11 | 0.0319 (9) | 0.0260 (8) | 0.0285 (9) | 0.0006 (7) | −0.0019 (7) | 0.0054 (7) |
| C10 | 0.0252 (8) | 0.0269 (8) | 0.0283 (9) | 0.0000 (6) | −0.0043 (7) | −0.0014 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C7 | 1.2537 (17) | C9—N3 | 1.3805 (19) |
| O2—C7 | 1.2796 (18) | C9—C8 | 1.427 (2) |
| C6—C1 | 1.394 (2) | C8—N2 | 1.343 (2) |
| C6—C5 | 1.396 (2) | C8—N1 | 1.3484 (19) |

| | | | |
|---|---|---|---|
| C6—C7 | 1.498 (2) | N1—C12 | 1.367 (2) |
| C1—C2 | 1.383 (2) | N1—H1N1 | 0.96 (2) |
| C1—H1A | 0.974 (19) | N2—H1N2 | 0.90 (2) |
| C2—C3 | 1.390 (3) | N2—H2N2 | 0.88 (2) |
| C2—H2A | 0.99 (2) | N3—H1N3 | 0.91 (2) |
| C3—C4 | 1.381 (3) | N3—H2N3 | 0.95 (2) |
| C3—H3A | 1.02 (2) | C12—C11 | 1.351 (2) |
| C4—C5 | 1.386 (2) | C12—H12A | 0.99 (2) |
| C4—H4A | 0.96 (2) | C11—C10 | 1.409 (2) |
| C5—H5A | 0.972 (19) | C11—H11A | 0.975 (18) |
| C9—C10 | 1.373 (2) | C10—H10A | 0.966 (18) |
| | | | |
| C1—C6—C5 | 118.94 (15) | N3—C9—C8 | 119.55 (15) |
| C1—C6—C7 | 119.56 (14) | N2—C8—N1 | 118.36 (14) |
| C5—C6—C7 | 121.50 (14) | N2—C8—C9 | 123.34 (14) |
| C2—C1—C6 | 120.50 (16) | N1—C8—C9 | 118.29 (14) |
| C2—C1—H1A | 121.0 (12) | C8—N1—C12 | 123.30 (14) |
| C6—C1—H1A | 118.5 (12) | C8—N1—H1N1 | 117.7 (12) |
| C1—C2—C3 | 120.25 (17) | C12—N1—H1N1 | 119.0 (12) |
| C1—C2—H2A | 120.4 (12) | C8—N2—H1N2 | 118.9 (12) |
| C3—C2—H2A | 119.3 (12) | C8—N2—H2N2 | 118.3 (14) |
| C4—C3—C2 | 119.53 (17) | H1N2—N2—H2N2 | 116.3 (18) |
| C4—C3—H3A | 121.2 (11) | C9—N3—H1N3 | 117.9 (13) |
| C2—C3—H3A | 119.3 (11) | C9—N3—H2N3 | 114.0 (12) |
| C3—C4—C5 | 120.59 (17) | H1N3—N3—H2N3 | 118.1 (17) |
| C3—C4—H4A | 120.4 (13) | C11—C12—N1 | 119.87 (15) |
| C5—C4—H4A | 119.0 (13) | C11—C12—H12A | 125.2 (11) |
| C4—C5—C6 | 120.18 (17) | N1—C12—H12A | 114.9 (11) |
| C4—C5—H5A | 119.9 (11) | C12—C11—C10 | 118.99 (16) |
| C6—C5—H5A | 119.9 (11) | C12—C11—H11A | 122.1 (11) |
| O1—C7—O2 | 123.33 (14) | C10—C11—H11A | 118.9 (11) |
| O1—C7—C6 | 118.52 (14) | C9—C10—C11 | 121.30 (16) |
| O2—C7—C6 | 118.15 (13) | C9—C10—H10A | 119.5 (10) |
| C10—C9—N3 | 122.21 (15) | C11—C10—H10A | 119.2 (10) |
| C10—C9—C8 | 118.22 (14) | | |
| | | | |
| C5—C6—C1—C2 | 0.5 (2) | C10—C9—C8—N2 | −179.52 (15) |
| C7—C6—C1—C2 | −179.77 (15) | N3—C9—C8—N2 | 1.9 (2) |
| C6—C1—C2—C3 | −0.3 (3) | C10—C9—C8—N1 | 1.4 (2) |
| C1—C2—C3—C4 | −0.1 (3) | N3—C9—C8—N1 | −177.16 (13) |
| C2—C3—C4—C5 | 0.5 (3) | N2—C8—N1—C12 | −179.52 (14) |
| C3—C4—C5—C6 | −0.3 (3) | C9—C8—N1—C12 | −0.4 (2) |
| C1—C6—C5—C4 | −0.1 (3) | C8—N1—C12—C11 | −0.4 (2) |
| C7—C6—C5—C4 | −179.90 (16) | N1—C12—C11—C10 | 0.2 (2) |
| C1—C6—C7—O1 | −10.6 (2) | N3—C9—C10—C11 | 176.89 (15) |
| C5—C6—C7—O1 | 169.17 (15) | C8—C9—C10—C11 | −1.7 (2) |
| C1—C6—C7—O2 | 169.17 (14) | C12—C11—C10—C9 | 0.8 (3) |
| C5—C6—C7—O2 | −11.1 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*N*1···O2 | 0.96 (2) | 1.77 (2) | 2.7218 (18) | 176 (2) |
| N2—H1*N*2···O1 | 0.90 (2) | 1.94 (2) | 2.8377 (18) | 173 (2) |
| N2—H2*N*2···O2[i] | 0.88 (2) | 2.01 (2) | 2.8873 (17) | 170 (2) |
| N3—H1*N*3···O2[i] | 0.91 (2) | 2.02 (2) | 2.9206 (19) | 173 (2) |
| N3—H2*N*3···O1[ii] | 0.95 (2) | 2.00 (2) | 2.9382 (19) | 170 (2) |

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