Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,3-Diaminopyridinium 4-nitrobenzoate

Kasthuri Balasubramani and Hoong-Kun Fun*‡

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

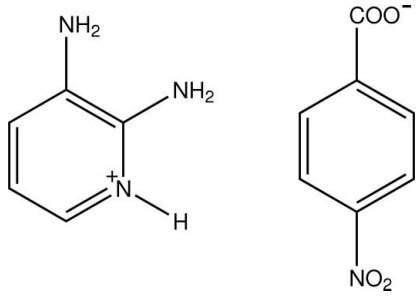
Received 22 May 2009; accepted 3 June 2009

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.116; data-to-parameter ratio = 12.3.

In the title salt, $C_5H_8N_3^+\cdot C_7H_4NO_4^-$, the pyridine N atom of the 2,3-diaminopyridine molecule is protonated. The protonated N atom and one of the two 2-amino groups are hydrogen bonded to the 4-nitrobenzoate anion through a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. The carboxylate mean plane of the 4-nitrobenzoate anion is twisted by 3.77 (5)° from the attached ring and the nitro group is similarly twisted by 2.28 (10)°. In the crystal, the molecules are linked by N—H···O and C—H···O interactions into sheets parallel to (100).

Related literature

For substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996); 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

$C_5H_8N_3^+\cdot C_7H_4NO_4^-$
M_r = 276.26
Monoclinic, $P2_1$
a = 8.0827 (2) Å
b = 6.7365 (1) Å
c = 11.4489 (3) Å
β = 101.967 (1)°
V = 609.83 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 100 K
0.25 × 0.17 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.972, T_{max} = 0.988
11659 measured reflections
2808 independent reflections
2155 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.116
S = 1.04
2808 reflections
229 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O4	0.99 (3)	1.70 (3)	2.671 (2)	167 (3)
N2—H1N2···O3	0.89 (3)	2.01 (3)	2.901 (2)	178 (5)
N2—H2N2···O3^{i}	0.86 (2)	2.06 (2)	2.903 (2)	171 (2)
N3—H1N3···O3^{i}	0.85 (3)	2.14 (3)	2.951 (3)	159 (2)
N3—H2N3···O2^{ii}	0.82 (3)	2.34 (3)	3.140 (2)	165 (3)
C10—H10A···O1^{ii}	0.98 (3)	2.53 (3)	3.507 (2)	177 (2)
C11—H11A···O4^{iii}	0.99 (2)	2.56 (2)	3.216 (3)	124 (2)

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

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).

HKF and KBS thank the Malaysian Government and Universiti Sains Malaysia for the Science Fund grant No. 305/PFIZIK/613312. KBS thanks Universiti Sains Malaysia for a post–doctoral research fellowship. HKF also thanks Universiti Sains Malaysia for the Research University Golden Goose grant No. 1001/PFIZIK/811012.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2462).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Jeffrey, G. A. (1997). In *An Introduction to Hydrogen Bonding*. Oxford University Press.
Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin: Springer.
Katritzky, A. R., Rees, C. W. & Scriven, E. F. V. (1996). In *Comprehensive Heterocyclic Chemistry II*. Oxford: Pergamon Press.
Pozharski, A. F., Soldatenkov, A. T. & Katritzky, A. R. (1997). In *Heterocycles in Life and Society*. New York: Wiley.

‡ Thomson Reuters ResearcherID: A-3561-2009.

Scheiner, S. (1997). In *Hydrogen Bonding, A Theoretical Perspective*. Oxford University Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2009). E**65**, o1511–o1512 [doi:10.1107/S160053680902100X]

2,3-Diaminopyridinium 4-nitrobenzoate

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 bonding interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). In order to study some interesting hydrogen bonding interactions, the synthesis and structure of the title salt (I) is presented here.

The asymmetric unit of (I), Fig. 1, contains a protonated 2,3-diaminopyridinium cation and a 4-nitrobenzoate anion. In the 2,3-diaminopyridinium cation, a wide angle (123.62 (17)°) is subtended at the protonated N1 atom. The 2,3-diaminopyridinium cation is planar, with a maximum deviation of 0.005 (2)Å for atom C1. The carboxylate group is twisted slightly from the ring; the dihedral angle between C1—C6 and O3/O4/C7/C6 planes is 5.41 (10)°. The nitro group is also slightly twisted away from its attached benzene ring by 2.28 (10)°.

In the crystal packing, Fig. 2, the protonated N1 atom and the 2-amino group (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O3 and O4) *via* a pair of N—H···O hydrogen bonds forming a ring motif, $R_2^2(8)$ (Bernstein *et al.*, 1995). The 2-amino groups (N2 and N3) are involved in N—H···O3 hydrogen bonding interactions to form a $R^1_2(7)$ ring motif. One of the amino group hydrogen atoms, H2N3, and the ring hydrogen atom, H10A, are connected to the 4-nitro group oxygen atoms (O1 and O2) to form an $R_2^2(8)$ ring motif (Table 1 and Fig. 2). These molecules are linked by these interactions into sheets parallel to (100). The crystal structure is further stabilized by a π-π stacking interactions between the aminopyridine- and carboxylate-rings with centroid-to-centroid distances of 3.8343 (10) Å.

S2. Experimental

Hot methanol solutions (20 ml) of 2,3-diaminopyridine (27 mg, Aldrich) and 4-nitrobenzoic acid (42 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 (I) appeared from the mother liquor after a few days.

S3. Refinement

All the H atoms were located from the difference Fourier map [N–H = 0.82 (3)–0.99 (3)Å and C–H = 0.91 (2)–0.99 (2) Å] and allowed to refine freely. In the absence of significant anomalous scattering effects, 2144 Friedel pairs were merged.

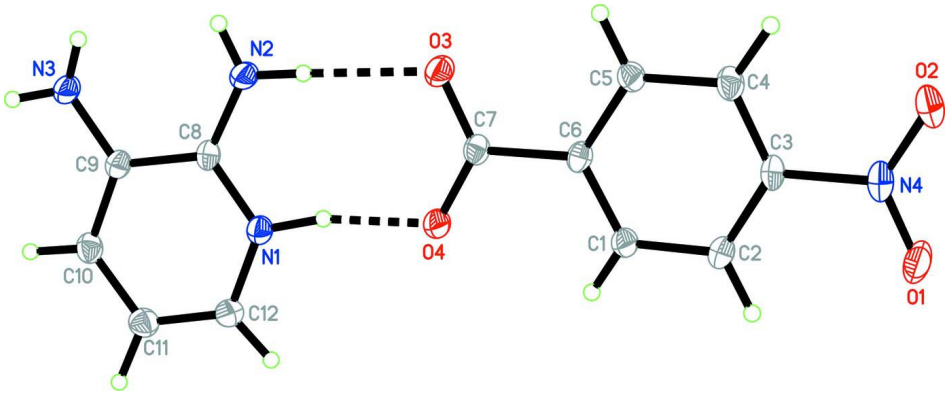


Figure 1

The molecular structures of the ions in (I), illustrating the primary mode of association between them, showing 50% probability displacement ellipsoids and the atom numbering scheme. Dashed lines indicate the hydrogen bonding.

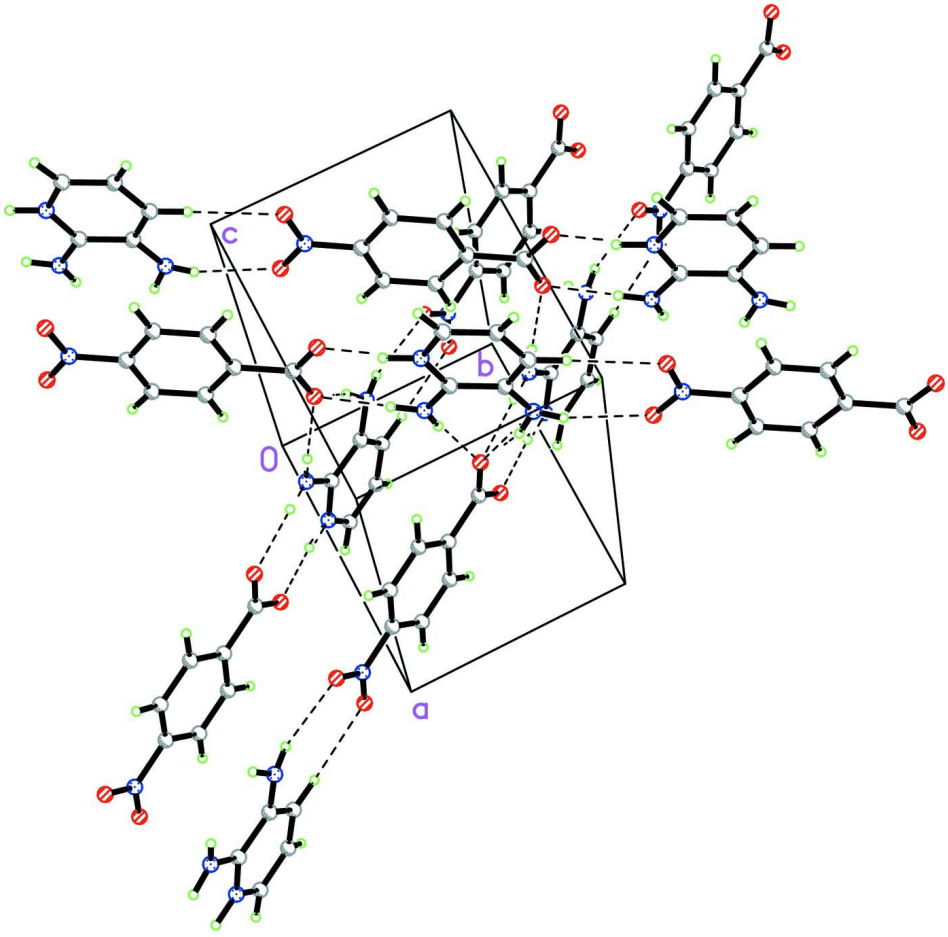


Figure 2

The crystal packing of (I). Dashed lines indicate the hydrogen bondings.

2,3-Diaminopyridinium 4-nitrobenzoate

Crystal data

$C_5H_8N_3^+ \cdot C_7H_4NO_4^-$
M_r = 276.26
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 8.0827 (2) Å
b = 6.7365 (1) Å
c = 11.4489 (3) Å
β = 101.967 (1)°
V = 609.83 (2) Å^3
Z = 2
$F(000)$ = 288
D_x = 1.504 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2526 reflections
θ = 2.8–31.7°
μ = 0.12 mm^{-1}
T = 100 K
Block, brown
0.25 × 0.17 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.972, T_{max} = 0.988
11659 measured reflections
2808 independent reflections
2155 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 34.9°, θ_{min} = 2.6°
$h = -12 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.116
S = 1.04
2808 reflections
229 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
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.026P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 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 s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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	−0.0506 (2)	−0.7085 (2)	0.85306 (17)	0.0306 (4)
O2	−0.04637 (19)	−0.7831 (2)	0.66897 (16)	0.0269 (4)

O3	0.35100 (19)	0.1109 (2)	0.60686 (14)	0.0223 (3)
O4	0.35695 (19)	0.1713 (2)	0.79972 (14)	0.0210 (3)
N4	−0.0141 (2)	−0.6717 (3)	0.75606 (18)	0.0213 (4)
C1	0.1816 (2)	−0.1740 (3)	0.82546 (19)	0.0178 (4)
C2	0.1021 (2)	−0.3532 (3)	0.8391 (2)	0.0183 (4)
C3	0.0723 (2)	−0.4824 (3)	0.7432 (2)	0.0178 (4)
C4	0.1172 (2)	−0.4421 (3)	0.6355 (2)	0.0196 (4)
C5	0.1973 (2)	−0.2624 (3)	0.6234 (2)	0.0180 (4)
C6	0.2309 (2)	−0.1287 (3)	0.71862 (19)	0.0162 (4)
C7	0.3201 (2)	0.0666 (3)	0.70675 (18)	0.0169 (4)
N1	0.5459 (2)	0.4983 (2)	0.80784 (16)	0.0179 (3)
N2	0.5600 (2)	0.4619 (3)	0.60992 (18)	0.0213 (4)
N3	0.7324 (2)	0.8308 (3)	0.62077 (18)	0.0212 (4)
C8	0.5959 (2)	0.5681 (3)	0.71027 (19)	0.0166 (4)
C9	0.6873 (2)	0.7522 (3)	0.72040 (19)	0.0168 (4)
C10	0.7217 (2)	0.8451 (3)	0.8301 (2)	0.0197 (4)
C11	0.6717 (2)	0.7629 (3)	0.9295 (2)	0.0213 (4)
C12	0.5820 (2)	0.5895 (3)	0.91644 (19)	0.0199 (4)
H1A	0.201 (3)	−0.084 (4)	0.887 (2)	0.020 (6)*
H2A	0.068 (3)	−0.384 (4)	0.914 (2)	0.020 (6)*
H4A	0.089 (3)	−0.535 (5)	0.569 (2)	0.033 (7)*
H5A	0.232 (3)	−0.233 (4)	0.547 (2)	0.021 (6)*
H10A	0.782 (3)	0.972 (5)	0.834 (2)	0.029 (7)*
H11A	0.711 (3)	0.821 (4)	1.010 (2)	0.027 (7)*
H12A	0.540 (3)	0.527 (4)	0.978 (2)	0.021 (6)*
H1N1	0.478 (3)	0.375 (5)	0.793 (3)	0.038 (8)*
H1N2	0.497 (4)	0.353 (5)	0.608 (3)	0.038 (8)*
H2N2	0.579 (3)	0.496 (4)	0.542 (2)	0.017 (6)*
H1N3	0.735 (3)	0.759 (5)	0.560 (2)	0.025 (7)*
H2N3	0.806 (4)	0.917 (5)	0.635 (3)	0.037 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0374 (9)	0.0213 (8)	0.0368 (10)	−0.0086 (6)	0.0162 (8)	0.0038 (7)
O2	0.0274 (7)	0.0170 (7)	0.0348 (10)	−0.0058 (6)	0.0027 (7)	−0.0027 (7)
O3	0.0293 (7)	0.0175 (6)	0.0226 (8)	−0.0035 (5)	0.0109 (6)	0.0002 (6)
O4	0.0281 (7)	0.0164 (6)	0.0199 (8)	−0.0056 (5)	0.0083 (6)	−0.0023 (6)
N4	0.0165 (7)	0.0146 (7)	0.0320 (10)	−0.0015 (6)	0.0030 (7)	0.0026 (8)
C1	0.0213 (8)	0.0139 (8)	0.0187 (10)	−0.0012 (7)	0.0053 (7)	−0.0008 (8)
C2	0.0185 (8)	0.0155 (8)	0.0215 (10)	−0.0007 (6)	0.0054 (7)	0.0030 (8)
C3	0.0166 (8)	0.0116 (7)	0.0255 (11)	−0.0015 (6)	0.0053 (7)	0.0010 (7)
C4	0.0216 (8)	0.0132 (8)	0.0249 (11)	−0.0008 (6)	0.0067 (8)	−0.0015 (8)
C5	0.0205 (8)	0.0146 (8)	0.0196 (10)	−0.0010 (7)	0.0056 (7)	−0.0018 (8)
C6	0.0176 (8)	0.0111 (8)	0.0201 (10)	0.0012 (6)	0.0043 (7)	0.0032 (7)
C7	0.0180 (8)	0.0128 (8)	0.0208 (10)	0.0003 (6)	0.0058 (7)	0.0008 (8)
N1	0.0188 (7)	0.0161 (7)	0.0191 (9)	−0.0021 (6)	0.0048 (6)	0.0004 (7)
N2	0.0300 (9)	0.0176 (8)	0.0182 (9)	−0.0056 (6)	0.0094 (7)	−0.0014 (7)

N3	0.0273 (8)	0.0178 (7)	0.0201 (9)	−0.0061 (7)	0.0089 (7)	−0.0003 (8)
C8	0.0158 (7)	0.0136 (8)	0.0208 (10)	−0.0012 (6)	0.0046 (7)	0.0007 (8)
C9	0.0157 (7)	0.0161 (8)	0.0189 (9)	0.0003 (6)	0.0042 (6)	0.0023 (8)
C10	0.0199 (8)	0.0168 (8)	0.0228 (11)	−0.0021 (7)	0.0055 (7)	−0.0018 (8)
C11	0.0210 (8)	0.0225 (9)	0.0206 (11)	−0.0001 (7)	0.0051 (7)	−0.0028 (8)
C12	0.0201 (8)	0.0223 (9)	0.0176 (10)	−0.0010 (7)	0.0045 (7)	0.0004 (8)

Geometric parameters (Å, º)

O1—N4	1.232 (2)	N1—C8	1.349 (3)
O2—N4	1.232 (2)	N1—C12	1.363 (3)
O3—C7	1.256 (2)	N1—H1N1	0.99 (3)
O4—C7	1.260 (2)	N2—C8	1.333 (3)
N4—C3	1.476 (2)	N2—H1N2	0.89 (3)
C1—C2	1.391 (3)	N2—H2N2	0.85 (3)
C1—C6	1.397 (3)	N3—C9	1.373 (3)
C1—H1A	0.92 (3)	N3—H1N3	0.85 (3)
C2—C3	1.383 (3)	N3—H2N3	0.82 (3)
C2—H2A	0.98 (3)	C8—C9	1.435 (3)
C3—C4	1.382 (3)	C9—C10	1.379 (3)
C4—C5	1.394 (3)	C10—C11	1.399 (3)
C4—H4A	0.98 (3)	C10—H10A	0.98 (3)
C5—C6	1.396 (3)	C11—C12	1.367 (3)
C5—H5A	0.99 (3)	C11—H11A	0.99 (3)
C6—C7	1.520 (3)	C12—H12A	0.94 (3)
O2—N4—O1	123.84 (17)	C8—N1—C12	123.62 (17)
O2—N4—C3	118.06 (18)	C8—N1—H1N1	113.8 (17)
O1—N4—C3	118.10 (18)	C12—N1—H1N1	122.6 (17)
C2—C1—C6	120.69 (19)	C8—N2—H1N2	119.0 (19)
C2—C1—H1A	119.4 (17)	C8—N2—H2N2	126.1 (17)
C6—C1—H1A	119.9 (17)	H1N2—N2—H2N2	114 (2)
C3—C2—C1	117.7 (2)	C9—N3—H1N3	121 (2)
C3—C2—H2A	122.2 (16)	C9—N3—H2N3	114 (2)
C1—C2—H2A	120.1 (16)	H1N3—N3—H2N3	115 (3)
C4—C3—C2	123.38 (18)	N2—C8—N1	118.49 (17)
C4—C3—N4	118.44 (18)	N2—C8—C9	123.34 (19)
C2—C3—N4	118.18 (18)	N1—C8—C9	118.16 (18)
C3—C4—C5	118.21 (19)	N3—C9—C10	122.90 (18)
C3—C4—H4A	120.7 (17)	N3—C9—C8	119.10 (19)
C5—C4—H4A	121.1 (17)	C10—C9—C8	117.97 (18)
C4—C5—C6	120.13 (19)	C9—C10—C11	121.58 (18)
C4—C5—H5A	118.6 (16)	C9—C10—H10A	116.5 (16)
C6—C5—H5A	121.2 (16)	C11—C10—H10A	121.9 (16)
C5—C6—C1	119.87 (17)	C12—C11—C10	119.1 (2)
C5—C6—C7	120.51 (17)	C12—C11—H11A	120.1 (16)
C1—C6—C7	119.62 (17)	C10—C11—H11A	120.5 (16)
O3—C7—O4	125.37 (18)	N1—C12—C11	119.6 (2)

O3—C7—C6	118.35 (18)	N1—C12—H12A	115.8 (16)
O4—C7—C6	116.28 (17)	C11—C12—H12A	124.6 (16)

C6—C1—C2—C3	−0.8 (3)	C1—C6—C7—O3	−174.40 (17)
C1—C2—C3—C4	−0.1 (3)	C5—C6—C7—O4	−174.72 (17)
C1—C2—C3—N4	−179.16 (16)	C1—C6—C7—O4	5.6 (2)
O2—N4—C3—C4	−1.9 (3)	C12—N1—C8—N2	177.00 (18)
O1—N4—C3—C4	178.55 (18)	C12—N1—C8—C9	−2.2 (3)
O2—N4—C3—C2	177.21 (18)	N2—C8—C9—N3	3.9 (3)
O1—N4—C3—C2	−2.3 (3)	N1—C8—C9—N3	−176.90 (17)
C2—C3—C4—C5	0.4 (3)	N2—C8—C9—C10	−177.88 (18)
N4—C3—C4—C5	179.44 (17)	N1—C8—C9—C10	1.3 (2)
C3—C4—C5—C6	0.2 (3)	N3—C9—C10—C11	178.94 (19)
C4—C5—C6—C1	−1.0 (3)	C8—C9—C10—C11	0.8 (3)
C4—C5—C6—C7	179.32 (16)	C9—C10—C11—C12	−2.1 (3)
C2—C1—C6—C5	1.3 (3)	C8—N1—C12—C11	0.9 (3)
C2—C1—C6—C7	−179.02 (17)	C10—C11—C12—N1	1.3 (3)
C5—C6—C7—O3	5.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O4	0.99 (3)	1.70 (3)	2.671 (2)	167 (3)
N2—H1*N*2···O3	0.89 (3)	2.01 (3)	2.901 (2)	178 (5)
N2—H2*N*2···O3^{i}	0.86 (2)	2.06 (2)	2.903 (2)	171 (2)
N3—H1*N*3···O3^{i}	0.85 (3)	2.14 (3)	2.951 (3)	159 (2)
N3—H2*N*3···O2^{ii}	0.82 (3)	2.34 (3)	3.140 (2)	165 (3)
C10—H10*A*···O1^{ii}	0.98 (3)	2.53 (3)	3.507 (2)	176.9 (16)
C11—H11*A*···O4^{iii}	0.99 (2)	2.56 (2)	3.216 (3)	123.5 (19)

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