

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(2-aminopyridinium) 2,5-dicarboxybenzene-1,4-dicarboxylate

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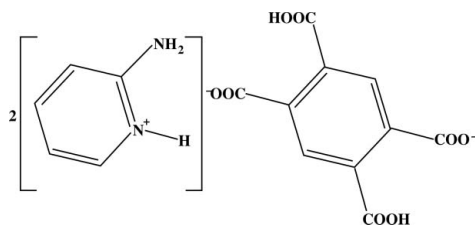
Received 16 April 2012; accepted 18 April 2012

Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 14.0.

In the title compound, $2\text{C}_5\text{H}_7\text{N}_2^+\cdot\text{C}_{10}\text{H}_4\text{O}_8^{2-}$, the 2-aminopyridinium (2-apyH) cation and 2,5-dicarboxybenzene-1,4-dicarboxylate (btch2) anion are both nearly planar, with r.m.s. deviations of 0.015 and 0.050 Å, respectively. The angle between the latter least-squares planes is 17.68 (9)°. The overall crystal structure results from the packing of two-dimensional networks, formed by alternating 2-apyH and btch2 linked by hydrogen bonds, parallel to (100).

Related literature

For similar and most common conformations of 2-aminopyridinium, see: Guelmami & Jouini (2011); Chitra *et al.* (2008); Quah *et al.* (2008); Bis & Zaworotko (2005); Büyükgüngör & Odabaşoğlu (2002); Odabaşoğlu *et al.* (2003); Acheson (1967). For similar and most common conformations of 2,5-dicarboxybenzene-1,4-dicarboxylate, see: Dong *et al.* (2011); Wang & Tang (2010). For graph-set analysis of hydrogen-bond patterns in organic crystals, see: Etter *et al.* (1990).



Experimental

Crystal data

$2\text{C}_5\text{H}_7\text{N}_2^+\cdot\text{C}_{10}\text{H}_4\text{O}_8^{2-}$
 $M_r = 442.38$
 Monoclinic, $P2_1/c$
 $a = 4.0165$ (1) Å

$b = 10.8098$ (4) Å
 $c = 21.4036$ (7) Å
 $\beta = 99.535$ (2)°
 $V = 916.45$ (5) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹

$T = 273$ K
 $0.3 \times 0.2 \times 0.15$ mm

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.755$, $T_{\max} = 1.000$

18838 measured reflections
 2209 independent reflections
 1652 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
 $S = 1.01$
 2209 reflections
 158 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.20$ e Å⁻³
 $\Delta\rho_{\min} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O2}$	0.913 (16)	1.904 (17)	2.7852 (15)	161.6 (15)
$\text{N1}-\text{H1A}\cdots\text{O1}$	0.913 (16)	2.478 (16)	3.2413 (16)	141.4 (13)
$\text{N2}-\text{H2A}\cdots\text{O3}^i$	0.831 (19)	2.125 (19)	2.9520 (17)	173.0 (17)
$\text{N2}-\text{H2B}\cdots\text{O1}$	0.880 (19)	2.14 (2)	2.9759 (17)	157.6 (16)
$\text{O4}-\text{H4A}\cdots\text{O1}$	1.06 (2)	1.31 (2)	2.3766 (15)	176.8 (17)

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

Data collection: APEX2 (Bruker–Nonius, 2004); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

This work was supported by funds from FEDER via the COMPETE (Programa Operacional Factores de Competitividade) programme and by the FCT (Fundação para a Ciência e a Tecnologia) (project PEst-C/FIS/UI0036/2011).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5880).

References

- Acheson, R. M. (1967). *An Introduction to the Chemistry of Heterocyclic Compounds*, 2nd ed., pp. 215–218. London: Wiley.
- Bis, J. A. & Zaworotko, M. J. (2005). *Cryst. Growth Des.* **5**, 1169–1179.
- Bruker (2003). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker–Nonius (2004). APEX2. Bruker–Nonius BV, Delft, The Netherlands.
- Büyükgüngör, O. & Odabaşoğlu, M. (2002). *Acta Cryst.* **C58**, o691–o692.
- Chitra, R., Roussel, P., Capet, F., Murli, C. & Choudhury, R. R. (2008). *J. Mol. Struct.* **891**, 103–109.
- Dong, G.-Y., Liu, T.-F., He, C.-H., Deng, X.-C. & Shi, X.-G. (2011). *Acta Cryst.* **E67**, o1696.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Guelmami, L. & Jouini, A. (2011). *J. Chem. Crystallogr.* **41**, 1268–1272.
- Odabasoglu, M., Büyükgüngör, O., Turgut, G., Karadag, A., Bulak, E. & Lönnecke, P. (2003). *J. Mol. Struct.* **648**, 133–138.
- Quah, C. K., Jebas, S. R. & Fun, H.-K. (2008). *Acta Cryst.* **E64**, o2230.
- Sheldrick, G. M. (2003). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Wang, Y.-J. & Tang, L.-M. (2010). *Chin. J. Struct. Chem.* **29**, 102–108.

supporting information

Acta Cryst. (2012). E68, o1524 [doi:10.1107/S1600536812017254]

Bis(2-aminopyridinium) 2,5-dicarboxybenzene-1,4-dicarboxylate

V. H. Rodrigues, Mohammad Hakimi and Elham Motieiyani

S1. Comment

This work is a further contribution to the broad family of structural studies of 2-aminopyridinium (2-apyH) systems with hydrogen-bond donors. A considerable number of analogous materials formed from 2-aminopyridine and a given carboxylic acid has already been reported (Guelmami & Jouini, 2011; Chitra *et al.*, 2008; Quah *et al.*, 2008; Bis & Zaworotko, 2005; Büyükgüngör & Odabasogonogocaron;lu, 2002; Odabasogonogocaron;lu *et al.*, 2003; *etc.*). This is due to the fact that 2-aminopyridine is protonated in acidic solutions. It is well known that the bonding of the H atom to the ring N atom of 2-aminopyridine, and not to the amino N atom, produces an ion for which an additional resonance structure must be considered (Acheson, 1967). We have inferred the positive charge in the 2-apyH ion lies on the amino group based on a difference fourier map, a common practice when allowed by the quality of the collected intensities. The charge state, related to the hydrogen loss, in each of the two candidate carboxylic acid groups belonging to the asymmetric unit was also inferred from a difference map and further reinforced by analysis of the C–O bond lengths.

Elucidation of the numbering scheme and a view of the H-bonds giving rise to two-dimensional networks parallel to (100) are shown in Figs. 1 and 2, respectively. Both the 2-apyH cation and 2,5-dicarboxybenzene-1,4-dicarboxylate (btcH₂) anion are nearly planar, with r.m.s. deviations of 0.015 and 0.050 Å, respectively. The angle between the latter idealized planes is 17.68 (9)°. The two-dimensional networks are formed by alternating 2-apyH and btcH₂ linked by H-bonds and include all H-bonds found. The first order network describing the H-bonding in the title compound is N₁=4DS(7), as established by applying the rules of graph-set analysis of hydrogen-bond patterns in organic crystals (Etter *et al.*, 1990).

Similar and most common conformations of 2,5-dicarboxybenzene-1,4-dicarboxylate were described by Dong *et al.* (2011) and Wang & Tang (2010).

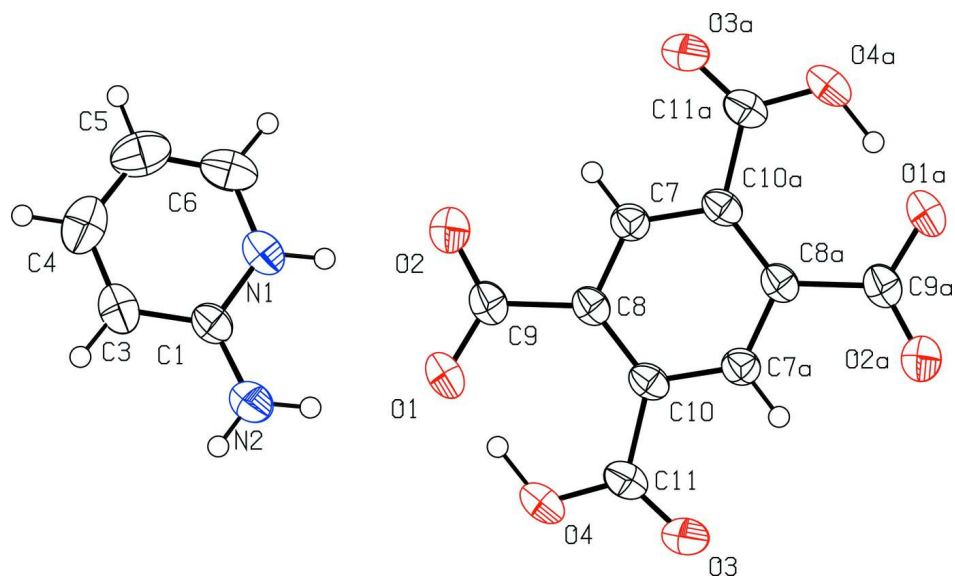
S2. Experimental

A solution of 0.254 g (1 mmol) benzene-1,2,4,5-tetracarboxylic acid in methanol (10 ml) was added to a solution of 2-aminopyridine (0.1 g, 1 mmol) in water (15 ml), and refluxed for 1 h. The resulting solution was light yellow in colour. After slow evaporation of the solvent at room-temperature colorless prisms of the compound were obtained.

S3. Refinement

The structure was solved by direct methods using *SHELXS97* (Sheldrick, 2008). H atoms bound to aromatic C were placed at idealized positions and refined as riding, with C—H=0.93 (Sheldrick, 2008); amine and carboxyl H atoms were found from a difference fourier map and their coordinates refined freely. $U_{\text{iso}}(\text{H})$ was fixed to 1.2 times U_{eq} of the heavy atom they are bonded to, for all hydrogen atoms.

Examination of the crystal structure with *PLATON* (Spek, 2009) showed that there are no solvent-accessible voids in the crystal lattice.

**Figure 1**

ORTEP plot of the title compound. Displacement ellipsoids are drawn at the 50% level.

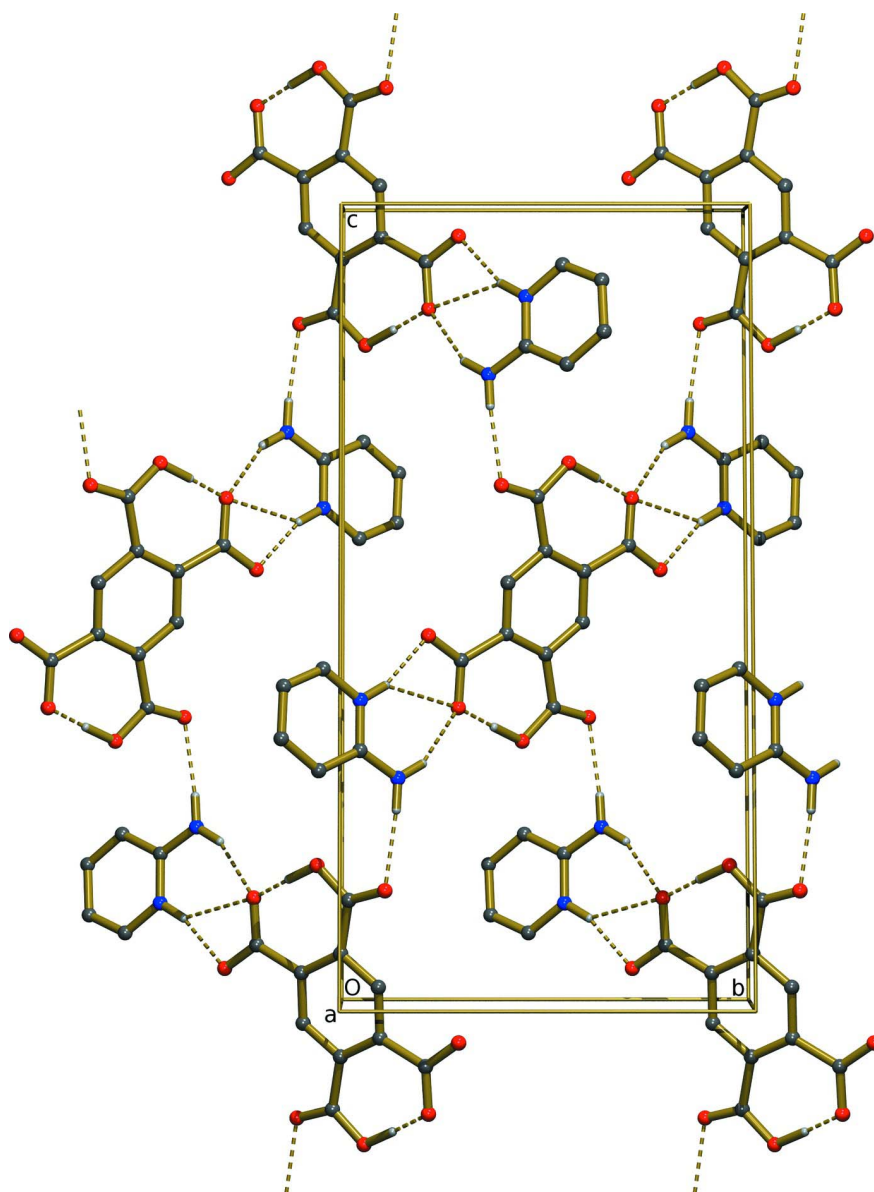


Figure 2

Representation of the two-dimensional networks, parallel to the (100) planes, of H-bonded molecules.

Bis(2-aminopyridinium) 2,5-dicarboxybenzene-1,4-dicarboxylate

Crystal data

$2\text{C}_5\text{H}_7\text{N}_2^+\cdot\text{C}_{10}\text{H}_4\text{O}_8^{2-}$

$M_r = 442.38$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 4.0165\ (1)\ \text{\AA}$

$b = 10.8098\ (4)\ \text{\AA}$

$c = 21.4036\ (7)\ \text{\AA}$

$\beta = 99.535\ (2)^\circ$

$V = 916.45\ (5)\ \text{\AA}^3$

$Z = 2$

$F(000) = 460$

$D_x = 1.603\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 7209 reflections

$\theta = 2.7\text{--}24.9^\circ$

$\mu = 0.13\ \text{mm}^{-1}$

$T = 273\ \text{K}$

Block, yellow

$0.3 \times 0.2 \times 0.15\ \text{mm}$

Data collection

Bruker–Nonius APEXII CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2003)
 $T_{\min} = 0.755$, $T_{\max} = 1.000$

18838 measured reflections
2209 independent reflections
1652 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 28.2^\circ$, $\theta_{\min} = 1.9^\circ$
 $h = -4 \rightarrow 5$
 $k = -13 \rightarrow 14$
 $l = -27 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
 $S = 1.01$
2209 reflections
158 parameters
0 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
 $w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.1584P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.014 (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.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.1547 (3)	0.04940 (11)	0.38178 (5)	0.0424 (3)
H1A	1.040 (4)	0.1095 (15)	0.3993 (8)	0.051*
C1	1.1679 (3)	0.04905 (12)	0.32019 (6)	0.0370 (3)
N2	1.0229 (4)	0.14007 (12)	0.28496 (6)	0.0511 (3)
H2A	1.021 (4)	0.1363 (16)	0.2461 (9)	0.061*
H2B	0.916 (5)	0.1990 (16)	0.3019 (9)	0.061*
C3	1.3390 (4)	-0.04878 (13)	0.29700 (7)	0.0469 (4)
H3	1.3508	-0.0532	0.2540	0.056*
C4	1.4882 (4)	-0.13741 (15)	0.33704 (9)	0.0569 (4)
H4	1.6042	-0.2019	0.3215	0.068*
C5	1.4684 (4)	-0.13228 (16)	0.40058 (9)	0.0587 (4)
H5	1.5712	-0.1922	0.4285	0.070*
C6	1.2984 (4)	-0.03922 (15)	0.42096 (7)	0.0523 (4)
H6	1.2786	-0.0356	0.4636	0.063*
C7	0.7030 (3)	0.40755 (11)	0.52514 (6)	0.0325 (3)

H7	0.8444	0.3440	0.5427	0.039*
C8	0.5869 (3)	0.40386 (11)	0.46123 (5)	0.0312 (3)
C9	0.7148 (3)	0.29317 (12)	0.42838 (6)	0.0380 (3)
O1	0.6529 (3)	0.28618 (10)	0.36938 (5)	0.0588 (3)
O2	0.8806 (3)	0.21344 (9)	0.45984 (5)	0.0591 (3)
C10	0.3760 (3)	0.50071 (11)	0.43487 (5)	0.0315 (3)
C11	0.2130 (3)	0.52081 (12)	0.36717 (6)	0.0386 (3)
O3	0.0283 (3)	0.60888 (10)	0.35332 (5)	0.0571 (3)
O4	0.2721 (3)	0.44339 (10)	0.32502 (4)	0.0556 (3)
H4A	0.448 (5)	0.3738 (17)	0.3439 (8)	0.067*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0464 (7)	0.0473 (7)	0.0338 (6)	-0.0050 (5)	0.0072 (5)	-0.0078 (5)
C1	0.0391 (7)	0.0395 (7)	0.0316 (7)	-0.0064 (5)	0.0038 (5)	-0.0049 (5)
N2	0.0690 (9)	0.0481 (7)	0.0339 (6)	0.0058 (6)	0.0017 (6)	-0.0040 (6)
C3	0.0463 (8)	0.0510 (9)	0.0452 (8)	-0.0037 (7)	0.0129 (6)	-0.0118 (7)
C4	0.0450 (8)	0.0447 (8)	0.0820 (12)	0.0006 (7)	0.0131 (8)	-0.0058 (8)
C5	0.0511 (9)	0.0552 (9)	0.0664 (11)	-0.0078 (7)	0.0001 (8)	0.0187 (8)
C6	0.0516 (9)	0.0648 (10)	0.0387 (8)	-0.0144 (8)	0.0025 (7)	0.0090 (7)
C7	0.0367 (6)	0.0310 (6)	0.0303 (6)	-0.0027 (5)	0.0067 (5)	0.0019 (5)
C8	0.0349 (6)	0.0316 (6)	0.0284 (6)	-0.0069 (5)	0.0091 (5)	-0.0015 (5)
C9	0.0437 (7)	0.0364 (7)	0.0351 (7)	-0.0050 (6)	0.0102 (6)	-0.0056 (5)
O1	0.0832 (8)	0.0600 (7)	0.0336 (6)	0.0173 (6)	0.0113 (5)	-0.0114 (5)
O2	0.0841 (8)	0.0469 (6)	0.0453 (6)	0.0203 (6)	0.0074 (5)	-0.0048 (5)
C10	0.0358 (6)	0.0336 (6)	0.0259 (6)	-0.0087 (5)	0.0069 (5)	0.0005 (5)
C11	0.0451 (7)	0.0429 (7)	0.0275 (6)	-0.0065 (6)	0.0055 (5)	0.0006 (5)
O3	0.0777 (7)	0.0550 (7)	0.0336 (6)	0.0151 (6)	-0.0053 (5)	0.0017 (4)
O4	0.0763 (8)	0.0634 (7)	0.0257 (5)	0.0096 (6)	0.0045 (5)	-0.0065 (5)

Geometric parameters (Å, °)

N1—C1	1.3281 (17)	C6—H6	0.9300
N1—C6	1.3392 (19)	C7—C8	1.3707 (17)
N1—H1A	0.913 (16)	C7—C10 ⁱ	1.3809 (17)
C1—N2	1.3154 (19)	C7—H7	0.9300
C1—C3	1.3964 (19)	C8—C10	1.4049 (18)
N2—H2A	0.831 (19)	C8—C9	1.5197 (17)
N2—H2B	0.880 (19)	C9—O2	1.2212 (16)
C3—C4	1.357 (2)	C9—O1	1.2483 (16)
C3—H3	0.9300	C10—C7 ⁱ	1.3809 (17)
C4—C5	1.377 (2)	C10—C11	1.5037 (17)
C4—H4	0.9300	C11—O3	1.2133 (17)
C5—C6	1.329 (2)	C11—O4	1.2811 (16)
C5—H5	0.9300	O4—H4A	1.06 (2)
C1—N1—C6	122.39 (13)	C5—C6—H6	119.1

C1—N1—H1A	121.0 (10)	N1—C6—H6	119.1
C6—N1—H1A	116.6 (10)	C8—C7—C10 ⁱ	124.36 (12)
N2—C1—N1	118.70 (13)	C8—C7—H7	117.8
N2—C1—C3	124.06 (13)	C10 ⁱ —C7—H7	117.8
N1—C1—C3	117.24 (13)	C7—C8—C10	117.52 (11)
C1—N2—H2A	117.8 (12)	C7—C8—C9	113.54 (11)
C1—N2—H2B	120.4 (12)	C10—C8—C9	128.93 (11)
H2A—N2—H2B	121.5 (17)	O2—C9—O1	120.93 (12)
C4—C3—C1	120.15 (14)	O2—C9—C8	119.73 (11)
C4—C3—H3	119.9	O1—C9—C8	119.33 (12)
C1—C3—H3	119.9	C7 ⁱ —C10—C8	118.12 (11)
C3—C4—C5	120.25 (15)	C7 ⁱ —C10—C11	112.67 (11)
C3—C4—H4	119.9	C8—C10—C11	129.20 (11)
C5—C4—H4	119.9	O3—C11—O4	121.18 (12)
C6—C5—C4	118.13 (15)	O3—C11—C10	119.99 (12)
C6—C5—H5	120.9	O4—C11—C10	118.83 (12)
C4—C5—H5	120.9	C11—O4—H4A	112.5 (9)
C5—C6—N1	121.83 (15)		
C6—N1—C1—N2	-179.42 (13)	C10—C8—C9—O2	-175.39 (13)
C6—N1—C1—C3	0.14 (19)	C7—C8—C9—O1	-173.10 (12)
N2—C1—C3—C4	178.46 (14)	C10—C8—C9—O1	5.7 (2)
N1—C1—C3—C4	-1.1 (2)	C7—C8—C10—C7 ⁱ	-0.56 (18)
C1—C3—C4—C5	0.8 (2)	C9—C8—C10—C7 ⁱ	-179.36 (11)
C3—C4—C5—C6	0.5 (2)	C7—C8—C10—C11	-179.96 (11)
C4—C5—C6—N1	-1.4 (2)	C9—C8—C10—C11	1.2 (2)
C1—N1—C6—C5	1.1 (2)	C7 ⁱ —C10—C11—O3	-1.71 (17)
C10 ⁱ —C7—C8—C10	0.60 (19)	C8—C10—C11—O3	177.72 (13)
C10 ⁱ —C7—C8—C9	179.58 (11)	C7 ⁱ —C10—C11—O4	178.55 (12)
C7—C8—C9—O2	5.76 (17)	C8—C10—C11—O4	-2.01 (19)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O2	0.913 (16)	1.904 (17)	2.7852 (15)	161.6 (15)
N1—H1A \cdots O1	0.913 (16)	2.478 (16)	3.2413 (16)	141.4 (13)
N2—H2A \cdots O3 ⁱⁱ	0.831 (19)	2.125 (19)	2.9520 (17)	173.0 (17)
N2—H2B \cdots O1	0.880 (19)	2.14 (2)	2.9759 (17)	157.6 (16)
O4—H4A \cdots O1	1.06 (2)	1.31 (2)	2.3766 (15)	176.8 (17)

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