Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,6-Diaminopyridinium 2-carboxybenzoate

Mohammad T. M. Al-Dajani,[a] Hassan H. Abdallah,[b] Nornisah Mohamed,[a]‡ Mohd Mustaqim Rosli[c] and Hoong-Kun Fun[c]*§

[a]School of Pharmaceutical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, [b]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

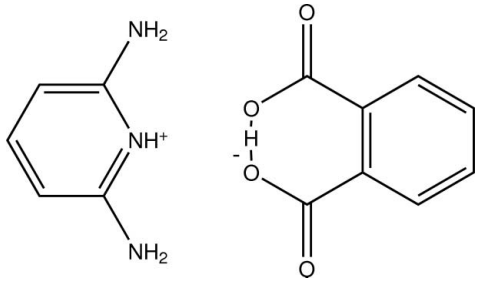
Received 17 July 2010; accepted 16 August 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.053; wR factor = 0.197; data-to-parameter ratio = 15.2.

In the crystal of the title molecular salt, $C_5H_8N_3^+\cdot C_8H_5O_4^-$, the diaminopyridine cation and the phthalate anion are linked by a pair of N—H···O hydrogen bonds. Within the phthalate anion, an almost symmetrical O—H···O hydrogen bond is observed. The ion pairs are linked by further N—H···O hydrogen bonds, generating a two-dimensional network lying parallel to $(10\bar{1})$.

Related literature

For background to 2,6-diaminopyridines, see: Abu Zuhri & Cox (1989); Inuzuka & Fujimoto (1990); El-Mossalamy (2001). For background and the biological activity of phthalic acid, see: Brike *et al.* (2002); Yamamoto *et al.* (1990). For related structures: see: Büyükgüngör & Odabąsoğlu (2006); Al-Dajani *et al.* (2009); Raissi Shabari *et al.* (2010). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_5H_8N_3^+\cdot C_8H_5O_4^-$
M_r = 275.26
Monoclinic, $C2/c$
a = 32.332 (11) Å
b = 3.7246 (14) Å
c = 24.184 (8) Å
β = 123.036 (6)°
V = 2441.5 (15) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.47 × 0.10 × 0.03 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.948, T_{max} = 0.996
5492 measured reflections
2757 independent reflections
1869 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.197
S = 1.06
2757 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1*O2*···O3	1.18	1.29	2.437 (3)	162
N1—H1*A*···O3	0.86	1.98	2.828 (3)	167
N2—H2*A*···O4	0.86	1.98	2.834 (3)	177
N2—H2*B*···O4^{i}	0.86	2.10	2.851 (3)	145
N3—H3*A*···O2^{ii}	0.86	2.35	3.042 (3)	138
N3—H3*B*···O1^{iii}	0.86	2.01	2.858 (3)	171

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

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

NM gratefully acknowledges funding from Universiti Sains Malaysia (USM) under the University Research Grant (No. 1001/PFARMASI/815025) and HHA gratefully acknowledges funding from Universiti Sains Malaysia (USM) under the University Research Grant (No. 1001/PKIMIA/811142). HKF 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: HB5557).

References

Abu Zuhri, A. Z. & Cox, J. A. (1989). *Mikrochim. Acta*, **11**, 277–283.
Al-Dajani, M. T. M., Salihin, A., Mohamed, N., Loh, W.-S. & Fun, H.-K. (2009). *Acta Cryst.* E**65**, o2931–o2932.
Brike, G., Hirsch, M. & Franz, V. (2002). US Patent No. 636 838 9B1.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Büyükgüngör, O. & Odabąsoğlu, M. (2006). *Acta Cryst.* E**62**, o3816–o3818.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
El-Mossalamy, E. H. (2001). *Pigm. Resin Technol.* **30**, 164–168.

‡ Additional correspondence author, e-mail: nornisah@usm.my.
§ Thomson Reuters ResearcherID: A-3561-2009.

Inuzuka, K. & Fujimoto, A. (1990). *Bull. Chem. Soc. Jpn*, **63**, 216–220.
Raissi Shabari, A., Safaeimovahed, M. & Pourayoubi, M. (2010). *Acta Cryst.* E**66**, o551.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Yamamoto, S., Nakadate, T., Aizu, E. & Kato, R. (1990). *Carcinogenesis*, **11**, 749–754.

supporting information

Acta Cryst. (2010). E**66**, o2433–o2434 [https://doi.org/10.1107/S1600536810032903]

2,6-Diaminopyridinium 2-carboxybenzoate

Mohammad T. M. Al-Dajani, Hassan H. Abdallah, Nornisah Mohamed, Mohd Mustaqim Rosli and Hoong-Kun Fun

S1. Comment

Phthalic acid is an aromatic dicarboxylic acid which can be used for the preparation of many organic and inorganic compounds such as dyes, perfumes and phthalates(Brike *et al.* 2002). Some of its derivatives have anti-tumor promoting action (Yamamoto *et al.* 1990). The diaminopyridine have an important role in the preparation of aromatic azo dyes (Abu Zuhri & Cox, 1989; Inuzuka & Fujimoto, 1990) and in many polarographic investigations (El-Mossalamy, 2001).

All geometrical parameters in the title compound, $C_5H_8N_3^+.C_8H_5O_4^-$,(I), are within normal ranges and are comparable with the related structures (Büyükgüngör & Odabąsoğlu, 2006; Al-Dajani *et al.*, 2009; Shabari *et al.*, 2010). In the crystal structure, the anion and the cation were linked by N1—H1A···O3 and N2—H2A···O4 interactions. In the phthalate anion, a strong intramolecular interaction of O2—H1O2···O3 was observed. Intermolecular N—H···O hydrogen bonds (Table 1) further contribute to the stabilization of crystal structure, forming an infinite two-dimensional network parallel to the $(10\bar{1})$ plane.

S2. Experimental

In a round bottom flask, 25ml of THF was mixed with 2,6-diaminopyridine (0.01 mol, 1.1 g) with stirring. Phthalic anhydrate (0.01 mol, 1.5 g) was dissolved in THF and then added in small portions into the round bottom flask and refluxed for 2 hours. The gray precipitate formed was filtrated and washed with THF. Brown plates of (I) were formed by dissolving the precipitate in hot water and letting it to cool at room temperature. The crystals was then filtered and dried at 60°C.

S3. Refinement

O-bound H atoms were located from a difference Fourier map and refined as riding with $U_{iso}(H) = 1.5U_{eq}(O)$.The remaining H atoms were positioned geometrically [N–H = 0.86Å, C–H = 0.93 Å and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(N,C)$].

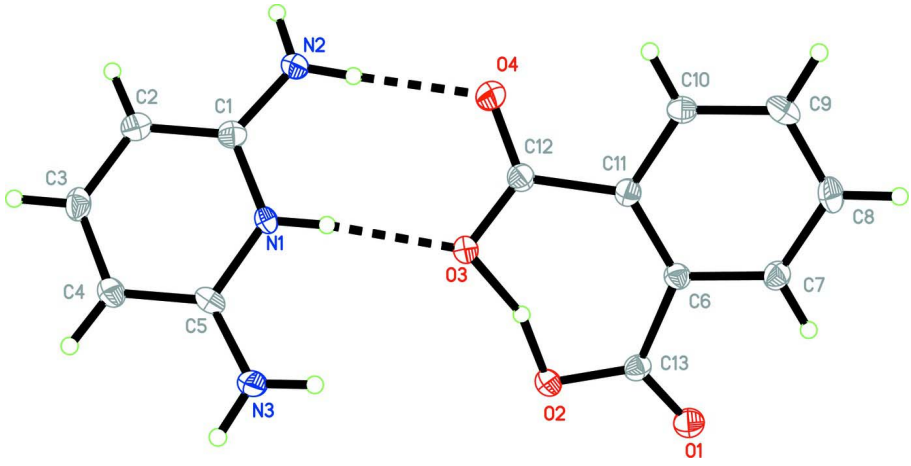


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids. Hydrogen atoms are shown as spheres of arbitrary radius. Dashed lines indicate the intermolecular hydrogen bonds.

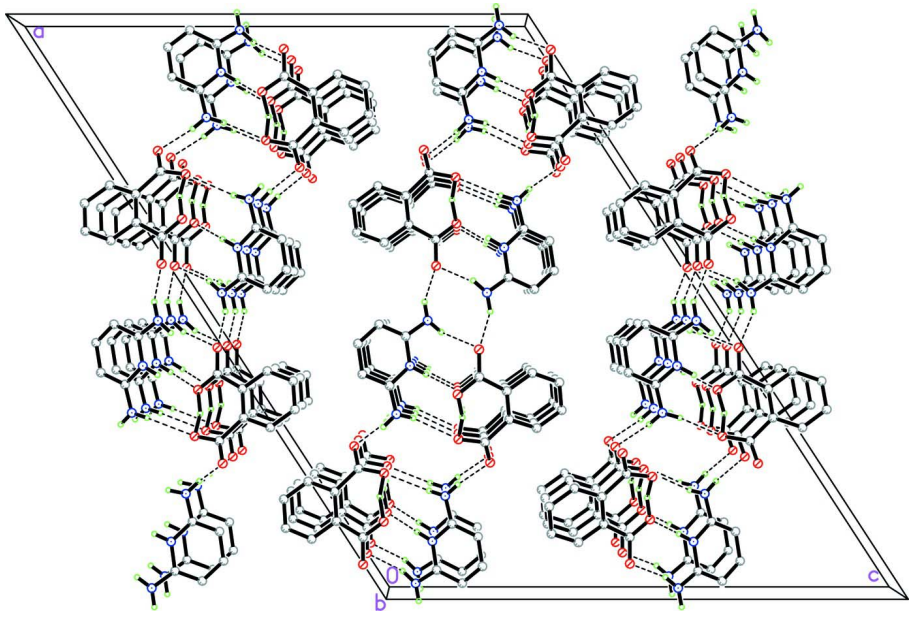


Figure 2

The crystal packing of (I) viewed down the b axis. Dashed lines indicate hydrogen bonds. H atoms not involved in the hydrogen bond interactions have been omitted for clarity.

2,6-Diaminopyridinium 2-carboxybenzoate

Crystal data

$C_5H_8N_3^+·C_8H_5O_4^-$
M_r = 275.26
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 32.332 (11) Å
b = 3.7246 (14) Å
c = 24.184 (8) Å
β = 123.036 (6)°
V = 2441.5 (15) Å^3
Z = 8
F(000) = 1152
D_x = 1.498 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 975 reflections

θ = 3.8–28.1°
μ = 0.11 mm^{-1}
T = 100 K

Plate, brown
0.47 × 0.10 × 0.03 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.948, T_{max} = 0.996

5492 measured reflections
2757 independent reflections
1869 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.5°, θ_{min} = 3.4°
h = −36→42
k = −4→4
l = −31→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.197
S = 1.06
2757 reflections
181 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1138P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 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 esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 > 2sigma(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}
N1	0.09892 (7)	0.9810 (6)	0.16036 (9)	0.0153 (5)
H1A	0.1109	0.8974	0.1388	0.018*
N2	0.02334 (7)	0.8089 (7)	0.07262 (10)	0.0195 (5)
H2A	0.0381	0.7329	0.0542	0.023*
H2B	−0.0082	0.7882	0.0526	0.023*
N3	0.17839 (7)	1.1355 (7)	0.24299 (10)	0.0210 (5)
H3A	0.1883	1.0487	0.2192	0.025*
H3B	0.1993	1.2268	0.2810	0.025*
C1	0.04920 (8)	0.9585 (7)	0.13210 (11)	0.0158 (5)
C2	0.02953 (9)	1.0896 (8)	0.16702 (11)	0.0179 (6)
H2C	−0.0042	1.0754	0.1494	0.021*

C3	0.06092 (9)	1.2402 (8)	0.22794 (12)	0.0191 (6)
H3C	0.0478	1.3309	0.2510	0.023*
C4	0.11140 (9)	1.2624 (8)	0.25640 (11)	0.0169 (5)
H4A	0.1319	1.3636	0.2980	0.020*
C5	0.13083 (8)	1.1287 (7)	0.22106 (11)	0.0153 (5)
O1	0.26121 (6)	−0.0595 (6)	0.12827 (8)	0.0228 (5)
O2	0.21888 (6)	0.2628 (6)	0.15685 (7)	0.0191 (4)
H1O2	0.1816	0.4181	0.1225	0.029*
O3	0.14264 (6)	0.6094 (5)	0.10279 (8)	0.0193 (5)
O4	0.06986 (6)	0.5317 (6)	0.01065 (9)	0.0272 (5)
C6	0.18695 (8)	0.1875 (7)	0.03925 (11)	0.0148 (5)
C7	0.20221 (9)	0.0642 (8)	−0.00144 (12)	0.0170 (5)
H7A	0.2336	−0.0336	0.0179	0.020*
C8	0.17220 (9)	0.0825 (8)	−0.06960 (12)	0.0193 (6)
H8A	0.1836	0.0045	−0.0955	0.023*
C9	0.12537 (9)	0.2173 (8)	−0.09827 (11)	0.0195 (6)
H9A	0.1045	0.2259	−0.1440	0.023*
C10	0.10903 (9)	0.3408 (7)	−0.05943 (11)	0.0159 (5)
H10A	0.0772	0.4316	−0.0797	0.019*
C11	0.13903 (8)	0.3330 (7)	0.00959 (11)	0.0145 (5)
C12	0.11507 (8)	0.4977 (7)	0.04302 (11)	0.0161 (5)
C13	0.22537 (8)	0.1262 (7)	0.11219 (11)	0.0154 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0160 (10)	0.0203 (12)	0.0105 (9)	0.0010 (9)	0.0079 (8)	−0.0016 (9)
N2	0.0140 (9)	0.0278 (13)	0.0146 (9)	−0.0007 (10)	0.0066 (8)	−0.0046 (10)
N3	0.0140 (9)	0.0340 (15)	0.0135 (9)	−0.0008 (10)	0.0064 (8)	−0.0042 (10)
C1	0.0162 (11)	0.0156 (13)	0.0147 (10)	0.0007 (10)	0.0079 (9)	0.0025 (10)
C2	0.0162 (11)	0.0185 (14)	0.0181 (11)	0.0005 (11)	0.0089 (10)	0.0018 (11)
C3	0.0236 (12)	0.0207 (14)	0.0175 (11)	0.0051 (12)	0.0141 (10)	0.0020 (11)
C4	0.0196 (11)	0.0175 (13)	0.0136 (11)	−0.0001 (11)	0.0091 (10)	−0.0004 (11)
C5	0.0170 (11)	0.0148 (13)	0.0111 (10)	−0.0031 (10)	0.0057 (9)	−0.0006 (10)
O1	0.0190 (9)	0.0286 (11)	0.0184 (8)	0.0056 (9)	0.0085 (7)	0.0023 (9)
O2	0.0170 (8)	0.0274 (11)	0.0127 (8)	0.0010 (8)	0.0078 (7)	−0.0007 (8)
O3	0.0155 (8)	0.0272 (11)	0.0151 (8)	0.0011 (8)	0.0084 (7)	−0.0045 (8)
O4	0.0152 (9)	0.0409 (13)	0.0235 (9)	−0.0007 (9)	0.0092 (7)	−0.0105 (10)
C6	0.0147 (10)	0.0162 (13)	0.0134 (10)	−0.0004 (10)	0.0076 (9)	0.0005 (10)
C7	0.0161 (11)	0.0185 (13)	0.0184 (11)	−0.0018 (11)	0.0107 (9)	−0.0010 (11)
C8	0.0261 (13)	0.0192 (14)	0.0191 (11)	−0.0028 (12)	0.0166 (10)	−0.0008 (11)
C9	0.0209 (12)	0.0205 (14)	0.0126 (10)	−0.0037 (11)	0.0062 (9)	−0.0003 (11)
C10	0.0141 (10)	0.0156 (13)	0.0162 (11)	−0.0024 (10)	0.0072 (9)	−0.0013 (10)
C11	0.0153 (10)	0.0127 (12)	0.0162 (11)	−0.0016 (10)	0.0090 (9)	−0.0017 (10)
C12	0.0159 (11)	0.0176 (14)	0.0161 (11)	−0.0023 (11)	0.0095 (9)	−0.0015 (11)
C13	0.0141 (10)	0.0166 (13)	0.0161 (11)	−0.0004 (10)	0.0086 (9)	0.0020 (10)

Geometric parameters (Å, º)

N1—C1	1.364 (3)	O2—C13	1.310 (3)
N1—C5	1.368 (3)	O2—H1O2	1.1764
N1—H1A	0.8600	O3—C12	1.285 (3)
N2—C1	1.329 (3)	O3—H1O2	1.2919
N2—H2A	0.8600	O4—C12	1.232 (3)
N2—H2B	0.8600	C6—C7	1.397 (3)
N3—C5	1.326 (3)	C6—C11	1.413 (3)
N3—H3A	0.8600	C6—C13	1.522 (3)
N3—H3B	0.8600	C7—C8	1.385 (3)
C1—C2	1.393 (3)	C7—H7A	0.9300
C2—C3	1.373 (3)	C8—C9	1.372 (3)
C2—H2C	0.9300	C8—H8A	0.9300
C3—C4	1.386 (3)	C9—C10	1.383 (3)
C3—H3C	0.9300	C9—H9A	0.9300
C4—C5	1.399 (3)	C10—C11	1.401 (3)
C4—H4A	0.9300	C10—H10A	0.9300
O1—C13	1.217 (3)	C11—C12	1.521 (3)
C1—N1—C5	123.8 (2)	C12—O3—H1O2	100.1
C1—N1—H1A	118.1	C7—C6—C11	118.6 (2)
C5—N1—H1A	118.1	C7—C6—C13	112.8 (2)
C1—N2—H2A	120.0	C11—C6—C13	128.5 (2)
C1—N2—H2B	120.0	C8—C7—C6	122.3 (2)
H2A—N2—H2B	120.0	C8—C7—H7A	118.8
C5—N3—H3A	120.0	C6—C7—H7A	118.8
C5—N3—H3B	120.0	C9—C8—C7	118.9 (2)
H3A—N3—H3B	120.0	C9—C8—H8A	120.5
N2—C1—N1	116.2 (2)	C7—C8—H8A	120.5
N2—C1—C2	125.2 (2)	C8—C9—C10	120.2 (2)
N1—C1—C2	118.5 (2)	C8—C9—H9A	119.9
C3—C2—C1	118.6 (2)	C10—C9—H9A	119.9
C3—C2—H2C	120.7	C9—C10—C11	122.0 (2)
C1—C2—H2C	120.7	C9—C10—H10A	119.0
C2—C3—C4	122.6 (2)	C11—C10—H10A	119.0
C2—C3—H3C	118.7	C10—C11—C6	117.9 (2)
C4—C3—H3C	118.7	C10—C11—C12	113.7 (2)
C3—C4—C5	118.3 (2)	C6—C11—C12	128.3 (2)
C3—C4—H4A	120.8	O4—C12—O3	122.4 (2)
C5—C4—H4A	120.8	O4—C12—C11	118.4 (2)
N3—C5—N1	118.0 (2)	O3—C12—C11	119.1 (2)
N3—C5—C4	123.9 (2)	O1—C13—O2	120.6 (2)
N1—C5—C4	118.1 (2)	O1—C13—C6	119.3 (2)
C13—O2—H1O2	99.9	O2—C13—C6	120.0 (2)
C5—N1—C1—N2	179.6 (2)	C9—C10—C11—C6	−1.2 (4)
C5—N1—C1—C2	−0.7 (4)	C9—C10—C11—C12	177.1 (2)

N2—C1—C2—C3	−179.5 (3)	C7—C6—C11—C10	0.9 (4)
N1—C1—C2—C3	0.9 (4)	C13—C6—C11—C10	−175.8 (2)
C1—C2—C3—C4	−0.9 (4)	C7—C6—C11—C12	−177.1 (3)
C2—C3—C4—C5	0.7 (4)	C13—C6—C11—C12	6.2 (4)
C1—N1—C5—N3	−179.8 (2)	C10—C11—C12—O4	19.0 (4)
C1—N1—C5—C4	0.5 (4)	C6—C11—C12—O4	−162.9 (3)
C3—C4—C5—N3	179.8 (3)	C10—C11—C12—O3	−158.2 (2)
C3—C4—C5—N1	−0.4 (4)	C6—C11—C12—O3	19.9 (4)
C11—C6—C7—C8	0.5 (4)	C7—C6—C13—O1	−9.9 (3)
C13—C6—C7—C8	177.8 (3)	C11—C6—C13—O1	167.0 (3)
C6—C7—C8—C9	−1.8 (4)	C7—C6—C13—O2	172.4 (2)
C7—C8—C9—C10	1.6 (4)	C11—C6—C13—O2	−10.8 (4)
C8—C9—C10—C11	−0.1 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*O2*···O3	1.18	1.29	2.437 (3)	162
N1—H1*A*···O3	0.86	1.98	2.828 (3)	167
N2—H2*A*···O4	0.86	1.98	2.834 (3)	177
N2—H2*B*···O4^{i}	0.86	2.10	2.851 (3)	145
N3—H3*A*···O2^{ii}	0.86	2.35	3.042 (3)	138
N3—H3*B*···O1^{iii}	0.86	2.01	2.858 (3)	171

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