St. Catherine University

From the SelectedWorks of Daron E Janzen

October, 2016

Ammonium Hydrogen bis[4-(2-phenyl-2H-tetra-zol-5-yl)benzoate]

Daron E Janzen, *St. Catherine University*
Kayla A. Lange, *St. Catherine University*
James A. Wollack, *St. Catherine University*

Ammonium hydrogen bis[4-(2-phenyl-2H-tetrazol-5-yl)benzoate]

Daron E. Janzen,* Kayla A. Lange and James W. Wollack

St. Catherine University, Dept. of Chemistry and Biochemistry, 2004 Randolph Avenue, St. Paul, MN 55105, USA. *Correspondence e-mail: dejanzen@stkate.edu

The title salt, $NH_4^+ \cdot H^+ \cdot 2C_{14}H_9N_4O_2^-$, is composed of an ammonium cation with a strong intermolecular negatively charge-assisted hydrogen-bonded acid/conjugate base-pair monoanion. The carboxylic acid H atom is located on an inversion center, while the N atom of the ammonium cation is located on a twofold rotation axis. In the crystal, the N—H bonds of each ammonium cation act as donors with carboxylate O-atom acceptors to form chains along the *a*-axis direction. The chains are linked by offset π–π interactions [intercentroid distances = 3.588 (2) and 3.686 (2) Å], forming layers parallel to the *ab* plane.

3D view

Chemical scheme
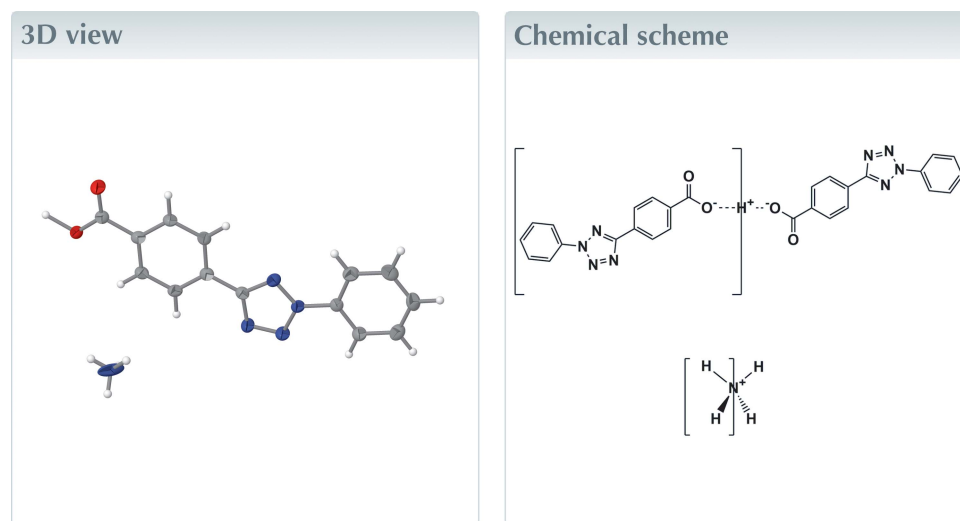
Structure description

Tetrazoles are an interesting class of compounds that are utilized in a bioorthogonal reaction called photoclick chemistry (Ramil & Lin, 2014). When tetrazoles are irradiated with UV light, a nitrile imine is formed which can subsequently complete a cycloaddition with olefins present *in situ* (Zheng *et al.*, 2009). After cycloaddition, a fluorescent pyrazoline is produced that can be used as a tag to monitor product formation. This technology has been successfully used to impart fluorescent properties onto alkene-containing proteins (Song *et al.*, 2008; Lim & Lin, 2011). Upon synthesizing 4-(2-phenyl-2H-tetrazol-5-yl)benzoic acid for this purpose, X-ray diffraction quality ammonium salt crystals of the title compound were produced and we report herein on its crystal structure.

The molecular structure of the title compound is illustrated in Fig. 1. The ammonium cation (N5) is located on a twofold rotation axis, and the carboxylic acid H atom (H1*A*), located on an inversion center, interacts with two inversion-related 4-(2-phenyl-2H-tetrazol-5-yl)benzoate ions (Fig. 1 and Table 1). The conjugate acid/base O1···O1($-x + 1$, $-y - 2$, $-z + 1$) distance of 2.561 (3) Å is short, consistent with a strong negatively charge-assisted hydrogen bond (Gilli *et al.*, 2009). The narrow range of bond lengths

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1A⋯O1^i	1.28	1.28	2.561 (3)	180
N5—H5A⋯O2^{ii}	0.80 (8)	2.09 (8)	2.815 (4)	151 (7)
N5—H5B⋯O1^{iii}	0.84 (11)	2.15 (10)	2.8513 (18)	140 (9)

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

[1.312 (3)–1.359 (3) Å] in the tetrazole moiety suggests significant conjugation in this ring. The 4-(2-phenyl-2H-tetrazol-5-yl)benzoate moiety is relatively planar. The phenyl (atoms C1–C6) and benzoate rings (atoms C8–C13) are inclined to the plane of the tetrazole ring (atoms N1–N4/C7) by 2.54 (15) and 6.10 (14)°, respectively, and by 3.84 (13)° to each another. The acetate group (C11/C14/O1/O2) is inclined to the benzene ring (C8–C13) to which it is attached by 10.44 (14)°.

In the crystal, intermolecular hydrogen bonding is present between the ammonium donor and four O-atom acceptors from two conjugate acid/base pairs. The hydrogen-bonding motif [$R_2^2(8)$] occurs as a chain of rings (joined at N5) along the a-axis direction plane (Table 1 and Fig. 2). This pattern of
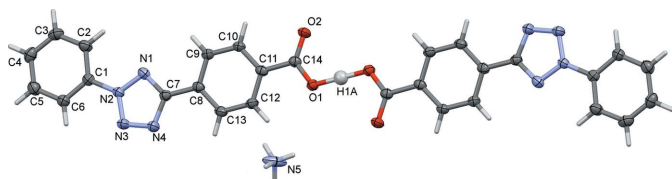

Figure 1
A view of the molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. The acidic H atom, H1A, is located on in inversion center, and unlabeled atoms of the anion are related to the labelled atoms by the inversion symmetry code ($-x + 1, -y - 2, -z + 1$).
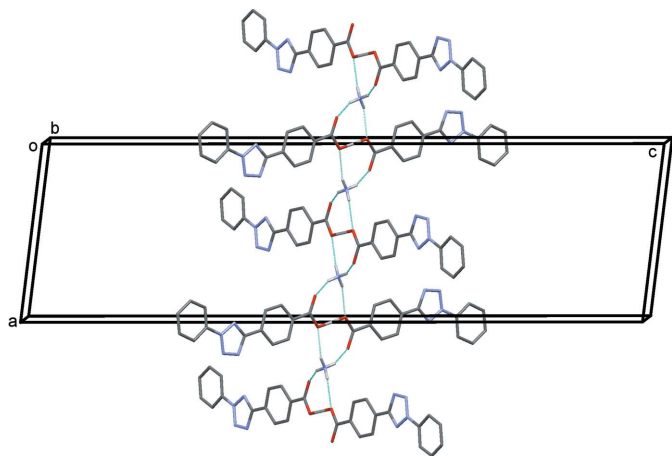

Figure 2
A view of the hydrogen bonding involving the ammonium cation. The hydrogen bonds are shown as dashed lines (see Table 1) and, for clarity, the C-bound H atoms have been omitted.

hydrogen bonding is unique to the small group of existing reported ammonium hydrogen bis(carboxylate) structures, which all exhibit hydrogen bonding of ammonium cations with carboxylate O atoms from four unique conjugate acid/base pairs (Chowdhury & Kariuki, 2006; Golic & Lazarini, 1975; Ichikawa, 1972; Nahringbauer, 1969; Perumalla & Sun, 2013). Adjacent chains are linked *via* offset π–π interactions, forming layers parallel to the ab plane; see Fig. 3 [$Cg1⋯Cg3^i$ = 3.588 (2) Å, interplanar distance = 3.480 (1) Å, slippage = 1.121 Å; $Cg1⋯Cg2^{ii}$ = 3.686 (2) Å, interplanar distance = 3.352 (1) Å, slippage = 1.384 Å; $Cg1$, $Cg2$, and $Cg3$ are the centroids of the N1–N4/C7, C1–C6 and C8–C13 rings, respectively; symmetry codes: (i) $x, y + 1, z$; (ii) $x, y - 1, z$].

Synthesis and crystallization

The title compound was synthesized using procedures adopted from multiple literature reports (Song *et al.*, 2008; Ito *et al.*, 1976). To a solution of 4-formylbenzoic acid (0.75 g, 5.0 mmol) in ethanol (50 ml) was added benzenesulfonohydrazide (0.86 g, 25 mmol) and the solution was stirred for 35 min. Water (200 ml) was then added and the beaker containing the reaction was placed in an ice bath to produce a precipitate, which was subsequently filtered off and dissolved in pyridine (30 ml). This was labeled solution **A**. In another flask aniline (0.47 g, 5.0 mmol) was dissolved in a solution consisting of water (4 ml), ethanol (4 ml), and concentrated HCl (1.3 ml). This solution was placed in an ice bath while a cooled solution of NaNO$_2$ (0.35 g, 5.0 mmol) in 2 ml water was added dropwise. This was labeled solution **B**. Solution **A** was then placed in an ice salt bath while solution **B** was added dropwise over 10 min under magnetic stirring. This solution was allowed to sit for 20 min, after which time it was extracted with ethyl acetate (3 × 30 ml). Then 3 M HCl (250 ml) was added to the combined organic extracts and the mixture was stirred for 15 min. The organic layer was then collected, concentrated, and recrystallized from hot ethyl acetate to produce 0.235 g of light-pink crystals of 4-(2-phenyl-2H-tetrazol-5-yl)benzoic acid (17.7% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.31 (*br s*, 1H), 8.27 (*d*, J = 8.7 Hz, 2H), 8.14 (*d*, J = 7.8, 2H), 8.12 (*d*,
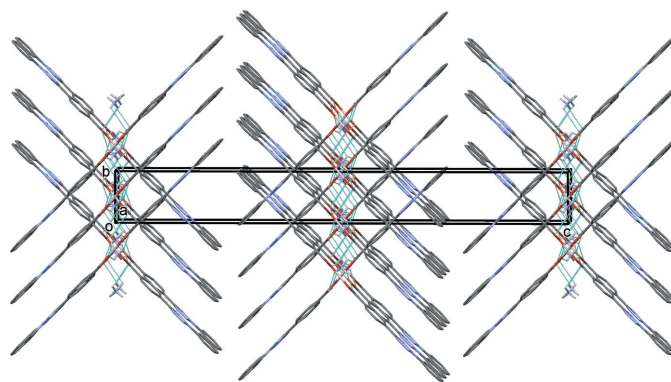

Figure 3
A view along the a axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1) and, for clarity, the C-bound H atoms have been omitted.

Table 2
Experimental details.

Crystal data	
Chemical formula	$NH_4^+ \cdot H^+ \cdot 2C_{14}H_9N_4O_2^-$
M_r	549.55
Crystal system, space group	Monoclinic, $I2/a$
Temperature (K)	173
a, b, c (Å)	12.350 (3), 4.8107 (13), 42.812 (11)
β (°)	97.569 (9)
V (Å^3)	2521.4 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	$0.43 \times 0.43 \times 0.08$
Data collection	
Diffractometer	Rigaku XtaLAB mini
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.679, 0.992
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	4744, 2206, 1788
R_{int}	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.128, 1.19
No. of reflections	2206
No. of parameters	195
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.21

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2011), *SIR2004* (Burla *et al.*, 2005), *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *CrystalStructure* (Rigaku, 2014).

J = 8.3 Hz, 2H), 7.68 (*dd*, J = 7.8, 8.7 Hz, 2H), 7.61 (*t*, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.6, 163.6, 136.0, 132.6 130.3, 130.2, 130.1, 126.7, 119.1.

Crystals of the title compound were prepared by dissolving 4-(2-phenyl-2*H*-tetrazol-5-yl)benzoic acid (30 mg) in 6 ml of a 2:1 solution of methanol–H$_2$O. This gave a cloudy solution which became clear on the addition of 6 drops of 6 *M* NH$_4$OH. The solution was allowed to sit in an open vial at room temperature, and yielded colourless prismatic crystals of the title compound after *ca* 10 d.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

References

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Chowdhury, M. & Kariuki, B. M. (2006). *Cryst. Growth Des.* **6**, 774–780.
Gilli, P., Pretto, L., Bertolasi, V. & Gilli, G. (2009). *Acc. Chem. Res.* **42**, 33–44.
Golic, L. & Lazarini, F. (1975). *Cryst. Struct. Commun.* **4**, 487–490.
Ichikawa, M. (1972). *Acta Cryst.* B**28**, 755–760.
Ito, S., Tanaka, Y., Kakehi, A. & Kondo, K. (1976). *Bull. Chem. Soc. Jpn*, **49**, 1920–1923.
Lim, R. K. & Lin, Q. (2011). *Acc. Chem. Res.* **44**, 828–839.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Nahringbauer, I. (1969). *Acta Chem. Scand.* **23**, 1653–1666.
Perumalla, S. R. & Sun, C. C. (2013). *CrystEngComm*, **15**, 5756–1559.
Ramil, C. P. & Lin, Q. (2014). *Curr. Opin. Chem. Biol.* **21**, 89–95.
Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2011). *CrystalClear-SM Expert*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2014). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Song, W., Wang, Y., Qu, J. & Lin, Q. (2008). *J. Am. Chem. Soc.* **130**, 9654–9655.
Zheng, S.-L., Wang, Y., Yu, Z., Lin, Q. & Coppens, P. J. (2009). *J. Am. Chem. Soc.* **131**, 18036–18037.

full crystallographic data

Ammonium hydrogen bis[4-(2-phenyl-2*H*-tetrazol-5-yl)benzoate]

Daron E. Janzen, Kayla A. Lange and James W. Wollack

Ammonium hydrogen bis[4-(2-phenyl-2*H*-tetrazol-5-yl)benzoate]

Crystal data

$NH_4^+ \cdot H^+ \cdot 2C_{14}H_9N_4O_2^-$
$M_r = 549.55$
Monoclinic, $I2/a$
$a = 12.350\ (3)$ Å
$b = 4.8107\ (13)$ Å
$c = 42.812\ (11)$ Å
$\beta = 97.569\ (9)°$
$V = 2521.4\ (12)$ Å^3
$Z = 4$

$F(000) = 1144.00$
$D_x = 1.448$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 4069 reflections
$\theta = 3.3–25.1°$
$\mu = 0.10$ mm^{-1}
$T = 173$ K
Prism, colourless
$0.43 \times 0.43 \times 0.08$ mm

Data collection

Rigaku XtaLAB mini
   diffractometer
Radiation source: sealed X-ray tube
Detector resolution: 6.849 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
   (REQAB; Rigaku, 1998)
$T_{min} = 0.679$, $T_{max} = 0.992$

4744 measured reflections
2206 independent reflections
1788 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int} = 0.031$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.3°$
$h = -14 \rightarrow 12$
$k = -5 \rightarrow 5$
$l = -50 \rightarrow 50$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.128$
$S = 1.19$
2206 reflections
195 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
$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 4.8932P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

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 was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.52029 (14)	−0.8059 (4)	0.48115 (4)	0.0259 (4)
O2	0.34227 (14)	−0.6986 (4)	0.47209 (5)	0.0359 (5)
N1	0.45919 (17)	0.2934 (5)	0.35894 (5)	0.0260 (5)
N2	0.51882 (16)	0.4507 (5)	0.34221 (5)	0.0248 (5)
N3	0.62631 (17)	0.4060 (5)	0.34874 (6)	0.0326 (6)
N4	0.63802 (18)	0.2133 (5)	0.37061 (6)	0.0321 (6)
N5	0.7500	0.1560 (9)	0.5000	0.0551 (14)
C1	0.4723 (2)	0.6455 (5)	0.31930 (6)	0.0242 (6)
C2	0.3595 (2)	0.6681 (6)	0.31350 (7)	0.0318 (7)
H2	0.3137	0.5576	0.3247	0.038*
C3	0.3158 (2)	0.8570 (6)	0.29087 (7)	0.0366 (7)
H3	0.2387	0.8747	0.2863	0.044*
C4	0.3818 (2)	1.0198 (6)	0.27481 (7)	0.0358 (7)
H4	0.3503	1.1480	0.2593	0.043*
C5	0.4942 (2)	0.9957 (6)	0.28133 (7)	0.0354 (7)
H5	0.5399	1.1084	0.2704	0.043*
C6	0.5402 (2)	0.8083 (6)	0.30370 (6)	0.0304 (7)
H6	0.6173	0.7917	0.3083	0.037*
C7	0.5358 (2)	0.1465 (6)	0.37659 (6)	0.0238 (6)
C8	0.5118 (2)	−0.0604 (6)	0.39962 (6)	0.0245 (6)
C9	0.4036 (2)	−0.1329 (6)	0.40206 (6)	0.0265 (6)
H9	0.3455	−0.0479	0.3887	0.032*
C10	0.3813 (2)	−0.3281 (6)	0.42394 (6)	0.0254 (6)
H10	0.3076	−0.3769	0.4254	0.030*
C11	0.4652 (2)	−0.4553 (6)	0.44397 (6)	0.0236 (6)
C12	0.5730 (2)	−0.3826 (6)	0.44126 (6)	0.0277 (6)
H12	0.6310	−0.4687	0.4546	0.033*
C13	0.5963 (2)	−0.1879 (6)	0.41957 (6)	0.0279 (6)
H13	0.6701	−0.1398	0.4181	0.034*
C14	0.4385 (2)	−0.6670 (6)	0.46713 (6)	0.0249 (6)
H1A	0.5000	−1.0000	0.5000	0.11 (2)*
H5A	0.770 (8)	0.061 (16)	0.4864 (18)	0.19 (4)*
H5B	0.806 (8)	0.25 (2)	0.507 (3)	0.31 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0212 (9)	0.0254 (10)	0.0312 (10)	0.0015 (8)	0.0033 (8)	0.0051 (8)
O2	0.0192 (10)	0.0465 (13)	0.0433 (12)	0.0006 (9)	0.0088 (8)	0.0150 (10)
N1	0.0245 (12)	0.0269 (12)	0.0278 (12)	−0.0017 (10)	0.0084 (10)	0.0009 (10)
N2	0.0194 (11)	0.0284 (13)	0.0277 (12)	−0.0011 (10)	0.0067 (9)	0.0024 (10)

N3	0.0188 (11)	0.0408 (15)	0.0387 (14)	0.0015 (11)	0.0062 (10)	0.0105 (12)
N4	0.0219 (12)	0.0390 (15)	0.0361 (14)	0.0018 (10)	0.0060 (10)	0.0125 (12)
N5	0.0184 (19)	0.022 (2)	0.126 (5)	0.000	0.014 (2)	0.000
C1	0.0252 (13)	0.0231 (14)	0.0244 (13)	0.0010 (11)	0.0036 (11)	−0.0015 (12)
C2	0.0247 (14)	0.0338 (16)	0.0383 (16)	0.0012 (13)	0.0090 (12)	0.0009 (14)
C3	0.0250 (15)	0.0414 (18)	0.0426 (18)	0.0058 (13)	0.0015 (13)	−0.0008 (15)
C4	0.0412 (17)	0.0316 (17)	0.0334 (16)	0.0078 (14)	0.0002 (13)	0.0039 (14)
C5	0.0366 (16)	0.0335 (17)	0.0378 (16)	−0.0003 (14)	0.0107 (13)	0.0049 (14)
C6	0.0255 (14)	0.0355 (16)	0.0309 (15)	0.0001 (13)	0.0058 (12)	0.0035 (14)
C7	0.0207 (13)	0.0265 (15)	0.0243 (13)	0.0016 (11)	0.0033 (11)	−0.0022 (12)
C8	0.0230 (13)	0.0262 (15)	0.0250 (14)	0.0007 (12)	0.0058 (11)	−0.0034 (12)
C9	0.0204 (13)	0.0301 (16)	0.0288 (14)	0.0017 (11)	0.0029 (11)	0.0022 (13)
C10	0.0176 (13)	0.0298 (15)	0.0291 (14)	−0.0001 (11)	0.0047 (11)	0.0010 (13)
C11	0.0217 (13)	0.0242 (14)	0.0260 (14)	0.0001 (11)	0.0067 (11)	−0.0043 (12)
C12	0.0189 (13)	0.0304 (15)	0.0332 (15)	0.0020 (11)	0.0013 (11)	0.0030 (13)
C13	0.0194 (13)	0.0317 (15)	0.0333 (15)	−0.0025 (12)	0.0052 (11)	0.0009 (13)
C14	0.0232 (14)	0.0243 (14)	0.0275 (14)	0.0016 (11)	0.0047 (11)	−0.0019 (12)

Geometric parameters (Å, º)

O1—C14	1.291 (3)	C4—H4	0.9500
O2—C14	1.244 (3)	C5—C6	1.382 (4)
N1—N2	1.329 (3)	C5—H5	0.9500
N1—C7	1.333 (3)	C6—H6	0.9500
N2—N3	1.337 (3)	C7—C8	1.458 (4)
N2—C1	1.422 (3)	C8—C9	1.399 (3)
N3—N4	1.312 (3)	C8—C13	1.400 (4)
N4—C7	1.359 (3)	C9—C10	1.379 (4)
N5—H5A	0.80 (8)	C9—H9	0.9500
N5—H5B	0.84 (11)	C10—C11	1.396 (4)
C1—C6	1.382 (4)	C10—H10	0.9500
C1—C2	1.387 (4)	C11—C12	1.396 (3)
C2—C3	1.385 (4)	C11—C14	1.489 (4)
C2—H2	0.9500	C12—C13	1.376 (4)
C3—C4	1.378 (4)	C12—H12	0.9500
C3—H3	0.9500	C13—H13	0.9500
C4—C5	1.384 (4)		
N2—N1—C7	101.8 (2)	N1—C7—N4	112.0 (2)
N1—N2—N3	113.7 (2)	N1—C7—C8	123.5 (2)
N1—N2—C1	123.0 (2)	N4—C7—C8	124.4 (2)
N3—N2—C1	123.3 (2)	C9—C8—C13	119.2 (2)
N4—N3—N2	106.0 (2)	C9—C8—C7	120.2 (2)
N3—N4—C7	106.5 (2)	C13—C8—C7	120.6 (2)
H5A—N5—H5B	103 (8)	C10—C9—C8	119.9 (2)
C6—C1—C2	121.9 (3)	C10—C9—H9	120.1
C6—C1—N2	119.4 (2)	C8—C9—H9	120.1
C2—C1—N2	118.7 (2)	C9—C10—C11	121.2 (2)

C3—C2—C1	117.8 (3)	C9—C10—H10	119.4
C3—C2—H2	121.1	C11—C10—H10	119.4
C1—C2—H2	121.1	C12—C11—C10	118.5 (2)
C4—C3—C2	121.4 (3)	C12—C11—C14	121.6 (2)
C4—C3—H3	119.3	C10—C11—C14	119.8 (2)
C2—C3—H3	119.3	C13—C12—C11	120.9 (2)
C3—C4—C5	119.7 (3)	C13—C12—H12	119.6
C3—C4—H4	120.2	C11—C12—H12	119.6
C5—C4—H4	120.2	C12—C13—C8	120.3 (2)
C6—C5—C4	120.3 (3)	C12—C13—H13	119.9
C6—C5—H5	119.8	C8—C13—H13	119.9
C4—C5—H5	119.9	O2—C14—O1	124.3 (2)
C5—C6—C1	119.0 (3)	O2—C14—C11	119.9 (2)
C5—C6—H6	120.5	O1—C14—C11	115.8 (2)
C1—C6—H6	120.5		
C7—N1—N2—N3	0.2 (3)	N3—N4—C7—C8	−179.8 (3)
C7—N1—N2—C1	179.5 (2)	N1—C7—C8—C9	6.1 (4)
N1—N2—N3—N4	−0.2 (3)	N4—C7—C8—C9	−174.2 (3)
C1—N2—N3—N4	−179.5 (2)	N1—C7—C8—C13	−173.7 (3)
N2—N3—N4—C7	0.1 (3)	N4—C7—C8—C13	6.1 (4)
N1—N2—C1—C6	177.7 (3)	C13—C8—C9—C10	0.0 (4)
N3—N2—C1—C6	−3.1 (4)	C7—C8—C9—C10	−179.8 (3)
N1—N2—C1—C2	−1.7 (4)	C8—C9—C10—C11	0.3 (4)
N3—N2—C1—C2	177.6 (3)	C9—C10—C11—C12	−0.6 (4)
C6—C1—C2—C3	1.3 (4)	C9—C10—C11—C14	−179.5 (2)
N2—C1—C2—C3	−179.4 (3)	C10—C11—C12—C13	0.6 (4)
C1—C2—C3—C4	−0.7 (4)	C14—C11—C12—C13	179.5 (3)
C2—C3—C4—C5	−0.1 (5)	C11—C12—C13—C8	−0.4 (4)
C3—C4—C5—C6	0.4 (5)	C9—C8—C13—C12	0.1 (4)
C4—C5—C6—C1	0.2 (4)	C7—C8—C13—C12	179.9 (3)
C2—C1—C6—C5	−1.1 (4)	C12—C11—C14—O2	169.8 (3)
N2—C1—C6—C5	179.6 (3)	C10—C11—C14—O2	−11.3 (4)
N2—N1—C7—N4	−0.1 (3)	C12—C11—C14—O1	−9.5 (4)
N2—N1—C7—C8	179.7 (2)	C10—C11—C14—O1	169.3 (2)
N3—N4—C7—N1	0.0 (3)		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1A⋯O1[i]	1.28	1.28	2.561 (3)	180
N5—H5A⋯O2[ii]	0.80 (8)	2.09 (8)	2.815 (4)	151 (7)
N5—H5B⋯O1[iii]	0.84 (11)	2.15 (10)	2.8513 (18)	140 (9)

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