IUCrData

ISSN 2414-3146

Diisopropylammonium hydrogen phthalate

Dame Seye,[a] Libasse Diop,[a]* Cheikh Abdoul Khadir Diop[a] and David K. Geiger[b]

[a]Laboratoire de Chimie Minérale et Analytique, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal, and [b]Department of Chemistry, SUNY-College at Geneseo, Geneseo, NY 14454, USA. *Correspondence e-mail: dlibasse@gmail.com

Received 16 April 2018
Accepted 8 May 2018

Edited by A. J. Lough, University of Toronto, Canada

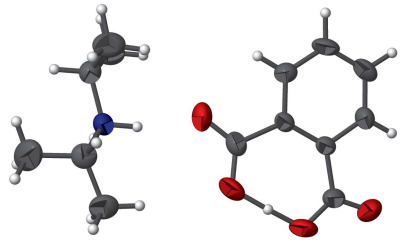
Keywords: crystal structure; hydrogen bonds; layered structure.

CCDC reference: 1842128

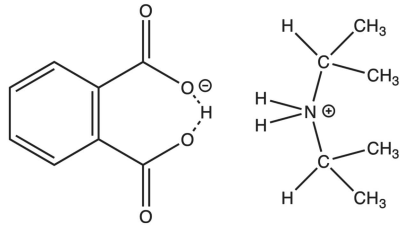
Structural data: full structural data are available from iucrdata.iucr.org

In the crystal of the title molecular salt, $C_6H_{16}N^+\cdot C_8H_5O_4^-$, the cation and anions are linked into [010] chains by N—H···O hydrogen bonds. The chains are connected to their neighbours through weak C—H···O hydrogen bonds, leading to a layered supramolecular architecture. The hydrogen phthalate anion exhibits an intramolecular O—H···O hydrogen bond in which the H atom is approximately equidistant to the two O atoms.

3D view



Chemical scheme



Structure description

Various ammonium hydrogen phthalate and phthalate salts have been synthesized by several groups (Edwards *et al.*, 2001; Pereira Silva *et al.*, 2006; Yu, 2012; Liu 2012; Shahid *et al.* 2015; Lin *et al.* 2011). These salts can react with metallic halides leading to complexes (Ma *et al.*, 2004; Askarinejad *et al.*, 2006; Döring & Jones, 2016). For several years, our group has been involved in the study of the interactions of similar salts with organotin(IV) and halotin(IV) compounds (Diop *et al.*, 2016; Sarr *et al.*, 2018). As part of our ongoing studies in this area, we now describe the synthesis and structure of the title molecular salt.

The title compound crystallizes in the monoclinic $P2_1/c$ space group with the asymmetric unit comprising of one diisopropylammonium cation and one hydrogen phthalate anion (Fig. 1). The C—C and C—N bonds within the cation are similar to those previously observed for compounds containing the $i\mathrm{Pr}_2\mathrm{NH}_2^+$ cation (Sarr *et al.*, 2018; Lin *et al.*, 2017). The C—C and C—O bonds of the hydrogen phthalate anion are close to the published values for salts containing this anion (Liu *et al.*, 2012; Shahid *et al.*, 2015). In the extended structure, the monomeric acidic inner (O1—H1···O3) hydrogen-bonded anions $[\mathrm{PhCO_2H(COO)}]^-$ are connected to the cations *via* hydrogen bonds (N1—H1*A*···O4^{i}, N1—H1*B*···O2; Table 1, Fig. 2), giving rise to zigzag chains of alternating cations and anions parallel to [010]. Weak intermolecular hydrogen bonds (C3—

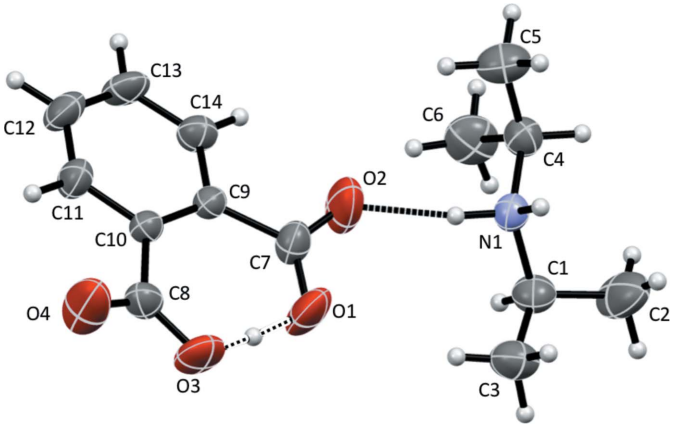


Figure 1
View of the title compound showing the atom-labelling scheme. Anisotropic displacement parameters of non-H atoms are drawn at the 50% probability level.

H3*C*···O1, C13—H13···O1, C12—H12···O3, C3—H3*A*···O4 and C6—H6···O2), which can be described as phthalate/phthalate and phthalate/cation interactions, occur leading to a supramolecular pleated sheet architecture.

A search of the Cambridge Structural Database (CSD Version 5.39, updates Nov 2017; Groom *et al.*, 2016) yielded 67 hits for diisopropylammonium salts while 101 hits were obtained in a search for the phthalate anion.

Synthesis and crystallization

All the chemicals were purchased from Aldrich (Germany) and used without further purification. Diisopropylammonium hydrogen phthalate [iPr$_2$NH$_2$·Ph(CO$_2$H)(CO$_2$)] was obtained from the partial neutralization of phthalic acid (Ph(COH)$_2$); 5 g, 3 mmol) by diisopropylamine (iPr$_2$NH; 3.05 g, 3 mmol) in ethanol (50 ml). The clear mixture was stirred for two h.

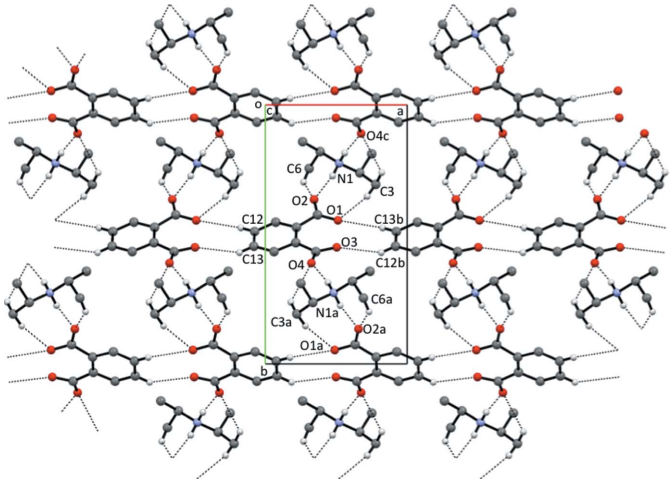


Figure 2
Partial packing diagram showing the hydrogen-bonding interactions. Only H atoms involved in the intermolecular interactions are shown. Symmetry identifiers: (*a*) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (*b*) $x+1, y, z$; (*c*) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O3	1.19 (4)	1.20 (4)	2.385 (3)	173 (3)
N1—H1*A*···O4^{i}	0.94 (3)	1.83 (3)	2.756 (3)	169 (2)
N1—H1*B*···O2	0.95 (3)	1.83 (3)	2.763 (2)	166 (2)
C3—H3*C*···O1	0.98	2.70	3.659 (3)	166
C3—H3*A*···O4^{i}	0.98	2.69	3.392 (4)	129
C6—H6*C*···O2	0.98	2.68	3.408 (4)	132
C12—H12···O3^{ii}	0.95	2.58	3.401 (2)	145
C13—H13···O1^{ii}	0.95	2.61	3.449 (3)	148

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_{16}N^+·C_8H_5O_4^-$
M_r	267.32
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	200
a, b, c (Å)	8.160 (3), 14.876 (5), 12.549 (5)
β (°)	93.192 (9)
V (Å^3)	1520.9 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.40 × 0.40 × 0.40
Data collection	
Diffractometer	Bruker Smart X2S benchtop
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.48, 0.97
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12641, 2772, 2240
R_{int}	0.071
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.164, 1.07
No. of reflections	2772
No. of parameters	188
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, −0.23

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

Crystals suitable for X-ray diffraction analysis were obtained after a week of slow solvent evaporation at room temperature (300 K).

Refinement

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

Funding information

The authors acknowledge the Cheikh Anta Diop University, Dakar, Senegal, for their support and the US Department of Education *via* a Congressionally directed grant (grant No. P116Z100020) for the X-ray diffractometer.

References

Askarinejad, A., Torabi, A. A. & Morsali, A. (2006). *Z. Naturforsch. B: Chem. Sci.* **61**, 565–569.

Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Diop, M. B., Diop, L., Plasseraud, L. & Maris, T. (2016). *Acta Cryst.* E**72**, 355–357.

Döring, C. & Jones, P. G. (2016). *Z. Anorg. Allg. Chem.* **642**, 930–936.

Edwards, S. H., Kahwa, I. A. & Mague, J. T. (2001). *Acta Cryst.* E**57**, o20–o21.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst*. B**72**, 171–179.

Lin, Z., Hu, K., Jin, S., Ding, A., Wang, Y., Dong, L., Gao, X. & Wang, D. (2017). *J. Mol. Struct.* **1146**, 577–591.

Lin, F., Jin, S., Tong, K., He, H. & Yu, Y. Q. (2011). *Acta Cryst.* E**67**, o2592.

Liu, M.-L. (2012). *Acta Cryst.* E**68**, o228.

Ma, C, Wang. W, Zhang. X, Chen. C, Liu. Q, Zhu. H, Liao. D & Li. L. (2004). *Eur. J. Inorg. Chem.* pp. 3522–3532.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Pereira Silva, P. S., Ramos Silva, M., Matos Beja, A. & Paixão, J. A. (2006). *Acta Cryst.* E**62**, o1067–o1069.

Sarr, B., Diop, C. A. K., Sidibé, M. & Rousselin, Y. (2018). *Acta Cryst.* E**74**, 502–504.

Shahid, M., Tahir, M. N., Salim, M. & Munawar, M. A. (2015). *Acta Cryst.* E**71**, o446.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Yu, C.-H. (2012). *Acta Cryst.* E**68**, o2295.

full crystallographic data

IUCrData (2018). **3**, x180704 [https://doi.org/10.1107/S2414314618007046]

Diisopropylammonium hydrogen phthalate

Dame Seye, Libasse Diop, Cheikh Abdoul Khadir Diop and David K. Geiger

Diisopropylammonium hydrogen phthalate

Crystal data

$C_6H_{16}N^+·C_8H_5O_4^-$
M_r = 267.32
Monoclinic, $P2_1/c$
a = 8.160 (3) Å
b = 14.876 (5) Å
c = 12.549 (5) Å
β = 93.192 (9)°
V = 1520.9 (10) Å^3
Z = 4
$F(000)$ = 576
D_x = 1.167 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5881 reflections
θ = 2.5–25.3°
μ = 0.09 mm^{-1}
T = 200 K
Block, colorless
0.40 × 0.40 × 0.40 mm

Data collection

Bruker Smart X2S benchtop diffractometer
Radiation source: sealed microfocus tube
Detector resolution: 8.3330 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.48, T_{max} = 0.97
12641 measured reflections
2772 independent reflections
2240 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 25.4°, θ_{min} = 2.5°
h = −7→9
k = −17→16
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.164
S = 1.07
2772 reflections
188 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 0.612P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 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. All hydrogen atoms were observed in difference fourier maps. The H atoms were refined using a riding model with a C— H distance of 0.98 Å for the methyl carbon atoms and 0.95 Å for the phenyl carbon atoms. The methyl C—H hydrogen atom isotropic displacement parameters were set using the and hydrogen-atom isotropic displacement parameters were set using the approximation $U_{iso}(H) = 1.2U_{eq}(C)$. The hydrogen atoms bonded to the oxygen and nitrogen atoms were refined freely, including isotropic displacement parameters.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.51102 (17)	0.44641 (14)	0.35313 (15)	0.0727 (6)
H1O	0.511 (4)	0.502 (2)	0.285 (3)	0.106 (11)*
O2	0.3436 (2)	0.36584 (14)	0.44266 (17)	0.0824 (6)
O3	0.50277 (17)	0.55055 (13)	0.20842 (16)	0.0687 (5)
O4	0.3243 (2)	0.61102 (16)	0.09499 (18)	0.0947 (8)
N1	0.51945 (19)	0.22605 (11)	0.53843 (13)	0.0386 (4)
H1A	0.559 (3)	0.1865 (17)	0.4879 (19)	0.059 (7)*
H1B	0.473 (3)	0.2747 (18)	0.4978 (19)	0.061 (7)*
C1	0.6655 (3)	0.26303 (15)	0.60386 (16)	0.0482 (5)
H1	0.6257	0.3097	0.6536	0.058*
C2	0.7504 (3)	0.1897 (2)	0.6693 (2)	0.0899 (11)
H2A	0.7802	0.1405	0.6221	0.135*
H2B	0.6764	0.167	0.7219	0.135*
H2C	0.8498	0.2139	0.7061	0.135*
C3	0.7788 (3)	0.30729 (17)	0.5290 (2)	0.0621 (6)
H3A	0.8208	0.2621	0.4807	0.093*
H3B	0.8708	0.3351	0.5703	0.093*
H3C	0.7186	0.3535	0.4872	0.093*
C4	0.3859 (2)	0.18111 (14)	0.59641 (17)	0.0466 (5)
H4	0.4352	0.1302	0.6392	0.056*
C5	0.2623 (3)	0.1430 (2)	0.5132 (2)	0.0690 (7)
H5A	0.215	0.192	0.4694	0.104*
H5B	0.1747	0.112	0.5491	0.104*
H5C	0.3174	0.1003	0.4677	0.104*
C6	0.3086 (3)	0.24578 (19)	0.6716 (2)	0.0703 (7)
H6A	0.3903	0.2641	0.7275	0.105*
H6B	0.2163	0.2163	0.7042	0.105*
H6C	0.2688	0.2989	0.6318	0.105*
C7	0.3676 (3)	0.42528 (14)	0.37800 (17)	0.0478 (5)
C8	0.3558 (2)	0.56711 (13)	0.17568 (18)	0.0456 (5)
C9	0.2187 (2)	0.47323 (12)	0.32552 (14)	0.0349 (4)
C10	0.2140 (2)	0.53271 (12)	0.23738 (15)	0.0352 (4)
C11	0.0605 (2)	0.56684 (14)	0.20079 (17)	0.0471 (5)
H11	0.0551	0.6057	0.1406	0.057*
C12	−0.0817 (2)	0.54627 (16)	0.24843 (19)	0.0546 (6)
H12	−0.1833	0.5709	0.2218	0.066*
C13	−0.0761 (2)	0.48961 (17)	0.33524 (19)	0.0541 (6)
H13	−0.1735	0.4755	0.3698	0.065*
C14	0.0725 (2)	0.45341 (14)	0.37176 (17)	0.0454 (5)

H14	0.0747	0.4134	0.4308	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0296 (8)	0.1033 (14)	0.0849 (12)	0.0125 (8)	0.0015 (8)	0.0280 (11)
O2	0.0646 (11)	0.0819 (13)	0.1007 (14)	0.0197 (9)	0.0037 (10)	0.0501 (11)
O3	0.0295 (8)	0.0905 (13)	0.0870 (12)	−0.0079 (7)	0.0117 (8)	0.0212 (10)
O4	0.0614 (11)	0.1140 (17)	0.1107 (15)	0.0077 (11)	0.0236 (11)	0.0737 (14)
N1	0.0379 (8)	0.0378 (9)	0.0399 (8)	0.0039 (7)	0.0005 (7)	−0.0007 (7)
C1	0.0480 (11)	0.0489 (12)	0.0470 (11)	−0.0057 (9)	−0.0030 (9)	−0.0059 (9)
C2	0.0626 (16)	0.112 (2)	0.092 (2)	−0.0162 (16)	−0.0300 (15)	0.0447 (19)
C3	0.0529 (13)	0.0613 (15)	0.0722 (15)	−0.0143 (11)	0.0049 (11)	0.0017 (12)
C4	0.0450 (11)	0.0441 (11)	0.0507 (11)	0.0002 (9)	0.0035 (9)	0.0058 (9)
C5	0.0527 (13)	0.0793 (18)	0.0743 (16)	−0.0156 (12)	−0.0026 (12)	−0.0062 (14)
C6	0.0672 (15)	0.0786 (18)	0.0678 (15)	−0.0016 (13)	0.0272 (13)	−0.0030 (14)
C7	0.0423 (11)	0.0489 (12)	0.0521 (11)	0.0105 (9)	0.0005 (9)	0.0048 (10)
C8	0.0378 (10)	0.0399 (10)	0.0600 (12)	−0.0010 (8)	0.0118 (9)	0.0041 (10)
C9	0.0291 (9)	0.0332 (9)	0.0423 (10)	0.0006 (7)	0.0000 (7)	−0.0015 (7)
C10	0.0283 (9)	0.0327 (9)	0.0445 (10)	−0.0001 (7)	0.0032 (7)	−0.0004 (7)
C11	0.0368 (10)	0.0512 (12)	0.0528 (11)	0.0052 (9)	−0.0028 (9)	0.0123 (10)
C12	0.0288 (10)	0.0684 (15)	0.0657 (14)	0.0047 (9)	−0.0054 (9)	0.0041 (11)
C13	0.0262 (9)	0.0707 (15)	0.0663 (13)	−0.0078 (9)	0.0099 (9)	0.0026 (12)
C14	0.0381 (10)	0.0492 (11)	0.0493 (11)	−0.0041 (8)	0.0062 (8)	0.0070 (9)

Geometric parameters (Å, º)

O1—C7	1.267 (3)	C4—C5	1.520 (3)
O1—H1O	1.19 (4)	C4—H4	1.0
O2—C7	1.223 (3)	C5—H5A	0.98
O3—C8	1.270 (3)	C5—H5B	0.98
O3—H1O	1.20 (4)	C5—H5C	0.98
O4—C8	1.220 (3)	C6—H6A	0.98
N1—C4	1.501 (3)	C6—H6B	0.98
N1—C1	1.513 (2)	C6—H6C	0.98
N1—H1A	0.94 (3)	C7—C9	1.526 (3)
N1—H1B	0.95 (3)	C8—C10	1.517 (3)
C1—C3	1.506 (3)	C9—C14	1.387 (3)
C1—C2	1.510 (3)	C9—C10	1.415 (3)
C1—H1	1.0	C10—C11	1.405 (3)
C2—H2A	0.98	C11—C12	1.369 (3)
C2—H2B	0.98	C11—H11	0.95
C2—H2C	0.98	C12—C13	1.376 (3)
C3—H3A	0.98	C12—H12	0.95
C3—H3B	0.98	C13—C14	1.382 (3)
C3—H3C	0.98	C13—H13	0.95
C4—C6	1.510 (3)	C14—H14	0.95

C7—O1—H1O	112.8 (17)	H5A—C5—H5B	109.5
C8—O3—H1O	112.7 (17)	C4—C5—H5C	109.5
C4—N1—C1	118.04 (15)	H5A—C5—H5C	109.5
C4—N1—H1A	109.7 (15)	H5B—C5—H5C	109.5
C1—N1—H1A	107.7 (15)	C4—C6—H6A	109.5
C4—N1—H1B	108.6 (15)	C4—C6—H6B	109.5
C1—N1—H1B	107.0 (14)	H6A—C6—H6B	109.5
H1A—N1—H1B	105.0 (19)	C4—C6—H6C	109.5
C3—C1—C2	112.1 (2)	H6A—C6—H6C	109.5
C3—C1—N1	108.24 (17)	H6B—C6—H6C	109.5
C2—C1—N1	110.86 (19)	O2—C7—O1	121.79 (19)
C3—C1—H1	108.5	O2—C7—C9	118.10 (19)
C2—C1—H1	108.5	O1—C7—C9	120.10 (19)
N1—C1—H1	108.5	O4—C8—O3	121.6 (2)
C1—C2—H2A	109.5	O4—C8—C10	118.17 (18)
C1—C2—H2B	109.5	O3—C8—C10	120.20 (19)
H2A—C2—H2B	109.5	C14—C9—C10	118.24 (16)
C1—C2—H2C	109.5	C14—C9—C7	113.74 (17)
H2A—C2—H2C	109.5	C10—C9—C7	128.02 (17)
H2B—C2—H2C	109.5	C11—C10—C9	117.81 (17)
C1—C3—H3A	109.5	C11—C10—C8	113.78 (17)
C1—C3—H3B	109.5	C9—C10—C8	128.41 (16)
H3A—C3—H3B	109.5	C12—C11—C10	122.57 (19)
C1—C3—H3C	109.5	C12—C11—H11	118.7
H3A—C3—H3C	109.5	C10—C11—H11	118.7
H3B—C3—H3C	109.5	C11—C12—C13	119.40 (18)
N1—C4—C6	111.06 (18)	C11—C12—H12	120.3
N1—C4—C5	107.78 (17)	C13—C12—H12	120.3
C6—C4—C5	112.4 (2)	C12—C13—C14	119.42 (19)
N1—C4—H4	108.5	C12—C13—H13	120.3
C6—C4—H4	108.5	C14—C13—H13	120.3
C5—C4—H4	108.5	C13—C14—C9	122.54 (19)
C4—C5—H5A	109.5	C13—C14—H14	118.7
C4—C5—H5B	109.5	C9—C14—H14	118.7

C4—N1—C1—C3	−178.07 (18)	O4—C8—C10—C11	−8.3 (3)
C4—N1—C1—C2	58.6 (3)	O3—C8—C10—C11	171.3 (2)
C1—N1—C4—C6	61.3 (2)	O4—C8—C10—C9	172.6 (2)
C1—N1—C4—C5	−175.11 (19)	O3—C8—C10—C9	−7.7 (3)
O2—C7—C9—C14	10.5 (3)	C9—C10—C11—C12	1.5 (3)
O1—C7—C9—C14	−170.6 (2)	C8—C10—C11—C12	−177.7 (2)
O2—C7—C9—C10	−168.8 (2)	C10—C11—C12—C13	−0.4 (4)
O1—C7—C9—C10	10.1 (3)	C11—C12—C13—C14	−1.0 (4)
C14—C9—C10—C11	−1.1 (3)	C12—C13—C14—C9	1.3 (3)
C7—C9—C10—C11	178.11 (19)	C10—C9—C14—C13	−0.2 (3)
C14—C9—C10—C8	177.85 (19)	C7—C9—C14—C13	−179.6 (2)
C7—C9—C10—C8	−2.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O3	1.19 (4)	1.20 (4)	2.385 (3)	173 (3)
N1—H1*A*···O4^{i}	0.94 (3)	1.83 (3)	2.756 (3)	169 (2)
N1—H1*B*···O2	0.95 (3)	1.83 (3)	2.763 (2)	166 (2)
C3—H3*C*···O1	0.98	2.70	3.659 (3)	166
C3—H3*A*···O4^{i}	0.98	2.69	3.392 (4)	129
C6—H6*C*···O2	0.98	2.68	3.408 (4)	132
C12—H12···O3^{ii}	0.95	2.58	3.401 (2)	145
C13—H13···O1^{ii}	0.95	2.61	3.449 (3)	148

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