

1,3-Bis(2,6-diisopropylphenyl)imidazolium perchlorate

Samuel A. Minaker,^a Ruiyao Wang^b and Manuel A. S. Aquino^{a*}

^aDepartment of Chemistry, St. Francis Xavier University, PO Box 5000, Antigonish, Nova Scotia, B2G 2W5, Canada, and

^bDepartment of Chemistry, Xi'an Jiaotong-Liverpool University, 111 Renai Road, Suzhou, Jiangsu 215123, People's Republic of China. *Correspondence e-mail: maquino@stfx.ca

Received 30 March 2018

Accepted 31 March 2018

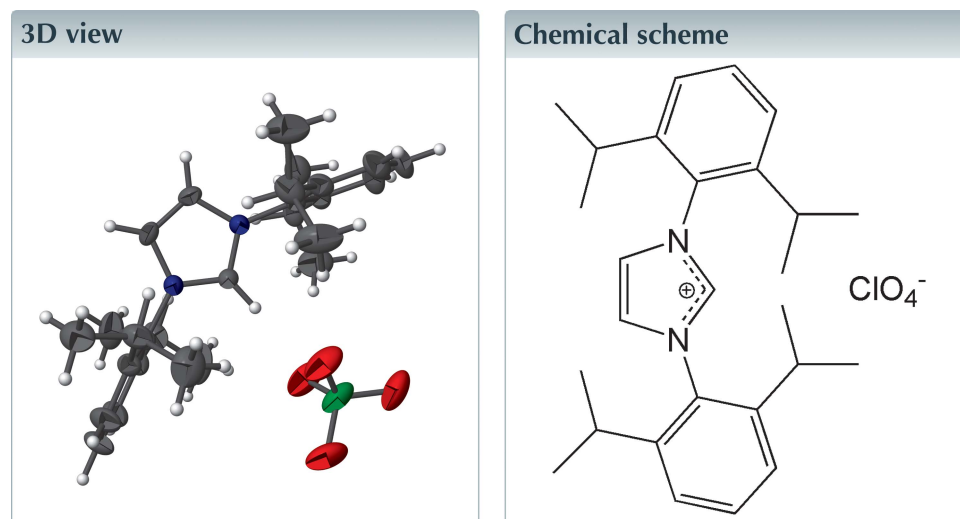
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; imidazolium; carbene.

CCDC reference: 1833992

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

The title salt, $C_{27}H_{37}N_2^+ \cdot ClO_4^-$, arose as an unexpected oxidation product of the carbene 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene in methanol. The five-membered cationic imidazolium ring is planar by symmetry and the complete cation is generated by a crystallographic twofold axis passing through the central N-bonded C atom and the mid-point of the C=C bond; the Cl atom of the perchlorate anion also lies on the rotation axis. The phenyl rings of the 2,6-diisopropylphenyl groups are each perpendicular to the imidazolium ring [dihedral angle = 90.0 (3)°]. In the crystal, weak C—H···O and bifurcated C—H···(O,O) interactions between the imidazolium ring H atoms and the perchlorate O atoms lead to [001] chains.



Structure description

Our ongoing research into the chemistry of diruthenium(II,III) tetracarboxylates led us to attempt axial coordination of N-heterocyclic carbenes to the diruthenium(II,III) core, as had successfully been accomplished on the analogous dirhodium(II,II) core (André *et al.*, 2008). Our attempts have been unsuccessful but we were able to isolate crystals of an oxidized imidazolium species as its title perchlorate salt in the course of one of our reactions.

The molecule consists of an imidazolium core with isopropylphenyl substituents attached to each heterocyclic nitrogen atom (Fig. 1). The bond lengths in the heterocycle: C2—C2($\frac{3}{2} - x, \frac{1}{2} - y, z$) = 1.340 (4), N1—C1 = 1.326 (2) and N1—C2 = 1.378 (3) Å, are consistent with a double bond between the C2 carbon atoms and bond delocalization over the N—C—N part of the ring, similar to other isopropylphenyl derivatives (*e.g.* Arduengo *et al.*, 1999; Berger *et al.*, 2012; Blue *et al.*, 2006). In the crystal, extensive C—H···O hydrogen bonding is seen (Table 1) involving the C1—H1 grouping and the

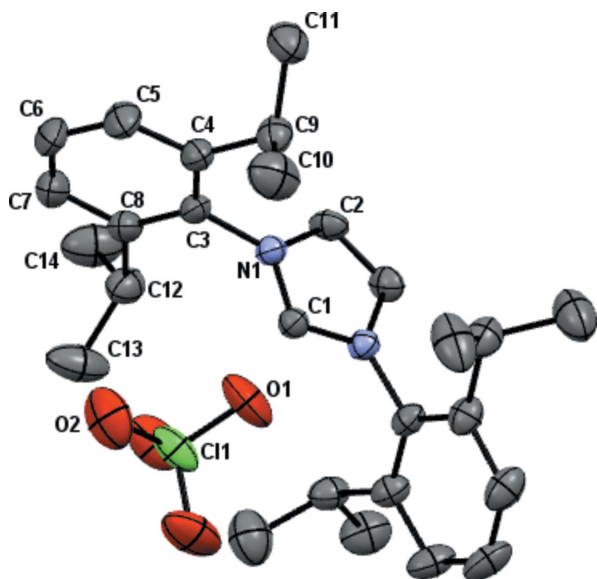


Figure 1
The molecular structure of the title compound with displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity and unlabelled atoms are generated by the symmetry operator $(-x + \frac{3}{2}, -y + \frac{1}{2}, z)$.

perchlorate anion (symmetrically bifurcating two of the perchlorate oxygen atoms) as well as the C2–H2A grouping and the other perchlorate oxygen atom, leading to [001] chains (Fig. 2).

Crystal structures of perchlorate salts of imidazolium derivatives are rare (Crees *et al.*, 2010; Pesch *et al.*, 2004; Fürstner *et al.*, 2006) and there are none for the isopropylphenyl derivative.

Synthesis and crystallization

Crystals of the title compound were isolated as a byproduct of the reaction of $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{MeOH})_2](\text{ClO}_4)$ (0.100 g, 0.166 mmol) in 10 ml of methanol with a twofold excess of the carbene 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (0.131 g, 0.333 mmol) in 5 ml of methanol.

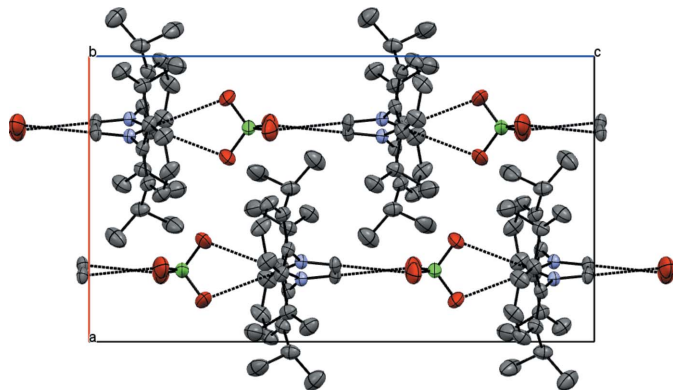


Figure 2
Packing diagram viewed along the [010] axis showing the hydrogen-bonding interactions.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$C1\text{---}H1A\cdots O1$	0.95	2.37	3.232 (3)	151
$C1\text{---}H1A\cdots O1^i$	0.95	2.37	3.232 (3)	151
$C2\text{---}H2A\cdots O2^{ii}$	0.95	2.32	3.096 (3)	138

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{27}\text{H}_{37}\text{N}_2^+\cdot\text{ClO}_4^-$
M_r	489.04
Crystal system, space group	Orthorhombic, $Pccn$
Temperature (K)	180
a, b, c (\AA)	11.0729 (12), 12.6284 (13), 19.6141 (19)
V (\AA^3)	2742.7 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.17
Crystal size (mm)	$0.15 \times 0.10 \times 0.08$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2010)
$T_{\text{min}}, T_{\text{max}}$	0.975, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7718, 2695, 1759
R_{int}	0.042
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.150, 1.04
No. of reflections	2695
No. of parameters	159
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.31, -0.42

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXT2018/1* (Sheldrick, 2015a), *SHELXL2018/1* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

This solution was stirred for 2 h and after slow evaporation yielded a brown powder (ruthenium complex) and crystals of the de-protonated, oxidized, imidazolium, 1,3-bis(2,6-diisopropylphenyl)imidazolium, as a perchlorate salt.

Refinement

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

Funding information

Funding for this research was provided by: Natural Sciences and Engineering Research Council of Canada (grant to Manuel Aquino).

References

- André, V., Duarte, M. T., Trindade, A. F., Góis, P. M. P. & Afonso, C. A. M. (2008). *Acta Cryst.* **C64**, m345–m348.
 Arduengo, A. J., Krafczyk, R. & Schmutzler, R. (1999). *Tetrahedron*, **55**, 14523–14534.

- Berger, M., Auner, N. & Bolte, M. (2012). *Acta Cryst.* **E68**, o1844.
- Blue, E. D., Gunnoe, T. B., Peterson, J. L. & Boyle, P. D. (2006). *J. Organomet. Chem.* **691**, 5988–5993.
- Bruker (2010). *APEX2*, *SAINTE*, and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Crees, R. S., Cole, M. L., Hanton, L. R. & Sumbly, C. J. (2010). *Inorg. Chem.* **49**, 1712–1719.
- Fürstner, A., Alcarazo, M., César, V. & Lehmann, C. W. (2006). *Chem. Commun.* 2176–2178.
- Pesch, J., Harms, K. & Bach, T. (2004). *Eur. J. Org. Chem.* pp. 2025–2035.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

full crystallographic data

IUCrData (2018). 3, x180516 [https://doi.org/10.1107/S2414314618005163]

1,3-Bis(2,6-diisopropylphenyl)imidazolium perchlorate

Samuel A. Minaker, Ruiyao Wang and Manuel A. S. Aquino

1,3-Bis(2,6-diisopropylphenyl)imidazolium perchlorate

Crystal data

$C_{27}H_{37}N_2^+ \cdot ClO_4^-$

$M_r = 489.04$

Orthorhombic, *Pccn*

$a = 11.0729$ (12) Å

$b = 12.6284$ (13) Å

$c = 19.6141$ (19) Å

$V = 2742.7$ (5) Å³

$Z = 4$

$F(000) = 1048$

$D_x = 1.184$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1213 reflections

$\theta = 2.5$ – 21.3°

$\mu = 0.17$ mm⁻¹

$T = 180$ K

Block, colourless

$0.15 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2010)

$T_{\min} = 0.975$, $T_{\max} = 0.986$

7718 measured reflections

2695 independent reflections

1759 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -10 \rightarrow 13$

$k = -15 \rightarrow 10$

$l = -18 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.150$

$S = 1.04$

2695 reflections

159 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

$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.6803P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.31$ e Å⁻³

$\Delta\rho_{\min} = -0.42$ 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 of the H atoms were placed in geometrically calculated positions, with C—H = 0.95 (aromatic), 1.00 (CH, aliphatic) and 0.98 Å (CH₃), and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C}(\text{methyl}))$, or $1.2 U_{\text{eq}}(\text{other C})$. In addition, the methyl groups were refined with AFIX 137, which allowed the rotation of the methyl groups whilst keeping the C—H distances and X—C—H angles fixed.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.78014 (16)	0.33094 (13)	0.41998 (9)	0.0274 (4)
C11	0.7500	0.2500	0.18392 (4)	0.0497 (3)
O1	0.85386 (16)	0.24115 (18)	0.22649 (9)	0.0646 (6)
O2	0.75960 (19)	0.34257 (19)	0.14182 (10)	0.0745 (7)
C1	0.7500	0.2500	0.38038 (16)	0.0275 (7)
H1A	0.7500	0.2500	0.3319	0.033*
C2	0.7687 (2)	0.30046 (17)	0.48715 (11)	0.0336 (5)
H2A	0.7845	0.3430	0.5261	0.040*
C3	0.8224 (2)	0.43217 (16)	0.39426 (11)	0.0303 (5)
C4	0.7371 (2)	0.51047 (17)	0.38081 (12)	0.0347 (5)
C5	0.7810 (2)	0.60378 (19)	0.35238 (14)	0.0470 (7)
H5A	0.7261	0.6589	0.3411	0.056*
C6	0.9023 (2)	0.61800 (19)	0.34024 (15)	0.0506 (7)
H6A	0.9300	0.6825	0.3209	0.061*
C7	0.9836 (2)	0.53943 (19)	0.35594 (14)	0.0467 (7)
H7A	1.0671	0.5509	0.3477	0.056*
C8	0.9462 (2)	0.44387 (17)	0.38346 (12)	0.0361 (6)
C9	0.6034 (2)	0.49721 (19)	0.39413 (13)	0.0399 (6)
H9A	0.5925	0.4311	0.4215	0.048*
C10	0.5331 (3)	0.4840 (3)	0.32793 (16)	0.0674 (9)
H10A	0.5674	0.4253	0.3016	0.101*
H10B	0.5382	0.5494	0.3012	0.101*
H10C	0.4483	0.4687	0.3384	0.101*
C11	0.5522 (3)	0.5888 (2)	0.43552 (15)	0.0548 (7)
H11A	0.5988	0.5969	0.4777	0.082*
H11B	0.4676	0.5743	0.4467	0.082*
H11C	0.5573	0.6542	0.4088	0.082*
C12	1.0364 (2)	0.35671 (19)	0.39863 (14)	0.0440 (6)
H12A	0.9918	0.2978	0.4216	0.053*
C13	1.0910 (3)	0.3128 (3)	0.33389 (16)	0.0695 (10)
H13A	1.0264	0.2959	0.3015	0.104*
H13B	1.1367	0.2484	0.3445	0.104*
H13C	1.1451	0.3656	0.3137	0.104*
C14	1.1353 (3)	0.3938 (3)	0.44702 (17)	0.0696 (9)
H14A	1.1877	0.3339	0.4586	0.104*
H14B	1.0986	0.4221	0.4887	0.104*
H14C	1.1832	0.4493	0.4249	0.104*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0325 (9)	0.0239 (9)	0.0257 (9)	-0.0005 (7)	0.0004 (8)	-0.0008 (8)
C11	0.0373 (5)	0.0842 (7)	0.0277 (5)	0.0176 (5)	0.000	0.000
O1	0.0438 (11)	0.1088 (17)	0.0412 (11)	0.0205 (11)	-0.0120 (9)	0.0006 (11)
O2	0.0759 (15)	0.1031 (17)	0.0445 (11)	0.0105 (13)	0.0023 (11)	0.0287 (12)
C1	0.0312 (15)	0.0269 (16)	0.0244 (15)	-0.0015 (13)	0.000	0.000
C2	0.0446 (13)	0.0339 (11)	0.0224 (11)	0.0038 (10)	-0.0015 (10)	-0.0053 (10)
C3	0.0377 (12)	0.0236 (11)	0.0295 (12)	-0.0040 (9)	0.0038 (10)	-0.0027 (10)
C4	0.0406 (13)	0.0277 (11)	0.0358 (13)	0.0009 (10)	0.0062 (11)	0.0003 (10)
C5	0.0529 (15)	0.0279 (12)	0.0602 (18)	0.0054 (11)	0.0120 (13)	0.0086 (13)
C6	0.0573 (17)	0.0284 (13)	0.0660 (19)	-0.0074 (12)	0.0207 (14)	0.0056 (13)
C7	0.0431 (14)	0.0384 (14)	0.0585 (18)	-0.0084 (11)	0.0150 (13)	-0.0054 (13)
C8	0.0367 (13)	0.0317 (12)	0.0400 (14)	-0.0008 (10)	0.0050 (10)	-0.0076 (11)
C9	0.0369 (13)	0.0338 (13)	0.0488 (16)	0.0047 (10)	0.0041 (11)	0.0082 (12)
C10	0.0490 (16)	0.081 (2)	0.072 (2)	0.0045 (16)	-0.0060 (15)	-0.0132 (19)
C11	0.0513 (16)	0.0511 (17)	0.0620 (18)	0.0074 (13)	0.0158 (14)	0.0025 (15)
C12	0.0354 (13)	0.0371 (13)	0.0596 (17)	0.0017 (10)	0.0020 (12)	-0.0050 (13)
C13	0.0500 (17)	0.082 (2)	0.076 (2)	0.0255 (16)	-0.0133 (15)	-0.0375 (19)
C14	0.068 (2)	0.069 (2)	0.071 (2)	0.0156 (17)	-0.0245 (18)	-0.0213 (18)

Geometric parameters (Å, °)

N1—C1	1.326 (2)	C7—H7A	0.9500
N1—C2	1.378 (3)	C8—C12	1.516 (3)
N1—C3	1.452 (3)	C9—C11	1.523 (3)
C11—O1	1.4255 (17)	C9—C10	1.523 (4)
C11—O1 ⁱ	1.4255 (17)	C9—H9A	1.0000
C11—O2	1.435 (2)	C10—H10A	0.9800
C11—O2 ⁱ	1.435 (2)	C10—H10B	0.9800
C1—N1 ⁱ	1.327 (2)	C10—H10C	0.9800
C1—H1A	0.9500	C11—H11A	0.9800
C2—C2 ⁱ	1.340 (4)	C11—H11B	0.9800
C2—H2A	0.9500	C11—H11C	0.9800
C3—C4	1.393 (3)	C12—C13	1.512 (4)
C3—C8	1.395 (3)	C12—C14	1.523 (4)
C4—C5	1.391 (3)	C12—H12A	1.0000
C4—C9	1.512 (3)	C13—H13A	0.9800
C5—C6	1.375 (3)	C13—H13B	0.9800
C5—H5A	0.9500	C13—H13C	0.9800
C6—C7	1.375 (4)	C14—H14A	0.9800
C6—H6A	0.9500	C14—H14B	0.9800
C7—C8	1.385 (3)	C14—H14C	0.9800
C1—N1—C2	108.75 (18)	C11—C9—C10	110.3 (2)
C1—N1—C3	123.79 (18)	C4—C9—H9A	107.7
C2—N1—C3	127.41 (17)	C11—C9—H9A	107.7

O1—C11—O1 ⁱ	108.30 (16)	C10—C9—H9A	107.7
O1—C11—O2	109.94 (12)	C9—C10—H10A	109.5
O1 ⁱ —C11—O2	109.44 (12)	C9—C10—H10B	109.5
O1—C11—O2 ⁱ	109.44 (12)	H10A—C10—H10B	109.5
O1 ⁱ —C11—O2 ⁱ	109.94 (12)	C9—C10—H10C	109.5
O2—C11—O2 ⁱ	109.75 (19)	H10A—C10—H10C	109.5
N1—C1—N1 ⁱ	108.3 (3)	H10B—C10—H10C	109.5
N1—C1—H1A	125.8	C9—C11—H11A	109.5
N1 ⁱ —C1—H1A	125.8	C9—C11—H11B	109.5
C2 ⁱ —C2—N1	107.09 (11)	H11A—C11—H11B	109.5
C2 ⁱ —C2—H2A	126.5	C9—C11—H11C	109.5
N1—C2—H2A	126.5	H11A—C11—H11C	109.5
C4—C3—C8	124.2 (2)	H11B—C11—H11C	109.5
C4—C3—N1	118.17 (19)	C13—C12—C8	111.4 (2)
C8—C3—N1	117.58 (19)	C13—C12—C14	110.4 (2)
C5—C4—C3	116.1 (2)	C8—C12—C14	111.9 (2)
C5—C4—C9	120.4 (2)	C13—C12—H12A	107.6
C3—C4—C9	123.5 (2)	C8—C12—H12A	107.6
C6—C5—C4	121.4 (2)	C14—C12—H12A	107.6
C6—C5—H5A	119.3	C12—C13—H13A	109.5
C4—C5—H5A	119.3	C12—C13—H13B	109.5
C7—C6—C5	120.4 (2)	H13A—C13—H13B	109.5
C7—C6—H6A	119.8	C12—C13—H13C	109.5
C5—C6—H6A	119.8	H13A—C13—H13C	109.5
C6—C7—C8	121.4 (2)	H13B—C13—H13C	109.5
C6—C7—H7A	119.3	C12—C14—H14A	109.5
C8—C7—H7A	119.3	C12—C14—H14B	109.5
C7—C8—C3	116.4 (2)	H14A—C14—H14B	109.5
C7—C8—C12	120.8 (2)	C12—C14—H14C	109.5
C3—C8—C12	122.7 (2)	H14A—C14—H14C	109.5
C4—C9—C11	111.9 (2)	H14B—C14—H14C	109.5
C4—C9—C10	111.4 (2)		
C2—N1—C1—N1 ⁱ	-0.03 (11)	C5—C6—C7—C8	0.8 (4)
C3—N1—C1—N1 ⁱ	177.7 (2)	C6—C7—C8—C3	-0.1 (4)
C1—N1—C2—C2 ⁱ	0.1 (3)	C6—C7—C8—C12	178.2 (3)
C3—N1—C2—C2 ⁱ	-177.6 (2)	C4—C3—C8—C7	-1.7 (4)
C1—N1—C3—C4	90.2 (2)	N1—C3—C8—C7	177.1 (2)
C2—N1—C3—C4	-92.5 (3)	C4—C3—C8—C12	-179.9 (2)
C1—N1—C3—C8	-88.6 (2)	N1—C3—C8—C12	-1.1 (3)
C2—N1—C3—C8	88.7 (3)	C5—C4—C9—C11	-52.5 (3)
C8—C3—C4—C5	2.5 (3)	C3—C4—C9—C11	128.8 (2)
N1—C3—C4—C5	-176.2 (2)	C5—C4—C9—C10	71.5 (3)
C8—C3—C4—C9	-178.8 (2)	C3—C4—C9—C10	-107.1 (3)
N1—C3—C4—C9	2.5 (3)	C7—C8—C12—C13	-66.9 (3)
C3—C4—C5—C6	-1.7 (4)	C3—C8—C12—C13	111.3 (3)

C9—C4—C5—C6	179.5 (3)	C7—C8—C12—C14	57.3 (3)
C4—C5—C6—C7	0.1 (4)	C3—C8—C12—C14	-124.6 (3)

Symmetry code: (i) $-x+3/2, -y+1/2, z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C1—H1A...O1	0.95	2.37	3.232 (3)	151
C1—H1A...O1 ⁱ	0.95	2.37	3.232 (3)	151
C2—H2A...O2 ⁱⁱ	0.95	2.32	3.096 (3)	138

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