Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetraphenyl piperazine-1,4-diyldiphosphonate

Mehrdad Pourayoubi* and Poorya Zargaran

Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, 91779, Iran
Correspondence e-mail: mehrdad_pourayoubi@yahoo.com

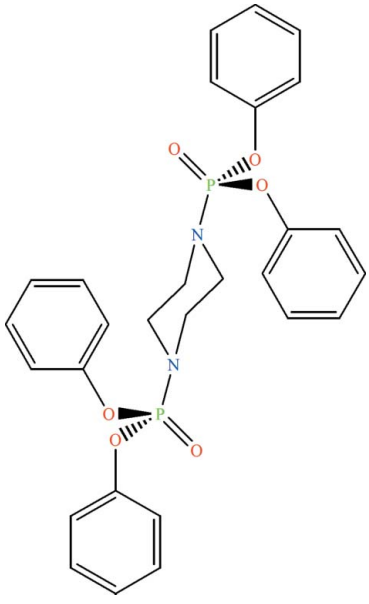
Received 10 November 2010; accepted 17 November 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.089; data-to-parameter ratio = 19.8.

The molecule of the title compound, $C_{28}H_{28}N_2O_6P_2$, is organized around an inversion center located at the centre of the piperazine ring. Both piperazine N atoms are substituted by $P(O)(OC_6H_5)_2$ phosphoester groups. The P atoms display a slightly distorted tetrahedral environment; the N atoms show some deviation from planarity. The O atoms of the P═O groups are involved in intermolecular C—H···O hydrogen bonds, building $R_2^2(22)$ rings, in extended chains parallel to the a axis. C—H···π interactions involving the phenyl rings further stabilize the packing.

Related literature

For the physical properties of bisphosphoramidates, see: Nguyen & Kim (2008). For related structures, see: Chen *et al.* (2007); Balakrishna *et al.* (2003, 2006); Rodriguez i Zubiri *et al.* (2002). For hydrogen-bond motifs, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{28}H_{28}N_2O_6P_2$
M_r = 550.46
Monoclinic, $P2_1/n$
a = 6.3117 (4) Å
b = 8.9530 (5) Å
c = 22.8630 (13) Å
β = 96.756 (1)°
V = 1282.99 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 100 K
0.55 × 0.40 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.890, T_{max} = 0.958
14864 measured reflections
3405 independent reflections
3071 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.089
S = 1.03
3405 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

*Cg*1 and *Cg*2 are the centroids of the C3–C8 and C11–C14 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···O1^{i}	0.95	2.49	3.4327 (15)	172
C11—H11A···Cg1^{ii}	0.95	2.74	3.3324 (12)	121
C7—H7A···Cg2^{iii}	0.95	2.59	3.4099 (13)	145

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Support of this investigation by Ferdowsi University of Mashhad is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2623).

References

Balakrishna, M. S., George, P. P. & Mague, J. T. (2003). *J. Chem. Res.* pp. 576–577.
Balakrishna, M. S., George, P. P. & Mague, J. T. (2006). *Phosphorus Sulfur Silicon Relat. Elem.* **181**, 141–146.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Chen, X., Xiao, W. & Jiao, P. (2007). *Acta Cryst.* E**63**, o4271.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Nguyen, C. & Kim, J. (2008). *Polym. Degrad. Stabil.* **93**, 1037–1043.
Rodriguez i Zubiri, M., Slawin, A. M. Z., Wainwright, M. & Woollins, J. D. (2002). *Polyhedron*, **21**, 1729–1736.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2010). E**66**, o3273–o3274 [https://doi.org/10.1107/S1600536810047860]

Tetraphenyl piperazine-1,4-diyldiphosphonate

Mehrdad Pourayoubi and Poorya Zargaran

S1. Comment

The thermal behavior and flame retardancies of some bisphosphoramidates, with a P(O)*X*P(O) skeleton, such as the title compound have been investigated by Nguyen & Kim (2008). Here, we report the crystal structure of the title compound.

The molecule of the title compound is organized around inversion center located in the middle of the piperazine ring. Both the nitrogen atoms of the piperazine are substituted by the $P(O)(OC_6H_5)_2$ phosphoester moieties (Fig. 1). The phosphorus atom has a distorted tetrahedral configuration with the bond angles in the range of 99.04 (4)° [O(2)–P(1)–O(3)] to 115.93 (5)° [O(1)–P(1)–O(2)]. As observed in related compounds containing piperazine ring substituted by phosphorus (Chen *et al.*, 2007; Balakrishna *et al.*, 2003, 2006; Rodriguez i Zubiri *et al.*, 2002), the N atom shows some deviation from planarity, indeed it is 0.25 (1)Å above the C1, C2, P1 plane.

The oxygen atom of P═O group are involved in a C–H···O hydrogen bond building a $R_2^2(22)$ ring (Etter *et al.*, 1990; Bernstein *et al.*, 1995) (Table 1, Fig. 2). Furthermore, these rings are interconnected building infinite chains parallel to the *a* axis. C–H···π interactions involving the phenyl rings stabilize the packing (Table 1).

S2. Experimental

To a solution of $(C_6H_5O)_2P(O)Cl$ in chloroform, a solution of piperazine and triethylamine (2:1:2 mole ratio) in chloroform was added at 273 K. After 4 h stirring, the solvent was removed and product was washed with distilled water and recrystallized from chloroform/n-heptane at room temperature. IR (KBr, cm^{-1}): 3051.2, 2913.8, 2866.3, 1592.5, 1490.4, 1383.3, 1334.6, 1261.7, 1198.5, 1135.3, 1067.1, 1013.7, 969.8, 931.6, 776.8, 686.8. Raman (cm^{-1}): 3066.5, 2526.4, 1593.0, 1469.5, 1452.2, 1265.1, 1218.8, 1168.7, 1157.1, 1024.0, 1006.6, 939.2, 771.4, 705.8, 617.1, 414.6, 262.2. $^{31}P\{^1H\}$ NMR (202.45 MHz, DMSO-d6, 300.0 K, H_3PO_4 external): -1.45 p.p.m. (*s*). ^1H NMR (500.13 MHz, DMSO-d6, 300.0 K, TMS): 3.01 (*s*, 8H, CH_2), 7.15–7.27 (*m*, 12H, Ar—H), 7.38–7.40 p.p.m. (*m*, 8H, Ar—H). ^{13}C NMR (125.75 MHz, DMSO-d6, 300.0 K, TMS): 43.98 (*d*, $^{2(\&3)}J(P,C)$ = 3.5 Hz, 4 C), 119.94 (*d*, $^3J(P,C)$ = 4.7 Hz, 8 C, C_{ortho}), 125.11 (*s*), 129.90 (*s*), 150.07 p.p.m. (*d*, $^2J(P,C)$ = 6.4 Hz, 4 C, C_{ipso}).

S3. Refinement

H atoms were placed in calculated positions and included in the refinement in a riding-model approximation with C–H = 0.93–0.97 Å, and $U_{iso}(H) = 1.2Ueq(C)$.

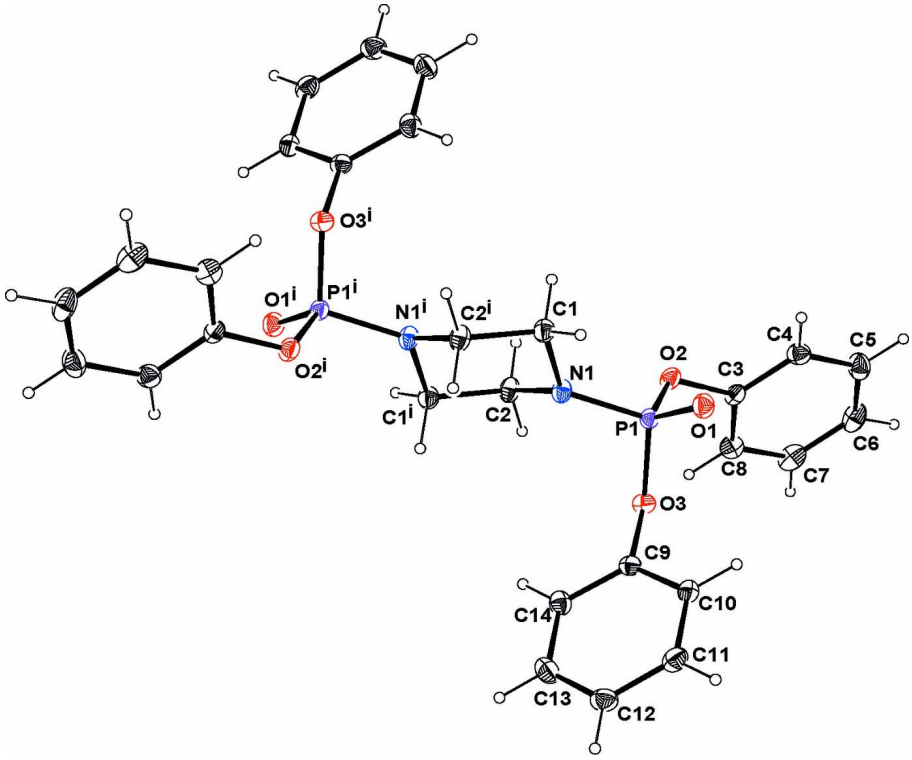


Figure 1

Molecular view with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

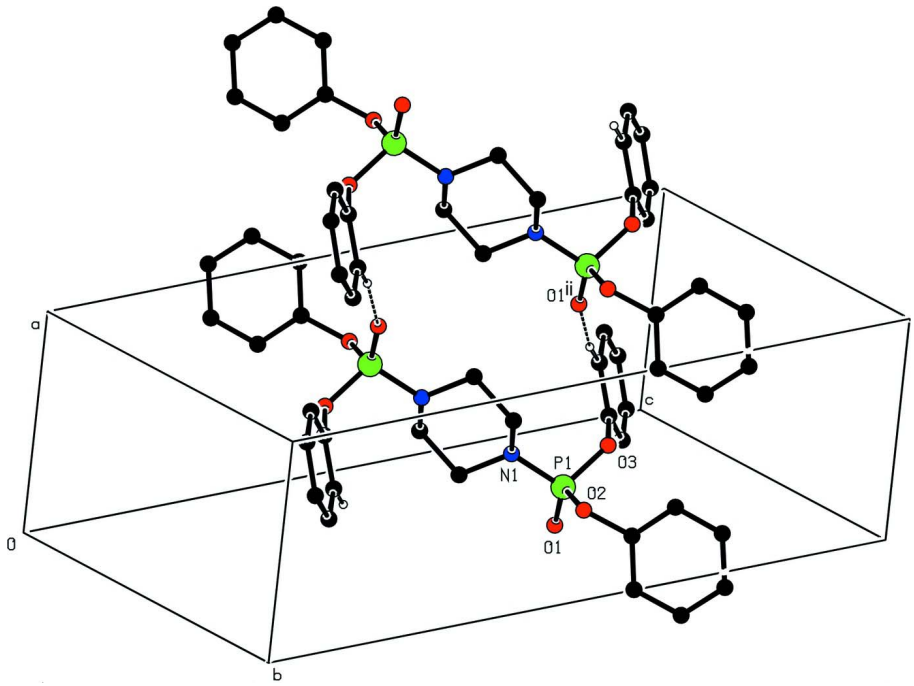


Figure 2

Partial packing view showing the formation of dimer through C–H···O interactions. H bonds are shown as dashed lines. [Symmetry codes: (ii) x+1, y, z]

Tetraphenyl piperazine-1,4-diyldiphosphonate

Crystal data

$C_{28}H_{28}N_2O_6P_2$
M_r = 550.46
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 6.3117 (4) Å
b = 8.9530 (5) Å
c = 22.8630 (13) Å
β = 96.756 (1)°
V = 1282.99 (13) Å^3
Z = 2
F(000) = 576
D_x = 1.425 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2258 reflections
θ = 3–29°
μ = 0.22 mm^{-1}
T = 100 K
Plate, colourless
0.55 × 0.40 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.890, T_{max} = 0.958
14864 measured reflections
3405 independent reflections
3071 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 29.0°, θ_{min} = 1.8°
h = −8→8
k = −12→12
l = −30→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.03$
3405 reflections
172 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
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.567P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.29408 (4)	0.70141 (3)	0.584588 (12)	0.01226 (9)
O1	0.08499 (13)	0.65211 (10)	0.59873 (4)	0.01722 (18)
O2	0.30060 (14)	0.86102 (9)	0.55434 (4)	0.01595 (17)
O3	0.46851 (13)	0.72855 (9)	0.63989 (3)	0.01431 (17)
N1	0.40456 (15)	0.59125 (11)	0.54033 (4)	0.01435 (19)
C1	0.27230 (18)	0.49056 (13)	0.50046 (5)	0.0154 (2)
H1A	0.2168	0.5452	0.4642	0.019*
H1B	0.1490	0.4557	0.5198	0.019*
C2	0.59794 (18)	0.64262 (13)	0.51554 (5)	0.0159 (2)
H2A	0.6852	0.7054	0.5448	0.019*
H2B	0.5564	0.7039	0.4800	0.019*
C3	0.24646 (19)	0.99346 (12)	0.58193 (5)	0.0141 (2)
C4	0.03688 (19)	1.04226 (13)	0.57405 (5)	0.0174 (2)
H4A	−0.0717	0.9831	0.5531	0.021*
C5	−0.0111 (2)	1.18012 (14)	0.59758 (6)	0.0213 (2)
H5A	−0.1538	1.2157	0.5925	0.026*
C6	0.1478 (2)	1.26566 (14)	0.62831 (6)	0.0224 (3)
H6A	0.1142	1.3603	0.6436	0.027*
C7	0.3561 (2)	1.21302 (14)	0.63680 (6)	0.0221 (3)
H7A	0.4642	1.2709	0.6586	0.026*
C8	0.40715 (19)	1.07579 (14)	0.61346 (5)	0.0181 (2)
H8A	0.5494	1.0393	0.6191	0.022*
C9	0.51165 (18)	0.61794 (12)	0.68335 (5)	0.0136 (2)
C10	0.36396 (19)	0.58904 (13)	0.72215 (5)	0.0160 (2)
H10A	0.2295	0.6380	0.7181	0.019*

C11	0.4174 (2)	0.48638 (14)	0.76736 (5)	0.0190 (2)
H11A	0.3176	0.4638	0.7941	0.023*
C12	0.6154 (2)	0.41695 (14)	0.77356 (5)	0.0203 (2)
H12A	0.6518	0.3486	0.8049	0.024*
C13	0.7607 (2)	0.44750 (14)	0.73384 (6)	0.0204 (2)
H13A	0.8957	0.3993	0.7380	0.025*
C14	0.70950 (18)	0.54823 (13)	0.68798 (5)	0.0168 (2)
H14A	0.8075	0.5688	0.6605	0.020*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01325 (14)	0.01125 (14)	0.01239 (14)	0.00080 (10)	0.00199 (10)	−0.00088 (9)
O1	0.0147 (4)	0.0193 (4)	0.0182 (4)	0.0001 (3)	0.0038 (3)	−0.0014 (3)
O2	0.0226 (4)	0.0125 (4)	0.0133 (4)	0.0031 (3)	0.0041 (3)	−0.0003 (3)
O3	0.0169 (4)	0.0121 (4)	0.0136 (4)	−0.0012 (3)	−0.0001 (3)	0.0006 (3)
N1	0.0137 (4)	0.0127 (4)	0.0170 (5)	−0.0015 (3)	0.0031 (3)	−0.0035 (3)
C1	0.0135 (5)	0.0158 (5)	0.0170 (5)	−0.0008 (4)	0.0017 (4)	−0.0036 (4)
C2	0.0165 (5)	0.0133 (5)	0.0187 (5)	−0.0013 (4)	0.0054 (4)	−0.0029 (4)
C3	0.0207 (5)	0.0103 (5)	0.0116 (5)	0.0014 (4)	0.0039 (4)	0.0008 (4)
C4	0.0195 (5)	0.0157 (5)	0.0166 (5)	0.0005 (4)	0.0005 (4)	0.0003 (4)
C5	0.0238 (6)	0.0170 (6)	0.0240 (6)	0.0060 (5)	0.0065 (5)	0.0036 (5)
C6	0.0344 (7)	0.0118 (5)	0.0229 (6)	0.0006 (5)	0.0112 (5)	−0.0009 (4)
C7	0.0290 (6)	0.0170 (6)	0.0206 (6)	−0.0073 (5)	0.0049 (5)	−0.0026 (4)
C8	0.0191 (5)	0.0177 (6)	0.0179 (5)	−0.0020 (4)	0.0033 (4)	0.0012 (4)
C9	0.0165 (5)	0.0107 (5)	0.0130 (5)	−0.0004 (4)	−0.0004 (4)	−0.0008 (4)
C10	0.0174 (5)	0.0157 (5)	0.0150 (5)	0.0024 (4)	0.0027 (4)	−0.0012 (4)
C11	0.0249 (6)	0.0178 (5)	0.0148 (5)	0.0005 (5)	0.0045 (4)	0.0005 (4)
C12	0.0268 (6)	0.0166 (6)	0.0167 (5)	0.0024 (5)	−0.0011 (5)	0.0019 (4)
C13	0.0181 (5)	0.0180 (6)	0.0245 (6)	0.0037 (4)	−0.0006 (5)	−0.0001 (5)
C14	0.0154 (5)	0.0157 (5)	0.0195 (5)	0.0000 (4)	0.0021 (4)	−0.0016 (4)

Geometric parameters (Å, º)

P1—O1	1.4633 (9)	C5—C6	1.3855 (19)
P1—O2	1.5901 (9)	C5—H5A	0.9500
P1—O3	1.5944 (8)	C6—C7	1.3885 (19)
P1—N1	1.6275 (10)	C6—H6A	0.9500
O2—C3	1.4040 (13)	C7—C8	1.3923 (17)
O3—C9	1.4066 (13)	C7—H7A	0.9500
N1—C1	1.4702 (14)	C8—H8A	0.9500
N1—C2	1.4783 (14)	C9—C10	1.3847 (16)
C1—C2^{i}	1.5155 (16)	C9—C14	1.3889 (16)
C1—H1A	0.9900	C10—C11	1.3946 (16)
C1—H1B	0.9900	C10—H10A	0.9500
C2—C1^{i}	1.5155 (16)	C11—C12	1.3880 (18)
C2—H2A	0.9900	C11—H11A	0.9500
C2—H2B	0.9900	C12—C13	1.3913 (18)

C3—C4	1.3846 (16)	C12—H12A	0.9500
C3—C8	1.3855 (17)	C13—C14	1.3919 (17)
C4—C5	1.3937 (17)	C13—H13A	0.9500
C4—H4A	0.9500	C14—H14A	0.9500

O1—P1—O2	115.93 (5)	C6—C5—H5A	119.7
O1—P1—O3	115.30 (5)	C4—C5—H5A	119.7
O2—P1—O3	99.04 (4)	C5—C6—C7	120.00 (11)
O1—P1—N1	114.71 (5)	C5—C6—H6A	120.0
O2—P1—N1	103.85 (5)	C7—C6—H6A	120.0
O3—P1—N1	106.20 (5)	C6—C7—C8	120.27 (12)
C3—O2—P1	122.92 (7)	C6—C7—H7A	119.9
C9—O3—P1	120.74 (7)	C8—C7—H7A	119.9
C1—N1—C2	112.78 (9)	C3—C8—C7	118.71 (11)
C1—N1—P1	120.23 (8)	C3—C8—H8A	120.6
C2—N1—P1	118.91 (7)	C7—C8—H8A	120.6
N1—C1—C2^{i}	110.39 (9)	C10—C9—C14	122.29 (11)
N1—C1—H1A	109.6	C10—C9—O3	119.68 (10)
C2^{i}—C1—H1A	109.6	C14—C9—O3	117.89 (10)
N1—C1—H1B	109.6	C9—C10—C11	118.39 (11)
C2^{i}—C1—H1B	109.6	C9—C10—H10A	120.8
H1A—C1—H1B	108.1	C11—C10—H10A	120.8
N1—C2—C1^{i}	109.99 (9)	C12—C11—C10	120.49 (11)
N1—C2—H2A	109.7	C12—C11—H11A	119.8
C1^{i}—C2—H2A	109.7	C10—C11—H11A	119.8
N1—C2—H2B	109.7	C11—C12—C13	119.99 (11)
C1^{i}—C2—H2B	109.7	C11—C12—H12A	120.0
H2A—C2—H2B	108.2	C13—C12—H12A	120.0
C4—C3—C8	121.97 (11)	C12—C13—C14	120.44 (11)
C4—C3—O2	119.17 (10)	C12—C13—H13A	119.8
C8—C3—O2	118.76 (10)	C14—C13—H13A	119.8
C3—C4—C5	118.47 (11)	C9—C14—C13	118.39 (11)
C3—C4—H4A	120.8	C9—C14—H14A	120.8
C5—C4—H4A	120.8	C13—C14—H14A	120.8
C6—C5—C4	120.55 (12)		

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

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the C3–C8 and C11–C14 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*A*···O1^{ii}	0.95	2.49	3.4327 (15)	172
C11—H11*A*···*Cg*1^{iii}	0.95	2.74	3.3324 (12)	121
C7—H7*A*···*Cg*2^{iv}	0.95	2.59	3.4099 (13)	145

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