research communications

Hydrogen bonding, π–π stacking and van der Waals forces-dominated layered regions in the crystal structure of 4-aminopyridinium hydrogen (9-phosphonononyl)phosphonate

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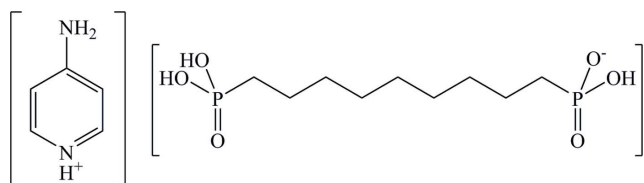
The asymmetric unit of the title molecular salt, $[C_5H_7N_2^+][(HO)_2OP(CH_2)_9PO_2(OH)^-]$, consists of one 4-aminopyridinium cation and one hydrogen (9-phosphonononyl)phosphonate anion, both in general positions. As expected, the 4-aminopyridinium moieties are protonated exclusively at their endocyclic nitrogen atom due to a mesomeric stabilization by the imine form which would not be given in the corresponding double-protonated dicationic species. In the crystal, the phosphonyl ($-PO_3H_2$) and hydrogen phosphonate ($-PO_3H$) groups of the anions form two-dimensional O—H···O hydrogen-bonded networks in the ab plane built from 24-membered hydrogen-bonded ring motifs with the graph-set descriptor $R_6^6(24)$. These networks are pairwise linked by the anions' alkylene chains. The 4-aminopyridinium cations are stacked in parallel displaced face-to-face arrangements and connect neighboring anionic substructures via medium–strong charge-supported N—H···O hydrogen bonds along the c axis. The resulting three-dimensional hydrogen-bonded network shows clearly separated hydrophilic and hydrophobic structural domains.

1. Chemical context

Salts of organophosphonic acids with organic cations, *e.g.* with protonated primary (Mahmoudkhani & Langer, 2002b), secondary (Wheatley *et al.*, 2001) and tertiary amines (Kan & Ma, 2011) are of growing interest in supramolecular chemistry and crystal engineering. Besides their interesting topologies and structural diversity, they seem to be feasible model compounds for metal phosphonates as they exhibit similar structural characteristics but are less difficult to crystallize. Mostly, these organic solids establish extended hydrogen-bonded networks which are characterized by a rich diversity of strong charge-supported hydrogen bonds (Aakeröy & Seddon, 1993) and can either be one-, two- or three-dimensional. This contribution forms part of our research on the principles of the arrangement of alkane-α,ω-diphosphonic acids (van Megen *et al.*, 2015) and their organic aminium salts (van Megen *et al.*, 2016). Moreover, aminopyridines and the related protonated cations are of crucial interest in the field of biochemistry (Muñoz-Caro & Niño, 2002; Bolliger *et al.*, 2011) and are also used as counter-cations to stabilize complex salts (Reiss & Leske, 2014a,b), in crystal engineering (Sertucha *et al.*, 1998; Surbella III *et al.*, 2016) as well as in polymer chemistry (Deng *et al.*, 2015).
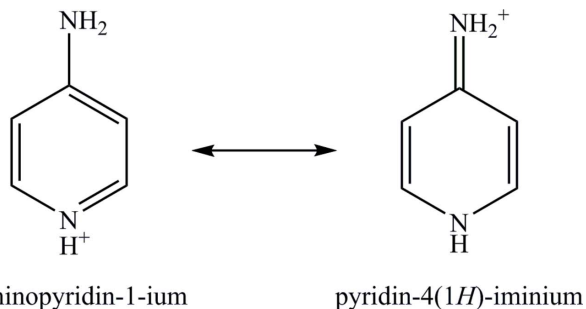
$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O3—H3$\cdots$O6^i	0.78 (3)	1.85 (3)	2.6171 (18)	166 (3)
O5—H5$\cdots$O1^{ii}	0.88 (3)	1.64 (3)	2.5059 (18)	168 (3)
O4—H4$\cdots$O2^{iii}	0.91 (3)	1.59 (3)	2.4977 (17)	178 (3)
N1—H1$\cdots$O6	0.96 (2)	1.74 (3)	2.696 (2)	173 (2)
N2—H22$\cdots$O2^{iv}	0.90 (3)	1.92 (3)	2.806 (2)	170 (2)
N2—H21$\cdots$O1^v	0.88 (3)	2.14 (3)	2.965 (2)	156 (3)

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

2. Structural commentary

The asymmetric unit of the title compound, [C$_5$H$_7$N$_2$$^+$][(HO)$_2$OP(CH$_2$)$_9PO_2(OH)^-$], consists of one 4-aminopyridinium cation and one hydrogen (9-phosphono-nonyl)phosphonate anion, both in general positions (Fig. 1). Generally, the first protonation of the 4-aminopyridine can take place at the exo- as well as at the endocyclic nitrogen atom. In the literature, all monoprotonated 4-aminopyridines characterized to date are protonated at the endocyclic nitrogen atom. Geometric parameters derived from the single-crystal diffraction experiment for the title compound show a short exocyclic N—C bond length [1.324 (2) Å] and slightly longer C—C and C—N bond lengths of the six-membered ring [1.350 (3)–1.425 (2) Å]. The bonding properties of this cation are best described by a pair of mesomeric structures: the enamine and the imine form (Scheme 2), which have been discussed in detail before (Koleva et al., 2008).

For the designation of the title compound, the systematic name of the amino form is used throughout this article. The bond lengths and angles of the anion are unexceptional and lie within the expected ranges. The alkylene chain of the anion shows nearly antiperiplanar conformations. In detail, the P—OH distances of the phosphonate moieties have values between 1.5535 (13) and 1.5786 (14) Å, longer than the P=O distances [1.5045 (13)–1.5149 (12) Å].

3. Supramolecular features

Within the crystal of the title compound, the phosphonyl and hydrogen phosphonate groups of the anions form two-dimensional O—H$\cdots$O hydrogen-bonded networks which propagate in the ab plane. These networks contain 24-membered rings classified as a third level graph set $R_6^6(24)$ (Etter et al., 1990; Fig. 2; Table 1). 24-Membered hydrogen-bonded rings have been well known for decades (e.g. Mootz & Poll, 1984). In particular, the $R_6^6(24)$ motif is very common (e.g. Gomathi & Muthiah, 2011; Maspoch et al., 2007). Along the c-axis direction, these networks are pairwise linked by the anions' alkylene chains to form a three-dimensional anionic substructure. The 4-aminopyridinium cations show π–π stacking interactions. The rings are oriented in parallel displaced face-to-face arrangements (Grimme, 2008; Fig. 3). The geometry of these π–π interactions is reflected by distances of 3.25 and 3.32 Å between neighbouring pyridinium
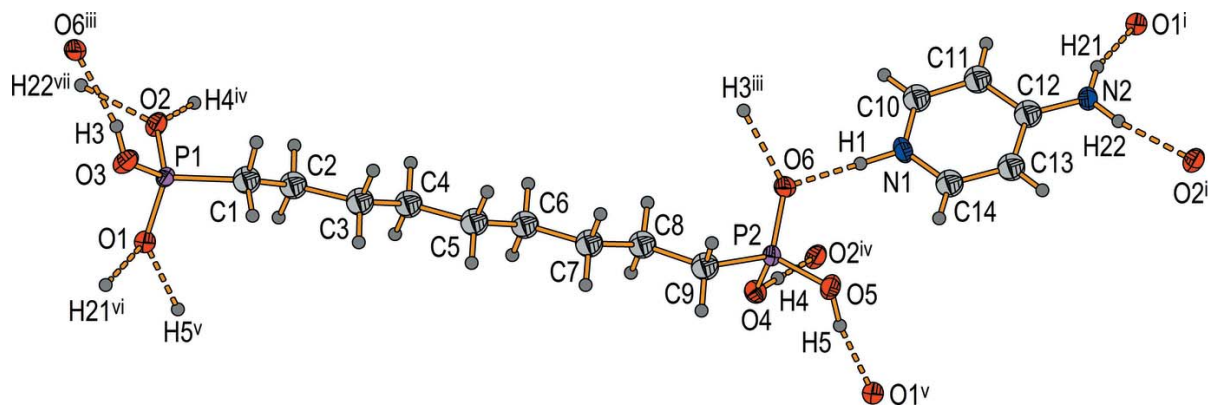
Figure 1
The asymmetric unit of the title compound plus symmetry-related hydrogen-bonded atoms [displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are drawn as spheres with arbitrary radii; symmetry codes: (i) $1+x, -1+y, 1+z$; (ii) $x, -1+y, 1+z$; (iii) $1-x, 2-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $-x, 1-y, 1-z$; (vi) $-1+x, 1+y, -1+z$; (vii) $x, 1+y, -1+z$].
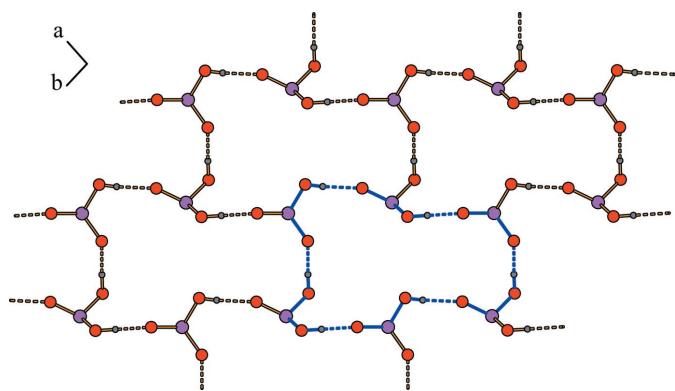
Figure 2
Two-dimensional hydrogen-bonded networks composed of phosphonyl and hydrogen phosphonate groups. The graph set $R_6^6(24)$ is indicated by blue bonds.

rings and centroid offsets of 2.37 and 2.42 Å. These findings are comparable to those found for other compounds containing pyridyl moieties (Janiak, 2000). Anions and cations are connected by medium–strong, charge-supported N—H⋯O hydrogen bonds (Steiner, 2002; Table 2) along the *c* axis. For these connections, each nitrogen-bound hydrogen atom forms one unbifurcated hydrogen bond (Fig. 1). The resulting three-dimensional hydrogen-bonded network clearly shows separated hydrophilic and hydrophobic regions (Fig. 3).

4. Related structures

For related phosphonate and bis(phosphonate) salts, see: Ferguson *et al.* (1998); Fu *et al.* (2004); Fuller & Heimer (1995); Glidewell *et al.* (2000); Kan & Ma (2011); Mahmoud-

khani & Langer (2002a,b,c); van Megen *et al.* (2016); Plabst *et al.* (2009); Wheatley *et al.* (2001). For related 4-amino-pyridinium salts, see: Sertucha *et al.* (1998); Reiss & Leske (2014a,b); Surbella III *et al.* (2016).

5. Synthesis and crystallization

Equimolar quantities (0.5 mmol) of 4-aminopyridine (47.1 mg) and nonane-1,9-diphosphonic acid (144.1 mg) were dissolved in methanol, separately. The solutions were mixed and stored in an open petri dish. Within several days, colorless platelet-shaped crystals of the title compound were obtained by slow evaporation of the solvent. 4-Aminopyridine was purchased from commercial sources and nonane-1,9-di-phosphonic acid was synthesized according to the literature (Schwarzenbach & Zurc, 1950; Moedritzer & Irani, 1961; Griffith *et al.*, 1998). Elemental analysis: $C_{14}H_{28}N_2O_6P_2$ (382.3): calculated C 44.0, H 7.4, N 7.3; found C 43.6, H 7.9, N 7.1. M. p.: 157 °C. The IR and Raman spectra of the title compound are shown in Fig. 4.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms bound to either nitrogen or oxygen atoms were identified in difference syntheses and refined without any geometric constraints or restraints with individual $U_{iso}(H)$ values. Carbon-bound hydrogen atoms were included using a riding model (AFIX23 option of the *SHELX* program for the methylene groups and AFIX43 option for the methine groups).
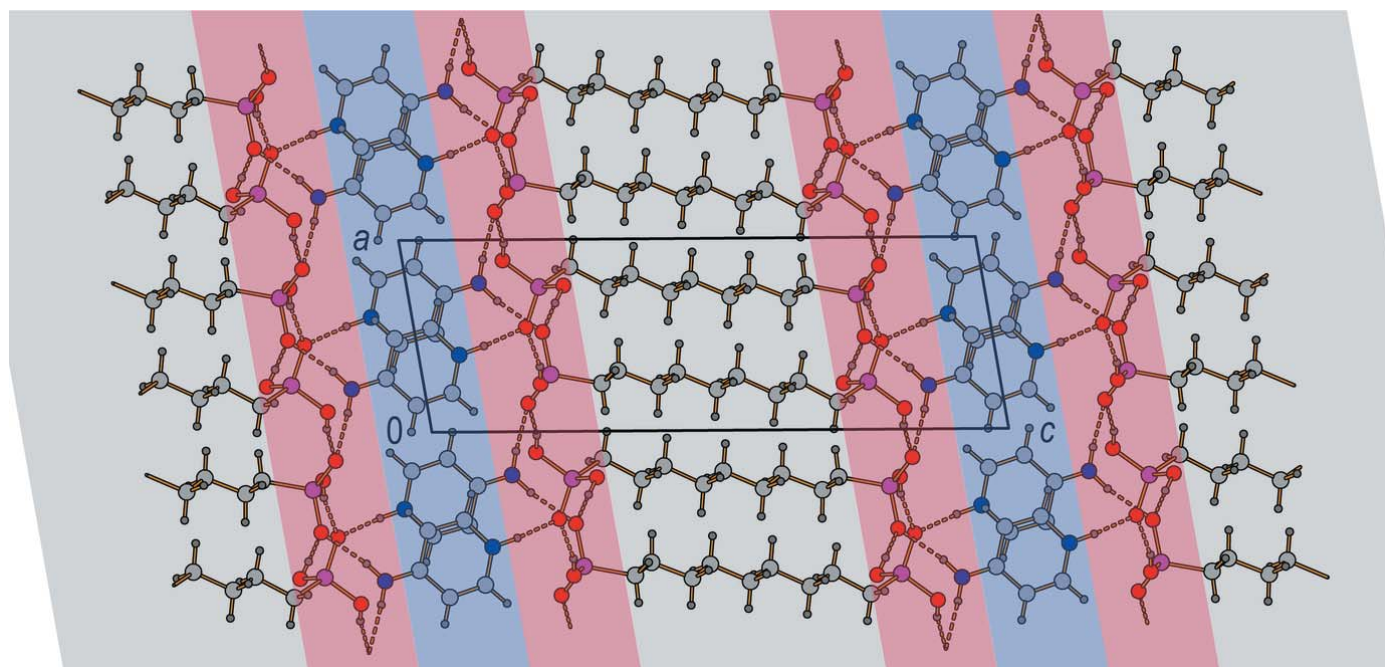

Figure 3
View along [010] of the title structure, showing the hydrogen bonding (red), π–π stacking (blue), and van der Waals forces (grey) dominated layered regions within the three-dimensional network.
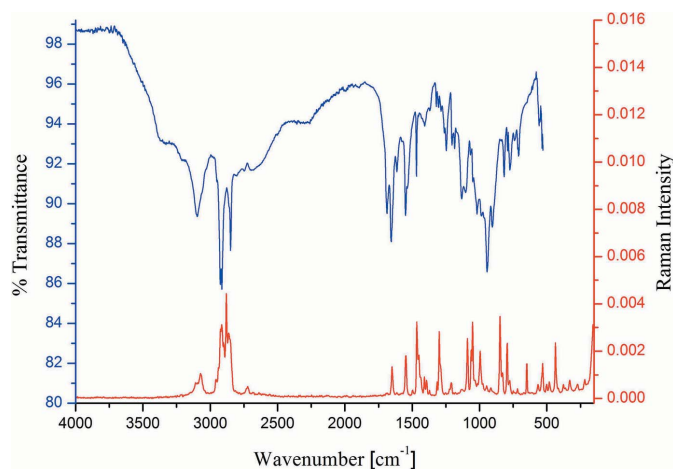
Figure 4
The IR (blue) and Raman (red) spectra of the title compound.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_7N_2^+\cdot C_9H_{21}O_6P_2^-$
M_r	382.32
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	123
a, b, c (Å)	6.7275 (4), 6.8963 (4), 20.0643 (10)
α, β, γ (°)	97.956 (4), 98.767 (4), 94.309 (5)
V (Å³)	906.73 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.27
Crystal size (mm)	0.33 × 0.07 × 0.03
Data collection	
Diffractometer	Stoe IPDS
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	8855, 4131, 3674
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.079, 1.02
No. of reflections	4131
No. of parameters	241
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.50, −0.36

Computer programs: *X-AREA* (Stoe & Cie, 2002), *SHELXT* (Sheldrick, 2015a), *SHELXL-2014/7* (Sheldrick, 2015b) and *DIAMOND* (Brandenburg, 2015).

supporting information

Hydrogen bonding, π–π stacking and van der Waals forces-dominated layered regions in the crystal structure of 4-aminopyridinium hydrogen (9-phosphono-nonyl)phosphonate

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL-2014/7* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2015).

4-Aminopyridinium hydrogen (9-phosphonononyl)phosphonate

Crystal data

$C_5H_7N_2^+ \cdot C_9H_{21}O_6P_2^-$	$Z = 2$
$M_r = 382.32$	$F(000) = 408$
Triclinic, $P\bar{1}$	$D_x = 1.400$ Mg m^{-3}
$a = 6.7275$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 6.8963$ (4) Å	Cell parameters from 6853 reflections
$c = 20.0643$ (10) Å	$\theta = 3.0$–$35.3°$
$\alpha = 97.956$ (4)°	$\mu = 0.27$ mm^{-1}
$\beta = 98.767$ (4)°	$T = 123$ K
$\gamma = 94.309$ (5)°	Platelet, colourless
$V = 906.73$ (9) Å^3	$0.33 \times 0.07 \times 0.03$ mm

Data collection

Stoe IPDS diffractometer	3674 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.029$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
8855 measured reflections	$h = -8 \rightarrow 8$
4131 independent reflections	$k = -8 \rightarrow 8$
	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 1.110P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4131 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
241 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
0 restraints	

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.29655 (6)	1.15924 (6)	0.22320 (2)	0.01579 (10)
O1	0.14667 (19)	1.0094 (2)	0.17549 (6)	0.0230 (3)
N1	0.5995 (3)	0.2836 (2)	0.92948 (8)	0.0257 (3)
H1	0.553 (4)	0.306 (4)	0.8838 (13)	0.036 (6)*
C1	0.2470 (3)	1.1616 (3)	0.30883 (8)	0.0179 (3)
H1A	0.3161	1.2802	0.3371	0.021*
H1B	0.1032	1.1663	0.3086	0.021*
P2	0.24757 (6)	0.29013 (6)	0.77082 (2)	0.01589 (10)
O2	0.51802 (18)	1.13618 (18)	0.22159 (6)	0.0199 (3)
N2	0.7740 (3)	0.1858 (3)	1.12583 (8)	0.0252 (3)
H21	0.901 (4)	0.169 (4)	1.1403 (14)	0.049 (8)*
H22	0.681 (4)	0.172 (4)	1.1527 (12)	0.035 (6)*
C2	0.3143 (3)	0.9827 (3)	0.34082 (8)	0.0191 (3)
H2A	0.2686	0.8640	0.3084	0.023*
H2B	0.4608	0.9929	0.3504	0.023*
O3	0.2486 (2)	1.3660 (2)	0.20293 (7)	0.0239 (3)
C3	0.2306 (3)	0.9668 (3)	0.40681 (8)	0.0191 (3)
H3A	0.2699	1.0891	0.4379	0.023*
H3B	0.0842	0.9503	0.3964	0.023*
H3	0.343 (5)	1.442 (5)	0.2068 (17)	0.070 (11)*
O4	0.24107 (19)	0.08343 (18)	0.72796 (6)	0.0188 (2)
C4	0.3028 (3)	0.7975 (3)	0.44244 (8)	0.0195 (3)
H4A	0.4490	0.8157	0.4542	0.023*
H4B	0.2664	0.6752	0.4112	0.023*
H4	0.330 (5)	0.006 (5)	0.7471 (16)	0.066 (9)*
O5	0.1083 (2)	0.27587 (19)	0.82576 (6)	0.0216 (3)
C5	0.2125 (3)	0.7822 (3)	0.50710 (9)	0.0195 (3)
H5A	0.2483	0.9055	0.5379	0.023*
H5B	0.0664	0.7648	0.4950	0.023*
H5	0.017 (5)	0.174 (5)	0.8191 (16)	0.064 (9)*
O6	0.45679 (19)	0.37295 (19)	0.80557 (6)	0.0220 (3)
C6	0.2806 (3)	0.6151 (3)	0.54491 (8)	0.0188 (3)
H6A	0.4264	0.6325	0.5579	0.023*
H6B	0.2450	0.4910	0.5146	0.023*
C7	0.1838 (3)	0.6074 (3)	0.60867 (8)	0.0179 (3)
H7A	0.0383	0.5858	0.5951	0.022*
H7B	0.2146	0.7341	0.6377	0.022*
C8	0.2526 (3)	0.4476 (3)	0.65035 (8)	0.0180 (3)
H8A	0.3972	0.4716	0.6661	0.022*

H8B	0.2261	0.3205	0.6214	0.022*
C9	0.1432 (3)	0.4431 (3)	0.71211 (8)	0.0175 (3)
H9A	0.0022	0.3966	0.6959	0.021*
H9B	0.1488	0.5762	0.7360	0.021*
C10	0.7973 (3)	0.2769 (3)	0.95325 (10)	0.0283 (4)
H10	0.8919	0.2928	0.9247	0.034*
C11	0.8604 (3)	0.2470 (3)	1.01867 (9)	0.0272 (4)
H11	0.9972	0.2420	1.0341	0.033*
C12	0.7189 (3)	0.2236 (3)	1.06310 (9)	0.0199 (3)
C13	0.5127 (3)	0.2384 (3)	1.03659 (9)	0.0214 (4)
H13	0.4144	0.2288	1.0642	0.026*
C14	0.4601 (3)	0.2665 (3)	0.97075 (10)	0.0242 (4)
H14	0.3249	0.2741	0.9537	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01293 (19)	0.0198 (2)	0.0158 (2)	0.00022 (16)	0.00233 (15)	0.00733 (16)
O1	0.0224 (6)	0.0286 (7)	0.0167 (6)	−0.0056 (5)	0.0023 (5)	0.0042 (5)
N1	0.0360 (9)	0.0236 (8)	0.0159 (7)	0.0009 (7)	−0.0008 (6)	0.0036 (6)
C1	0.0179 (8)	0.0202 (8)	0.0161 (8)	−0.0003 (6)	0.0038 (6)	0.0048 (6)
P2	0.0175 (2)	0.0167 (2)	0.01360 (19)	−0.00040 (16)	0.00111 (15)	0.00535 (15)
O2	0.0163 (6)	0.0239 (6)	0.0228 (6)	0.0042 (5)	0.0057 (5)	0.0111 (5)
N2	0.0187 (8)	0.0392 (10)	0.0194 (7)	0.0036 (7)	0.0035 (6)	0.0097 (7)
C2	0.0185 (8)	0.0237 (9)	0.0162 (8)	0.0015 (7)	0.0030 (6)	0.0072 (6)
O3	0.0158 (6)	0.0267 (7)	0.0328 (7)	0.0026 (5)	0.0047 (5)	0.0162 (6)
C3	0.0195 (8)	0.0229 (9)	0.0163 (8)	0.0003 (7)	0.0047 (6)	0.0066 (6)
O4	0.0190 (6)	0.0194 (6)	0.0178 (6)	0.0029 (5)	0.0014 (5)	0.0036 (5)
C4	0.0201 (8)	0.0239 (9)	0.0161 (8)	0.0009 (7)	0.0038 (6)	0.0079 (6)
O5	0.0280 (7)	0.0206 (6)	0.0170 (6)	−0.0021 (5)	0.0070 (5)	0.0041 (5)
C5	0.0209 (8)	0.0217 (8)	0.0169 (8)	0.0002 (7)	0.0039 (6)	0.0063 (6)
O6	0.0216 (6)	0.0228 (6)	0.0202 (6)	−0.0045 (5)	−0.0032 (5)	0.0091 (5)
C6	0.0193 (8)	0.0221 (8)	0.0161 (8)	0.0008 (7)	0.0041 (6)	0.0056 (6)
C7	0.0195 (8)	0.0199 (8)	0.0153 (7)	0.0014 (6)	0.0029 (6)	0.0060 (6)
C8	0.0191 (8)	0.0200 (8)	0.0157 (7)	0.0019 (6)	0.0027 (6)	0.0058 (6)
C9	0.0178 (8)	0.0198 (8)	0.0157 (7)	0.0020 (6)	0.0027 (6)	0.0054 (6)
C10	0.0305 (10)	0.0338 (11)	0.0206 (9)	0.0008 (8)	0.0077 (7)	0.0020 (8)
C11	0.0206 (9)	0.0390 (11)	0.0215 (9)	0.0018 (8)	0.0038 (7)	0.0032 (8)
C12	0.0212 (8)	0.0192 (8)	0.0184 (8)	0.0008 (7)	0.0025 (6)	0.0014 (6)
C13	0.0206 (8)	0.0207 (8)	0.0232 (9)	0.0010 (7)	0.0039 (7)	0.0047 (7)
C14	0.0249 (9)	0.0206 (9)	0.0254 (9)	0.0022 (7)	−0.0020 (7)	0.0046 (7)

Geometric parameters (Å, º)

P1—O1	1.5088 (13)	C4—H4A	0.9700
P1—O2	1.5149 (12)	C4—H4B	0.9700
P1—O3	1.5786 (14)	O5—H5	0.88 (3)
P1—C1	1.7974 (17)	C5—C6	1.526 (2)

N1—C10	1.350 (3)	C5—H5A	0.9700
N1—C14	1.352 (3)	C5—H5B	0.9700
N1—H1	0.96 (2)	C6—C7	1.527 (2)
C1—C2	1.534 (2)	C6—H6A	0.9700
C1—H1A	0.9700	C6—H6B	0.9700
C1—H1B	0.9700	C7—C8	1.530 (2)
P2—O6	1.5045 (13)	C7—H7A	0.9700
P2—O4	1.5535 (13)	C7—H7B	0.9700
P2—O5	1.5601 (13)	C8—C9	1.537 (2)
P2—C9	1.7880 (17)	C8—H8A	0.9700
N2—C12	1.324 (2)	C8—H8B	0.9700
N2—H21	0.88 (3)	C9—H9A	0.9700
N2—H22	0.90 (3)	C9—H9B	0.9700
C2—C3	1.530 (2)	C10—C11	1.365 (3)
C2—H2A	0.9700	C10—H10	0.9300
C2—H2B	0.9700	C11—C12	1.415 (3)
O3—H3	0.78 (3)	C11—H11	0.9300
C3—C4	1.523 (2)	C12—C13	1.425 (2)
C3—H3A	0.9700	C13—C14	1.359 (3)
C3—H3B	0.9700	C13—H13	0.9300
O4—H4	0.91 (3)	C14—H14	0.9300
C4—C5	1.527 (2)		
O1—P1—O2	116.41 (8)	C6—C5—C4	114.77 (15)
O1—P1—O3	105.96 (8)	C6—C5—H5A	108.6
O2—P1—O3	108.76 (7)	C4—C5—H5A	108.6
O1—P1—C1	109.09 (8)	C6—C5—H5B	108.6
O2—P1—C1	109.62 (7)	C4—C5—H5B	108.6
O3—P1—C1	106.51 (8)	H5A—C5—H5B	107.6
C10—N1—C14	120.49 (16)	C5—C6—C7	112.06 (14)
C10—N1—H1	121.8 (15)	C5—C6—H6A	109.2
C14—N1—H1	117.6 (15)	C7—C6—H6A	109.2
C2—C1—P1	113.66 (12)	C5—C6—H6B	109.2
C2—C1—H1A	108.8	C7—C6—H6B	109.2
P1—C1—H1A	108.8	H6A—C6—H6B	107.9
C2—C1—H1B	108.8	C6—C7—C8	114.51 (14)
P1—C1—H1B	108.8	C6—C7—H7A	108.6
H1A—C1—H1B	107.7	C8—C7—H7A	108.6
O6—P2—O4	113.40 (7)	C6—C7—H7B	108.6
O6—P2—O5	109.15 (7)	C8—C7—H7B	108.6
O4—P2—O5	108.70 (7)	H7A—C7—H7B	107.6
O6—P2—C9	111.12 (8)	C7—C8—C9	111.67 (14)
O4—P2—C9	105.43 (8)	C7—C8—H8A	109.3
O5—P2—C9	108.89 (8)	C9—C8—H8A	109.3
C12—N2—H21	119.9 (18)	C7—C8—H8B	109.3
C12—N2—H22	119.6 (16)	C9—C8—H8B	109.3
H21—N2—H22	120 (2)	H8A—C8—H8B	107.9
C3—C2—C1	112.06 (14)	C8—C9—P2	113.70 (12)

C3—C2—H2A	109.2	C8—C9—H9A	108.8
C1—C2—H2A	109.2	P2—C9—H9A	108.8
C3—C2—H2B	109.2	C8—C9—H9B	108.8
C1—C2—H2B	109.2	P2—C9—H9B	108.8
H2A—C2—H2B	107.9	H9A—C9—H9B	107.7
P1—O3—H3	115 (2)	N1—C10—C11	120.95 (18)
C4—C3—C2	113.89 (15)	N1—C10—H10	119.5
C4—C3—H3A	108.8	C11—C10—H10	119.5
C2—C3—H3A	108.8	C10—C11—C12	120.38 (18)
C4—C3—H3B	108.8	C10—C11—H11	119.8
C2—C3—H3B	108.8	C12—C11—H11	119.8
H3A—C3—H3B	107.7	N2—C12—C11	121.92 (17)
P2—O4—H4	113 (2)	N2—C12—C13	121.32 (17)
C3—C4—C5	112.68 (15)	C11—C12—C13	116.75 (16)
C3—C4—H4A	109.1	C14—C13—C12	119.77 (17)
C5—C4—H4A	109.1	C14—C13—H13	120.1
C3—C4—H4B	109.1	C12—C13—H13	120.1
C5—C4—H4B	109.1	N1—C14—C13	121.60 (18)
H4A—C4—H4B	107.8	N1—C14—H14	119.2
P2—O5—H5	117 (2)	C13—C14—H14	119.2
O1—P1—C1—C2	74.30 (14)	O6—P2—C9—C8	66.99 (14)
O2—P1—C1—C2	−54.24 (14)	O4—P2—C9—C8	−56.25 (14)
O3—P1—C1—C2	−171.74 (12)	O5—P2—C9—C8	−172.75 (12)
P1—C1—C2—C3	−167.86 (12)	C14—N1—C10—C11	1.9 (3)
C1—C2—C3—C4	−176.88 (14)	N1—C10—C11—C12	−0.4 (3)
C2—C3—C4—C5	−178.52 (15)	C10—C11—C12—N2	176.98 (19)
C3—C4—C5—C6	−179.83 (15)	C10—C11—C12—C13	−1.7 (3)
C4—C5—C6—C7	−179.62 (14)	N2—C12—C13—C14	−176.38 (18)
C5—C6—C7—C8	−177.72 (15)	C11—C12—C13—C14	2.3 (3)
C6—C7—C8—C9	−177.78 (14)	C10—N1—C14—C13	−1.3 (3)
C7—C8—C9—P2	−169.70 (12)	C12—C13—C14—N1	−0.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O6[i]	0.78 (3)	1.85 (3)	2.6171 (18)	166 (3)
O5—H5···O1[ii]	0.88 (3)	1.64 (3)	2.5059 (18)	168 (3)
O4—H4···O2[iii]	0.91 (3)	1.59 (3)	2.4977 (17)	178 (3)
N1—H1···O6	0.96 (2)	1.74 (3)	2.696 (2)	173 (2)
N2—H22···O2[iv]	0.90 (3)	1.92 (3)	2.806 (2)	170 (2)
N2—H21···O1[v]	0.88 (3)	2.14 (3)	2.965 (2)	156 (3)

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