

# Crystal structure of diethyl [(4-nitrophenylamino)(2-hydroxyphenyl)methyl]-phosphonate methanol monosolvate

QingMing Wang,<sup>a</sup> Feng Su,<sup>b</sup> TingTing Yang,<sup>a</sup> LiPing Lu<sup>b</sup> and MiaoLi Zhu<sup>b\*</sup>

<sup>a</sup>School of Pharmacy, Yancheng Teachers' University, Yancheng, Jiangsu 224051, People's Republic of China, and <sup>b</sup>Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China. \*Correspondence e-mail: miaoli@sxu.edu.cn

Received 9 July 2014; accepted 17 August 2014

Edited by S. Parkin, University of Kentucky, USA

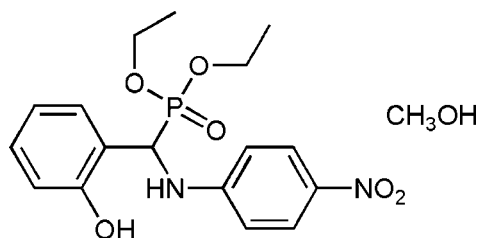
In the title compound,  $C_{17}H_{21}N_2O_6P \cdot CH_3OH$ , the planes of the 4-nitroaniline and 2-hydroxyphenyl groups form a dihedral angle of  $84.04(8)^\circ$ . The P atom exhibits tetrahedral geometry involving two *O*-ethyl groups, a  $C\alpha$  atom and a double-bonded O atom. In the crystal,  $O-H \cdots O$ ,  $N-H \cdots O$  and  $C-H \cdots O$  hydrogen bonds link the  $\alpha$ -aminophosphonic acid and methanol molecules into chains that propagate parallel to the *a* axis.

**Keywords:** crystal structure;  $\alpha$ -aminophosphonic acids; phosphonate salts; hydrogen bonding.

**CCDC reference:** 1019639

## 1. Related literature

For background to the synthesis and properties of  $\alpha$ -aminophosphonic acids, see: Allen *et al.* (1978); Arizpe *et al.* (2011); Cherkasov & Galkin (1998); Sieńczyk & Oleksyszyn (2009). For structures of related compounds, see: Li *et al.* (2008); Wang *et al.* (2012).



## 2. Experimental

### 2.1. Crystal data

$C_{17}H_{21}N_2O_6P \cdot CH_4O$   
 $M_r = 412.37$   
 Triclinic,  $P\bar{1}$   
 $a = 9.401(6) \text{ \AA}$   
 $b = 10.061(6) \text{ \AA}$   
 $c = 11.963(7) \text{ \AA}$   
 $\alpha = 101.328(10)^\circ$   
 $\beta = 94.183(10)^\circ$   
 $\gamma = 104.549(9)^\circ$   
 $V = 1065.0(12) \text{ \AA}^3$   
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.17 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 $0.40 \times 0.34 \times 0.30 \text{ mm}$

### 2.2. Data collection

Bruker SMART 1K CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)  
 $T_{\min} = 0.935$ ,  $T_{\max} = 0.951$   
 14569 measured reflections  
 5230 independent reflections  
 2934 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.138$   
 $S = 1.01$   
 5230 reflections  
 262 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D-H \cdots A$           | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--------------------------|----------|--------------|--------------|----------------|
| $O7-H7A \cdots O4^i$     | 0.82     | 2.00         | 2.819 (3)    | 172            |
| $O1-H1 \cdots O7$        | 0.82     | 1.95         | 2.757 (3)    | 170            |
| $C10-H10 \cdots O5^{ii}$ | 0.93     | 2.53         | 3.308 (4)    | 141            |
| $N1-H1A \cdots O4^{iii}$ | 0.82 (2) | 2.14 (2)     | 2.959 (3)    | 171 (2)        |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *S SAINT* (Bruker, 2000); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

## Acknowledgements

This work was supported financially by the National Natural Science Foundation for Young Scientists of China (grant No. 21301150), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (grant No. 13KJB150037), the Foundation of Jiangsu Provincial Key Laboratory of Solonchak (grant No. JKLBS2012022), the Doctor and Professor Foundation of Yancheng Teachers' University (grant No. 12YSYJB0117) and the Practice Innovation Training Program Projects for the Jiangsu College Students (grant Nos. 201310324034Y and 201410324038Y).

Supporting information for this paper is available from the IUCr electronic archives (Reference: PK2529).

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## supporting information

*Acta Cryst.* (2014). E70, o1053–o1054 [doi:10.1107/S1600536814018649]

## Crystal structure of diethyl [(4-nitrophenylamino)(2-hydroxyphenyl)methyl]-phosphonate methanol monosolvate

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### S1. Introduction

As mimics of natural amino acids,  $\alpha$ -aminophosphonic acids and related derivatives are currently attracting a great deal of interest in medicinal chemistry due to their important biological effects (Arizpe, *et al.*, 2011). They have been reported to possess a wide range of biological functions. These include antibacterial activities (Allen *et al.*, 1978), action as inhibitors of enzymes such as rennin, HIV proteases, serine proteases and so on (Sieńczyk, *et al.*, 2009).

### S2. Experimental

#### S2.1. Synthesis and crystallization

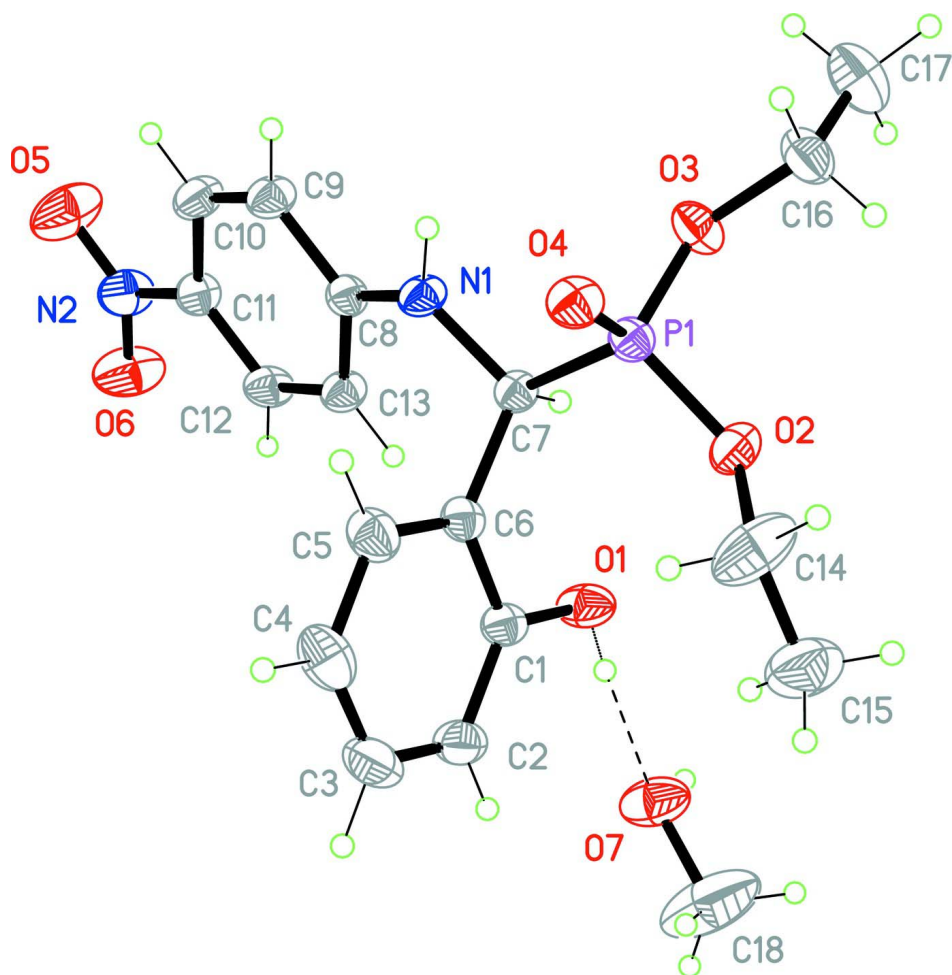
The synthesis of *o*-cresol  $\alpha$ -aminophosphonate N-derivatives with rigid structures was achieved through the Pudovik reaction reaction (Cherkasov *et al.*, 1998). We obtained the title compound following our earlier report (Wang *et al.*, 2012). The synthesis involved two steps: a) the Schiff bases were first prepared in a condensation of 4-nitroaniline and salicylaldehyde in methanol solvent by refluxing equimolar amounts of reagents; b) reaction of Schiff base with a diethyl phosphonate in methanol solvent under reflux. The title compound was obtained from the filtrate after three days.

#### S2.2. Refinement

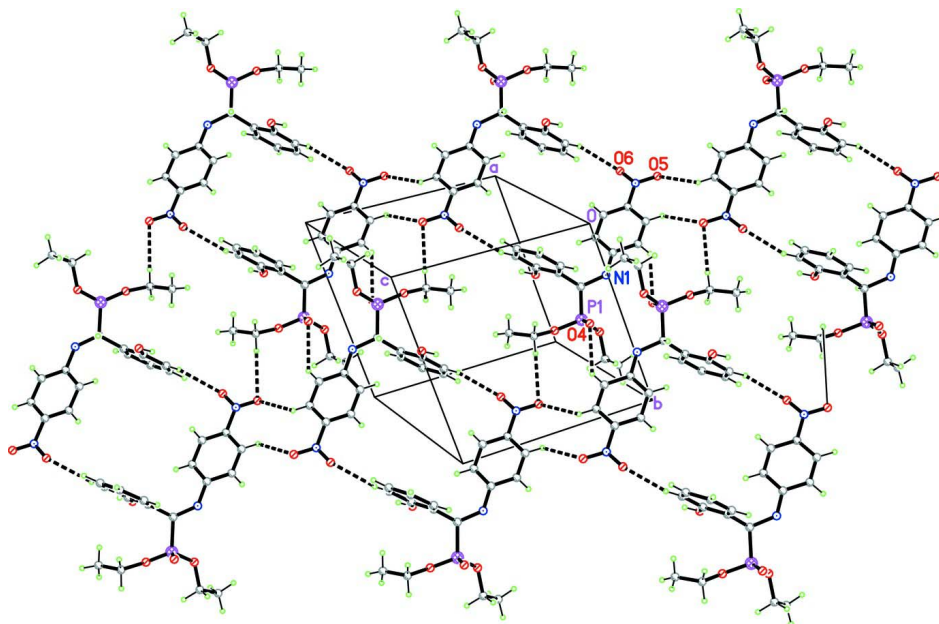
The amine H atom was located in a difference Fourier map and refined freely. All other H atoms were placed in geometrically idealized positions and refined as riding, with C–H = 0.93–0.98 Å, O–H = 0.82 Å, and the Uiso(H) = 1.2Ueq (C) for benzene ring, C7, C14, C16 and Uiso(H) = 1.5Ueq (O, C) for O–H groups and C15, C17, C18.

### S3. Results and discussion

The crystal structure of the title compound is triclinic, with space group  $P\bar{1}$ . As seen from Fig. 1, the P atom has tetrahedral geometry involving two O-ethyl groups (O2, O3), one  $C\alpha$  atom (C7), and a double bond O atom (O4), which is the same as our earlier reports (Li *et al.*, 2008; Wang *et al.*, 2012). The C–P and P=O bond lengths are comparable to those in similar structures (Li *et al.* 2008; Wang *et al.*, 2012). Several hydrogen bonding interactions [O7—H7A $\cdots$ O4<sup>i</sup> ( $i = x+1, y, z$ ), O1—H1 $\cdots$ O7, C10—H10 $\cdots$ O5<sup>ii</sup> ( $ii = -x, -y, -z-1$ ), N1—H1A $\cdots$ O4<sup>iii</sup> ( $iii = -x, -y+1, -z$ )] exist within in the crystal structure. The dihedral angle formed by the planes of the 4-nitroaniline and 2-hydroxyphenyl groups is 84.08 (8)°.

**Figure 1**

A view of the structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

**Figure 2**

Crystal packing of the title compound, drawn so as to highlight the hydrogen-bonding interactions between molecules.

### Diethyl [(4-nitrophenylamino)(2-hydroxyphenyl)methyl]phosphonate methanol monosolvate

#### Crystal data

$C_{17}H_{21}N_2O_6P \cdot CH_4O$

$M_r = 412.37$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 9.401\ (6)\ \text{\AA}$

$b = 10.061\ (6)\ \text{\AA}$

$c = 11.963\ (7)\ \text{\AA}$

$\alpha = 101.328\ (10)^\circ$

$\beta = 94.183\ (10)^\circ$

$\gamma = 104.549\ (9)^\circ$

$V = 1065.0\ (12)\ \text{\AA}^3$

$Z = 2$

$F(000) = 436$

$D_x = 1.286\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1930 reflections

$\theta = 1.8\text{--}28.3^\circ$

$\mu = 0.17\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, yellow

$0.4 \times 0.34 \times 0.3\ \text{mm}$

#### Data collection

Bruker SMART 1K CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2000)

$T_{\min} = 0.935$ ,  $T_{\max} = 0.951$

14569 measured reflections

5230 independent reflections

2934 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\max} = 28.2^\circ$ ,  $\theta_{\min} = 1.8^\circ$

$h = -12 \rightarrow 12$

$k = -13 \rightarrow 13$

$l = -15 \rightarrow 15$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.138$

$S = 1.01$

5230 reflections

262 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

$$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.0659P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

|      | <i>x</i>   | <i>y</i>   | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|------------|---------------|----------------------------------|
| C1   | 0.4255 (3) | 0.3224 (2) | 0.17400 (19)  | 0.0408 (5)                       |
| C2   | 0.4364 (3) | 0.2362 (3) | 0.2493 (2)    | 0.0538 (7)                       |
| H2   | 0.5292     | 0.2347     | 0.2808        | 0.065*                           |
| C3   | 0.3111 (4) | 0.1532 (3) | 0.2778 (2)    | 0.0655 (8)                       |
| H3   | 0.3192     | 0.0962     | 0.3291        | 0.079*                           |
| C4   | 0.1720 (4) | 0.1538 (3) | 0.2302 (3)    | 0.0692 (8)                       |
| H4   | 0.0868     | 0.0979     | 0.2497        | 0.083*                           |
| C5   | 0.1618 (3) | 0.2385 (3) | 0.1535 (2)    | 0.0538 (7)                       |
| H5   | 0.0688     | 0.2379     | 0.1207        | 0.065*                           |
| C6   | 0.2871 (3) | 0.3241 (2) | 0.12431 (18)  | 0.0378 (5)                       |
| C7   | 0.2760 (2) | 0.4232 (2) | 0.04485 (17)  | 0.0348 (5)                       |
| H7   | 0.3749     | 0.4597     | 0.0239        | 0.042*                           |
| C8   | 0.2056 (2) | 0.2631 (2) | -0.14895 (19) | 0.0372 (5)                       |
| C9   | 0.1083 (3) | 0.2150 (2) | -0.2517 (2)   | 0.0467 (6)                       |
| H9   | 0.0257     | 0.2492     | -0.2595       | 0.056*                           |
| C10  | 0.1327 (3) | 0.1185 (3) | -0.3410 (2)   | 0.0526 (7)                       |
| H10  | 0.0681     | 0.0884     | -0.4092       | 0.063*                           |
| C11  | 0.2548 (3) | 0.0660 (2) | -0.3287 (2)   | 0.0449 (6)                       |
| C12  | 0.3527 (3) | 0.1124 (3) | -0.2294 (2)   | 0.0472 (6)                       |
| H12  | 0.4347     | 0.0772     | -0.2227       | 0.057*                           |
| C13  | 0.3303 (3) | 0.2105 (2) | -0.1397 (2)   | 0.0428 (6)                       |
| H13  | 0.3976     | 0.2422     | -0.0729       | 0.051*                           |
| C14  | 0.3182 (4) | 0.6256 (4) | 0.3468 (2)    | 0.0941 (12)                      |
| H14A | 0.2782     | 0.7004     | 0.3841        | 0.113*                           |
| H14B | 0.2476     | 0.5363     | 0.3455        | 0.113*                           |
| C15  | 0.4561 (4) | 0.6334 (4) | 0.4116 (3)    | 0.0989 (12)                      |
| H15A | 0.5020     | 0.5674     | 0.3700        | 0.148*                           |
| H15B | 0.4377     | 0.6111     | 0.4846        | 0.148*                           |
| H15C | 0.5206     | 0.7269     | 0.4237        | 0.148*                           |

|      |              |              |               |              |
|------|--------------|--------------|---------------|--------------|
| C16  | 0.2262 (3)   | 0.8152 (3)   | 0.0724 (2)    | 0.0600 (7)   |
| H16A | 0.2731       | 0.8615       | 0.1500        | 0.072*       |
| H16B | 0.1208       | 0.8069       | 0.0696        | 0.072*       |
| C17  | 0.2894 (4)   | 0.8987 (3)   | -0.0089 (3)   | 0.0853 (10)  |
| H17A | 0.3945       | 0.9110       | -0.0026       | 0.128*       |
| H17B | 0.2697       | 0.9891       | 0.0087        | 0.128*       |
| H17C | 0.2453       | 0.8505       | -0.0858       | 0.128*       |
| C18  | 0.8676 (5)   | 0.4263 (6)   | 0.3596 (3)    | 0.154 (2)    |
| H18A | 0.9379       | 0.3743       | 0.3716        | 0.232*       |
| H18B | 0.7854       | 0.3987       | 0.4010        | 0.232*       |
| H18C | 0.9143       | 0.5253       | 0.3868        | 0.232*       |
| N1   | 0.1748 (2)   | 0.3567 (2)   | -0.06050 (16) | 0.0415 (5)   |
| N2   | 0.2802 (3)   | -0.0373 (3)  | -0.4225 (2)   | 0.0650 (7)   |
| O1   | 0.54719 (18) | 0.4078 (2)   | 0.14493 (15)  | 0.0566 (5)   |
| H1   | 0.6220       | 0.4018       | 0.1811        | 0.085*       |
| O2   | 0.33759 (18) | 0.63846 (17) | 0.22920 (13)  | 0.0518 (4)   |
| O3   | 0.25022 (19) | 0.67641 (16) | 0.04156 (14)  | 0.0525 (5)   |
| O4   | 0.06458 (17) | 0.53339 (17) | 0.14848 (13)  | 0.0478 (4)   |
| O5   | 0.1927 (3)   | -0.0771 (3)  | -0.51111 (19) | 0.1029 (9)   |
| O6   | 0.3885 (3)   | -0.0818 (2)  | -0.41134 (17) | 0.0919 (8)   |
| O7   | 0.8177 (2)   | 0.3987 (3)   | 0.24407 (17)  | 0.0785 (6)   |
| H7A  | 0.8843       | 0.4359       | 0.2104        | 0.118*       |
| P1   | 0.21847 (7)  | 0.57045 (6)  | 0.12230 (5)   | 0.03809 (18) |
| H1A  | 0.107 (3)    | 0.391 (2)    | -0.077 (2)    | 0.045 (7)*   |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|-------------|--------------|--------------|
| C1  | 0.0458 (14) | 0.0433 (14) | 0.0362 (12) | 0.0202 (11) | 0.0041 (11)  | 0.0060 (11)  |
| C2  | 0.0633 (18) | 0.0542 (16) | 0.0482 (15) | 0.0253 (14) | -0.0009 (13) | 0.0122 (13)  |
| C3  | 0.092 (2)   | 0.0552 (18) | 0.0595 (18) | 0.0284 (17) | 0.0110 (17)  | 0.0260 (14)  |
| C4  | 0.073 (2)   | 0.0569 (18) | 0.081 (2)   | 0.0077 (16) | 0.0271 (17)  | 0.0307 (16)  |
| C5  | 0.0478 (16) | 0.0494 (16) | 0.0677 (18) | 0.0133 (12) | 0.0112 (13)  | 0.0202 (14)  |
| C6  | 0.0427 (13) | 0.0345 (12) | 0.0383 (12) | 0.0170 (10) | 0.0074 (10)  | 0.0043 (10)  |
| C7  | 0.0304 (12) | 0.0384 (12) | 0.0371 (12) | 0.0127 (10) | 0.0051 (10)  | 0.0069 (10)  |
| C8  | 0.0386 (13) | 0.0356 (12) | 0.0384 (12) | 0.0127 (10) | 0.0057 (10)  | 0.0070 (10)  |
| C9  | 0.0420 (14) | 0.0532 (15) | 0.0473 (14) | 0.0244 (12) | -0.0002 (11) | 0.0041 (12)  |
| C10 | 0.0521 (16) | 0.0589 (16) | 0.0433 (14) | 0.0201 (13) | -0.0072 (12) | 0.0010 (12)  |
| C11 | 0.0521 (15) | 0.0439 (14) | 0.0401 (13) | 0.0229 (12) | 0.0043 (11)  | 0.0008 (11)  |
| C12 | 0.0491 (15) | 0.0530 (15) | 0.0478 (15) | 0.0301 (12) | 0.0070 (12)  | 0.0093 (12)  |
| C13 | 0.0401 (13) | 0.0476 (14) | 0.0421 (13) | 0.0196 (11) | 0.0015 (11)  | 0.0047 (11)  |
| C14 | 0.077 (2)   | 0.154 (4)   | 0.0440 (17) | 0.040 (2)   | 0.0036 (17)  | -0.005 (2)   |
| C15 | 0.131 (3)   | 0.117 (3)   | 0.0546 (19) | 0.058 (3)   | -0.007 (2)   | 0.008 (2)    |
| C16 | 0.0649 (18) | 0.0428 (15) | 0.0774 (19) | 0.0221 (14) | 0.0101 (15)  | 0.0153 (14)  |
| C17 | 0.102 (3)   | 0.0560 (19) | 0.106 (3)   | 0.0203 (18) | 0.030 (2)    | 0.0333 (19)  |
| C18 | 0.090 (3)   | 0.273 (6)   | 0.081 (3)   | -0.008 (3)  | -0.006 (2)   | 0.074 (4)    |
| N1  | 0.0372 (11) | 0.0475 (12) | 0.0416 (11) | 0.0229 (10) | -0.0020 (9)  | 0.0017 (9)   |
| N2  | 0.0834 (18) | 0.0676 (16) | 0.0481 (14) | 0.0422 (14) | -0.0002 (13) | -0.0021 (12) |

|    |             |             |             |             |              |              |
|----|-------------|-------------|-------------|-------------|--------------|--------------|
| O1 | 0.0382 (10) | 0.0749 (13) | 0.0640 (12) | 0.0186 (9)  | 0.0022 (9)   | 0.0298 (10)  |
| O2 | 0.0484 (10) | 0.0560 (11) | 0.0440 (10) | 0.0116 (8)  | -0.0047 (8)  | 0.0020 (8)   |
| O3 | 0.0708 (12) | 0.0400 (9)  | 0.0556 (11) | 0.0256 (9)  | 0.0171 (9)   | 0.0143 (8)   |
| O4 | 0.0395 (9)  | 0.0560 (10) | 0.0531 (10) | 0.0234 (8)  | 0.0092 (8)   | 0.0094 (8)   |
| O5 | 0.1169 (19) | 0.120 (2)   | 0.0634 (14) | 0.0713 (16) | -0.0256 (14) | -0.0358 (13) |
| O6 | 0.1136 (18) | 0.1124 (18) | 0.0664 (14) | 0.0860 (16) | -0.0014 (13) | -0.0079 (12) |
| O7 | 0.0485 (12) | 0.1205 (19) | 0.0717 (14) | 0.0160 (12) | 0.0039 (10)  | 0.0441 (13)  |
| P1 | 0.0382 (3)  | 0.0382 (3)  | 0.0402 (3)  | 0.0168 (3)  | 0.0047 (3)   | 0.0059 (3)   |

*Geometric parameters (Å, °)*

|          |           |               |             |
|----------|-----------|---------------|-------------|
| C1—O1    | 1.360 (3) | C14—C15       | 1.438 (4)   |
| C1—C2    | 1.382 (3) | C14—O2        | 1.458 (3)   |
| C1—C6    | 1.396 (3) | C14—H14A      | 0.9700      |
| C2—C3    | 1.370 (4) | C14—H14B      | 0.9700      |
| C2—H2    | 0.9300    | C15—H15A      | 0.9600      |
| C3—C4    | 1.390 (4) | C15—H15B      | 0.9600      |
| C3—H3    | 0.9300    | C15—H15C      | 0.9600      |
| C4—C5    | 1.383 (4) | C16—O3        | 1.451 (3)   |
| C4—H4    | 0.9300    | C16—C17       | 1.469 (4)   |
| C5—C6    | 1.386 (3) | C16—H16A      | 0.9700      |
| C5—H5    | 0.9300    | C16—H16B      | 0.9700      |
| C6—C7    | 1.522 (3) | C17—H17A      | 0.9600      |
| C7—N1    | 1.454 (3) | C17—H17B      | 0.9600      |
| C7—P1    | 1.812 (2) | C17—H17C      | 0.9600      |
| C7—H7    | 0.9800    | C18—O7        | 1.377 (4)   |
| C8—N1    | 1.371 (3) | C18—H18A      | 0.9600      |
| C8—C9    | 1.401 (3) | C18—H18B      | 0.9600      |
| C8—C13   | 1.407 (3) | C18—H18C      | 0.9600      |
| C9—C10   | 1.371 (3) | N1—H1A        | 0.82 (2)    |
| C9—H9    | 0.9300    | N2—O6         | 1.219 (3)   |
| C10—C11  | 1.389 (3) | N2—O5         | 1.225 (3)   |
| C10—H10  | 0.9300    | O1—H1         | 0.8200      |
| C11—C12  | 1.372 (3) | O2—P1         | 1.5557 (18) |
| C11—N2   | 1.450 (3) | O3—P1         | 1.5638 (18) |
| C12—C13  | 1.376 (3) | O4—P1         | 1.4734 (18) |
| C12—H12  | 0.9300    | O7—H7A        | 0.8200      |
| C13—H13  | 0.9300    |               |             |
| O1—C1—C2 | 122.1 (2) | O2—C14—H14A   | 109.3       |
| O1—C1—C6 | 117.4 (2) | C15—C14—H14B  | 109.3       |
| C2—C1—C6 | 120.6 (2) | O2—C14—H14B   | 109.3       |
| C3—C2—C1 | 120.4 (3) | H14A—C14—H14B | 108.0       |
| C3—C2—H2 | 119.8     | C14—C15—H15A  | 109.5       |
| C1—C2—H2 | 119.8     | C14—C15—H15B  | 109.5       |
| C2—C3—C4 | 120.2 (3) | H15A—C15—H15B | 109.5       |
| C2—C3—H3 | 119.9     | C14—C15—H15C  | 109.5       |
| C4—C3—H3 | 119.9     | H15A—C15—H15C | 109.5       |



|              |             |               |             |
|--------------|-------------|---------------|-------------|
| C5—C4—C3     | 119.2 (3)   | H15B—C15—H15C | 109.5       |
| C5—C4—H4     | 120.4       | O3—C16—C17    | 109.0 (2)   |
| C3—C4—H4     | 120.4       | O3—C16—H16A   | 109.9       |
| C4—C5—C6     | 121.5 (3)   | C17—C16—H16A  | 109.9       |
| C4—C5—H5     | 119.3       | O3—C16—H16B   | 109.9       |
| C6—C5—H5     | 119.3       | C17—C16—H16B  | 109.9       |
| C5—C6—C1     | 118.2 (2)   | H16A—C16—H16B | 108.3       |
| C5—C6—C7     | 121.6 (2)   | C16—C17—H17A  | 109.5       |
| C1—C6—C7     | 120.2 (2)   | C16—C17—H17B  | 109.5       |
| N1—C7—C6     | 113.91 (19) | H17A—C17—H17B | 109.5       |
| N1—C7—P1     | 109.45 (15) | C16—C17—H17C  | 109.5       |
| C6—C7—P1     | 108.85 (14) | H17A—C17—H17C | 109.5       |
| N1—C7—H7     | 108.2       | H17B—C17—H17C | 109.5       |
| C6—C7—H7     | 108.2       | O7—C18—H18A   | 109.5       |
| P1—C7—H7     | 108.2       | O7—C18—H18B   | 109.5       |
| N1—C8—C9     | 119.2 (2)   | H18A—C18—H18B | 109.5       |
| N1—C8—C13    | 122.4 (2)   | O7—C18—H18C   | 109.5       |
| C9—C8—C13    | 118.4 (2)   | H18A—C18—H18C | 109.5       |
| C10—C9—C8    | 121.1 (2)   | H18B—C18—H18C | 109.5       |
| C10—C9—H9    | 119.5       | C8—N1—C7      | 123.21 (19) |
| C8—C9—H9     | 119.5       | C8—N1—H1A     | 115.2 (17)  |
| C9—C10—C11   | 119.4 (2)   | C7—N1—H1A     | 119.4 (17)  |
| C9—C10—H10   | 120.3       | O6—N2—O5      | 121.8 (2)   |
| C11—C10—H10  | 120.3       | O6—N2—C11     | 119.1 (2)   |
| C12—C11—C10  | 120.7 (2)   | O5—N2—C11     | 119.1 (2)   |
| C12—C11—N2   | 119.7 (2)   | C1—O1—H1      | 109.5       |
| C10—C11—N2   | 119.6 (2)   | C14—O2—P1     | 125.58 (18) |
| C11—C12—C13  | 120.4 (2)   | C16—O3—P1     | 121.48 (16) |
| C11—C12—H12  | 119.8       | C18—O7—H7A    | 109.5       |
| C13—C12—H12  | 119.8       | O4—P1—O2      | 114.76 (10) |
| C12—C13—C8   | 120.0 (2)   | O4—P1—O3      | 114.66 (10) |
| C12—C13—H13  | 120.0       | O2—P1—O3      | 104.51 (10) |
| C8—C13—H13   | 120.0       | O4—P1—C7      | 114.21 (10) |
| C15—C14—O2   | 111.4 (3)   | O2—P1—C7      | 105.37 (10) |
| C15—C14—H14A | 109.3       | O3—P1—C7      | 101.94 (10) |
| O1—C1—C2—C3  | 179.0 (2)   | C9—C8—C13—C12 | -1.3 (3)    |
| C6—C1—C2—C3  | -1.2 (4)    | C9—C8—N1—C7   | -173.7 (2)  |
| C1—C2—C3—C4  | 0.7 (4)     | C13—C8—N1—C7  | 7.8 (3)     |
| C2—C3—C4—C5  | 0.4 (4)     | C6—C7—N1—C8   | -72.5 (3)   |
| C3—C4—C5—C6  | -0.9 (4)    | P1—C7—N1—C8   | 165.39 (18) |
| C4—C5—C6—C1  | 0.4 (4)     | C12—C11—N2—O6 | 0.2 (4)     |
| C4—C5—C6—C7  | -176.7 (2)  | C10—C11—N2—O6 | 179.3 (3)   |
| O1—C1—C6—C5  | -179.6 (2)  | C12—C11—N2—O5 | -179.4 (3)  |
| C2—C1—C6—C5  | 0.6 (3)     | C10—C11—N2—O5 | -0.3 (4)    |
| O1—C1—C6—C7  | -2.4 (3)    | C15—C14—O2—P1 | 150.2 (2)   |
| C2—C1—C6—C7  | 177.8 (2)   | C17—C16—O3—P1 | 170.2 (2)   |
| C5—C6—C7—N1  | -49.0 (3)   | C14—O2—P1—O4  | 21.6 (3)    |

|                 |            |              |              |
|-----------------|------------|--------------|--------------|
| C1—C6—C7—N1     | 133.9 (2)  | C14—O2—P1—O3 | 148.0 (2)    |
| C5—C6—C7—P1     | 73.4 (2)   | C14—O2—P1—C7 | -104.9 (2)   |
| C1—C6—C7—P1     | -103.7 (2) | C16—O3—P1—O4 | 58.8 (2)     |
| N1—C8—C9—C10    | -178.1 (2) | C16—O3—P1—O2 | -67.7 (2)    |
| C13—C8—C9—C10   | 0.5 (4)    | C16—O3—P1—C7 | -177.30 (19) |
| C8—C9—C10—C11   | 0.9 (4)    | N1—C7—P1—O4  | 56.04 (18)   |
| C9—C10—C11—C12  | -1.6 (4)   | C6—C7—P1—O4  | -69.04 (17)  |
| C9—C10—C11—N2   | 179.3 (2)  | N1—C7—P1—O2  | -177.09 (14) |
| C10—C11—C12—C13 | 0.8 (4)    | C6—C7—P1—O2  | 57.82 (17)   |
| N2—C11—C12—C13  | 179.9 (2)  | N1—C7—P1—O3  | -68.20 (17)  |
| C11—C12—C13—C8  | 0.6 (4)    | C6—C7—P1—O3  | 166.71 (15)  |
| N1—C8—C13—C12   | 177.3 (2)  |              |              |

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H $\cdots$ <i>A</i>     | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O7—H7A $\cdots$ O4 <sup>i</sup>   | 0.82        | 2.00                | 2.819 (3)                  | 172                           |
| O1—H1 $\cdots$ O7                 | 0.82        | 1.95                | 2.757 (3)                  | 170                           |
| C10—H10 $\cdots$ O5 <sup>ii</sup> | 0.93        | 2.53                | 3.308 (4)                  | 141                           |
| N1—H1A $\cdots$ O4 <sup>iii</sup> | 0.82 (2)    | 2.14 (2)            | 2.959 (3)                  | 171 (2)                       |

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