Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

# The crystal structure of baeocystin

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Received 20 April 2022
Accepted 27 April 2022

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

**Keywords:** crystal structure; tryptamines; indoles; hydrogen bonding.

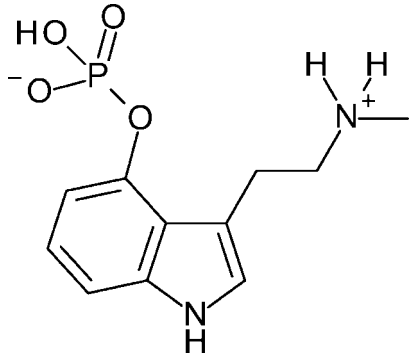
**CCDC reference**: 2169087

**Supporting information**: this article has supporting information at journals.iucr.org/e

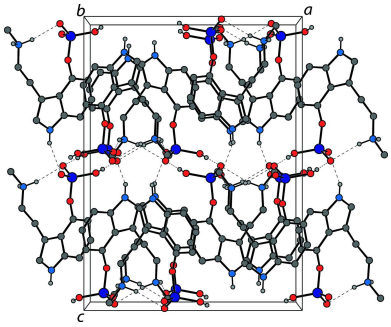
The title compound, baeocystin or 4-phosphoryloxy-*N*-methyltryptamine {systematic name: 3-[2-(methylazaniumyl)ethyl]-1*H*-indol-4-yl hydrogen phosphate}, $C_{11}H_{15}N_2O_4P$, has a single zwitterionic molecule in the asymmetric unit. The molecule has an intramolecular N—H···O hydrogen bond between the ammonium cation and the hydrophosphate anion. In the crystal, the molecules are linked by N—H···O and O—H···O hydrogen bonds into a three-dimensional network.

## 1. Chemical context

'Magic' mushrooms are a group of psilocybin-containing fungi that induce psychoactive effects in humans, and have been used for recreational and sacramental purposes for centuries (Geiger *et al.*, 2018). Recent studies have shown that psilocybin (4-phosphoryloxy-*N*,*N*-dimethyltryptamine, $C_{12}H_{17}N_2O_4P$), a naturally occurring tryptamine found in these mushrooms, has great potential in the treatment of mood disorders including anxiety, addiction, depression and post-traumatic stress disorder (Johnson & Griffiths, 2017; Nutt, 2019; McClure-Begley & Roth, 2022). Upon ingestion, psilocybin is converted, *via* hydrolysis of the phosphate ester, to psilocin (4-hydroxy-*N*,*N*-dimethyltryptamine, $C_{12}H_{16}N_2O$), which acts as an agonist of the serotonin (5-hydroxytryptamine or 5-HT) 2A receptor, mediating its psychoactive effects.




In addition to psilocybin, these mushrooms contain several other structurally similar tryptamines, including norbaeocystin, baeocystin, aeruginascin and norpsilocin. Baeocystin is the *N*-demethylated analog of psilocybin (4-phosphoryloxy-*N*-methyltryptamine). This minor tryptamine natural product was first isolated from the *Psilocybe baeocystis* mushroom in 1968 (Leung & Paul, 1968), and has since been found in a number of other mushroom species (Repke *et al.*, 1977; Gartz,



1987). The Hoffmeister lab has identified baeocystin as an enzymatic substrate in the synthesis of psilocybin (Fricke *et al.*, 2017), and also identified norpsilocin (4-hydroxy-*N*-methyltryptamine), the metabolite of baeocystin, as a *Psilocybe* natural product (Lenz *et al.*, 2017). It was not until 2020 that a scalable synthesis of baeocystin was reported (Sherwood *et al.*, 2020), with a prior synthesis appearing in the literature in 1988 (Brenneisen *et al.*, 1988).

Baeocystin's hydrolysis product and metabolite norpsilocin has been shown to be a full agonist of the 5-$HT_{2A}$ receptor. However, baeocystin does not induce a head-twitch response (HTR) in mice, which is strongly correlated with 5-$HT_{2A}$ receptor-mediated psychoactive effects (Sherwood *et al.*, 2020). While HTR experiments indicated that baeocystin alone does not induce psychoactive effects, it is still unclear whether it modulates psilocybin's pharmacology when co-administered. It has been shown that mushroom extracts are an order of magnitude more potent than pure psilocybin in HTR assays (Zhuk *et al.*, 2015). Additionally, human anecdotal evidence suggests that the experiential psychedelic effects vary between different species of 'magic' mushrooms, where the ratios of the different tryptamines can vary significantly.

Our understanding of 'magic' mushroom pharmacology has been limited by access to pure, well-characterized chemicals for biological assays. Recent studies have demonstrated the significance of crystallographic characterization of molecules in this area, and in potential pharmaceuticals more broadly (Sherwood *et al.*, 2022; Toby, 2022). Herein we report the solid-state structure of the natural product baeocystin, $C_{11}H_{15}N_2O_4P$, for the first time.

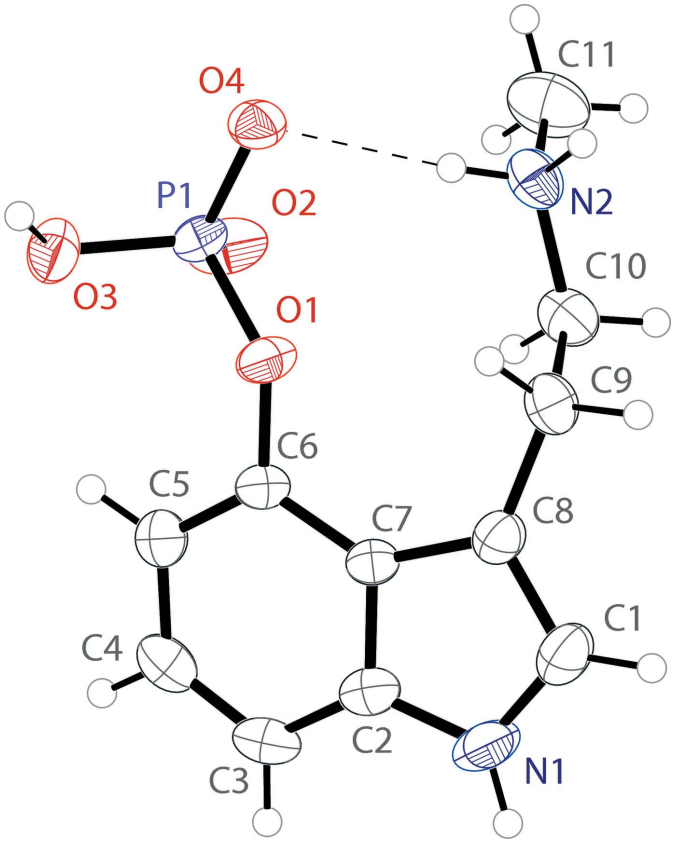



**Figure 1**
The molecular structure of baeocystin showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is shown as a dashed line.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | 0.87 (1) | 2.16 (1) | 2.969 (2) | 156 (3) |
| O3—H3···O4$^{ii}$ | 0.89 (1) | 1.67 (1) | 2.5560 (18) | 173 (3) |
| N2—H2*A*···O4 | 0.90 (1) | 2.04 (1) | 2.913 (2) | 165 (2) |
| N2—H2*B*···O2$^{iii}$ | 0.90 (1) | 1.85 (1) | 2.698 (2) | 157 (2) |

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

## 2. Structural commentary

The asymmetric unit of the baeocystin structure consists of a single zwitterionic tryptamine molecule with a protonated secondary ammonium group and a singly deprotonated phosphoryloxy unit (Fig. 1). The phosphate unit shows longer P—O distances with single-bond character for the two-coordinate oxygen atoms, with values of 1.5480 (14) Å for P1—O3 and 1.6032 (12) Å for P1—O1. The bonding about the two one-coordinate oxygen atoms appears to be delocalized, with distances of 1.4848 (14) Å for P1—O2 and 1.5019 (13) Å for P1—O4. The molecule has a near planar indole unit, with an r.m.s. deviation from planarity of 0.016 Å. The ethylamino arm is turned away from the indole plane, with a C7—C8—C9—C10 torsion angle of 67.7 (2)° and a C9—C10—N2—C11 unit showing an *anti* conformation with a torsion angle of 178.96 (18)°. The phosphoryloxy group is similarly turned away from the indole plane, with a C5—C6—O1—P1 torsion angle of 33.8 (3)°. Both groups are turned to the same side of the indole ring, which is likely supported by an intramolecular N2—H2*A*···O4 hydrogen bond (Table 1).

## 3. Supramolecular features

In the crystal, the baeocystin molecules are held together by various N—H···O and O—H···O hydrogen bonds that produce a three-dimensional network in the extended structure. The most significant hydrogen bonding observed is the dimerization of two molecules through the phosphate groups, consisting of two O—H···O hydrogen bonds. One of the ammonium hydrogen atoms participates in an intramolecular hydrogen bond as described above, while the other has an intermolecular N—H···O hydrogen bond to a phosphate oxygen atom of a symmetry-generated baeocystin molecule. The indole nitrogen atom shows an N—H···O hydrogen bond to a phosphate oxygen atom of another symmetry-generated baeocystine molecule. One of the phosphate O atoms without a proton is partner in both the intramolecular N—H···O hydrogen bond and the phosphate dimer O—H···O hydrogen bond. The other phosphate O atom without a proton is the

acceptor to both intermolecular N—H···O hydrogen bonds. Fig. 2 shows the hydrogen bonding about a single baeocystin molecule, which is also summarized in Table 1. The crystal packing of baeocystin is shown in Fig. 3. It is of note that the anhydrate of baeocystin forms from an aqueous solution, while psilocybin readily forms the trihydrate when isolated in a similar fashion. Even the storage of psilocybin anhydrate under humid conditions results in the conversion to the trihydrate, so the ready formation of baeocystin anhydrate is notable (Kuhnert-Brandstätter & Heindl, 1976).

## 4. Database survey

Perhaps the most closely associated molecule to baeocystin is the well-known psychedelic, psilocybin, whose structure was first reported in 1974 [Weber & Petcher, 1974: Cambridge Structural Database (CSD; Groom *et al.*, 2016) refcode PSILOC], and whose crystalline forms have undergone extensive study recently (Sherwood *et al.*, 2022: TAVZID, TAVZID01; Greenan *et al.*, 2020: OKOKAD). Similar to baeocystin, psilocybin exists in a zwitterionic form in the solid state. The other closely associated structure to baeocystin is its putative metabolite, norpsilocin, which has been reported as both its free base and its fumarate salt (Chadeayne *et al.*, 2020: MULXAV, MULXEZ). The only other mono-alkyltryptamine structure in the CSD is the free base of 5-methoxy-*N*-methyltryptamine (Bergin *et al.*, 1968: QQQAHA) and the only other 4-phosphoryloxytryptamine structure is of the psilocybin analogue 4-phosphoryloxy-*N*,*N*-diethyltryptamine (Baker *et al.*, 1973: KOWHOT).

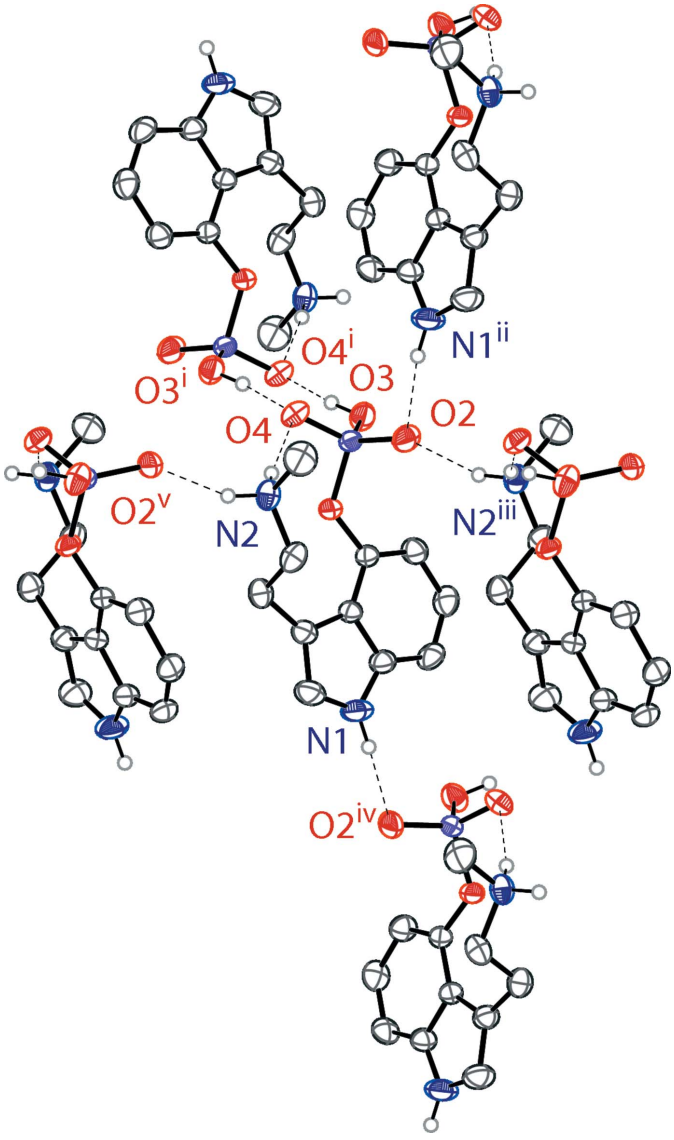



**Figure 2**
The hydrogen-bonding interactions between the baeocystin molecules (Table 1). Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Symmetry codes: (1) $1-x, 1-y, 1-z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, -\frac{1}{2}+y, z$; (iv) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, z$.

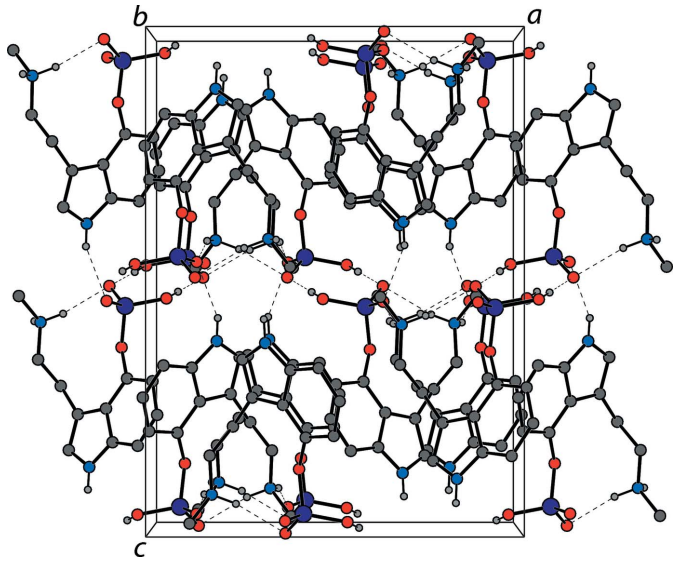



**Figure 3**
The crystal packing of baeocystin viewed along the *b*-axis direction. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity.

## 5. Synthesis and crystallization

Baeocystin was prepared according to the literature procedure (Sherwood *et al.*, 2020). Single crystals suitable for X-ray diffraction studies were grown by the slow evaporation of an aqueous solution.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms H1, H2*A*, H2*B* and H3 were found in a difference-Fourier map and were refined isotropically, using DFIX restraints with an N—H(indole) distance of 0.87 (1) Å, N—H(ammonium) distances of 0.90 (1) Å, and an O—H distance of 0.90 (1) Å. Isotropic displacement parameters were set to 1.2 $U_{eq}$ of the parent nitrogen atoms and 1.5 $U_{eq}$ of the parent oxygen atom. All other hydrogen atoms were placed in calculated positions [C—

H = 0.93 Å ($sp^2$), 0.97 Å ($sp^3$)]. Isotropic displacement parameters were set to 1.2 $U_{eq}$ of the parent carbon atoms.


## Acknowledgements

Financial statements and conflict of interest: This study was funded by CaaMTech, Inc. ARC reports an ownership interest in CaaMTech, Inc., which owns US and worldwide patent applications, covering new tryptamine compounds, compositions, formulations, novel crystalline forms, and methods of making and using the same.

## Funding information

Funding for this research was provided by: National Science Foundation, Directorate for Mathematical and Physical Sciences (grant No. CHE-1429086).


**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{11}H_{15}N_2O_4P$ |
| $M_r$ | 270.22 |
| Crystal system, space group | Orthorhombic, *Pbca* |
| Temperature (K) | 297 |
| *a*, *b*, *c* (Å) | 13.229 (1), 10.5551 (7), 17.8346 (13) |
| *V* (Å$^3$) | 2490.3 (3) |
| *Z* | 8 |
| Radiation type | Mo *Kα* |
| $\mu$ (mm$^{-1}$) | 0.23 |
| Crystal size (mm) | 0.25 × 0.20 × 0.03 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 Venture CMOS |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2018) |
| $T_{min}$, $T_{max}$ | 0.680, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 58953, 2551, 2155 |
| $R_{int}$ | 0.070 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.626 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.037, 0.096, 1.07 |
| No. of reflections | 2551 |
| No. of parameters | 180 |
| No. of restraints | 4 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.21, −0.35 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

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# supporting information

*Acta Cryst.* (2022). E**78**, 550-553 [https://doi.org/10.1107/S2056989022004467]

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### Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### 3-[2-(Methylazaniumyl)ethyl]-1*H*-indol-4-yl hydrogen phosphate

*Crystal data*

$C_{11}H_{15}N_2O_4P$
$M_r$ = 270.22
Orthorhombic, *Pbca*
$a$ = 13.229 (1) Å
$b$ = 10.5551 (7) Å
$c$ = 17.8346 (13) Å
$V$ = 2490.3 (3) Å$^3$
$Z$ = 8
$F$(000) = 1136
$D_x$ = 1.441 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9978 reflections
$\theta$ = 2.7–26.2°
$\mu$ = 0.23 mm$^{-1}$
$T$ = 297 K
Block, colourless
0.25 × 0.20 × 0.03 mm

*Data collection*

Bruker D8 Venture CMOS diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2018)
$T_{min}$ = 0.680, $T_{max}$ = 0.745
58953 measured reflections
2551 independent reflections
2155 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.070
$\theta_{max}$ = 26.4°, $\theta_{min}$ = 2.8°
$h$ = −16→16
$k$ = −13→13
$l$ = −22→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.096
$S$ = 1.07
2551 reflections
180 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 1.4406P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.35 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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| P1 | 0.41763 (4) | 0.35224 (4) | 0.45000 (2) | 0.02770 (14) |
| O1 | 0.40570 (10) | 0.39542 (12) | 0.36428 (7) | 0.0347 (3) |
| O2 | 0.37058 (12) | 0.22578 (13) | 0.46057 (8) | 0.0471 (4) |
| O3 | 0.53246 (11) | 0.34327 (13) | 0.46581 (8) | 0.0409 (4) |
| O4 | 0.36978 (10) | 0.46089 (12) | 0.49120 (7) | 0.0355 (3) |
| N1 | 0.31807 (15) | 0.33361 (18) | 0.11856 (9) | 0.0481 (5) |
| N2 | 0.17536 (12) | 0.48828 (15) | 0.41629 (10) | 0.0361 (4) |
| C1 | 0.25753 (18) | 0.4233 (2) | 0.15158 (11) | 0.0462 (5) |
| H1A | 0.206731 | 0.468024 | 0.127137 | 0.055* |
| C2 | 0.38408 (15) | 0.28696 (17) | 0.17085 (10) | 0.0341 (4) |
| C3 | 0.45759 (16) | 0.19289 (19) | 0.16549 (11) | 0.0393 (5) |
| H3A | 0.469351 | 0.150336 | 0.120666 | 0.047* |
| C4 | 0.51182 (15) | 0.16557 (19) | 0.22883 (12) | 0.0402 (5) |
| H4 | 0.560213 | 0.101749 | 0.226826 | 0.048* |
| C5 | 0.49710 (15) | 0.23030 (18) | 0.29663 (11) | 0.0366 (4) |
| H5 | 0.536699 | 0.211304 | 0.338222 | 0.044* |
| C6 | 0.42355 (14) | 0.32217 (16) | 0.30106 (9) | 0.0281 (4) |
| C7 | 0.36420 (13) | 0.35111 (15) | 0.23867 (9) | 0.0279 (4) |
| C8 | 0.28245 (14) | 0.43741 (17) | 0.22544 (10) | 0.0339 (4) |
| C9 | 0.23077 (15) | 0.51840 (18) | 0.28322 (11) | 0.0376 (4) |
| H9A | 0.185375 | 0.577128 | 0.258397 | 0.045* |
| H9B | 0.280986 | 0.567456 | 0.310198 | 0.045* |
| C10 | 0.17092 (15) | 0.43738 (18) | 0.33870 (11) | 0.0393 (5) |
| H10A | 0.100926 | 0.433429 | 0.322673 | 0.047* |
| H10B | 0.197693 | 0.351832 | 0.338375 | 0.047* |
| C11 | 0.1188 (2) | 0.4085 (2) | 0.47055 (14) | 0.0580 (6) |
| H11A | 0.125189 | 0.443908 | 0.519921 | 0.087* |
| H11B | 0.146014 | 0.324199 | 0.470236 | 0.087* |
| H11C | 0.048792 | 0.405930 | 0.456596 | 0.087* |
| H1 | 0.315 (2) | 0.309 (2) | 0.0722 (7) | 0.069 (8)* |
| H3 | 0.563 (2) | 0.4153 (17) | 0.4793 (17) | 0.084 (10)* |
| H2A | 0.2389 (9) | 0.491 (2) | 0.4340 (12) | 0.044 (6)* |
| H2B | 0.1541 (18) | 0.5695 (11) | 0.4179 (13) | 0.055 (7)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| P1 | 0.0344 (3) | 0.0263 (2) | 0.0224 (2) | −0.00431 (18) | −0.00240 (18) | −0.00125 (16) |
| O1 | 0.0512 (8) | 0.0307 (6) | 0.0223 (6) | 0.0085 (6) | −0.0036 (5) | −0.0021 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 0.0692 (10) | 0.0373 (8) | 0.0347 (7) | −0.0214 (7) | 0.0057 (7) | −0.0022 (6) |
| O3 | 0.0394 (8) | 0.0343 (7) | 0.0491 (8) | 0.0059 (6) | −0.0141 (6) | −0.0085 (6) |
| O4 | 0.0346 (7) | 0.0397 (7) | 0.0323 (7) | −0.0039 (6) | 0.0015 (6) | −0.0110 (6) |
| N1 | 0.0615 (12) | 0.0582 (11) | 0.0245 (8) | 0.0060 (9) | −0.0079 (8) | −0.0055 (8) |
| N2 | 0.0324 (9) | 0.0300 (8) | 0.0459 (10) | 0.0012 (7) | 0.0046 (7) | −0.0029 (7) |
| C1 | 0.0491 (12) | 0.0536 (12) | 0.0360 (10) | 0.0095 (10) | −0.0119 (10) | 0.0025 (9) |
| C2 | 0.0404 (11) | 0.0362 (10) | 0.0257 (9) | −0.0040 (8) | 0.0026 (8) | −0.0012 (7) |
| C3 | 0.0467 (12) | 0.0391 (10) | 0.0321 (10) | −0.0009 (9) | 0.0118 (9) | −0.0078 (8) |
| C4 | 0.0379 (10) | 0.0366 (10) | 0.0461 (12) | 0.0079 (8) | 0.0092 (9) | −0.0033 (8) |
| C5 | 0.0350 (10) | 0.0386 (10) | 0.0364 (10) | 0.0067 (8) | −0.0022 (8) | 0.0009 (8) |
| C6 | 0.0339 (9) | 0.0275 (8) | 0.0231 (8) | −0.0001 (7) | 0.0023 (7) | −0.0006 (6) |
| C7 | 0.0316 (9) | 0.0288 (8) | 0.0232 (8) | −0.0011 (7) | 0.0021 (7) | 0.0008 (6) |
| C8 | 0.0359 (10) | 0.0355 (9) | 0.0302 (9) | 0.0030 (8) | −0.0032 (7) | 0.0017 (7) |
| C9 | 0.0350 (10) | 0.0331 (9) | 0.0447 (11) | 0.0060 (8) | 0.0007 (8) | 0.0011 (8) |
| C10 | 0.0352 (10) | 0.0369 (10) | 0.0458 (11) | −0.0047 (8) | 0.0053 (9) | −0.0095 (9) |
| C11 | 0.0616 (15) | 0.0559 (14) | 0.0565 (14) | −0.0113 (12) | 0.0208 (12) | 0.0013 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| P1—O1 | 1.6032 (12) | C3—H3A | 0.9300 |
| P1—O2 | 1.4848 (14) | C3—C4 | 1.369 (3) |
| P1—O3 | 1.5480 (14) | C4—H4 | 0.9300 |
| P1—O4 | 1.5019 (13) | C4—C5 | 1.402 (3) |
| O1—C6 | 1.387 (2) | C5—H5 | 0.9300 |
| O3—H3 | 0.893 (10) | C5—C6 | 1.376 (3) |
| N1—C1 | 1.372 (3) | C6—C7 | 1.396 (2) |
| N1—C2 | 1.369 (3) | C7—C8 | 1.434 (2) |
| N1—H1 | 0.866 (10) | C8—C9 | 1.503 (3) |
| N2—C10 | 1.486 (3) | C9—H9A | 0.9700 |
| N2—C11 | 1.485 (3) | C9—H9B | 0.9700 |
| N2—H2A | 0.899 (10) | C9—C10 | 1.529 (3) |
| N2—H2B | 0.902 (10) | C10—H10A | 0.9700 |
| C1—H1A | 0.9300 | C10—H10B | 0.9700 |
| C1—C8 | 1.366 (3) | C11—H11A | 0.9600 |
| C2—C3 | 1.393 (3) | C11—H11B | 0.9600 |
| C2—C7 | 1.411 (2) | C11—H11C | 0.9600 |
| | | | |
| O2—P1—O1 | 109.59 (8) | C6—C5—C4 | 119.41 (18) |
| O2—P1—O3 | 109.47 (9) | C6—C5—H5 | 120.3 |
| O2—P1—O4 | 116.60 (8) | O1—C6—C7 | 115.48 (15) |
| O3—P1—O1 | 106.72 (8) | C5—C6—O1 | 124.04 (16) |
| O4—P1—O1 | 102.00 (7) | C5—C6—C7 | 120.42 (16) |
| O4—P1—O3 | 111.79 (7) | C2—C7—C8 | 107.72 (16) |
| C6—O1—P1 | 126.86 (11) | C6—C7—C2 | 118.27 (16) |
| P1—O3—H3 | 116 (2) | C6—C7—C8 | 134.01 (16) |
| C1—N1—H1 | 125.8 (19) | C1—C8—C7 | 105.75 (17) |
| C2—N1—C1 | 109.14 (16) | C1—C8—C9 | 127.83 (18) |
| C2—N1—H1 | 125.0 (19) | C7—C8—C9 | 126.27 (16) |

| | | | |
|---|---|---|---|
| C10—N2—H2A | 112.1 (15) | C8—C9—H9A | 109.4 |
| C10—N2—H2B | 111.2 (15) | C8—C9—H9B | 109.4 |
| C11—N2—C10 | 112.48 (16) | C8—C9—C10 | 111.17 (15) |
| C11—N2—H2A | 105.2 (15) | H9A—C9—H9B | 108.0 |
| C11—N2—H2B | 111.1 (16) | C10—C9—H9A | 109.4 |
| H2A—N2—H2B | 104 (2) | C10—C9—H9B | 109.4 |
| N1—C1—H1A | 124.8 | N2—C10—C9 | 112.34 (16) |
| C8—C1—N1 | 110.38 (18) | N2—C10—H10A | 109.1 |
| C8—C1—H1A | 124.8 | N2—C10—H10B | 109.1 |
| N1—C2—C3 | 130.90 (18) | C9—C10—H10A | 109.1 |
| N1—C2—C7 | 107.01 (17) | C9—C10—H10B | 109.1 |
| C3—C2—C7 | 122.07 (17) | H10A—C10—H10B | 107.9 |
| C2—C3—H3A | 121.3 | N2—C11—H11A | 109.5 |
| C4—C3—C2 | 117.34 (17) | N2—C11—H11B | 109.5 |
| C4—C3—H3A | 121.3 | N2—C11—H11C | 109.5 |
| C3—C4—H4 | 118.8 | H11A—C11—H11B | 109.5 |
| C3—C4—C5 | 122.42 (18) | H11A—C11—H11C | 109.5 |
| C5—C4—H4 | 118.8 | H11B—C11—H11C | 109.5 |
| C4—C5—H5 | 120.3 | | |

| | | | |
|---|---|---|---|
| P1—O1—C6—C5 | −33.8 (3) | C2—C3—C4—C5 | −1.5 (3) |
| P1—O1—C6—C7 | 149.11 (14) | C2—C7—C8—C1 | −0.6 (2) |
| O1—C6—C7—C2 | 175.07 (15) | C2—C7—C8—C9 | 175.11 (18) |
| O1—C6—C7—C8 | −4.2 (3) | C3—C2—C7—C6 | 2.8 (3) |
| O2—P1—O1—C6 | −45.56 (17) | C3—C2—C7—C8 | −177.82 (18) |
| O3—P1—O1—C6 | 72.88 (16) | C3—C4—C5—C6 | 2.1 (3) |
| O4—P1—O1—C6 | −169.73 (14) | C4—C5—C6—O1 | −177.12 (17) |
| N1—C1—C8—C7 | 0.3 (2) | C4—C5—C6—C7 | −0.2 (3) |
| N1—C1—C8—C9 | −175.36 (19) | C5—C6—C7—C2 | −2.1 (3) |
| N1—C2—C3—C4 | −179.2 (2) | C5—C6—C7—C8 | 178.63 (19) |
| N1—C2—C7—C6 | −178.69 (17) | C6—C7—C8—C1 | 178.7 (2) |
| N1—C2—C7—C8 | 0.7 (2) | C6—C7—C8—C9 | −5.6 (3) |
| C1—N1—C2—C3 | 177.8 (2) | C7—C2—C3—C4 | −1.0 (3) |
| C1—N1—C2—C7 | −0.6 (2) | C7—C8—C9—C10 | −67.7 (2) |
| C1—C8—C9—C10 | 107.1 (2) | C8—C9—C10—N2 | 143.00 (17) |
| C2—N1—C1—C8 | 0.2 (3) | C11—N2—C10—C9 | −178.96 (18) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | 0.87 (1) | 2.15 (1) | 2.969 (2) | 156 (3) |
| O3—H3···O4$^{ii}$ | 0.89 (1) | 1.67 (1) | 2.5560 (18) | 173 (3) |
| N2—H2*A*···O4 | 0.90 (1) | 2.04 (1) | 2.913 (2) | 165 (2) |
| N2—H2*B*···O2$^{iii}$ | 0.90 (1) | 1.85 (1) | 2.698 (2) | 157 (2) |

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