The crystal structure of baeocystin

Marilyn Naeem,a Alexander M. Sherwood,b Andrew R. Chadeayne,c James A. Golen,a and David R. Mankeb*

aUniversity of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA, bUsona Institute, 2780 Woods Hollow Rd., Madison, WI 53711, USA, and cCaaMTech, Inc., 56 East Sunset Way, Suite 209, Issaquah, WA 98027, USA. *Correspondence e-mail: dmanke@umassd.edu

The title compound, baeocystin or 4-phosphoryloxy-N-methyltryptamine [systematic name: 3-[2-(methylazaniumyl)ethyl]-1H-indol-4-yl hydrogen phosphate], C11H15N2O4P, 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, C12H17N2O4P), 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, C12H16N2O), 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 norbaecocystin, 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,
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-HT2A receptor. However, baeocystin does not induce a head-twitch response (HTR) in mice, which is strongly correlated with 5-HT2A 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, C11H15N2O4P, for the first time.

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 35.8 (3)°. Both groups are turned to the same side of the indole ring, which is likely supported by an intramolecular N2—H2A···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

![Figure 1](image)

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···O2i                  | 0.87 (1) | 2.16 (1) | 2.969 (2) | 156 (3) |
| O3—H3···O4ii                 | 0.89 (1) | 1.67 (1) | 2.556 (18) | 173 (3) |
| N2—H2A···O4                  | 0.90 (1) | 2.04 (1) | 2.913 (2) | 165 (2) |
| N2—H2B···O4ii                | 0.90 (1) | 1.85 (1) | 2.698 (2) | 157 (2) |

Symmetry codes: (i) −x, −y + 1, −z; (ii) −x + 1, −y + 1, −z + 1; (iii) x + 1, y + ½, z.
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: MULXA V, 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).

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, H2A, H2B and H3 were found in a difference-Fourier map and were refined isotropically, using DEFIX 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 (sp³), 0.97 Å (sp²)]. 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).

References

Baker, R. W., Chothia, C., Pauling, P. & Weber, H. P. (1973). Mol. Pharmacol. 9, 23–32.
Bergin, R., Carlström, D., Falkenberg, G. & Ringertz, H. (1968). Acta Cryst. B24, 882.
Brenneisen, R., Borner, S., Peter-Oesch, N. & Schlunegger, U. P. (1988). Arch. Pharm. Pharm. Med. Chem. 321, 487–489.
Bruner, T.A., APEX3, SAINT, and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Chadeayne, A. R., Pham, D. N. K., Golen, J. A. & Manke, D. R. (2020). Acta Cryst. E76, 589–593.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Fricke, J., Blei, F. & Hoffmeister, D. (2017). Angew. Chem. Int. Ed. 56, 12352–12355.
Gartz, J. (1987). Plant Med. 53, 290–291.
Geiger, H. A., Wurst, M. G. & Daniels, R. N. (2018). ACS Chem. Neurosci. 9, 2438–2447.
Greenan, C., Arlin, J.-B., Lorimer, K., Kaylo, K., Kargbo, R., Meisenheimer, P., Tarpley, W. G. & Sherwood, A. (2020). ResearchGate, https://doi.org/10.13140/RG.2.2.32357.14560.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Johnson, M. W. & Griffiths, R. R. (2017). Neurotherapeutics, 14, 734–740.
Kuhnert-Brandstätter, M. & Heindl, W. (1976). Arch. Pharm. Pharm. Med. Chem. 309, 699–706.
Lenz, C., Wick, J. & Hoffmeister, D. (2017). J. Nat. Prod. 80, 2835–2838.
Leung, A. Y. & Paul, A. G. (1968). J. Pharm. Sci. 57, 1667–1671.
McClure-Begley, T. D. & Roth, B. L. (2022). Nat. Rev. Drug Discov. 21, https://doi.org/10.1038/s41573-022-00421-7.

Table 2

Experimental details.

| Crystal data | Chemical formula | C_{11}H_{15}N_2O_4P |
|--------------|------------------|-------------------|
| M_0          | Orthorhombic, Pbca |
| Temperature (K) | 297             |
| V (Å³)       | 13.229 (1), 10.5551 (7), 17.8346 (13) |
| Z            | 8                |
| Radiation type | Mo Kα          |
| μ (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 \(|I| > 2σ(I)\) reflections:

\[ R_{int} (\sin θ/λ)_{max} (\text{Å}^{-1}) \]

\[ 0.037, 0.096, 1.07 \]

No. of restraints: 4
H-atom treatment:

\[ Δρ_{max}, Δρ_{min} (e Å⁻³) \]

\[ 0.21, −0.35 \]

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

Nutt, D. (2019). Dialogues Clin. Neurosci. 21, 139–147.
Repke, D. B., Leslie, D. T. & Guzmán, G. (1977). Lloydia, 40, 566–578.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Sherwood, A. M., Halberstadt, A. L., Klein, A. K., McCorvy, J. D., Kaylo, K. W., Kargbo, R. B. & Meisenheimer, P. (2020). J. Nat. Prod. 83, 461–467.
Sherwood, A. M., Kargbo, R. B., Kaylo, K. W., Cozzi, N. V., Meisenheimer, P. & Kaduk, J. A. (2022). Acta Cryst. C78, 36–55.
Toby, B. H. (2022). Acta Cryst. C78, 70–71.
Weber, H. P. & Petcher, T. J. (1974). J. Chem. Soc. Perkin Trans. 2, 942–946.
Westrip, S. P. (2010). J. Appl. Cryst. 43, 920–925.
Zhuk, O., Jasicka-Misiak, I., Poliwoda, A., Kazakova, A., Godovan, V., Halama, M. & Wieczorek, P. (2015). Toxins, 7, 1018–1029.
The crystal structure of baecystin

Marilyn Naeem, Alexander M. Sherwood, Andrew R. Chadeayne, James A. Golen and David R. Manke

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]-1H-indol-4-yl hydrogen phosphate

Crystal data
C\textsubscript{11}H\textsubscript{15}N\textsubscript{2}O\textsubscript{4}P

\[D_a = 1.441 \text{ Mg m}^{-3}\]

Mo K\textalpha\ radiation, \(\lambda = 0.71073 \text{ Å}\)

Cell parameters from 9978 reflections

\[\theta = 2.7-26.2^\circ\]

\[\mu = 0.23 \text{ mm}^{-1}\]

\[T = 297 \text{ K}\]

Block, colourless

0.25 \times 0.20 \times 0.03 \text{ mm}

Data collection
Bruker D8 Venture CMOS diffractometer

\[\phi \text{ and } \omega \text{ scans}\]

Absorption correction: multi-scan

(SADABS; Bruker, 2018)

\[T_{\text{min}} = 0.680, T_{\text{max}} = 0.745\]

58953 measured reflections

2551 independent reflections

2155 reflections with \(I > 2\sigma(I)\)

\[R_{\text{int}} = 0.070\]

\[\theta_{\text{max}} = 26.4^\circ, \theta_{\text{min}} = 2.8^\circ\]

\[h = -16\rightarrow16\]

\([k = -13\rightarrow13]\]

\([l = -22\rightarrow22]\]

Refinement
Refinement on \(F^2\)

\[R(F^2 > 2\sigma(F^2)) = 0.037\]

\[wR(F^2) = 0.096\]

\[S = 1.07\]

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 \(P = (F_o^2 + 2F_c^2)/3\)

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

\[\Delta\rho_{\text{max}} = 0.21 \text{ e} \text{ Å}^{-3}\]

\[\Delta\rho_{\text{min}} = -0.35 \text{ e} \text{ Å}^{-3}\]
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   | Uiso*/Ueq |
|------|-----|-----|-----|-----------|
| 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) | 0.32217 (16) | 0.30106 (9) | 0.0281 (4) |
| 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) |
| H6A  | 0.473451 | 0.150336 | 0.120666 | 0.047* |
| 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)

|      | U11 | U22 | U33 | U12 | U13 | U23 |
|------|-----|-----|-----|-----|-----|-----|
| 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) |
Geometric parameters (Å, °)

| Bond                  | Distance | Angle       |
|-----------------------|----------|-------------|
| 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) | C10—H10A 0.9700 |
| N2—H2B                | 0.902 (10) | C10—H10B 0.9700 |
| C1—H1A                | 0.9300 | C11—H11A 0.9600 |
| C1—C8                 | 1.366 (3) | C11—H11B 0.9600 |
| C2—C3                 | 1.393 (3) | C11—H11C 0.9600 |
| C2—C7                 | 1.411 (2) | C6—C5—C4 119.41 (18) |
| O2—P1—O1              | 109.59 (8) | C6—C5—H5 120.3 |
| O2—P1—O3              | 109.47 (9) | C6—C5—C7 115.48 (15) |
| O2—P1—O4              | 116.60 (8) | O1—C6—C7 124.04 (16) |
| O3—P1—O1              | 106.72 (8) | C5—C6—O1 120.42 (16) |
| O4—P1—O1              | 102.00 (7) | C5—C6—C7 107.72 (16) |
| O4—P1—O3              | 111.79 (7) | C2—C7—C2 118.27 (16) |
| C6—O1—P1              | 126.86 (11) | C6—C7—C8 134.01 (16) |
| P1—O3—H3              | 116 (2) | C1—C8—C7 105.75 (17) |
| C1—N1—H1              | 125.8 (19) | C1—C8—C9 127.83 (18) |
| C2—N1—C1              | 109.14 (16) | 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 (2)  C10—C9—H9B 109.4  
N1—C1—N1 110.38 (18)  N2—C10—H10A 109.1  
C8—C1—N1 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  
C4—C3—H3A 117.34 (17)  N2—C11—H11A 109.5  
C4—C3—H3A 121.3  N2—C11—H11B 109.5  
C3—C4—C5 118.8  N2—C11—H11C 109.5  
C3—C4—H4 122.42 (18)  H11A—C11—H11B 109.5  
C5—C4—H4 118.8  H11A—C11—H11C 109.5  
C4—C5—H5 120.3  

| P1—O1—C6—C5 | −33.8 (3) | C2—C3—C4—C5 | −1.5 (3) |
| O1—C6—C7—C2 | 149.11 (14) | C2—C7—C8—C1 | −0.6 (2) |
| O1—C6—C7—C8 | 175.07 (15) | C2—C7—C8—C9 | 175.11 (18) |
| 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, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| N1—H1···O2i | 0.87 (1) | 2.15 (1) | 2.969 (2) | 156 (3) |
| O3···H3···O4ii | 0.89 (1) | 1.67 (1) | 2.5560 (18) | 173 (3) |
| N2···O4 | 0.90 (1) | 2.04 (1) | 2.913 (2) | 165 (2) |
| N2···O2iii | 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.