

Trimethylphosphine oxide dihydrate

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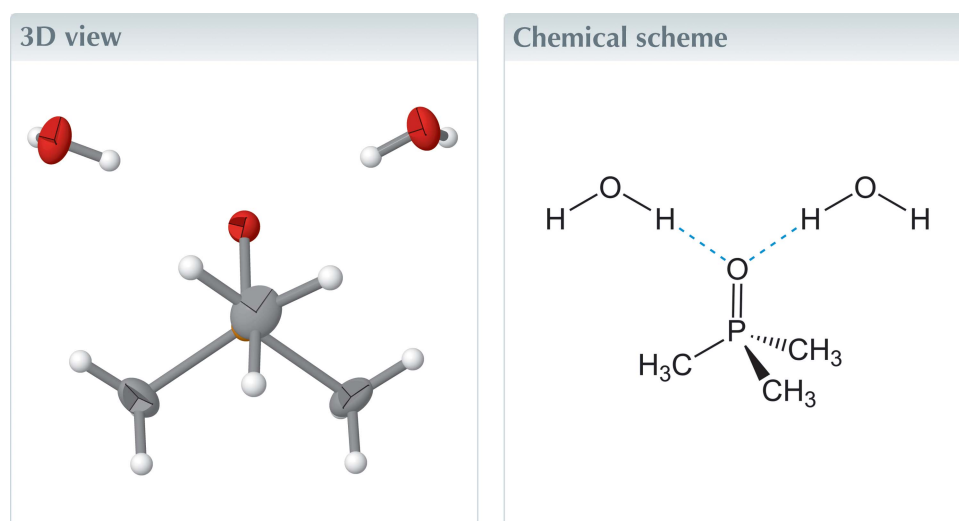
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The title hydrate, $\text{Me}_3\text{PO}\cdot 2\text{H}_2\text{O}$, crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell. The extended structure displays $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonding, with Me_3PO molecules as acceptors and water molecules acting as donors and acceptors of hydrogen bonds, forming hydrogen-bonded layers, which propagate in the *ac* plane.



Structure description

Tertiary phosphine oxides, $R_3\text{P}=\text{O}$ (R = alkyl/aryl), are good hydrogen-bond acceptors and have been employed for co-crystallization and stabilization of hydrogen-bond donor species such as hydrogen peroxide (Arp *et al.*, 2019) and di(hydroperoxy)alkanes (Ahn *et al.*, 2015). However, only a limited number of simple tertiary phosphine oxide hydrates have been structurally characterized by single-crystal X-ray diffraction. For example: tricyclohexylphosphine oxide hydrate, $\text{Cy}_3\text{PO}\cdot\text{H}_2\text{O}$ (Cambridge Structural Database refcode ZOQHEU; Hilliard *et al.* 2014; Thomas *et al.*, 2019); triphenylphosphine oxide hemihydrate, $\text{Ph}_3\text{PO}\cdot 0.5\text{H}_2\text{O}$ (JEDTOB; Baures & Silverton, 1990; Baures, 1991; Ng, 2009); tri-*p*-tolylphosphine oxide hemihydrate *p*-Tol₃PO·0.5H₂O (JULBAT; Churchill *et al.*, 1993); tris(2,4,6-trimethoxyphenyl)phosphine oxide hydrate, $[(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2]_3\text{PO}\cdot\text{H}_2\text{O}$ (WAMXIR; Chaloner *et al.*, 1993); tris(2,4,6-trimethoxyphenyl)phosphine oxide dihydrate, $[(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2]_3\text{PO}\cdot 2\text{H}_2\text{O}$ (LICVUO; Dunbar & Haefner, 1994); di-*o*-tolylphenylphosphine oxide hydrate, *o*-Tol₂PhPO·H₂O (POMRUH; Arp *et al.*, 2019). The absence of crystal structures of trialkylphosphine oxide hydrates with a short alkyl chain is particularly noteworthy. Herein, the crystal structure of the title phosphine oxide hydrate is reported.

Trimethylphosphine oxide dihydrate crystallizes in the orthorhombic space group *Pbca* with one Me_3PO and two H_2O molecules in the asymmetric unit (Fig. 1). The P=O bond length [1.5067 (7) Å] and P—C distances [1.7805 (12), 1.7809 (11), and 1.7819 (11) Å] are

in good agreement with the bond distances reported in crystal structures of trimethylphosphine oxide (FAKLUY; Engelhardt *et al.*, 1986; Begimova *et al.*, 2016).

The trimethylphosphine oxide molecule is an acceptor of two $O \cdots H-O$ hydrogen bonds, whereas both water molecules are donors of hydrogen bonds to Me_3PO and H_2O , and acceptors of hydrogen bonds from adjacent water molecules (Table 1, Fig. 2). Two Me_3PO and six H_2O molecules form a hydrogen-bonded 16-membered ring (Fig. 2) with an $R_6^6(16)$ graph-set motif (Etter, 1990). Each water molecule participates in three rings, whereas the trimethylphosphine molecule participates in two rings. These rings are interconnected into layers that extend parallel to the ac plane, whereby each ring is surrounded by six other rings (Figs. 2, 3). Hydrogen-bonded

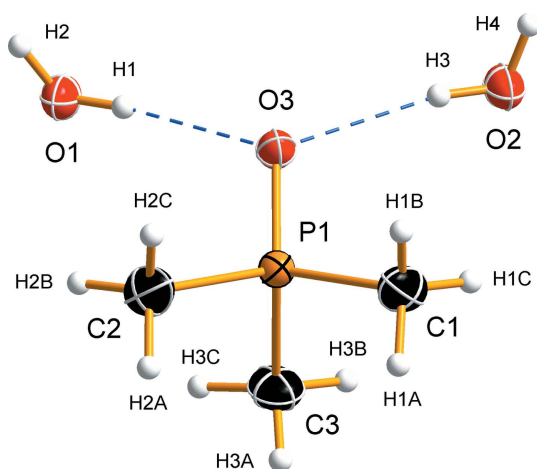


Figure 1
The asymmetric unit and the atom-labelling scheme of the $Me_3PO \cdot 2H_2O$ crystal structure. Displacement ellipsoids are depicted at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radius, and hydrogen bonds are indicated by blue dashed lines.

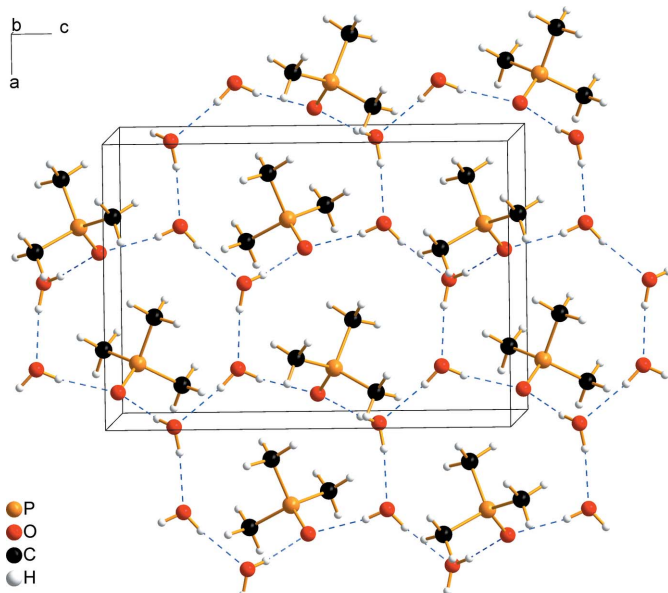


Figure 2
Hydrogen-bonded rings (depicted by blue dashed lines) are conjoined into layers parallel to the ac -plane.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1 \cdots O3$	0.807 (17)	1.976 (18)	2.7787 (10)	173.2 (16)
$O2-H3 \cdots O3$	0.789 (18)	2.046 (18)	2.8261 (11)	169.7 (15)
$O1-H2 \cdots O2^i$	0.873 (18)	1.981 (18)	2.8460 (12)	170.6 (14)
$O2-H4 \cdots O1^{ii}$	0.834 (17)	1.993 (17)	2.8218 (11)	172.0 (14)

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

layers and layers of Me_3P groups are stacked along the b -axis direction (Fig. 3).

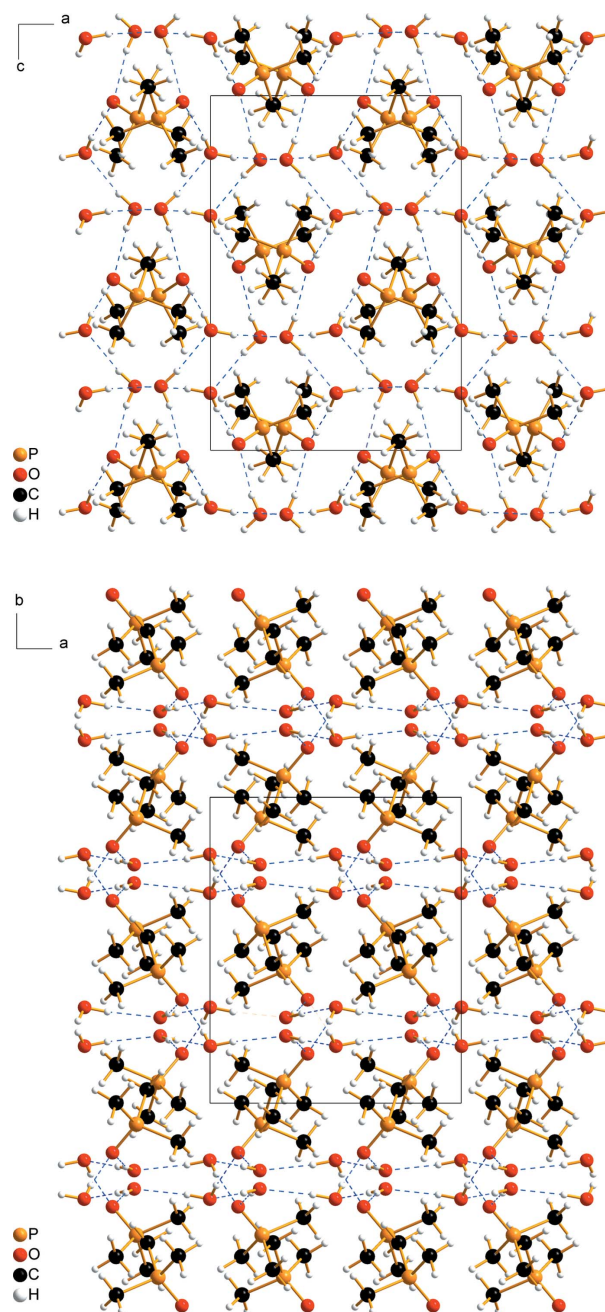


Figure 3
Crystal packing and the unit cell of $Me_3PO \cdot 2H_2O$ viewed along the crystallographic b -axis (top) and c -axis (bottom). Hydrogen bonds are indicated by blue dashed lines.

Synthesis and crystallization

Trimethylphosphine oxide (2.3 mg) was dissolved in a mixture of acetone- d_6 (0.6 ml) and diethyl ether- d_{10} (0.3 ml) in an NMR tube that was capped and cooled to $-20\text{ }^\circ\text{C}$ in an ethanol cooling bath. The Dewar flask containing the bath and sample was sealed and placed in a freezer at $-80\text{ }^\circ\text{C}$. Crystals of $\text{Me}_3\text{PO}\cdot 2\text{H}_2\text{O}$ grew within 3 days. The single crystals were examined, selected, and transferred to the diffractometer employing a previously described low-temperature crystal-mounting procedure (Lozinšek *et al.*, 2021). The crystals melt at room temperature.

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. Positions and isotropic thermal displacement parameters of hydrogen atoms were freely refined (Cooper *et al.*, 2010).

Acknowledgements

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References

- Ahn, S. H., Cluff, K. J., Bhuvanesh, N. & Blümel, J. (2015). *Angew. Chem. Int. Ed.* **54**, 13341–13345.
- Arp, F. F., Bhuvanesh, N. & Blümel, J. (2019). *Dalton Trans.* **48**, 14312–14325.
- Baures, P. W. (1991). *Acta Cryst.* **C47**, 2715–2716.
- Baures, P. W. & Silvertson, J. V. (1990). *Acta Cryst.* **C46**, 715–717.
- Begimova, G., Tupikina, E. Yu., Yu, V. K., Denisov, G. S., Bodensteiner, M. & Shenderovich, I. G. (2016). *J. Phys. Chem. C*, **120**, 8717–8729.
- Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Chaloner, P. A., Harrison, R. M. & Hitchcock, P. B. (1993). *Acta Cryst.* **C49**, 1072–1075.
- Churchill, M. R., See, R. F., Randall, S. L. & Atwood, J. D. (1993). *Acta Cryst.* **C49**, 345–347.
- Cooper, R. I., Thompson, A. L. & Watkin, D. J. (2010). *J. Appl. Cryst.* **43**, 1100–1107.

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_3\text{H}_9\text{OP}\cdot 2\text{H}_2\text{O}$
M_r	128.10
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	150
a, b, c (Å)	9.33514 (8), 11.39118 (9), 13.23961 (11)
V (Å ³)	1407.88 (2)
Z	8
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.88
Crystal size (mm)	0.70 × 0.24 × 0.13
Data collection	
Diffractometer	SuperNova, Dual, Cu at home/ near, Atlas
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
$T_{\text{min}}, T_{\text{max}}$	0.299, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24977, 1451, 1417
R_{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.023 0.628
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.057, 1.04
No. of reflections	1451
No. of parameters	117
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.27, -0.24

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009), *DIAMOND* (Brandenburg, 2005) and *publCIF* (Westrip, 2010).

- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Dunbar, K. R. & Haefner, S. C. (1994). *Polyhedron*, **13**, 727–736.
- Engelhardt, L. M., Raston, C. L., Whitaker, C. R. & White, A. H. (1986). *Aust. J. Chem.* **39**, 2151–2154.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Hilliard, C. R., Kharel, S., Cluff, K. J., Bhuvanesh, N., Gladysz, J. A. & Blümel, J. (2014). *Chem. Eur. J.* **20**, 17292–17295.
- Lozinšek, M., Mercier, H. P. A. & Schrobilgen, G. J. (2021). *Angew. Chem. Int. Ed.* **60**, 8149–8156.
- Ng, S. W. (2009). *Acta Cryst.* **E65**, o1431.
- Rigaku OD (2023). *CrysAlis PRO*. Rigaku Corporation, Wrocław, Poland.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Thomas, S. D., Tizzard, G. J., Coles, S. J. & Owen, G. R. (2019). *CSD Communication* (CCDC 1970272). CCDC, Cambridge, England.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2023). **8**, x230314 [https://doi.org/10.1107/S2414314623003140]

Trimethylphosphine oxide dihydrate

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(Dimethylphosphoryl)methane dihydrate

Crystal data

$C_3H_9OP \cdot 2H_2O$

$M_r = 128.10$

Orthorhombic, *Pbca*

$a = 9.33514$ (8) Å

$b = 11.39118$ (9) Å

$c = 13.23961$ (11) Å

$V = 1407.88$ (2) Å³

$Z = 8$

$F(000) = 560$

$D_x = 1.209$ Mg m⁻³

Cu *Kα* radiation, $\lambda = 1.54184$ Å

Cell parameters from 18569 reflections

$\theta = 3.3$ – 75.4°

$\mu = 2.88$ mm⁻¹

$T = 150$ K

Block, colourless

$0.70 \times 0.24 \times 0.13$ mm

Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 5.2466 pixels mm⁻¹

ω scans

Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.299$, $T_{\max} = 1.000$

24977 measured reflections

1451 independent reflections

1417 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 75.5^\circ$, $\theta_{\min} = 7.0^\circ$

$h = -11 \rightarrow 11$

$k = -14 \rightarrow 14$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.057$

$S = 1.04$

1451 reflections

117 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 0.4017P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.27$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ e Å⁻³

Extinction correction: *SHELXL2019/2*

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0019 (4)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.29293 (2)	0.43133 (2)	0.43709 (2)	0.01874 (11)
O3	0.38810 (7)	0.33831 (6)	0.48229 (5)	0.02332 (17)
O1	0.50092 (9)	0.18661 (7)	0.33846 (6)	0.02949 (19)
O2	0.30184 (8)	0.28005 (8)	0.68067 (6)	0.0309 (2)
C3	0.12748 (12)	0.37348 (12)	0.39205 (10)	0.0361 (3)
C1	0.25087 (15)	0.54386 (11)	0.52559 (9)	0.0360 (3)
C2	0.37390 (13)	0.50121 (11)	0.33118 (9)	0.0363 (3)
H1	0.4749 (17)	0.2314 (14)	0.3820 (13)	0.049 (4)*
H3	0.3357 (17)	0.2929 (13)	0.6272 (13)	0.044 (4)*
H1A	0.1928 (16)	0.6023 (14)	0.4936 (12)	0.049 (4)*
H3A	0.0705 (17)	0.4349 (13)	0.3682 (13)	0.049 (4)*
H2	0.5911 (19)	0.2011 (13)	0.3261 (11)	0.048 (4)*
H3B	0.0772 (19)	0.3342 (15)	0.4489 (14)	0.062 (5)*
H4	0.3659 (17)	0.2931 (12)	0.7231 (12)	0.042 (4)*
H2A	0.3129 (17)	0.5592 (14)	0.3018 (13)	0.050 (4)*
H3C	0.148 (2)	0.3195 (15)	0.3342 (15)	0.068 (5)*
H2B	0.395 (2)	0.4400 (15)	0.2808 (14)	0.063 (5)*
H1C	0.2035 (16)	0.5079 (16)	0.5804 (12)	0.055 (5)*
H2C	0.457 (2)	0.5422 (15)	0.3541 (14)	0.066 (5)*
H1B	0.337 (2)	0.5830 (16)	0.5464 (14)	0.067 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01726 (15)	0.02106 (16)	0.01790 (16)	0.00154 (8)	0.00075 (7)	0.00121 (8)
O3	0.0247 (3)	0.0246 (3)	0.0206 (3)	0.0062 (3)	0.0018 (2)	0.0022 (3)
O1	0.0265 (4)	0.0370 (4)	0.0249 (4)	0.0048 (3)	0.0004 (3)	-0.0075 (3)
O2	0.0240 (4)	0.0472 (5)	0.0214 (4)	-0.0027 (3)	0.0013 (3)	0.0014 (3)
C3	0.0252 (5)	0.0464 (7)	0.0366 (6)	-0.0071 (5)	-0.0062 (5)	0.0026 (5)
C1	0.0422 (7)	0.0322 (5)	0.0336 (6)	0.0156 (5)	-0.0049 (6)	-0.0071 (5)
C2	0.0336 (6)	0.0393 (6)	0.0359 (6)	0.0022 (5)	0.0068 (5)	0.0174 (5)

Geometric parameters (\AA , $^\circ$)

P1—O3	1.5067 (7)	C3—H3B	0.993 (18)
P1—C3	1.7819 (11)	C3—H3C	1.001 (19)
P1—C1	1.7805 (12)	C1—H1A	0.957 (17)
P1—C2	1.7809 (11)	C1—H1C	0.943 (17)
O1—H1	0.807 (17)	C1—H1B	0.96 (2)
O1—H2	0.873 (18)	C2—H2A	0.955 (17)
O2—H3	0.789 (18)	C2—H2B	0.985 (18)
O2—H4	0.834 (17)	C2—H2C	0.958 (19)
C3—H3A	0.934 (16)		
O3—P1—C3	112.58 (5)	H3B—C3—H3C	113.3 (13)

O3—P1—C1	112.02 (5)	P1—C1—H1A	109.6 (10)
O3—P1—C2	112.13 (5)	P1—C1—H1C	107.3 (11)
C1—P1—C3	107.18 (7)	P1—C1—H1B	109.7 (11)
C1—P1—C2	106.85 (7)	H1A—C1—H1C	112.1 (13)
C2—P1—C3	105.64 (6)	H1A—C1—H1B	106.2 (14)
H1—O1—H2	107.7 (14)	H1C—C1—H1B	112.0 (15)
H3—O2—H4	106.5 (15)	P1—C2—H2A	112.1 (10)
P1—C3—H3A	109.3 (9)	P1—C2—H2B	107.6 (10)
P1—C3—H3B	108.8 (10)	P1—C2—H2C	108.3 (11)
P1—C3—H3C	108.3 (11)	H2A—C2—H2B	109.5 (14)
H3A—C3—H3B	108.9 (14)	H2A—C2—H2C	106.1 (13)
H3A—C3—H3C	108.2 (14)	H2B—C2—H2C	113.3 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O3	0.807 (17)	1.976 (18)	2.7787 (10)	173.2 (16)
O2—H3...O3	0.789 (18)	2.046 (18)	2.8261 (11)	169.7 (15)
O1—H2...O2 ⁱ	0.873 (18)	1.981 (18)	2.8460 (12)	170.6 (14)
O2—H4...O1 ⁱⁱ	0.834 (17)	1.993 (17)	2.8218 (11)	172.0 (14)

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