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Crystal structure of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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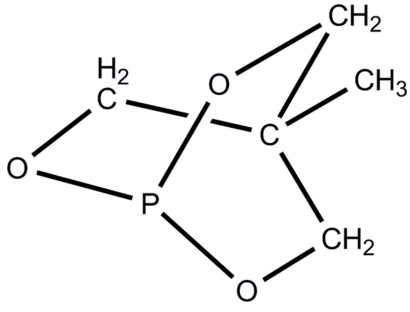
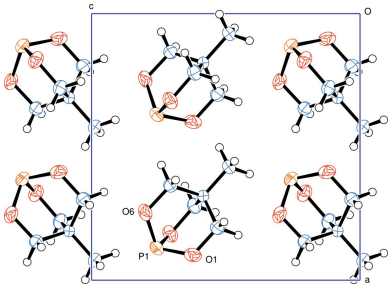
The title molecule, $C_5H_9O_3P$, has a bicyclo[2.2.2] structure with the P atom at the prow and the bridge-head C atom, with the bonded methyl group, at the stern. The three six-membered rings in the bicyclo[2.2.2] structure have essentially identical good boat conformations.

1. Chemical context

Phosphorus-based ligands bind strongly to transition metals and these complexes offer a wide range of properties due to the high volume of accessible substituents (Downing & Smith, 2004; Tolman, 1977; Joslin *et al.*, 2012). Complexation experiments with these ligands can yield mono- or bi-nuclear complexes (van den Beuken *et al.*, 1997). Phosphorus-based complexes are an important class of compounds in homogeneous catalysis and coordination chemistry (Downing & Smith, 2004; Kühl, 2005). In particular, we have noted interesting studies comparing the donor ability of bicyclic phosphites and the related acyclic phosphites; the phosphorus atom in the former shows more positive charge than in the acyclic phosphites and, hence, the donor ability of bicyclic phosphites is lower than that of the related acyclic phosphites (Vande Griend *et al.*, 1977; Joslin *et al.*, 2012). The present work is a continuation of an investigation into the synthesis and study of bi- and tri-cyclic, penta- and hexa-coordinated phosphoranes to form anionic, neutral and zwitterionic compounds (Said *et al.* 1996; Timosheva, *et al.* 2006; Kumara Swamy & Satish Kumar, 2006). In this paper, we report the synthesis, clean isolation and crystal structure of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (Tolman, 1977; Joslin *et al.*, 2012).





2. Structural commentary

The molecular structure of the title compound, Fig. 1, shows a bicyclo[2.2.2] structure with the phosphorus atom as one

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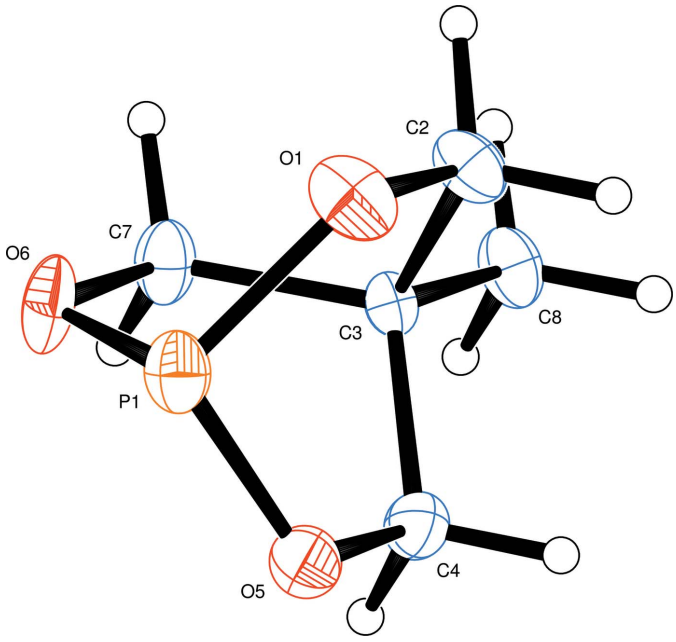
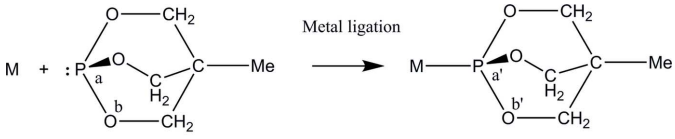


Figure 1
A view of a molecule of *bicyclo*-P(OCH$_2$)$_3$CMe, indicating the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

bridge-head atom and C3, with the bonded methyl group, as the other. The three six-membered rings in the bicyclo[2.2.2] structure have essentially identical, good boat conformations. The P—O bond lengths are very similar, lying in the range 1.613 (2)–1.616 (2) Å; the O—P—O angles at the prow have angles in the range 100.17 (9)–101.34 (10)°, whereas the C—P—C angles at the stern lie in the range 107.99 (17)–109.08 (18)°.



Scheme 1. Bicyclic phosphite upon metal ligation

A comparison between acyclic and bicyclic phosphites based on the 'hinge' effect has shown (Vande Griend *et al.*, 1977; Joslin *et al.*, 2012) that the O—P—O and P—O—C angles, a and b in Scheme 1, change upon ligation with a metal. Due to the steric profile of the bicyclic phosphite, the changes here in a, a′ and b, b′ upon metal ligation are less than in acyclic phosphites. Verkade had pointed out earlier that the *p*-orbital overlap between P and O in bicyclic phosphites is less than in acyclic phosphites, making P more positive and therefore reducing the basicity of P relative to that in acyclic phosphites (Vande Griend *et al.*, 1977); hence, the coordination ability of acyclic phosphites is higher than that of bicyclic phosphites (Verkade, 1972). A variety of multi-cyclic phosphorus compounds including their coordination to various metals has been studied. Based on the trends found in

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O6^{i}	0.97	2.58	3.495 (4)	158

Symmetry code: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z-\frac{1}{2}$.

basicity, it is expected that the title compound would show a donating ability to metal centres very similar to that of the more commonly studied bicyclic phosphite P(OCH$_2$)$_3$CEt (Verkade, 1972). The average of O—P—O bond angle (a, Scheme 1) in our study is 100.7°, whereas the average O—P—O bond angle in coordinated phosphites (a′, Scheme 1) is larger, *e.g.* in Ru{P(OCH$_2$)$_3$CEt}Cl$_2$, it is 102.5° (Joslin *et al.*, 2012), the same as in [Rh$_2$I$_2$(C$_6$H$_5$N$_2$O$_2$)$_2$(COMe)$_2${-P(OCH$_2$)$_3$CMe}$_2$] (Venter *et al.*, 2009); this suggests a slightly larger Tolman angle (Tolman *et al.*, 1977) after metal ligation. In another study, the enhanced π-accepting ability of the bicyclic phosphite ligand compared to the PPh$_3$ and other phosphine ligands was demonstrated clearly in the shorter *M*—P bond distances in the bicyclic phosphite complexes (Erasmus *et al.*, 1998).

3. Supramolecular features

Contacts between molecules are at normal van der Waals distances, the shortest of which is H4*B*···O6′, at 2.58 Å (Table 1). The nearest neighbours of the phosphorus atom are hydrogen atoms at distances of at least 3.09 Å. A view of the packing along the *b* axis is shown in Fig. 2.

4. Database survey

From a selection of crystal structure results for bicyclic phosphites from the Cambridge Structural Database (Groom *et al.*, 2016), we note that the P—O bond distances:

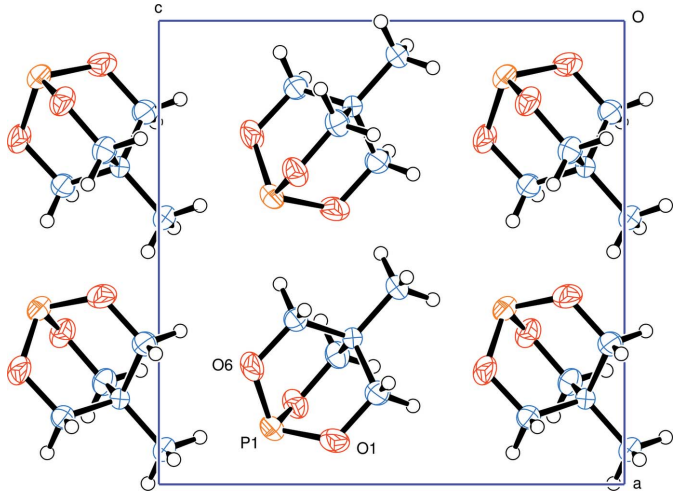


Figure 2
A view along the crystallographic *b* axis.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_9O_3P$
M_r	148.09
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	140
a, b, c (Å)	10.4408 (6), 6.2129 (5), 10.5052 (5)
V (Å^3)	681.45 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.34
Crystal size (mm)	0.65 × 0.17 × 0.07
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3/ Sapphire3 CCD
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.684, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10309, 1561, 1405
R_{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.084, 1.11
No. of reflections	1561
No. of parameters	82
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.12
Absolute structure	Flack x determined using 605 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.07 (6)

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEPIII* (Johnson, 1976) and *ORTEP-3 for Windows* (Farrugia, 2012) and *WinGX* (Farrugia, 2012).

1) are shortest in phosphonium ions, as in $[Ph_3C\{P(OCH_2)_3CMe\}]^+$ (Fang *et al.*, 2000), at *ca* 1.552 Å,

2) in the phosphates, as O═P$(OCH_2)_3$C*R*, (*e.g.* Nimrod *et al.*, 1968; Santarsiero, 1992) are *ca* 1.57 Å,

3) in the metal-coordinated phosphites, *M*–{P$(OCH_2)_3$CR} (*e.g.* Aroney *et al.*, 1994; Venter *et al.*, 2009; Davis & Verkade, 1990; Predvoditelev *et al.*, 2009; Basson *et al.*, 1992; Erasmus *et al.*, 1998; Joslin *et al.*, 2012; Albright *et al.*, 1977) are *ca* 1.59 Å, and

4) in our results, correlate with those of other unsubstituted phosphites, (*e.g.* Wojczykowski & Jutzi, 2006; Milbrath *et al.*, 1976; Predvoditelev *et al.*, 2009) with P—O bond lengths of *ca* 1.62 Å.

Within each group, there is very little variation in the P—O distances. The bond angles in the bicyclic structure are quite constrained, but we do note a trend, down the four groups of increasing P—O distances, of a corresponding decrease in O—P—O angles from *ca* 107 to 100°.

5. Synthesis and crystallization

To 4.26 g (35.46 mmol) of 2-(hydroxymethyl)-2-methylpropane-1,3-diol in 70 mL of dry benzene at RT was added 4.26 g (106.38 mmoles in mineral oil 60%) of NaH in small portions over a period of 20 minutes. The mixture was stirred for 3h before 4.87 g (35.46 mmol) of PCl_3 were added dropwise over a period of 20 mins in benzene (10 mL) using a dropping funnel. The reaction mixture was stirred overnight before NaCl was removed by filtration under nitrogen cover. Benzene was removed completely under low pressure. 5 mL of diethyl ether was added, followed by 3 mL of *n*-hexane. The mixture was placed in deep freeze to afford the title compound as a white solid (yield 4.52 g, 86%; m.p. 369–373 K). The product was purified further by sublimation at 393 K/0.5 mm to yield crystals. ^{1}H NMR (CDCl3, 400 MHz): 0.73 (*s*, 3H, CH_3), 3.94 (*s*, 6H, CH_2). ^{13}C NMR ($CDCl_3$, 400 MHz): 16.60 (*s*, 1C, CH3), 31.98 [*d*, 1C, C$(CH_3)_3$], 71.80 (*s*, 3C, CH_2). ^{31}P NMR ($CDCl_3$, 400 MHz): 91.45 p.p.m. IR cm^{-1}: 2950, 1380. Elemental analysis: calculated: C, 40.55; H, 6.13; found: C, 40.83; H, 6.19.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

The H atoms were included in idealized positions and treated as riding atoms: C—H = 0.93– 0.97 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and = 1.2U_{eq}(C) for methylene H atoms.

Acknowledgements

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supporting information

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Crystal structure of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEPIII* (Johnson, 1976) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012).

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

Crystal data

$C_5H_9O_3P$
M_r = 148.09
Orthorhombic, $Pna2_1$
a = 10.4408 (6) Å
b = 6.2129 (5) Å
c = 10.5052 (5) Å
V = 681.45 (7) Å^3
Z = 4
F(000) = 312
D_x = 1.443 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2685 reflections
θ = 3.3–32.3°
μ = 0.34 mm^{-1}
T = 140 K
Prism, colourless
0.65 × 0.17 × 0.07 mm

Data collection

Oxford Diffraction Xcalibur 3/Sapphire3 CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0050 pixels mm^{-1}
Thin slice φ and ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2013)
T_{min} = 0.684, T_{max} = 1.000
10309 measured reflections
1561 independent reflections
1405 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.5°, θ_{min} = 3.8°
h = −13→13
k = −8→8
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.084
S = 1.11
1561 reflections
82 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.0252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Absolute structure: Flack *x* determined using 605 quotients $[(I^{+})-(I^{-})]/[(I^{+})+(I^{-})]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.07 (6)

Special details

Experimental. CrysAlisPro, Agilent Technologies, Version 1.171.36.21 Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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	0.87893 (7)	0.45449 (13)	0.75670 (8)	0.0380 (2)
O1	0.9057 (2)	0.5737 (4)	0.6228 (3)	0.0470 (6)
C2	0.8029 (3)	0.5722 (6)	0.5302 (3)	0.0373 (7)
H2A	0.8308	0.4974	0.4541	0.045*
H2B	0.7816	0.7189	0.5068	0.045*
C3	0.6847 (2)	0.4614 (5)	0.5841 (2)	0.0253 (5)
C4	0.7208 (3)	0.2300 (4)	0.6164 (3)	0.0349 (6)
H4A	0.6473	0.1566	0.6524	0.042*
H4B	0.7456	0.1549	0.5393	0.042*
O5	0.8263 (2)	0.2254 (4)	0.7070 (2)	0.0399 (5)
O6	0.7460 (2)	0.5660 (4)	0.7998 (2)	0.0457 (7)
C7	0.6445 (3)	0.5749 (6)	0.7058 (3)	0.0371 (7)
H7A	0.6242	0.7240	0.6871	0.045*
H7B	0.5681	0.5070	0.7397	0.045*
C8	0.5752 (3)	0.4642 (6)	0.4878 (3)	0.0370 (7)
H8A	0.6017	0.3921	0.4113	0.055*
H8B	0.5021	0.3919	0.5231	0.055*
H8C	0.5530	0.6105	0.4683	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0322 (4)	0.0504 (4)	0.0314 (4)	0.0023 (3)	−0.0076 (4)	−0.0037 (5)
O1	0.0297 (11)	0.0630 (15)	0.0483 (14)	−0.0148 (10)	−0.0050 (10)	0.0112 (12)
C2	0.0313 (15)	0.047 (2)	0.0340 (16)	−0.0046 (13)	−0.0002 (13)	0.0088 (13)
C3	0.0232 (12)	0.0319 (13)	0.0209 (13)	−0.0003 (11)	−0.0002 (10)	−0.0004 (11)
C4	0.0391 (16)	0.0332 (15)	0.0323 (14)	0.0001 (13)	−0.0036 (12)	−0.0026 (13)
O5	0.0448 (12)	0.0399 (12)	0.0350 (11)	0.0094 (10)	−0.0096 (9)	0.0025 (9)
O6	0.0455 (13)	0.0625 (17)	0.0292 (11)	0.0128 (11)	−0.0079 (9)	−0.0209 (10)
C7	0.0295 (16)	0.0508 (18)	0.0310 (14)	0.0082 (13)	−0.0008 (12)	−0.0080 (13)
C8	0.0305 (16)	0.053 (2)	0.0274 (15)	−0.0001 (14)	−0.0049 (12)	0.0014 (13)

Geometric parameters (Å, º)

P1—O5	1.613 (2)	C4—O5	1.456 (4)
P1—O1	1.614 (3)	C4—H4A	0.9700
P1—O6	1.616 (2)	C4—H4B	0.9700
O1—C2	1.449 (4)	O6—C7	1.450 (4)
C2—C3	1.522 (4)	C7—H7A	0.9700
C2—H2A	0.9700	C7—H7B	0.9700
C2—H2B	0.9700	C8—H8A	0.9600
C3—C7	1.519 (4)	C8—H8B	0.9600
C3—C4	1.524 (4)	C8—H8C	0.9600
C3—C8	1.527 (4)		
O5—P1—O1	100.46 (13)	C3—C4—H4A	109.5
O5—P1—O6	100.17 (13)	O5—C4—H4B	109.5
O1—P1—O6	101.34 (14)	C3—C4—H4B	109.5
C2—O1—P1	117.00 (18)	H4A—C4—H4B	108.1
O1—C2—C3	110.7 (2)	C4—O5—P1	116.88 (18)
O1—C2—H2A	109.5	C7—O6—P1	116.95 (18)
C3—C2—H2A	109.5	O6—C7—C3	110.7 (2)
O1—C2—H2B	109.5	O6—C7—H7A	109.5
C3—C2—H2B	109.5	C3—C7—H7A	109.5
H2A—C2—H2B	108.1	O6—C7—H7B	109.5
C7—C3—C2	109.1 (3)	C3—C7—H7B	109.5
C7—C3—C4	108.6 (2)	H7A—C7—H7B	108.1
C2—C3—C4	108.0 (2)	C3—C8—H8A	109.5
C7—C3—C8	110.2 (2)	C3—C8—H8B	109.5
C2—C3—C8	110.8 (2)	H8A—C8—H8B	109.5
C4—C3—C8	110.1 (2)	C3—C8—H8C	109.5
O5—C4—C3	110.5 (2)	H8A—C8—H8C	109.5
O5—C4—H4A	109.5	H8B—C8—H8C	109.5
O5—P1—O1—C2	50.4 (3)	C3—C4—O5—P1	1.8 (3)
O6—P1—O1—C2	−52.3 (3)	O1—P1—O5—C4	−52.8 (2)
P1—O1—C2—C3	2.4 (4)	O6—P1—O5—C4	50.8 (2)
O1—C2—C3—C7	57.2 (3)	O5—P1—O6—C7	−54.0 (3)
O1—C2—C3—C4	−60.7 (3)	O1—P1—O6—C7	49.0 (3)
O1—C2—C3—C8	178.7 (3)	P1—O6—C7—C3	3.3 (4)
C7—C3—C4—O5	−60.0 (3)	C2—C3—C7—O6	−60.4 (3)
C2—C3—C4—O5	58.2 (3)	C4—C3—C7—O6	57.1 (3)
C8—C3—C4—O5	179.2 (2)	C8—C3—C7—O6	177.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O6^{i}	0.97	2.58	3.495 (4)	158

Symmetry code: (i) −*x*+3/2, *y*−1/2, *z*−1/2.