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Triethynylphosphine oxide

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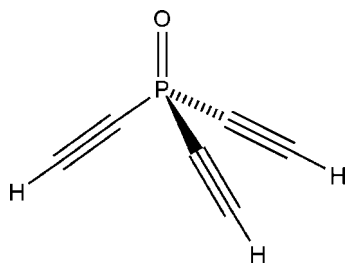
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
R factor = 0.030; wR factor = 0.084; data-to-parameter ratio = 19.1.

In the solid state, the title compound, $\text{C}_6\text{H}_3\text{OP}$, lies on a crystallographic mirror plane, with the $\text{P}=\text{O}$ as well as one of the acetylene units bisected by this plane. The central P atom exhibits pseudo-tetrahedral geometry. The crystallographic packing is dominated by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds between all of the acetylene H atoms and the O atom, which form a heavily interconnected hydrogen-bonding network. Two of the hydrogen bonds, related by the mirror plane, are coplanar with each other and with the $\text{P}=\text{O}$ unit, while the third $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond is at an angle of 67.49 (7) $^\circ$ to this plane; the $\text{H}\cdots\text{P}=\text{O}$ angles are 134 and 112 $^\circ$, respectively. The three-dimensional structure formed by the hydrogen-bond interactions consists of two independent interpenetrating networks.

Related literature

For geometry, see: Allen (2002); Herbstein (2000). For NMR data, see: Yang *et al.* (1992); Rosenberg & Drenth (1972).



Experimental

Crystal data

$\text{C}_6\text{H}_3\text{OP}$
 $M_r = 122.05$
Orthorhombic, $Pnma$

$a = 6.8646$ (9) Å
 $b = 9.7823$ (13) Å
 $c = 9.3277$ (12) Å

$V = 626.37$ (14) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 0.33$ mm⁻¹
 $T = 100$ (2) K
 $0.48 \times 0.23 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD
diffractometer
Absorption correction: multi-scan
(*SADABS* in *SAINTE-Plus*;
Bruker, 2003)
 $T_{\min} = 0.708$, $T_{\max} = 0.930$

7459 measured reflections
821 independent reflections
796 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.084$
 $S = 1.12$
821 reflections

43 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------------------------------|-------------|-----------------------------------|------------|
| $\text{P1}-\text{C1}^i$ | 1.7443 (12) | | |
| $\text{O1}-\text{P1}-\text{C1}^i$ | 113.25 (5) | $\text{C1}-\text{P1}-\text{C1}^i$ | 104.52 (8) |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C4}-\text{H4}\cdots\text{O1}^{\text{ii}}$ | 0.95 | 2.26 | 3.210 (2) | 179 |
| $\text{C2}-\text{H2}\cdots\text{O1}^{\text{iii}}$ | 0.95 | 2.30 | 3.2433 (14) | 174 |

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE-Plus* (Bruker, 2003); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The diffractometer was funded by NSF grant 0087210, by Ohio Board of Regents grant CAP-491, and by YSU.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2164).

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Triethynylphosphine oxide

R. Kallamadi, J. A. Jackson and M. Zeller

Comment

As an aspect of our research into the Diels-Alder chemistry of electron poor alkynyl phosphonates we attempted the synthesis of bis(2,2,2-trifluoroethyl)(trimethylsilyl)ethynyl phosphonate by reacting lithium trimethylsilyl acetylide with bis(2,2,2-trifluoroethyl)phosphorochloridate as shown in Figure 1. Displacement of not only the chlorine but also of the two $-\text{OCH}_2\text{CF}_3$ groups resulted, after aqueous workup and loss of the trimethylsilyl group, in the unplanned formation of triethynylphosphine oxide in 25% yield. While the triethynylphosphine oxide is mentioned in some spectroscopic publications (Yang *et al.*, 1992; Rosenberg & Drenth, 1972) no synthesis is reported in the scientific literature.

In the solid state the title compound is found to be located on a crystallographic mirror plane with the P=O as well as one of the acetylene units bisected by this plane (Figure 2). The phosphorus center exhibits pseudo-tetrahedral geometry with three acetylene substituents and the double bonded oxygen atom. The bond distances and angles are unexceptional.

Crystal packing is dominated by hydrogen bonds between the acetylenic H atoms and the P=O oxygen with all three acetylene units forming relatively strong C—H \cdots O hydrogen bonds. Two of the three hydrogen bonds towards each oxygen atom are symmetry related by the crystallographic mirror plane and are coplanar with each other and the P=O unit. The third C—H \cdots O hydrogen bond is at an angle of 67.49 (7) ° to this plane (as given by the angles between the lines defined by P1—O1 and O1—C4ⁱⁱⁱ (symmetry code $iv = x - 1, y, z$). (Figure 3)

The Cambridge crystallographic database does not have any other entries for hydrogen bonds between acetylene and O=P units, but the parameters observed here are in good agreement with those listed for hydrogen bonds towards other O=X units such as ketones or aldehydes (Cambridge Structural Database, V5.28; Allen 2002). The H \cdots P=O angles of the title compound are 133.70° for H2^v \cdots O1—P1 and 112.35° for H4^{iv} \cdots O1—P1, respectively (symmetry code $v = 1/2 - x, 1 - y, 1 - z$).

The three dimensional crystal structure thus formed by the hydrogen bonding interactions actually consists of two interpenetrating networks that are each heavily interconnected *via* H-bonding, but that are not connected *via* such interactions with each other (Figures 4 and 5).

Experimental

To a solution of trimethylsilylacetylene (5 mmol, 0.71 ml) in anhydrous pentane (5 ml) and anhydrous ether (5 ml), was added n-BuLi (1.6 M) solution in hexane (6 mmol, 3.8 ml) in a dropwise manner at 195 K (−78 °C). The reaction solution was stirred continuously for 1 h. Then bis(2,2,2-trifluoroethyl)phosphorochloridate was added dropwise at the same temperature and the mixture was stirred for an additional hour. The reaction solution was stirred overnight at ambient temperature and was then quenched with a saturated aqueous solution of ammonium chloride. The organic layer was separated and washed with water. The aqueous layers were washed with ether, and the organic fractions were combined, washed with saturated NaCl solution and dried over MgSO₄. The oxide was purified by column chromatography (hexane/ethyl acetate, 1/1) and

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crystals of sufficient quality for single-crystal diffraction analysis were obtained from ethyl acetate by slow evaporation. ^1H NMR (400 MHz, CDCl_3) δ 3.30 (d, 3H, $J = 12.45$ Hz), ^{13}C NMR (100 MHz) δ 92.12 (d, 3 C, $J = 45.45$ Hz), 77.35 (d, 3 C, $J = 233.88$ Hz), ^{31}P NMR (162 MHz) δ -55.3..

Refinement

Treatment of hydrogen atoms: All hydrogen atoms were added in calculated positions with a C—H bond distance of 0.95 Å and were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

The e.s.d. values of the cell parameters are taken from the software recognizing that the values are unreasonably small (Herbstein, 2000).

Figures



Fig. 1. Synthesis of the title compound.

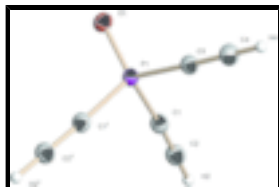


Fig. 2. Molecular structure showing 50% probability displacement ellipsoids (symmetry code i: $x, -y + 3/2, z$).

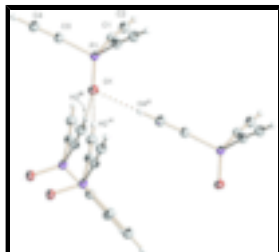


Fig. 3. Hydrogen bonding environment for one P=O unit, 50% probability displacement ellipsoids. Hydrogen bonds are indicated by dotted lines (symmetry codes: ii = $x + 1, y, z$; iii = $-x + 1/2, -y + 1, z + 1/2$; vi = $-x + 1, y + 1/2, z + 1/2$).

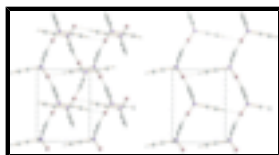


Fig. 4. Packing view along the b axis, 50% probability displacement ellipsoids. Hydrogen bonds are indicated as dotted lines. Left: both interpenetrating networks shown, right: only one of the interpenetrating networks shown.



Fig. 5. Packing view along the a axis, 50% probability displacement ellipsoids. Hydrogen bonds are indicated as dotted lines. Left: both interpenetrating networks shown, right: only one of the interpenetrating networks shown.

Triethynylphosphine oxide

Crystal data

$\text{C}_6\text{H}_3\text{OP}$

$M_r = 122.05$

$D_x = 1.294 \text{ Mg m}^{-3}$

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

Orthorhombic, *Pnma*

$a = 6.8646$ (9) Å

$b = 9.7823$ (13) Å

$c = 9.3277$ (12) Å

$V = 626.37$ (14) Å³

$Z = 4$

$F_{000} = 248$

Cell parameters from 7248 reflections

$\theta = 3.0\text{--}30.6^\circ$

$\mu = 0.33$ mm⁻¹

$T = 100$ (2) K

Block, colorless

$0.48 \times 0.23 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100$ (2) K

ω scans

Absorption correction: multi-scan
(SADABS in SAINT-Plus; Bruker, 2003)

$T_{\min} = 0.708$, $T_{\max} = 0.930$

7459 measured reflections

821 independent reflections

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

$R_{\text{int}} = 0.018$

$\theta_{\max} = 28.3^\circ$

$\theta_{\min} = 3.0^\circ$

$h = -9 \rightarrow 9$

$k = -13 \rightarrow 13$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.084$

$S = 1.12$

821 reflections

43 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.2795P]$

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

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

$\Delta\rho_{\max} = 0.45$ e Å⁻³

$\Delta\rho_{\min} = -0.33$ e Å⁻³

Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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.

supplementary materials

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 | 0.42049 (6) | 0.7500 | 0.53431 (4) | 0.01596 (17) |
| O1 | 0.29767 (18) | 0.7500 | 0.40356 (13) | 0.0205 (3) |
| C1 | 0.37974 (17) | 0.60900 (12) | 0.64477 (12) | 0.0199 (2) |
| C4 | 0.8405 (3) | 0.7500 | 0.47595 (18) | 0.0235 (4) |
| H4 | 0.9760 | 0.7500 | 0.4552 | 0.028* |
| C3 | 0.6715 (3) | 0.7500 | 0.50180 (18) | 0.0191 (3) |
| C2 | 0.33869 (17) | 0.51443 (13) | 0.71937 (12) | 0.0230 (3) |
| H2 | 0.3060 | 0.4390 | 0.7788 | 0.028* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|---------------|-------------|
| P1 | 0.0142 (2) | 0.0159 (2) | 0.0178 (2) | 0.000 | -0.00015 (13) | 0.000 |
| O1 | 0.0186 (6) | 0.0219 (6) | 0.0209 (6) | 0.000 | -0.0035 (4) | 0.000 |
| C1 | 0.0181 (5) | 0.0199 (5) | 0.0217 (5) | 0.0000 (4) | 0.0004 (4) | -0.0012 (4) |
| C4 | 0.0196 (9) | 0.0248 (9) | 0.0261 (9) | 0.000 | 0.0001 (6) | 0.000 |
| C3 | 0.0190 (8) | 0.0182 (7) | 0.0200 (7) | 0.000 | 0.0007 (6) | 0.000 |
| C2 | 0.0227 (6) | 0.0222 (6) | 0.0242 (6) | -0.0002 (4) | 0.0022 (4) | -0.0001 (5) |

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

| | | | |
|-----------------------|-------------|------------------------|-------------|
| P1—O1 | 1.4826 (12) | C1—C2 | 1.1914 (17) |
| P1—C1 | 1.7443 (12) | C4—C3 | 1.185 (3) |
| P1—C1 ⁱ | 1.7443 (12) | C4—H4 | 0.9500 |
| P1—C3 | 1.7495 (18) | C2—H2 | 0.9500 |
| O1—P1—C1 | 113.25 (5) | C1 ⁱ —P1—C3 | 105.09 (5) |
| O1—P1—C1 ⁱ | 113.25 (5) | C2—C1—P1 | 175.54 (11) |
| C1—P1—C1 ⁱ | 104.52 (8) | C3—C4—H4 | 180.0 |
| O1—P1—C3 | 114.67 (8) | C4—C3—P1 | 178.24 (17) |
| C1—P1—C3 | 105.09 (5) | C1—C2—H2 | 180.0 |

Symmetry codes: (i) $x, -y+3/2, z$.

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| C4—H4 \cdots O1 ⁱⁱ | 0.95 | 2.26 | 3.210 (2) | 179 |
| C2—H2 \cdots O1 ⁱⁱⁱ | 0.95 | 2.30 | 3.2433 (14) | 174 |

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

Fig. 1

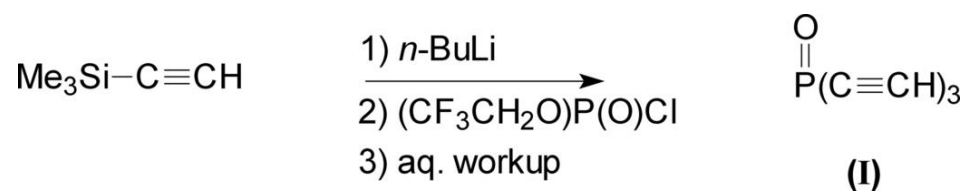


Fig. 2

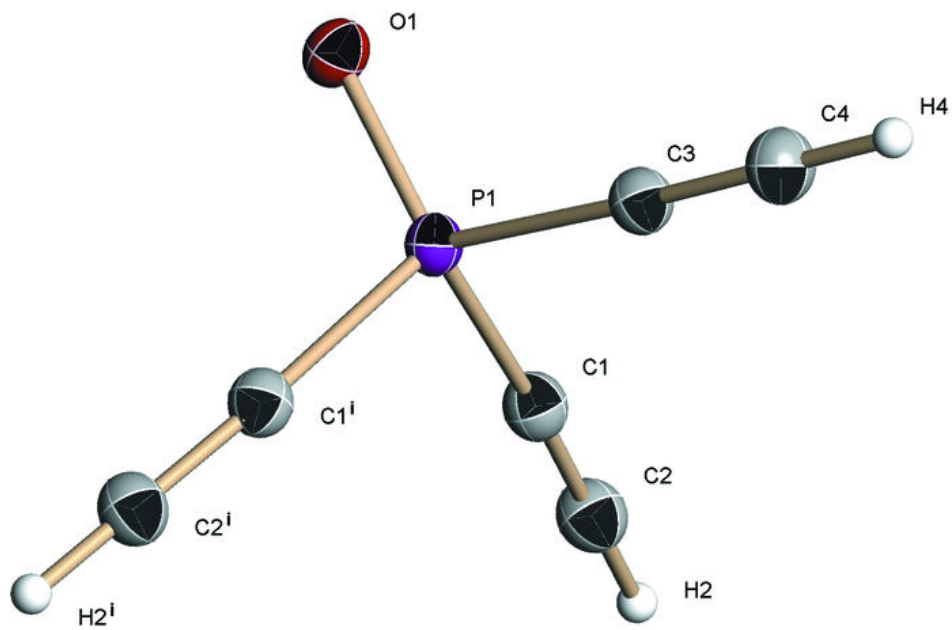


Fig. 3

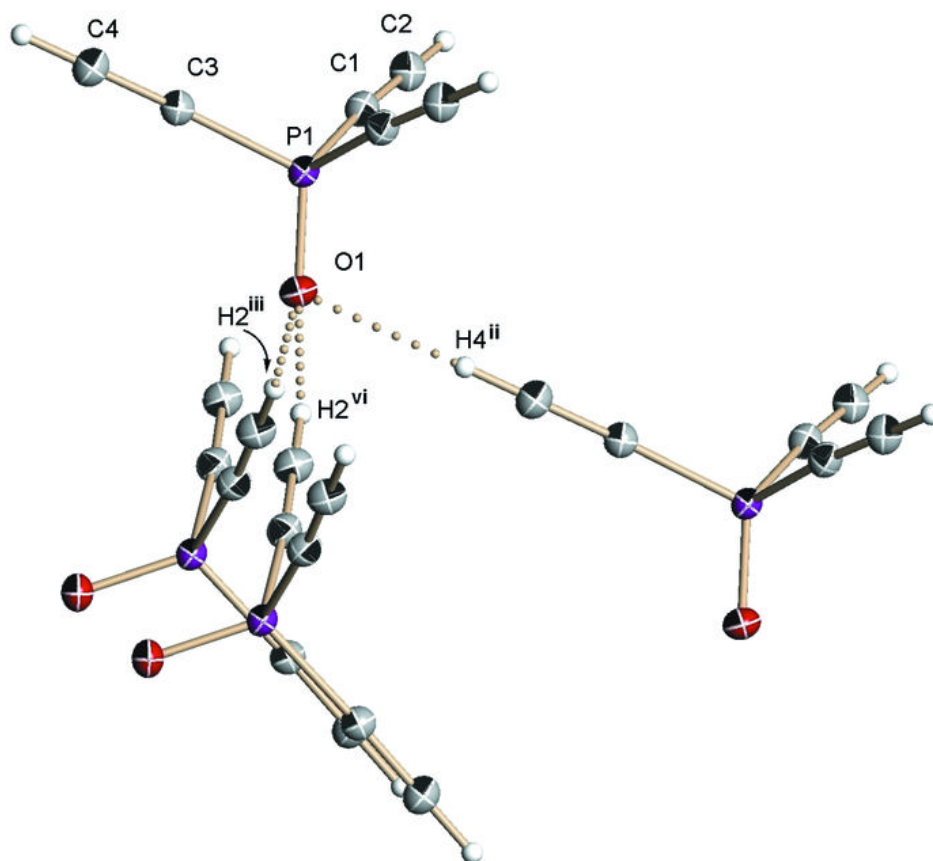


Fig. 4

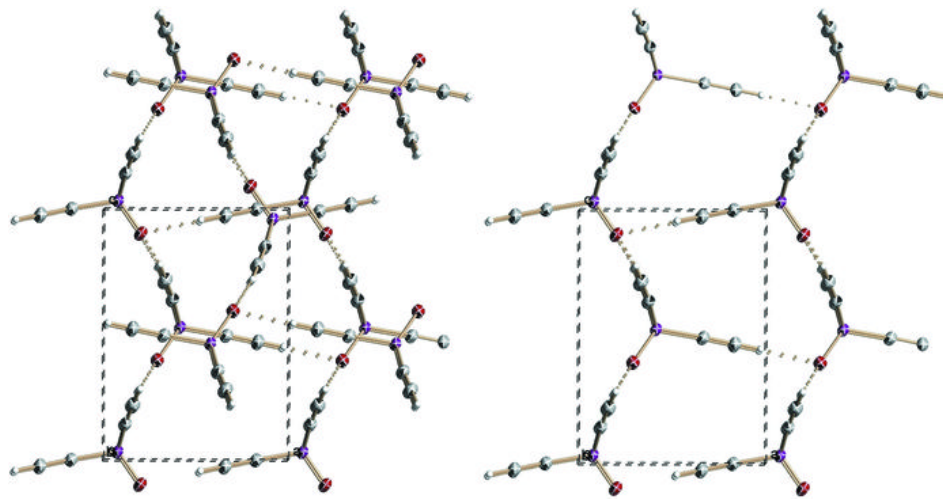


Fig. 5

