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## Tris(*n*-butyl)phosphine, Tris(*tert*-butyl)phosphine and Tris(trimethylsilyl)phosphine

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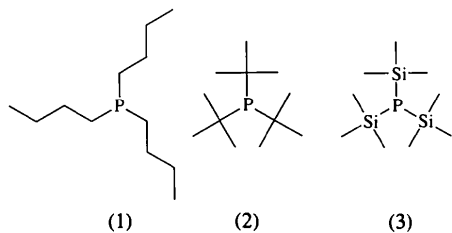
(Received 24 August 1994; accepted 9 December 1994)

### Abstract

Single crystals of the title compounds, C<sub>12</sub>H<sub>27</sub>P (1), C<sub>12</sub>H<sub>27</sub>P (2), and C<sub>9</sub>H<sub>27</sub>PSi<sub>3</sub> (3), were grown in capillaries at low temperature using zone-melting techniques [Brodalla, Mootz, Boese & Osswald (1985). *J. Appl. Cryst.* **18**, 316–319]. The molecular and crystal structures of all three compounds were determined at 102 K. Compound (1) has a pseudo-mirror plane and C—P—C angles between 100.5 (1) and 102.7 (1)°. Compound (2) has a pseudosymmetric threefold rotation axis and C—P—C angles of 107.1 (1), 107.4 (1) and 107.8 (1)°. Isomorphous compound (3) has Si—P—Si angles between 105.8 (1) and 106.5 (1)°.

### Comment

In our systematic investigation of phosphine ligands, we crystallized tris(*n*-butyl)phosphine [P(*n*-butyl)<sub>3</sub>], (1). The C—P—C angles are between 100.5 (1) and 102.7 (1)° (Table 2, Fig. 1). These values are as expected for non-bulky and flexible ligands such as *n*-butyl. The C—C distances tend to lower values with increasing distance from the P atom (Table 2). The C atoms of each



*n*-butyl group compose a plane [torsion angles range from 177.3 (3) to 179.3 (3)°]. Plane 1 (C1, C2, C3, C4)

and plane 2 (C5, C6, C7, C8) are oriented nearly parallel to one another [the dihedral angle between 1 and 2 is 5 (1)°], and both are almost perpendicular to plane 3 (P, C9, C10, C11, C12) [the dihedral angles between 1 and 3, and 2 and 3 are 90 (1) and 95 (1)°, respectively]. Plane 3 is an approximate mirror. The cone angle  $\theta$  (for a definition see Tolman, 1977; Bruckmann & Krüger, 1995) is determined as  $159 \pm 2^\circ$ . Tolman (1970) measured  $130 \pm 4^\circ$  as the minimum cone angle, using CPK atomic models, by folding back the flexible substituents on the P atom, while maintaining threefold symmetry (Tolman, 1970, 1977).

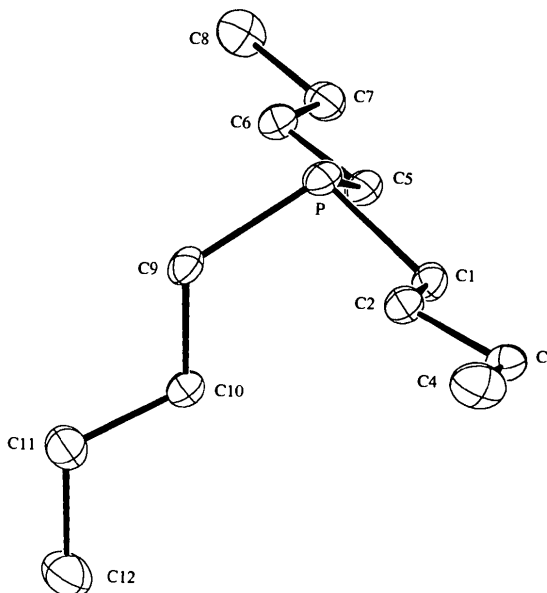


Fig. 1. An ORTEP (Johnson, 1976) view of P(*n*-butyl)<sub>3</sub> with displacement ellipsoids drawn at the 50% probability level.

The dimensions and general molecular structure of tris(*tert*-butyl)phosphine [P(*tert*-butyl)<sub>3</sub>], (2), are as expected. Although the *tert*-butyl groups are crystallographically independent, they are arranged in a pseudosymmetric way generated by a threefold rotation axis passing through the P atom (Fig. 2). Corresponding angles show no significant differences, but five of the six tetrahedral angles at every tertiary C atom are significantly different. All C—C distances are within the same range (Table 4). H atoms were located and are in good agreement with the threefold pseudosymmetry. In (2), the C—P—C angles are widened to 107.1 (1), 107.4 (1) and 107.8 (1)° by steric effects. These effects are also evident from the large angles involving the P atom, the tertiary C atoms and atoms C4, C7 and C12 [118.0 (1), 117.8 (1) and 117.4 (1)°, respectively]. The values of all other P—C—C angles are about 10° smaller (Table 4). The P—C distances are more than 0.06 Å longer than in (1). This reflects the bulkiness of the *tert*-butyl groups. The cone angle  $\theta$  is  $176 \pm 2^\circ$  and differs slightly from the value of  $182 \pm 2^\circ$  given by Tolman (1970).

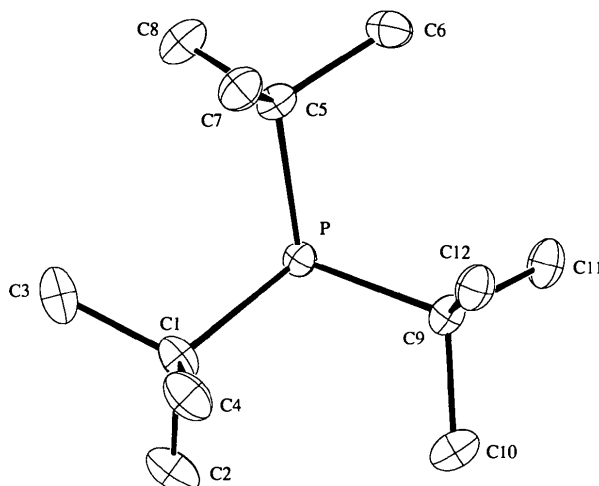


Fig. 2. An ORTEP drawing of  $P(\text{tert-butyl})_3$  with 50% probability displacement ellipsoids.

Crystals of tris(trimethylsilyl)phosphine [ $P(\text{trimethylsilyl})_3$ ], (3), are isomorphous with those of  $P(\text{tert-butyl})_3$  (Fig. 3). Because of the larger Si atoms replacing the tertiary C atoms, compound (3) is less strained, as can be seen from the Si—P—Si angles [105.8 (1), 105.8 (1) and 106.5 (1)°], as well as from the angles involving P, Si, and either C1, C4 or C7 [115.5 (1), 116.5 (1) and 116.0 (1)°, respectively]. All other angles at the Si atoms are close to tetrahedral angles. There are no more significant differences in the pertinent angles (Table 6). The cone angle  $\theta$  of (3) is  $178 \pm 2^\circ$ .

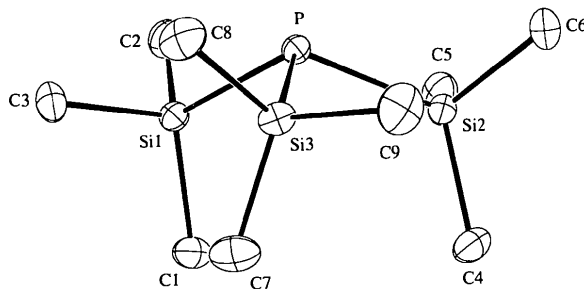


Fig. 3. An ORTEP plot of  $P(\text{trimethylsilyl})_3$  with displacement ellipsoids shown at the 50% probability level.

## Experimental

All three title compounds were grown by a zone-melting technique in an argon-filled capillary of diameter 0.2 mm with a focused halogen lamp as heat source (Brodalla *et al.*, 1985). Compound (1) used pentane solvent and had a  $T_{\text{melt}}$  of 213 and a  $T_{\text{growth}}$  of 195 K. Compound (2) used a pentane solvent,  $T_{\text{melt}} = 292$  and  $T_{\text{growth}} = 281$  K. Compound (3) had  $T_{\text{melt}} = 295$  and  $T_{\text{growth}} = 293$  K.

### Compound (1)

#### Crystal data

$\text{C}_{12}\text{H}_{27}\text{P}$   
 $M_r = 202.32$

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

Monoclinic  
 $P2_1/n$   
 $a = 12.569 (4) \text{ \AA}$   
 $b = 5.1148 (7) \text{ \AA}$   
 $c = 21.74 (1) \text{ \AA}$   
 $\beta = 104.04 (4)^\circ$   
 $V = 1356.1 (8) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 0.99 \text{ Mg m}^{-3}$

#### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
Absorption correction: none  
3441 measured reflections  
3011 independent reflections  
2482 observed reflections [ $I > 2\sigma(I)$ ]

Cell parameters from 25 reflections  
 $\theta = 6-18^\circ$   
 $\mu = 0.162 \text{ mm}^{-1}$   
 $T = 102 \text{ K}$   
Cylindrical  
height: 0.6 mm  
diameter: 0.2 mm  
Colourless

$R_{\text{int}} = 0.0058$   
 $\theta_{\text{max}} = 27.4^\circ$   
 $h = -15 \rightarrow 15$   
 $k = 0 \rightarrow 6$   
 $l = 0 \rightarrow 28$   
3 standard reflections  
frequency: 30 min  
intensity decay: 11.4%

#### Refinement

Refinement on  $F$   
 $R = 0.041$   
 $wR = 0.049$   
 $S = 2.0$   
2482 reflections  
226 parameters  
All H-atom parameters refined isotropically

$w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0.04$   
 $\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$   
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (1)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
P	0.1600 (1)	0.0006 (1)	0.0314 (1)	0.019 (1)
C(1)	0.1422 (1)	-0.2244 (3)	-0.0366 (1)	0.019 (1)
C(2)	0.1820 (1)	-0.1032 (3)	-0.0911 (1)	0.020 (1)
C(3)	0.1438 (1)	-0.2512 (4)	-0.1533 (1)	0.023 (1)
C(4)	0.1853 (2)	-0.1295 (5)	-0.2067 (1)	0.034 (1)
C(5)	0.1255 (1)	-0.2177 (3)	0.0910 (1)	0.019 (1)
C(6)	0.1466 (1)	-0.0904 (3)	0.1564 (1)	0.020 (1)
C(7)	0.0926 (1)	-0.2337 (3)	0.2020 (1)	0.022 (1)
C(8)	0.1110 (2)	-0.1032 (4)	0.2663 (1)	0.029 (1)
C(9)	0.3107 (1)	0.0256 (3)	0.0581 (1)	0.020 (1)
C(10)	0.3787 (1)	-0.2241 (3)	0.0701 (1)	0.021 (1)
C(11)	0.5014 (1)	-0.1708 (4)	0.0920 (1)	0.029 (1)
C(12)	0.5700 (2)	-0.4175 (4)	0.1011 (1)	0.033 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1)

P—C(1)	1.843 (2)	P—C(5)	1.841 (2)
P—C(9)	1.847 (2)	C(1)—C(2)	1.527 (2)
C(2)—C(3)	1.523 (2)	C(3)—C(4)	1.517 (3)
C(5)—C(6)	1.528 (2)	C(6)—C(7)	1.520 (2)
C(7)—C(8)	1.515 (3)	C(9)—C(10)	1.525 (2)
C(10)—C(11)	1.525 (2)	C(11)—C(12)	1.514 (3)
C(9)—P—C(5)	102.7 (1)	C(9)—P—C(1)	102.2 (1)
C(5)—P—C(1)	100.5 (1)	C(2)—C(1)—P	111.7 (1)
C(3)—C(2)—C(1)	113.3 (1)	C(4)—C(3)—C(2)	112.5 (2)
C(6)—C(5)—P	112.3 (1)	C(7)—C(6)—C(5)	113.4 (1)
C(8)—C(7)—C(6)	113.4 (1)	C(10)—C(9)—P	119.1 (1)
C(11)—C(10)—C(9)	112.7 (1)	C(12)—C(11)—C(10)	113.1 (2)

**Compound (2)***Crystal data*C<sub>12</sub>H<sub>27</sub>P*M<sub>r</sub>* = 202.32

Monoclinic

P2<sub>1</sub>/n*a* = 9.219 (1) Å*b* = 13.768 (5) Å*c* = 11.133 (2) Å

β = 111.36 (1)°

*V* = 1316.0 (6) Å<sup>3</sup>*Z* = 4*D<sub>x</sub>* = 1.02 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 8–16°

μ = 0.167 mm<sup>-1</sup>*T* = 102 K

Cylindrical

height: 0.4 mm

diameter: 0.2 mm

Colourless

C(9)—P—C(5)	107.1 (1)
C(5)—P—C(1)	107.8 (1)
C(4)—C(1)—C(2)	109.2 (2)
C(3)—C(1)—C(2)	105.2 (2)
C(2)—C(1)—P	106.9 (1)
C(8)—C(5)—C(6)	105.1 (1)
C(7)—C(5)—C(6)	108.2 (1)
C(6)—C(5)—P	108.8 (1)
C(12)—C(9)—C(10)	108.2 (1)
C(11)—C(9)—C(10)	105.0 (1)
C(10)—C(9)—P	109.0 (1)

C(9)—P—C(1)	107.4 (1)
C(4)—C(1)—C(3)	108.2 (1)
C(4)—C(1)—P	118.0 (1)
C(3)—C(1)—P	108.6 (1)
C(8)—C(5)—C(7)	109.4 (1)
C(8)—C(5)—P	106.9 (1)
C(7)—C(5)—P	117.8 (1)
C(12)—C(9)—C(11)	109.3 (1)
C(12)—C(9)—P	117.4 (1)
C(11)—C(9)—P	107.2 (1)

*Data collection*

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction: none

3270 measured reflections

2973 independent reflections

2412 observed reflections

[*I* > 2σ(*I*)]*R*<sub>int</sub> = 0.0071θ<sub>max</sub> = 27.4°*h* = -11 → 11*k* = 0 → 17*l* = 0 → 14

3 standard reflections

frequency: 30 min

intensity decay: 6.9%

*Refinement*Refinement on *F**R* = 0.040*wR* = 0.045*S* = 1.8

2412 reflections

226 parameters

All H-atom parameters refined isotropically

*w* = 1/σ<sup>2</sup>(*F*)(Δ/σ)<sub>max</sub> = 0.05Δρ<sub>max</sub> = 0.51 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.29 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)**Compound (3)***Crystal data*C<sub>9</sub>H<sub>27</sub>PSi<sub>3</sub>*M<sub>r</sub>* = 250.55

Monoclinic

P2<sub>1</sub>/n*a* = 9.859 (2) Å*b* = 15.010 (6) Å*c* = 11.947 (5) Å

β = 113.91 (2)°

*V* = 1616 (1) Å<sup>3</sup>*Z* = 4*D<sub>x</sub>* = 1.03 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 8–15°

μ = 0.344 mm<sup>-1</sup>*T* = 102 K

Cylindrical

height: 0.4 mm

diameter: 0.2 mm

Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction: none

3767 measured reflections

3442 independent reflections

2878 observed reflections

[*I* > 2σ(*I*)]*R*<sub>int</sub> = 0.0020θ<sub>max</sub> = 27.5°*h* = -12 → 12*k* = 0 → 19*l* = 0 → 15

3 standard reflections

frequency: 30 min

intensity decay: 10.2%

*Refinement*Refinement on *F**R* = 0.034*wR* = 0.046*S* = 1.9

2878 reflections

226 parameters

All H-atom parameters refined isotropically

*w* = 1/σ<sup>2</sup>(*F*)(Δ/σ)<sub>max</sub> = 0.05Δρ<sub>max</sub> = 0.42 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.37 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
P	0.2437 (1)	0.2495 (1)	0.4644 (1)	0.015 (1)
C(1)	0.4370 (2)	0.2849 (1)	0.4499 (2)	0.023 (1)
C(2)	0.4015 (2)	0.3674 (2)	0.3494 (2)	0.032 (1)
C(3)	0.4937 (2)	0.1997 (2)	0.3896 (2)	0.032 (1)
C(4)	0.5713 (2)	0.3163 (2)	0.5730 (2)	0.029 (1)
C(5)	0.2693 (2)	0.1238 (1)	0.5430 (1)	0.019 (1)
C(6)	0.1351 (2)	0.1058 (1)	0.5905 (2)	0.025 (1)
C(7)	0.4230 (2)	0.1026 (1)	0.6547 (2)	0.024 (1)
C(8)	0.2457 (2)	0.0487 (1)	0.4346 (2)	0.028 (1)
C(9)	0.2063 (2)	0.3388 (1)	0.5810 (1)	0.019 (1)
C(10)	0.2283 (2)	0.4428 (1)	0.5408 (2)	0.029 (1)
C(11)	0.0318 (2)	0.3317 (1)	0.5605 (2)	0.025 (1)
C(12)	0.3037 (2)	0.3271 (1)	0.7250 (2)	0.023 (1)

Table 4. Selected geometric parameters (Å, °) for (2)

P—C(1)	1.911 (2)	P—C(5)	1.915 (2)
P—C(9)	1.908 (2)	C(1)—C(2)	1.544 (3)
C(1)—C(3)	1.534 (3)	C(1)—C(4)	1.538 (3)
C(5)—C(6)	1.534 (2)	C(5)—C(7)	1.535 (3)
C(5)—C(8)	1.544 (3)	C(9)—C(10)	1.536 (2)
C(9)—C(11)	1.544 (2)	C(9)—C(12)	1.535 (2)

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (3)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
P	0.2299 (1)	0.2511 (1)	-0.0269 (1)	0.015 (1)
Si(1)	0.1894 (1)	0.1581 (1)	0.1030 (1)	0.016 (1)
Si(2)	0.2688 (1)	0.3856 (1)	0.0631 (1)	0.018 (1)
Si(3)	0.4470 (1)	0.2086 (1)	-0.0298 (1)	0.020 (1)
C(1)	0.3110 (2)	0.1751 (2)	0.2686 (2)	0.024 (1)
C(2)	-0.0093 (2)	0.1721 (2)	0.0799 (2)	0.024 (1)
C(3)	0.2137 (3)	0.0418 (1)	0.0587 (2)	0.026 (2)
C(4)	0.4517 (3)	0.4028 (2)	0.1945 (2)	0.028 (1)
C(5)	0.1182 (3)	0.4058 (2)	0.1172 (2)	0.026 (1)
C(6)	0.2487 (3)	0.4689 (2)	-0.0581 (2)	0.029 (2)
C(7)	0.5902 (3)	0.1676 (2)	0.1182 (2)	0.032 (2)
C(8)	0.4035 (3)	0.1185 (2)	-0.1473 (3)	0.033 (2)
C(9)	0.5250 (3)	0.3052 (2)	-0.0823 (3)	0.038 (2)

Table 6. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (3)

P—Si(1)	2.241 (1)	P—Si(2)	2.246 (1)
P—Si(3)	2.248 (1)	Si(1)—C(1)	1.870 (3)
Si(1)—C(2)	1.876 (2)	Si(1)—C(3)	1.868 (2)
Si(2)—C(4)	1.868 (3)	Si(2)—C(5)	1.869 (3)
Si(2)—C(6)	1.862 (3)	Si(3)—C(7)	1.865 (3)
Si(3)—C(8)	1.870 (3)	Si(3)—C(9)	1.865 (3)
Si(3)—P—Si(2)	106.5 (1)	Si(3)—P—Si(1)	105.8 (1)
Si(2)—P—Si(1)	105.8 (1)	C(3)—Si(1)—C(2)	108.0 (1)
C(3)—Si(1)—C(1)	109.0 (1)	C(3)—Si(1)—P	107.9 (1)
C(2)—Si(1)—C(1)	108.9 (1)	C(2)—Si(1)—P	107.3 (1)
C(1)—Si(1)—P	115.5 (1)	C(6)—Si(2)—C(5)	108.1 (1)
C(6)—Si(2)—C(4)	108.8 (1)	C(6)—Si(2)—P	106.7 (1)
C(5)—Si(2)—C(4)	108.5 (1)	C(5)—Si(2)—P	107.8 (1)
C(4)—Si(2)—P	116.5 (1)	C(9)—Si(3)—C(8)	108.1 (1)
C(9)—Si(3)—C(7)	108.6 (1)	C(9)—Si(3)—P	108.0 (1)
C(8)—Si(3)—C(7)	109.2 (1)	C(8)—Si(3)—P	106.7 (1)
C(7)—Si(3)—P	116.0 (1)		

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965). Structure solution: direct methods using *SHELX86* (Sheldrick, 1990). Structure refinement: *SHELXL93* (Sheldrick, 1993) and *GFMLX* (Flack, 1983). Molecular graphics: *ORTEPII* (Johnson, 1976), *XANADU* (Roberts & Sheldrick, 1976) and *SYBYL* (Tripos Associates Inc., 1994). Preparation of material for publication: *DAESD* (Davis & Harris, 1970).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and complete geometry for (3) only, including H-atom geometry, have been deposited with the IUCr for all three structures (Reference: HR1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 1155–1158

## Trimethylphosphine and Triethylphosphine in the Solid State

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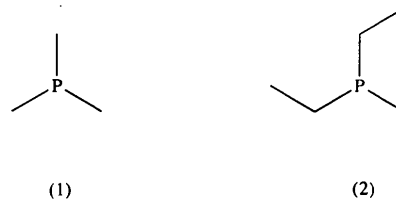
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### Abstract

Crystals of the title compounds,  $\text{C}_3\text{H}_9\text{P}$  (1) and  $\text{C}_6\text{H}_{15}\text{P}$  (2), were grown in glass capillaries using zone-melting techniques [Brodalla, Mootz, Boese & Osswald (1985). *J. Appl. Cryst.* **18**, 316–319]. Data sets were collected at 102 K. The asymmetric unit of (1) contains two independent half molecules which are situated on mirror planes. A small amount of disorder was observed for the P atoms (94/6). The C—P—C angles lie between  $99.1(1)$  and  $99.4(1)^\circ$ . In (2), the atoms are arranged in a pseudo-threefold-rotation symmetry. The C—P—C angles are in the range  $98.8(1)$ – $100.2(1)^\circ$ .

### Comment

Phosphines are important ligands in organometallic chemistry. To rationalize the steric effects in phosphine-exchange equilibria of organo-nickel compounds, the cone angle,  $\theta$ , concept was introduced by Tolman (1970). The cone angle  $\theta$  was correlated with the relative stabilities of complexes containing tertiary substituted phosphines, as well as with spectroscopic observations for these phosphine complexes (Tolman, 1970; Rahman, Liu, Eriks, Prock & Giering, 1989). The steric parameter  $\theta$  for triply substituted phosphines is the apex angle of a cone, centered  $2.28 \text{ \AA}$  from the P atom, which touches the van der Waals radii of the outermost atom of each ligand (Tolman, 1977). The crystal structures of  $\text{PMe}_3$ , (1), and  $\text{PEt}_3$ , (2), were studied as part of a program to systematically examine the structures of uncoordinated phosphine ligands.



In  $\text{PMe}_3$ , Bartell & Brockway (1960) determined the C—P—C angle as  $98.6(3)^\circ$  and the C—P distance as  $1.847(3) \text{ \AA}$  by means of electron diffraction. Magnusson (1986) undertook *ab initio* calculations and computed