

Table 6. Selected geometric parameters (\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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Trimethylphosphine and Triethylphosphine in the Solid State

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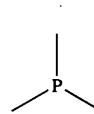
(Received 24 August 1994; accepted 9 December 1994)

Abstract

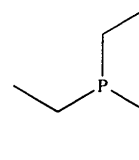
Crystals of the title compounds, $\text{C}_3\text{H}_9\text{P}$ (1) and $\text{C}_6\text{H}_{15}\text{P}$ (2), were grown in glass capillaries using zone-melting techniques [Brodalla, Mootz, Boese & Osswald (1985). *J. Appl. Cryst.* **18**, 316–319]. Data sets were collected at 102 K. The asymmetric 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, θ , concept was introduced by Tolman (1970). The cone angle θ 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 θ for triply substituted phosphines is the apex angle of a cone, centered 2.28 \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 PMe_3 , (1), and PEt_3 , (2), were studied as part of a program to systematically examine the structures of uncoordinated phosphine ligands.



(1)



(2)

In 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

values of 99.1° and 1.843 Å; *MM3* force-field calculations resulted in values of 98.6° and 1.8456 Å (Fox, Bowen & Allinger, 1992).

In our X-ray experiment, two independent half molecules were found in the asymmetric unit of (1) with a mirror plane passing through the P atom and one of the C atoms (Fig. 1). Significant residual electron density (1.1 e Å⁻³) was found 1.7 Å from the P atom. This electron density was located opposite the lone pair of the P atom. When a 6% disorder of the P atom (Fig. 2) is included, the *R* factor improves from 0.049 to 0.037 and the *wR* factor improves from 0.058 to 0.049. The minimum intermolecular distance of a 6% P atom from a 94% P atom is 3.43 (4) Å. As alkyl phosphines show no inversion at the P atom (Rademacher, 1987), as known, for example, from PH₃ and related compounds, the observed disorder cannot be attributed to dynamic inversion.

The C—P_{94%}—C angles are in the range 99.1 (1)–99.4 (1)° and the C—P_{94%} distances range between 1.827 (3) and 1.841 (5) Å (Table 2). Geometric data at the 6% disordered P atom are of lower accuracy and differ significantly from the values of the main part of the P atom.

A comparison of all experimental data, including gas-phase data (Lide & Mann, 1958; Bartell & Brockway, 1960; Hillier & Saunders, 1970; Rahman, Liu, Eriks,

Prock & Giering, 1989) with theoretical results (Hillier & Saunders, 1970; Guest, Hillier & Saunders, 1972; Xiao, Trogler, Ellis & Berkovitch-Yellin, 1983; Magnusson, 1986), reflects the dominant (60%) *p* character of the HOMO (highest-energy occupied molecular orbital) (Xiao, Trogler, Ellis & Berkovitch-Yellin, 1983).

The cone angle θ was calculated as 113 ± 2° and is in fair agreement with the value of 118 ± 4° given by Tolman (1970), from measurements using CPK atomic models, and the value of 117° from *MM2* calculations as determined by Chin, Durst, Head, Bock & Mosbo (1994).

Molecule (2) displays a pseudosymmetrical threefold-rotation axis passing through the P atom (Fig. 3). The P—C distances are between 1.841 (2) and 1.844 (2) Å, and the C—C distances average 1.527 (3) and 1.528 (3) Å. This is in agreement with the values obtained for P(*n*-butyl)₃ (Bruckmann & Krüger, 1995). The C—P—C angles are 98.8 (1), 99.4 (1) and 100.2 (1)° (Table 4). These statistically significant internal differences in bond angles may be due to packing effects. *Ab initio* computations for PEt₃ by Magnusson (1986) gave a C—P—C angle of 100.0° and a P—C distance of 1.850 Å, assuming a threefold-rotation axis passing through the P atom.

The cone angle θ was determined as 162 ± 2°. This is in excellent agreement with the value obtained by Chin, Durst, Head, Bock & Mosbo (1994) for an *MM2*-optimized geometry. Tolman (1970) lists a value of 132 ± 4°, obtained by folding back the flexible C₂H₅ substituents on phosphorus while maintaining threefold symmetry.

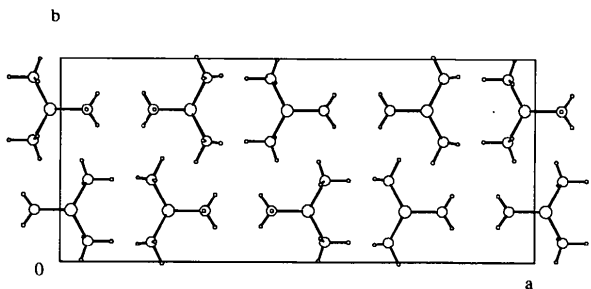


Fig. 1. ORTEPII (Johnson, 1976) plot of the cell contents of PMe₃ viewed along the *c* axis.

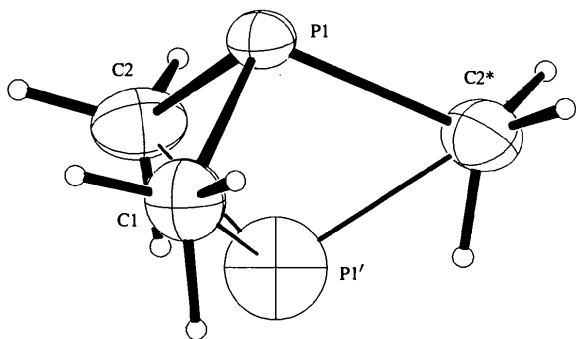


Fig. 2. ORTEPII plot of PMe₃ with only one of the two independent molecules of the asymmetric unit shown. The displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as circles of arbitrary size.

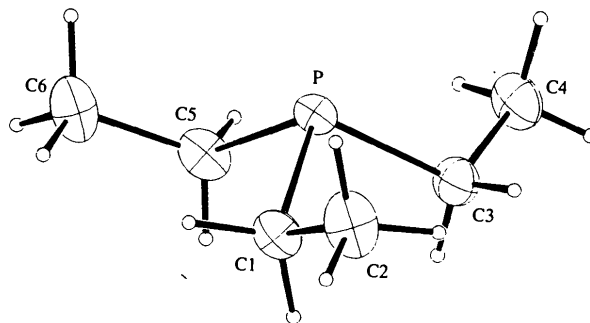


Fig. 3. ORTEPII plot of PEt₃ showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as spheres of arbitrary size.

Experimental

Crystals of (1) and (2) were grown by zone-melting techniques in argon-filled glass capillaries with a focused halogen lamp as heat source (Brodalla, Mootz, Boese & Osswald, 1985). For (1), pentane was used as solvent, *T*_{melt} was 188 and *T*_{growth} was 184 K. For (2), *T*_{melt} was 187 and *T*_{growth} was 185 K.

Compound (1)*Crystal data*C₃H₉P*M_r* = 76.08

Orthorhombic

*Pnma**a* = 21.472 (5) Å*b* = 9.117 (1) Å*c* = 5.186 (1) Å*V* = 1015.2 (3) Å³*Z* = 8*D_x* = 1.00 Mg m⁻³Mo *K*α radiation*λ* = 0.71069 Å

Cell parameters from 25 reflections

θ = 13–18°*μ* = 0.348 mm⁻¹*T* = 102 K

Cylindrical

height: 0.4 mm

diameter: 0.2 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω–2*θ* scans

Absorption correction: none

1383 measured reflections

1221 independent reflections

880 observed reflections

[*I* > 2σ(*I*)]*Refinement*Refinement on *F**R* = 0.037*wR* = 0.049*S* = 1.9

880 reflections

87 parameters

w = 1/σ²(*F*)*R*_{int} = 0.01*θ*_{max} = 27.5°*h* = 0 → 6*k* = 0 → 11*l* = 0 → 27

3 standard reflections

frequency: 30 min

intensity decay: 2.7%

(*Δ*/σ)_{max} = 0.03*Δρ*_{max} = 0.25 e Å⁻³*Δρ*_{min} = -0.34 e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography*

(1974, Vol. IV)

Monoclinic

*P*2₁/*a**a* = 9.495 (4) Å*b* = 7.421 (1) Å*c* = 11.151 (3) Å*β* = 90.71 (2)°*V* = 785.7 (4) Å³*Z* = 4*D_x* = 1.00 Mg m⁻³*Data collection*

Enraf–Nonius CAD-4 diffractometer

ω–2*θ* scans

Absorption correction: none

9739 measured reflections

1805 independent reflections

1727 observed reflections

[*I* > 2σ(*I*)]*Refinement*Refinement on *F**R* = 0.059*wR* = 0.068*S* = 4.7

1727 reflections

124 parameters

w = 1/σ²(*F*)

Cell parameters from 25 reflections

θ = 10–23°*μ* = 0.243 mm⁻¹*T* = 102 K

Cylindrical

height: 0.6 mm

diameter: 0.3 mm

Colourless

*R*_{int} = 0.0476*θ*_{max} = 27.5°*h* = -12 → 12*k* = 0 → 9*l* = 0 → 14

3 standard reflections

frequency: 30 min

intensity decay: 9.8%

(*Δ*/σ)_{max} = 0.04*Δρ*_{max} = 1.04 e Å⁻³*Δρ*_{min} = -0.68 e Å⁻³

Atomic scattering factors

from *International Tables**for X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C(1)	-0.0546 (2)	1/4	0.7476 (8)	0.037 (3)
C(2)	0.0580 (2)	0.0971 (4)	0.7734 (5)	0.038 (2)
C(3)	0.3055 (2)	1/4	0.2795 (8)	0.032 (2)
C(4)	0.1930 (2)	0.0975 (3)	0.2495 (5)	0.032 (2)
P(1)	0.0225 (1)	1/4	0.5973 (1)	0.025 (1)
P(2)	0.2276 (1)	1/4	0.4276 (2)	0.023 (1)
P(1')	0.018 (3)	1/4	0.935 (7)	0.11 (1)
P(2')	0.228 (1)	1/4	0.095 (4)	0.049 (5)

Table 2. Selected geometric parameters (Å, °) for (1)

C(1)—P(1)	1.830 (5)	C(1)—P(1')	1.85 (5)
C(2)—P(1)	1.833 (3)	C(2)—P(1')	1.835 (3)
C(3)—P(2)	1.841 (5)	C(3)—P(2')	1.92 (3)
C(4)—P(2)	1.827 (3)	C(4)—P(2')	1.772 (3)
C(2')—P(1)—C(2)	99.1 (1)	C(2)—P(1)—C(1)	99.4 (1)
C(4')—P(2)—C(4)	99.1 (1)	C(4)—P(2)—C(3)	99.1 (1)
C(2')—P(1')—C(2)	99 (2)	C(2)—P(1')—C(1)	98.7 (1)
C(4')—P(2')—C(4)	103 (1)	C(4)—P(2')—C(3)	98.1 (1)

Symmetry code: (i) *x*, ½ - *y*, *z*.**Compound (2)***Crystal data*C₆H₁₅P*M_r* = 118.16Mo *K*α radiation*λ* = 0.71069 ÅTable 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
P	0.1752 (1)	0.1711 (1)	0.2565 (1)	0.020 (1)
C(1)	0.0330 (2)	0.0143 (3)	0.2964 (2)	0.027 (1)
C(2)	0.0383 (3)	-0.1625 (3)	0.2266 (2)	0.037 (1)
C(3)	0.0987 (2)	0.2666 (3)	0.1180 (2)	0.029 (1)
C(4)	0.1942 (3)	0.4034 (3)	0.0571 (2)	0.034 (1)
C(5)	0.1358 (3)	0.3536 (3)	0.3631 (2)	0.028 (1)
C(6)	0.1883 (3)	0.3119 (3)	0.4902 (2)	0.036 (1)

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

P—C(1)	1.842 (2)	P—C(3)	1.841 (2)
P—C(5)	1.844 (2)	C(1)—C(2)	1.527 (3)
C(3)—C(4)	1.527 (3)	C(5)—C(6)	1.528 (3)
C(5)—P—C(3)	100.2 (1)	C(5)—P—C(1)	98.8 (1)
C(3)—P—C(1)	99.4 (1)	C(2)—C(1)—P	113.0 (2)
C(4)—C(3)—P	113.5 (2)	C(6)—C(5)—P	112.5 (2)

For (1), 94% of H atoms and 6% of P' atoms were located and refined isotropically. 6% of H atoms were calculated and kept fixed in the final stage of refinement. In (2), all H atoms were located and refined isotropically.

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 have been deposited with the IUCr (Reference: HR1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Cyano-2-methylsparteine

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Abstract

In the title compound, [7*S*-(7 α ,7 α ,14 α ,14 α)]-dodecahydro-4-methyl-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:

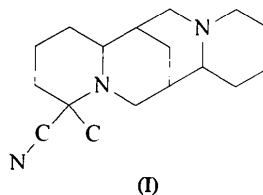
1',2'-*e*][1,5]diazocine-4-carbonitrile, C₁₇H₂₇N₃, the two quinolizidine moieties have been found to have *trans* *A/B* and *trans* *C/D* configurations. The piperidine rings *A*, *B*, *C* and *D* assume chair, chair, boat and chair conformations, respectively. The methyl substituent has been shown to adopt an equatorial orientation, with the cyano substituent in an axial position.

Comment

This work is a continuation of our studies on sparteine derivatives. Sparteine is the most common among the bisquinolizidine alkaloids isolated from lupine plants. It has been widely used as a model compound for the study of factors influencing conformational–configurational changes. The *A/B* ring system is not susceptible to conformational changes, whereas the *C/D* system is, owing to an easy inversion at the N16 atom.

Generally, free bases of sparteine derivatives have a *trans* configuration/boat–chair conformation of the *C/D* fragment, while the cations show a *cis* configuration/chair–chair conformation of this fragment, e.g. sparteine (Skolik, Krueger & Wiewiórowski, 1970) and the sparteine cation (Borowiak, Bokii & Struchkov, 1973), and 2-phenylsparteine (Katrusiak, Figas, Kałuski & Lesiewicz, 1989) and its cation (Kubicki, Borowiak & Boczoń, 1991). In these examples, the *A/B* fragment was found to have a *trans* configuration/chair–chair conformation in the free base as well as in the cation.

In this paper, we present the results of an X-ray structural analysis of 2-cyano-2-methylsparteine (I) (Fig. 1). The structure is similar to the examples cited above. The piperidine rings *A*, *B* and *D* adopt chair conformations with ring *C* having a boat conformation. The *A/B* junction is *trans* [torsion angles C2–N1–C6–C5 –52.5 (3) and C7–C6–N1–C10 56.5 (3)°], as is the *C/D* junction [torsion angles C9–C11–N16–C17 –54.0 (3) and C12–C11–N16–C15 59.0 (3)°]. The proper enantiomorph has been selected on the



basis of the absolute configuration of naturally occurring sparteine derivatives (Klyne, Scopes, Thomas, Skolik, Gawroński & Wiewiórowski, 1974) to be C7-(*S*), C9-(*S*).

The methyl substituent occupies an equatorial position with torsion angles C4–C3–C2–C20 and C6–N1–C2–C20 of –178.9 (2) and 174.9 (2)°, respectively. The cyano group is axial with torsion angles C4–C3–C2–C18 64.2 (3) and C6–C1–C2–C18 –64.9 (3)°.