Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Triclinic polymorphs of triphenylphosphine and triphenylphosphine sulfide

Burkhard Ziemer, Annegrit Rabis and Hans-Uwe Steinberger

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Triclinic polymorphs of triphenylphosphine and triphenylphosphine sulfide

Burkhard Ziemer,* Annegrit Rabis and Hans-Uwe Steinberger

Institut für Chemie, Humboldt-Universität zu Berlin, Hessische Str. 1-2, 10115 Berlin, Germany
Correspondence e-mail: burkhard=ziemer@chemie.hu-berlin.de

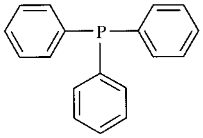
Received 16 December 1999
Accepted 23 December 1999

Data validation number: IUC0000007

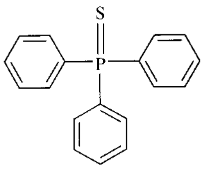
New triclinic polymorphs of triphenylphosphine, (I), and triphenylphosphine sulfide, (II), were crystallized. For the structure of (I), it is obvious that the highest peaks in the final difference electron-density map are located at the 'lone-pair regions' of P atoms. We have observed this effect in two further phosphorous-containing structures.

Comment

By reaction of triphenylphosphine, (I), with pyridinedithiomonometaphosphoryl chloride, an insertion of sulfur into triphenylphosphine takes place and a new triclinic polymorph of triphenylphosphine sulfide, (II), was isolated. The analogous reaction of triphenylphosphine with pyridinedithiomonometaphosphoryl fluoride yields in addition to the abovementioned sulfide a new crystallographic modification of triclinic triphenylphosphine. Both compounds form monoclinic structures, too, which have been described previously by Howells *et al.* (1954) and Codding & Kerr (1978), respectively.



(I)



(II)

In the unit cell of triphenylphosphine there are four independent molecules. Here, it is obvious that the four highest peaks in the final difference electron-density map [1.08 (4), 0.69 (4), 0.64 (4) and 0.31 (4) e Å^{-3}] are observed at the 'lone-pair regions' of P1—P4. The distances between those peaks and the corresponding P atoms are 1.25, 1.35, 1.35 and 1.22 Å, respectively.

Experimental

A solution of triphenylphosphine in benzene was slowly dropped to a suspension of pyridinedithiomonometaphosphoryl chloride or fluoride in benzene. After 1 h, the solid products were filtrated and recrystallized from benzene.

Compound (I)

Crystal data

C$_{18}$H$_{15}$P
$M_r = 262.27$
Triclinic, $P\overline{1}$
$a = 11.0306$ (19) Å
$b = 15.111$ (3) Å
$c = 17.554$ (3) Å
$\alpha = 84.38$ (2)°
$\beta = 80.36$ (2)°
$\gamma = 85.82$ (2)°
$V = 2866.0$ (8) Å^3
$Z = 8$
$D_x = 1.216$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 2.5$–25.0°
$\mu = 0.175$ mm^{-1}
$T = 180$ (2) K
Block, colorless
0.48 × 0.48 × 0.28 mm

Data collection

Stoe IPDS diffractometer
φ-oscill., φ-incr. = 1.4°, 164 exposure
Absorption correction: refdelf see publ section exptl prep
$T_{\min} = 0.921$, $T_{\max} = 0.953$
17 345 measured reflections
9738 independent reflections
6818 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0324$
$\theta_{\max} = 25.25°$
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0422$
$wR(F^2) = 0.1114$
$S = 0.919$
9738 reflections
685 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 1.02$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Compound (II)

Crystal data

C$_{18}$H$_{15}$PS
$M_r = 294.33$
Triclinic, $P\overline{1}$
$a = 9.542$ (3) Å
$b = 11.207$ (3) Å
$c = 14.537$ (4) Å
$\alpha = 88.89$ (4)°
$\beta = 80.39$ (4)°
$\gamma = 78.28$ (3)°
$V = 1500.5$ (8) Å^3
$Z = 4$
$D_x = 1.303$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 2.5$–25.0°
$\mu = 0.309$ mm^{-1}
$T = 180$ (2) K
Prism, yellow
0.72 × 0.38 × 0.11 mm

Data collection

Stoe IPDS diffractometer
φ-oscill., φ-incr. = 1.5°, 160 exposures
Absorption correction: refdelf see publ section exptl prep
$T_{\min} = 0.808$, $T_{\max} = 0.967$
13 389 measured reflections
5111 independent reflections
4117 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0502$
$\theta_{\max} = 25.24°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0293$
$wR(F^2) = 0.0786$
$S = 0.974$
5111 reflections
481 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

For the studied crystals, a ΔF^2-based absorption correction was carried out. The calculation was performed with *ABSCOR* (Stoe & Cie, 1997), a modification of *DIFABS* (Walker & Stuart, 1983). In

e58 Burkhard Ziemer *et al.* • C$_{18}$H$_{15}$PS and C$_{18}$H$_{15}$P *Acta Cryst.* (2000). C**56**, e58–e59

contrary of *DIFABS, ABSCOR* loads and provides F^2 values instead of *F* ones.

For both compounds, data collection: *IPDS*-2.87 (Stoe & Cie, 1997); cell refinement: *IPDS*-2.87 (Stoe & Cie, 1997); data reduction: *IPDS*-2.87 (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XSTEP*-2.18 (Stoe & Cie, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

References

Codding, P. W. & Kerr, K. A. (1978). *Acta Cryst.* B**34**, 3785–3787.

Howells, E. R., Lovell, F. M., Rogers, D. & Wilson, A. J. C. (1954). *Acta Cryst.* **7**, 298–299.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Stoe & Cie (1997). *IPDS*-2.87, *XRED*, *ABSCOR* and *XSTEP*-2.18. Stoe & Cie, Darmstadt, Germany.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.