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Hexaphenylhexaphosphinane benzene solvate

Jan J. Weigand,[a]* Andreas Decken[b] and Neil Burford[c]

[a]WWU Münster, Institut für Anorganische und Analytische Chemie, Corrensstrasse 28/30, Münster D-48149, Germany, [b]Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2, and [c]Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B4H 4J3
Correspondence e-mail: jweigand@uni-muenster.de

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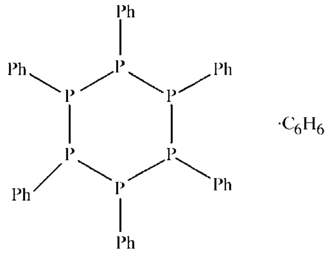
In the molecular crystal of hexaphenylhexaphosphinane benzene solvate, $C_{36}H_{30}P_6 \cdot C_6H_6$, representing the trigonal form of phosphobenzene as a solvate, the six-membered ring of P atoms adopts a chair conformation wherein the six phenyl groups are located in equatorial positions. The molecules [molecular symmetry $\overline{3}$ (C_{3i})] are stacked infinitely along the *c*-axial direction.

Comment

Oligophosphines (Baudler & Glinka, 1994), such as hexaphenylhexaphosphinane $(PPh)_6$, provide analogies with cycloalkanes since the CR_2 methylene unit is isolobal with the phosphine (PR) unit. The familiar cationic phosphonium center is also isolobal with this unit and is obtained, for example, through methylation reactions of phosphines (Burford *et al.*, 2005). *catena*-Phosphorus cations represent a newly developing family of compounds and we are currently establishing a comprehensive series of high yielding and facile methods for the synthesis of prototypical polyphosphonium salts from oligophosphines (Weigand *et al.*, 2007). Recently, we reported the synthesis and crystal structures of cyclohexaphosphorus dications, containing a P_6 homocycle composed of two phosphonium centers (1,4-positions) and four phosphine centers (Weigand *et al.*, 2006). In further investigations, we attempted the synthesis of hexaphenylhexaphosphinane, $(PPh)_6$, according to a modification of the procedure of Henderson *et al.* (1963). The $(PPh)_6$ hexamer exists in at least four crystalline forms (Daly, 1965, 1966; Daly & Maier, 1964, 1966). However, for the title solvate, (I), only the cell dimensions of the trigonal crystal system were reported, with $a = 12.68$ Å and $c = 20.96$ Å (Daly & Maier, 1964). Therefore, we have reinvestigated the crystal structure of hexaphenylhexaphosphinane benzene solvate, which is, to our knowledge, only the second crystallographic characterization of a solvated cyclooligophosphine after $(2,5\text{-}Me_2C_6H_3)_6P_6 \cdot CHCl_3$ (Schmutzler *et al.*, 1993).

A displacement ellipsoid drawing of (I) is shown in Fig. 1 with the corresponding numbering scheme. The centers of both the $(PPh)_6$ and the benzene molecules are located on the threefold axis as well as the symmetry center, and thus the ring entities are constructed from a single unique P—Ph fragment for the $(PPh)_6$ molecule and a unique C-atom position for the solvate. The molecules of the cyclohexamer contain an all-phosphorus ring framework adopting a chair conformation with the phenyl groups located in equatorial positions, as required by the $\overline{3}$ symmetry. X-ray investigation shows that the P—P length of 2.2207 (8) Å does not significantly differ from those reported for the other four crystalline forms, with an average value of 2.237 (3) Å. The average aromatic C—C bond length found in the phenyl ring attached to the P atom is 1.384 (2) Å and the C atoms of the phenyl group do not deviate significantly from a regular hexagon. Similar to the trigonal form of solvent-free $(PPh)_6$ (Daly, 1965), a slight deviation of the molecule from $\overline{3}m$ (D_{3d}) symmetry is observed. The P—P—C values differ slightly by 1.62 (5)° from each other, the phenyl ring makes an angle of 7.6 (3)° with the $\overline{3}$ axis of the puckered central ring, and the P atom deviates from the phenyl ring plane by 0.041 (2) Å. Distances and angles for the benzene molecule are also presented in Table 1.



(I)

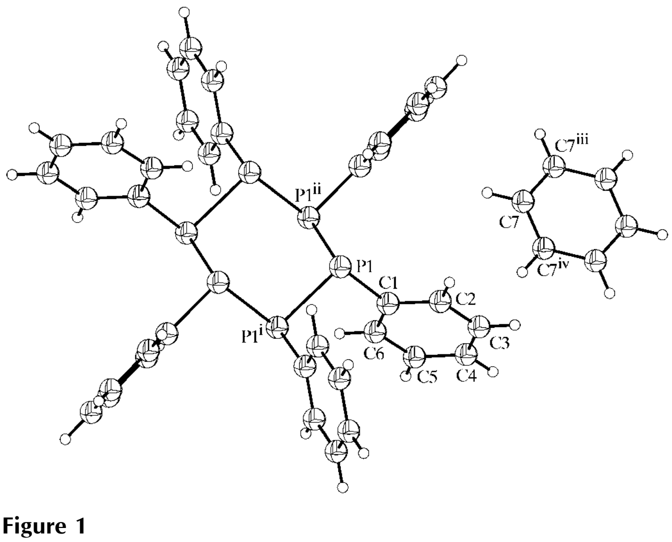


Figure 1
A view of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x - y, x, -z + 1$; (ii) $y, -x + y, -z + 1$; (iii) $x - y + \frac{1}{3}, x - \frac{1}{3}, -z + \frac{2}{3}$; (iv) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$.]

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Specific interactions between the $(PPh)_6$ molecules and the benzene solvent molecules are not observed. All intermolecular distances are longer than the sum of the appropriate van der Waals radii.

Fig. 2 presents the packing arrangement of the molecules in the unit cell, depicted along the *b* and *c* axes. All hexamers in this structure are positioned with their molecular threefold axes parallel to the *c* axis. The packing of the cyclopolyphosphine molecules in (I) corresponds to layers in a hexagonal arrangement. These body-centered packing layers have an *ABC* sequence separated by the benzene molecules, which also form layers and are located in the 'octahedral holes'. Thus, the benzene is surrounded by six individual $(PPh)_6$ molecules arranged in a pseudo-octahedron. Short van der Waals contacts of less than 4.0 Å are observed between the phenyl groups and the solvent molecule. However, there are no contacts of less than 4.0 Å involving the P atom. Nevertheless, this packing is surprisingly similar to that of the unsolvated trigonal $(PPh)_6$. The difference lies mainly in a more effective layer stacking of the latter caused by the absence of solvent molecules.

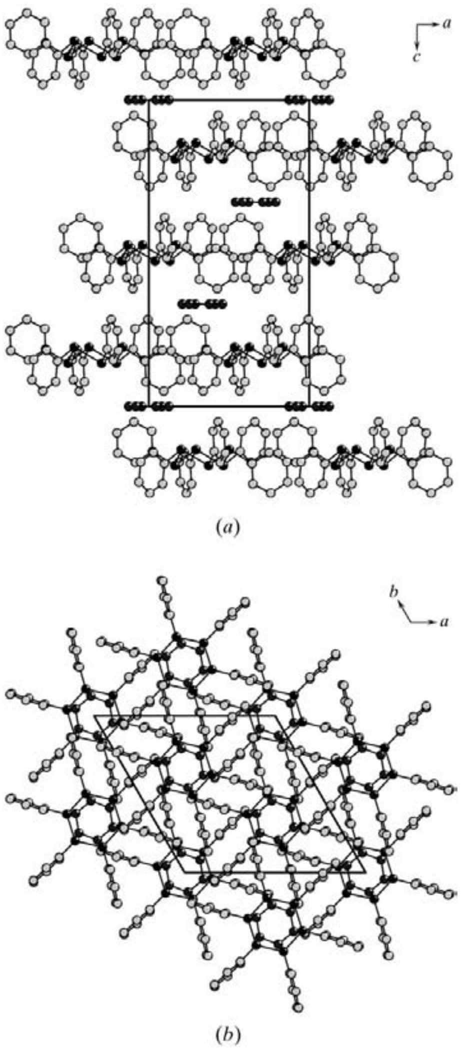

Figure 2
Views along (*a*) the *b* axis and (*b*) the *c* axis, showing the packing of (I) in its molecular structure. H atoms have been omitted for clarity. Light gray denotes phenyl C atoms, medium gray denotes benzene C atoms and black denotes P atoms.

Experimental

All manipulations were performed under an inert atmosphere of argon. To a solution of $PhPCl_2$ (179 mg, 1 mmol) in benzene (6 ml) was added $PhP(SiMe_3)_2$ (254 mg, 1 mmol) in one portion and the solution stirred for 6 h. From the reaction mixture, very small amounts of colorless block-shaped crystals were obtained after two weeks and crystallographically identified as the title compound, (I). The analytical data for the $^{31}P\{^1H\}$ NMR shift ($\delta = -26.4$ p.p.m.) is in agreement with that previously reported (Henderson *et al.*, 1963).

Crystal data

$C_{36}H_{30}P_6{\cdot}C_6H_6$
$M_r = 726.53$
Trigonal, $R\overline{3}$
$a = 12.533$ (5) Å
$c = 20.763$ (6) Å
$V = 2824.4$ (18) Å^3
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 0.32$ mm^{-1}
$T = 173$ (1) K
0.45 × 0.40 × 0.15 mm

Data collection

Bruker SMART1000/*P*4 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.871$, $T_{\max} = 0.954$
6465 measured reflections
1426 independent reflections
1279 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.088$
$S = 1.10$
1426 reflections
73 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—C1	1.8446 (15)	P1—P1$^{\rm i}$	2.2207 (8)
C1—P1—P1$^{\rm i}$	97.83 (5)	P1$^{\rm i}$—P1—P1$^{\rm ii}$	98.17 (2)
C1—P1—P1$^{\rm ii}$	96.21 (5)		

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

H atoms were included in calculated positions, with distances fixed at 0.95 Å and isotropic displacement parameters corresponding to $1.2U_{\rm eq}$ of the carrier C atom. The data set was truncated at $2\theta = 55°$ as only statistically insignificant data were present above the limit. The largest residual electron-density peaks were found within 0.83 and 1.02 Å of atoms C1 and P1, respectively.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3071). Services for accessing these data are described at the back of the journal.

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