Structure of 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene and of 2,4-Di-*tert*-butyl-1,3-diphosphabenzene: X-ray Analysis, Photoelectron Spectra and Molecular Orbital Calculations☆

Rolf Gleiter*[a], Holger Lange[a], Paul Binger*[b], Jörg Stannek[b], Carl Krüger[b], Joachim Bruckmann[b], Ulrich Zenneck*[c], and Susanne Kummer[c]

Organisch-Chemisches Institut der Universität Heidelberg[a],
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany,

Max-Planck-Institut für Kohlenforschung[b],
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim a. d. Ruhr, Germany,

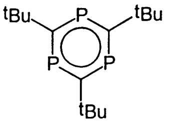
Institut für Anorganische Chemie der Universität Erlangen-Nürnberg[c],
Egerlandstraße 1, D-91058 Erlangen, Germany

Received June 16, 1998

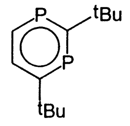
Keywords: 1,3,5-Triphosphabenzene / 1,3-Diphosphabenzene / Photoelectron spectroscopy / Molecular orbital calculations

The structure of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) as well as the He(I) photoelectron spectra of **1** and 2,4-di-*tert*-butyl-1,3-diphosphabenzene (**2**) have been investigated. It was found that **1** is planar with average C–P–C angles of 109.3° (±0.3°) and P–C–P angles of 130.7° (± 0.4°). All P–C bond lengths amount to 1.727 (± 0.008) Å. The PE spectra were interpreted by comparison with the results of ab initio calculations (RHF/ 6-31G*). They reveal a splitting of the lone pairs on P in **2** of 0.7 eV.

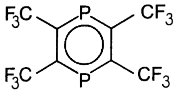
With the synthesis of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (2,4,6-tri-*tert*-butyl-1λ^3,3λ^3,5λ^3-triphosphinine) (**1**)[1] and of 2,4-di-*tert*-butyl-1,3-diphosphabenzene (2,4-di-*tert*-butyl-1λ^3,3λ^3-diphosphinine) (**2**)[2] the family of phosphorus-containing heterobenzenes is now nearly complete. Earlier investigations led to the synthesis of λ^3-phosphinine **4**[3], numerous substituted λ^3-phosphinines[4] and also of one example of a 1λ^3,4λ^3-diphosphinine **3**.[5] The latter compound, 2,3,5,6-tetrakis(trifluormethyl)-1λ^3,4λ^3-diphosphinine, is stable only in solution. According to their NMR-spectroscopic data (^{31}P, ^{1}H, ^{13}C) mono-, di- and triphosphinines can be conceived as 6π heteroarenes and therefore their trivial names as phosphabenzenes are justified.



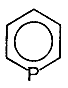
1



2



3



4

In order to gain more information about the electronic structure of the two recently prepared diphospha- and triphosphabenzenes **2** and **1**[1][2], we investigated their PE spectra and interpreted the results on the basis of Hartree-Fock ab initio calculations adopting a 6-31G* basis. Furthermore, we present the results of a single-crystal structure analysis of the triphosphabenzene **1** in this paper.

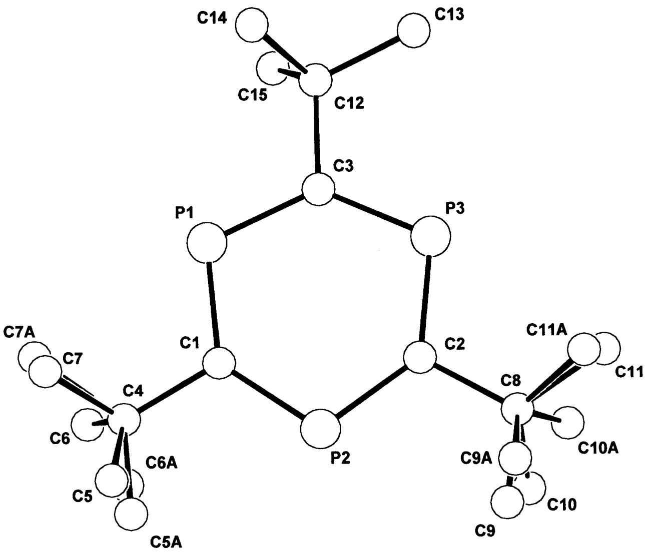
Suitable crystals of compound **1** for an X-ray analysis were obtained as little yellow plates from a pentane solution of **1** at −30°C. As shown in Figure 1 the triphosphabenzene derivative **1** is completely planar. However, in contrast to benzene or pyridine, but in accordance with phosphinines[4] 1,3,5-triphosphinine **1** is far from being regular hexagonal. The average C−P−C angles are 109.3° (±0.3°) (C−C−C angle in benzene 120°, C−N−C angle in pyridine 117°, C−P−C angle in phosphine 101−103°C). In order to accommodate this angular change the P−C−P angles have to exceed 120°. In triphosphabenzene **1** the average P−C−P angles are 130.7° (±0.4°) (P−C−C and C−C−C angles in phosphinines 122−120°[4]). All P−C bond lengths of the P_3C_3 ring are equal with average bond lengths of 1.727 (±0.008) Å, and are in the range of those found for phosphinines (1.73−1.75 Å),[4] considerably longer than P=C bond lengths in phosphaalkenes (1.66−1.68 Å).[6] All these results point towards a delocalization of the six π-electrons of the triphosphabenzene **1**. Our calculations (C_3 symmetry, RHF/6-31G*) reveal geometrical parameters for **1** which are close to the experiment (C=P: calcd. 1.730 Å, found 1.727 Å; C−P−C: calcd. 110.6°, found 109.6°; P−C−P: calcd. 129.4°, found 130.3°).[7]

The He(I) photoelectron (PE) spectra of **1** and **2** are shown in Figure 2. The vertical ionization energies, $I_{\mathrm{v,j}}$, are collected in Table 1. The PE spectrum of **1** shows one broad band centered at 8.2 eV separated by 1.8 eV from the next one at 10.0 eV. The PE spectrum of **2** shows also a broad peak at 8.6 eV and a smaller one at 9.5 eV. The ratio between the areas below both peaks in **2** is approximately 3:1.

To assign the PE spectra of **1** and **2** to various ionization processes we assume the validity of Koopmans′ theorem[8] which allows us to correlate the recorded vertical ionization

1434−1948/98/1111−1619 $ 17.50+.50/0

Figure 1. Molecular structure of **1**[a]



[a] Selected bond lengths [Å] and angles [°]: P1−C1 1.725(5), P1−C3 1.729(5), P2−C1 1.724(5), P2−C2 1.719(4), P3−C2 1.727(4), P3−C3 1.718(4), C3−C12 1.558(6), C1−C4 1.551(7); P1−C1−P2 130.3(3), P2−C2−P3 130.8(3), P1−C3−P3 130.9(3), C1−P1−C3 109.3(2), C1−P2−C2 109.6(2), C2−P3−C3 109.0(2).

Figure 2. He(I) photoelectron spectra of **1** and **2**

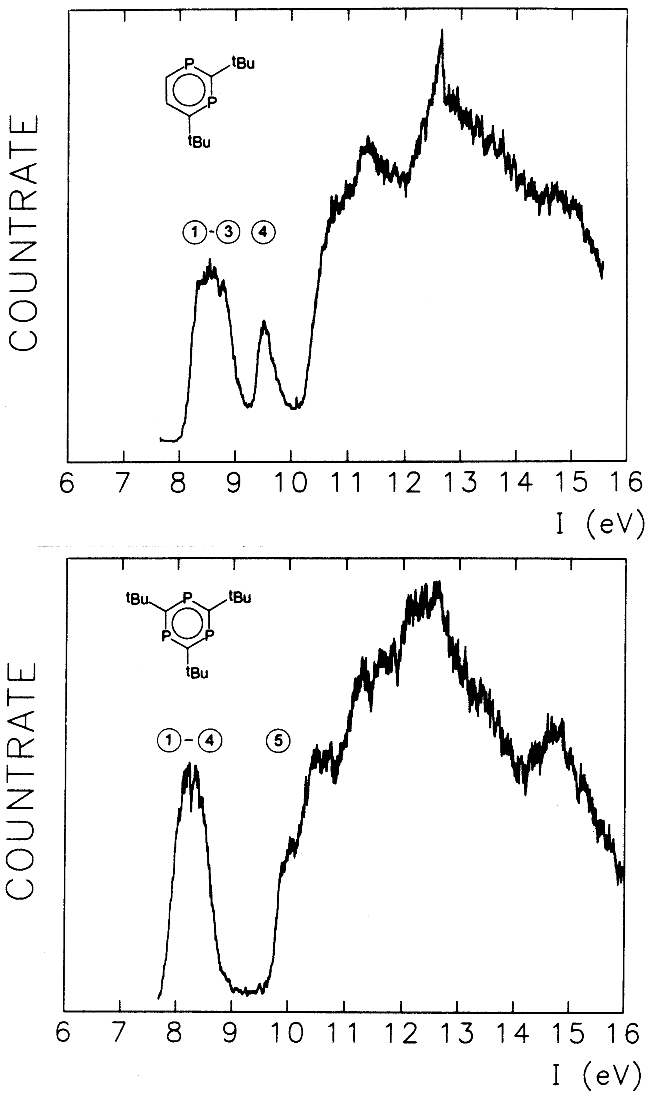


Table 1. Vertical ionization energies, $I_{v,j}$, and calculated orbital energies, $-\varepsilon_j$, of **1** and **2**

	band	$I_{v,j}$ [eV]	assignment	$-\varepsilon_j$ [eV]
1	1 2	8.2	27 e (π)	8.51
	3 4	8.3	26e (n)	9.16
	5	10.0	27a (π)	11.46
2	1	8.5	61a (π)	8.38
	2	8.6	60a (π)	8.93
	3	8.8	59a (n-)	9.29
	4	9.5	58a (n+)	10.76

energies, $I_{v,j}$, with the calculated orbital energies, $-\varepsilon_j$. To derive the orbital energies we use the Hartree-Fock ab initio method adopting a 6-31G* basis.[9] The results of our calculations are based on the optimized geometries of **1** and **2** and are listed in Table 1.

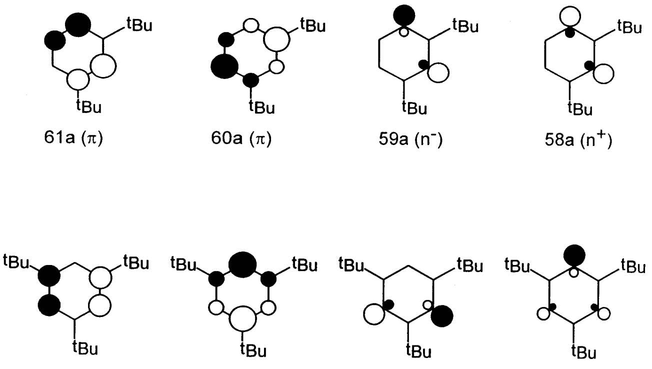
The calculations predict for **2** three relatively close-lying occupied molecular orbitals (MOs) at 8.38, 8.93 and 9.29 eV, well separated from a fourth one at 10.76 eV.

We assume that the ionizations from these four MOs give rise to two peaks; the first one is due to the overlap of three close-lying bands. The calculations predict that the two highest occupied MOs are of π type followed by linear combinations of the phosphorus lone pairs. All four are shown schematically in Figure 3.

The plausibility of this assignment can be checked by comparing the PE spectrum of **2** with that of phosphabenzene (**4**)[10] and 1,3,5-tri-*tert*-butylphosphabenzene (**5**).[11] The ionization energy of the phosphorous lone pair of **4** was found at 10.0 eV and of **5** at 8.6 eV. These values allow us to estimate the inductive effect of one *tert*-butyl group to 0.47 eV. This leads to the center of gravity of the two lone pairs in **2** at 9.1 eV. This value agrees very well with that found for bands 3 and 4 in the PE spectrum of **2**. A comparison between the energy difference of band 3 and 4 in the PE spectrum of **2** and the values for the corresponding orbital energies show that the calculated energy splitting of the lone pairs is twice as large as the measured one. The splitting of the bands assigned to the lone pairs in **2** (0.7 eV) is half the value found in the PE spectrum of pyrimidine.[12] We ascribe this to the higher p character of the lone pairs in pyrimidine (73%) as compared to 2,4-di-*tert*-butyl-1,3-diphosphabenzene **2** (41%).

Our assignment of the first bands of the PE spectrum of **1** is also based on the comparison between the results of a HF-SCF calculation and the PE experiment. This comparison suggests to assign the first peak in the PE spectrum of **1** to four strongly overlapping bands corresponding to the transition from 27e(π) and 26e(n). The shoulder at 10 eV is assigned to 27a(π). All four MOs are shown in Figure 3.

Figure 3. Schematic representation of the highest occupied molecular orbitals of **1**and **2**



61a (π) 60a (π) 59a (n⁻) 58a (n⁺)

27e (π) 26e (n)

The assignment of the π bands of **1** yields a center of gravity of 8.8 eV. This value is close to that found for **5** (8.9 eV).

We are grateful to *A. Flatow* for recording the PE spectra of **1** and **2**. We thank the *Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Phosphor als Bindeglied verschiedener chemischer Disziplinen“)*, the *Fonds der Chemischen Industrie* and the *BASF Aktiengesellschaft*, Ludwigshafen, for financial support.

Experimental Section

The He(I) PE spectra of **1** and **2** were recorded with a PS18 spectrometer (Perkin Elmer). The recording temperatures were 80°C for **1** and 25°C for **2**. The calibration was performed with Ar and Xe. A resolution of 20 meV on the $P_{3/2}$ Ar line was obtained. The MO calculations on **1** and **2** were carried out with the Gaussian 94 program.[9] The orbital energies are based on the optimized geometries of **1** and **2**.

Crystal Structure Analysis of **1**[13]: Enraf-Nonius CAD4 diffractometer (Cu-K_α radiation), T = 293 K; structure solution by heavy atom method (SHELXS-86[14]) and structure refinement by SHELXL-93[15]; monoclinic, space group $C2/c$, lattice constants a = 31.281(3), b = 6.047(1), c = 19.458(1) Å, β = 93.96(3)°, V = 3672.0(6) Å^3, Z = 8, μ(Mo-K_α) = 2.876 mm^{-1}, crystal size 0.25 × 0.24 × 0.11 mm, Θ_{max} = 33.16°, 4206 measured reflections (R_{int} = 0.04), 3756 independent of which 2262 were considered observed with $I > 2\sigma(I)$, ψscan absorption correction; min./max, transmission 0.860/0.999, max. residual electronic density 0.54 e/Å^3. 157 parameters C and P anisotropic (except the disordered atoms at C4 and C8), the positions of the H atoms were calculated for idealized positions (d_{C-H} = 0.980 Å), R_1 = 0.0909, wR^2 = 0.2438.

☆ Dedicated to Professor *Hans Bock* on the occasion of his 70th birthday.

[1] P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227.

[2] D. Böhm, F. Knoch, S. Kummer, U. Schmidt, U. Zenneck, *Angew. Chem.* **1995**, *107*, 251; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 198.

[3] A. J. Ashe III, *J. Am. Chem. Soc.* **1971**, *93*, 3293.

[4] G. Märkl in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Ed. M. Regitz, O. J. Scherer), Thieme, Stuttgart **1990**, p. 220.

[5] Y. Kobayashi, J. Kumadaki, A. Ohsawa, H. Hamana, *Tetrahedron Lett.* **1977**, 867; C. G. Krespan, B. C. McKusick, T. L. Cairns, *J. Am. Chem. Soc.* **1960**, *82*, 1515; C. G. Krespan, *J. Am. Chem. Soc.* **1961**, *83*, 3432.

[6] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Tayler, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[7] The calculated values for **1** would also be in line with the MP2/6-31G* results of S. R. Bachrach. P. Magdalinos, *J. Molec. Struct. (Theochem.)* **1996**, *368*, 1, reported for the parent system if one assumes that the authors have mixed up the C−P−C and P−C−P angles for 1,3,5-triphosphabenzene.

[8] T. Koopmans, *Physica* **1934**, *1*, 104.

[9] We used the *Gaussian 94* program by M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov. A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1995**.

[10] C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe III, D. T. Clark, K. T. Bobley, D. Kilcast, I. Scanlan, *J. Am. Chem. Soc.* **1973**, *95*, 928.

[11] H. Oehling, W. Schäfer, A. Schweig, *Angew. Chem.* **1971**, *83*, 723; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 656.

[12] R. Gleiter, E. Heilbronner, V. Hornung, *Helv. Chim. Acta* **1972**, *55*, 255.

[13] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101646. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

[14] G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Solution*, Universität Göttingen, **1986**.

[15] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, Universität Göttingen, **1993**.

[98188]