Photoelectron Spectra of λ^5-Di- and -Triphosphabenzenes[1]

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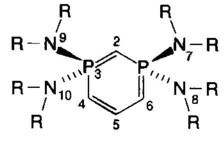
The He(I) photoelectron spectra of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphabenzene (**1a**), 1,1,3,3,5,5-hexakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^5$-triphosphabenzene (**2a**), 4-*tert*-butyl-1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^3$-triphosphabenzene (**3a**), and the substitution products **4a** and **5a** of **1a** have been recorded. The assignment of the PE spectra is based on a comparison of the PE spectra of related species with the MO calculations carried out by using the MNDO procedure. The investigations reveal that the first bands correspond to π-MOs which are mainly localized on the C atoms of the six-membered ring. The MO calculations predict a strong negative net charge for the ring carbon atoms adjacent to the P atoms and strong positive net charges for the P atoms.

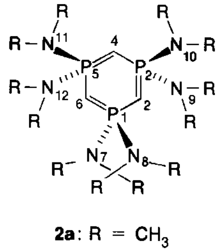
In recent years the electronic structures of many hetero-substituted benzenes have been studied by He(I) photoelectron (PE) spectroscopy. The π-bands of most of these spectra, for example pyridine[1], phosphabenzene[2], arsabenzene[2], stibabenzene[2], and bismabenzene[3] have been explained by the perturbing effect of the heteroatom and could be correlated with the π-bands of benzene[2–4]. In contrast to these species, the electronic structure of the six-membered phosphazenes (e.g. six-membered phosphonitrile halides) is very different[5,6]. Although 6π-electrons are available, the π-system is not delocalized; instead, it is described by localized three-center π-bonds[5,6]. The electronic structure of diphosphazenes[7] as well as diphosphacyclobutadienes[8] can also be rationalized by using the island model[5]. The recently synthesized 1,1,3,3-tetrakis-(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphabenzene (**1a**)[9], 1,1,3,3,5,5-hexakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^5$-triphosphabenzene (**2a**)[10], 4-*tert*-butyl-1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5,5\lambda^3$-triphosphabenzene (**3a**)[11] as well as the substitution products of **1**, **4a** and **5a**[9,12] provide good test cases to check the bonding models for such phosphorus species. The method of choice to investigate the electronic structure of **1**–**5** is photoelectron spectroscopy.

PE Spectra and Calculations

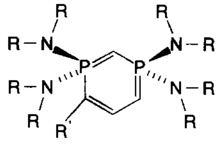
The PE spectra of **1a**–**3a** are shown in Figure 1. The data recorded for **1a**–**5a** are collected in Table 1. Common to all five spectra are two peaks in the low-energy region between 6 and 7.5 eV, followed by a very intense and broad peak between 8 and 9 eV. To interpret these data we make use of the observation that Koopmans' approximation also holds[13] for phosphorus compounds, as exemplified on many occasions[3,4,8,14–16]. We can hence set as equal the negative value of the calculated orbital energies, $-\varepsilon_i$, to the measured vertical ionization energies, $I_{v,j}$. The calculations were carried out by using the MNDO method[17] for the model compounds **1b**–**5b**. The calculations are based on the X-ray



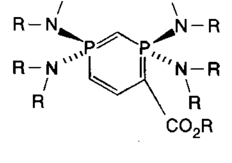
1a: R = CH_3
b: R = H



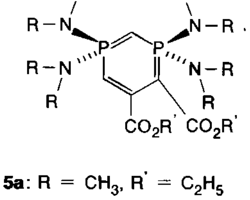
2a: R = CH_3
b: R = H



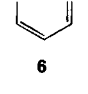
3a: R = CH_3, R' = *t*Bu
b: R = H, R' = CH_3



4a: R = CH_3
b: R = H



5a: R = CH_3, R' = C_2H_5
b: R = R' = H



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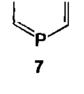

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data available for **2a**[10], **3a**[11], and **5a**[12]. For **1b** and **4b** we have optimized all geometrical parameters with respect to the total energy. The calculated geometrical parameters for **1b**–**5b** are in close agreement with the experimental ones. Besides the comparison between experimental results and MO calculations, our assignment of the PE bands is confirmed by a comparison with PE data of related species. The MO calculations are summarized in Table 1. For the sake of simplicity and comparability, the group-theoretical assignments refer to C_{2v} (**1** and **3**–**5**) and D_{3h} (**2**).

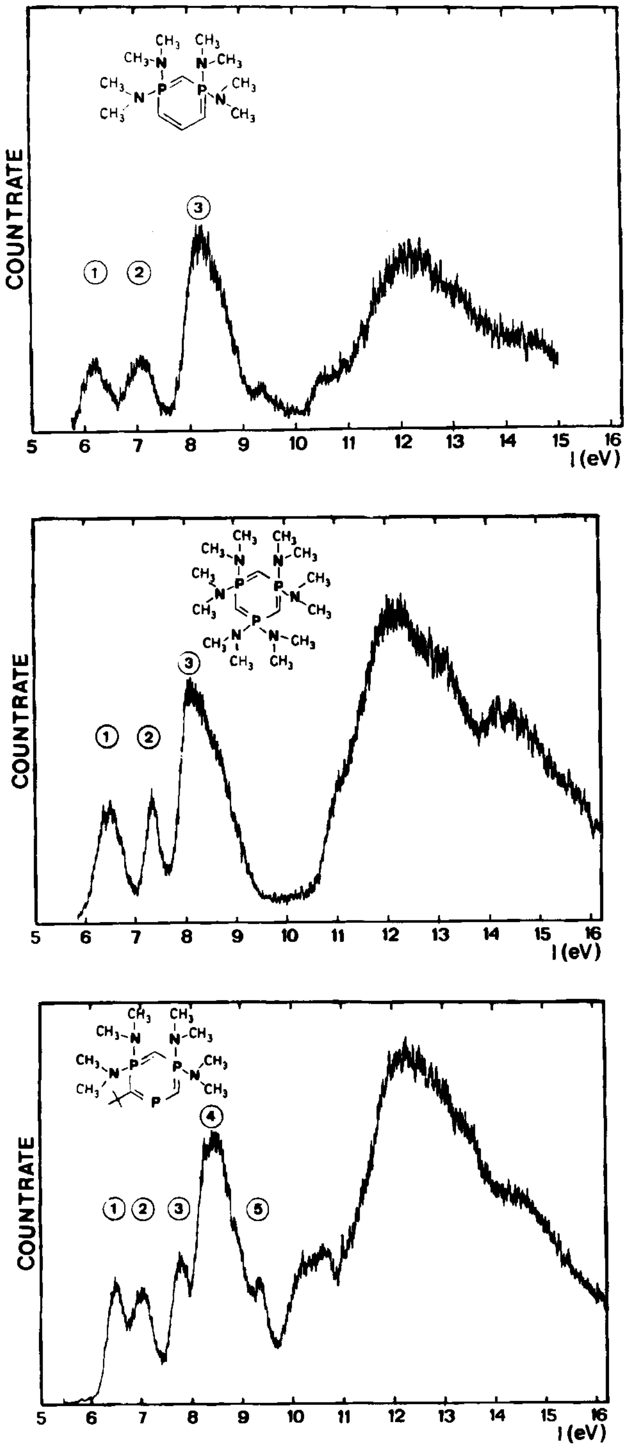


Figure 1. PE spectra of **1a**–**3a**

Table 1. Comparison between the recorded vertical ionization energies, $I_{v,j}$, for **1a**–**5a** and the calculated orbital energies, ε_j, for **1b**–**5b**. All values in eV

Compound	Band	$I_{v,J}$	Assignment	$-\varepsilon_j$(MNDO)
1	1	6.2	$5a_2(\pi)$[a]	7.81
	2	7.1	$6b_1(\pi)$	8.56
	3	8.1–8.7	$10a_1(n_N)$	10.81
			$8b_2(n_N)$	10.84
			$5b_1(\pi)$	10.94
			$4a_2(n_N)$	12.07
			$4b_1(n_N)$	12.29
2	1	6.5	$5e''(\pi)$[a]	8.55
	2	7.3	$4a_2''(\pi)$	8.76
	3	8.1–8.8	$7e'(n_N)$	10.69
			$5a_1(n_N)$	11.34
			$4e''(n_N)$	12.00
			$3a_2''(n_N)$	12.22
3	1	6.5	$a_2(\pi)$	8.06
	2	7.0	$b_1(\pi)$	8.91
	3	7.8	$b_1(\pi)$	10.87
	4	8.2–8.7	$b_2(n_N)$	10.88
			$a_1(n_N)$	11.56
			$a_2(n_N)$	12.23
			$b_1(n_N)$	12.50
	5	9.3	$a_1(n_P)$	10.20
4	1	6.1	$a_2(\pi)$	7.96
	2	7.4	$b_1(\pi)$	8.88
	3	8.2–9.2	$b_2\ (n_N)$	10.88
			n_O	11.13
			$b_1\ (\pi)$	11.18
			$\pi\ (CO_2)$	11.55
			$a_1\ (n_N)$	11.57
			$a_2\ (n_N)$	12.26
			$b_1\ (n_N)$	12.49
5	1	6.6	$a_2(\pi)$	7.95
	2	7.1	$b_1(\pi)$	8.86
	3	8.2–10.3	$b_2(n_N)$	10.85
			n_O	11.10
			$b_1(\pi)$	11.17
			$\pi(CO_2)$	11.46
			$a_2(n_N)$	11.54
			$a_1(n_N)$	12.23
			$b_1(n_N)$	12.46

[a] The numbering of the irreducible reprcsentation corresponds to **1b** and **2b**, respectively.

According to the MNDO calculations the first two bands in **1a** and **3a**–**5a** should be assigned to two π-MOs localized at the carbon atoms of the ring. In Figure 2 we have compared a schematic drawing of the three occupied π-MOs of **1** with those of $1\lambda^3,3\lambda^3$-diphosphabenzene (**6**). Although all three π-MOs of both compounds belong to the irreducible representations a_2 and b_1 in the point group C_{2v}, they show different localization properties. In the case of the π-MOs of **6** the resemblance to the π-MOs of benzene is evident. The π-MOs of **1**, however, are localized on the carbon skeleton. This strong localization on the carbon framework also shows up in a strong charge polarization (Table 2), that is a strong positive charge is predicted for the phosphorus atoms and a negative charge for carbon atoms adjacent to the phosphorus centers.

The broad peak between 8 and 9 eV in the PE spectra of **1a** and **3a**–**5a** is assigned to four bands arising from the four linear combinations of the lone pairs at the nitrogen

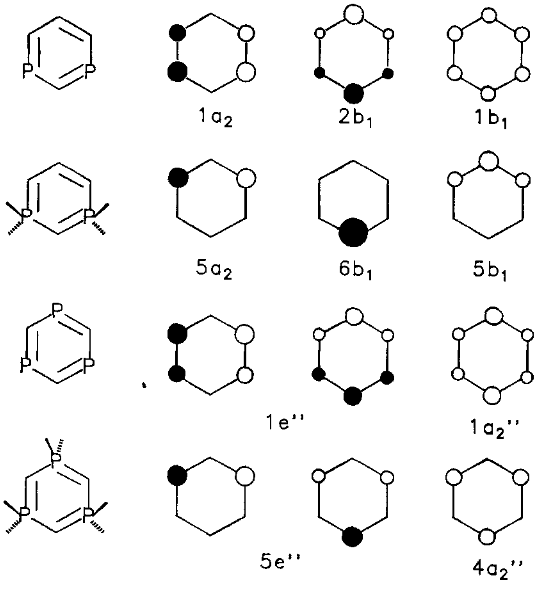


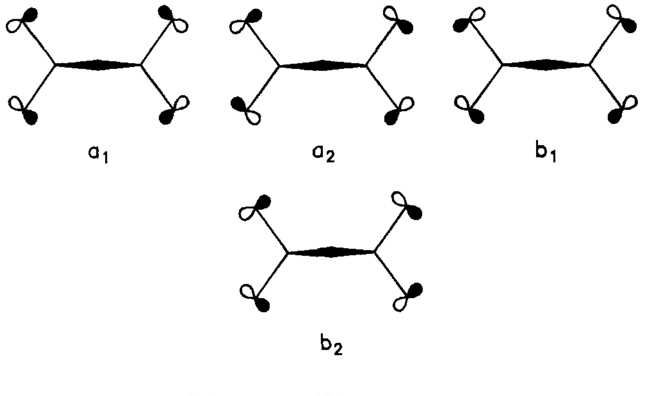
Figure 2. Schematic representation of the highest occupied MOs of **1**, **2**, **6**, and **7**

Table 2. Calculated (MNDO) net charges of **1b**, **2b**, **6** and **7**

Position	1b	2b	6	7
1	0.90	0.99	0.23	0.26
2	−0.92	−0.92	−0.33	−0.36
3	0.90	0.99	0.33	0.26
4	−0.50	−0.92	−0.18	−0.36
5	0.18	0.99	−0.06	0.26
7	−0.33	−0.34	–	–

centers, as shown in Scheme 1. In the case of **4a** and **5a**, linear combinations localized at the ester group(s) are also anticipated. Supporting this assignment are PE results on different aminophosphines[8,14,17] which show ionization energies for the nitrogen lone pairs between 8 and 9 eV. In the PE spectrum of **3a** there are two further bands (3, 5) to be assigned. According to the calculations we assign band 3 to the lone pair at the λ^3-phosphorus and band 5 to the lowest occupied π-MO. We prefer the reverse order (see Table 1) since the lone pair at P is found in phosphabenzene at 9.8 eV[2,3].

Scheme 1



The ratio of the areas below the envelopes of the first two bands of the PE spectrum of **2a** is approximately 2:1. Therefore, we have assigned two transitions to the first band at 6.5 eV. This assignment is in accordance with the results of MNDO calculations on **2b** summarized in Table 1. For the HOMO a degenerate pair (5e'',π) is predicted, followed by another π-MO of a_2'' symmetry. As discussed in the case of **1**, the π-MOs of **2** are also very strongly localized at the carbon atoms (see Figure 2), a consequence which leads to a strong polarization of charges. In Table 2 we compare the calculated net charges of **2b** with those of $1\lambda^3,3\lambda^3,5\lambda^3$-triphosphabenzene (**7**). A similar pattern is obtained by a comparison of **1b** with **6**. For the broad peak between 8 and 9 eV (Figure 1) the calculation predicts six linear combinations of the nitrogen lone pairs. This band has been anticipated from a discussion of the PE spectrum of **1a** and **3a**–**5a**.

Conclusion

Our PE spectroscopic investigations, together with model calculations, reveal similar electronic structures for **1**–**5**. A strong localization of negative charge on the ring carbon atoms adjacent to the strongly positively charged phosphorus atoms is found. This description is in agreement with Dewar's island model. It also corresponds to the case of 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete[8].

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Experimental

The syntheses of **1a**–**5a** have been described[9–12]. The He(I) photoelectron spectra of the analytically pure compounds have been recorded on a Perkin Elmer PS 18 instrument. The recording temperatures were: **1a**: 82°C, **2a**: 84°C, **3a**: 69°C, **4a**: 102°C, **5a**: 115°C. The calibration was carried out with the lines of Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of ca. 20 meV on the $^2P_{3/2}$ Ar line was achieved.

CAS Registry Numbers

1a: 131575-23-0 / **1b**: 133778-86-6 / **2a**: 129777-79-3 / **2b**: 133778-87-7 / **3a**: 105020-52-8 / **3b**: 133778-88-8 / **4a**: 131575-20-7 / **4b**: 133778-89-9 / **5a**: 126179-06-4 / **5b**: 133778-90-2 / **6**: 6050-23-3 / **7**: 79793-11-6

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[1] Dedicated to Professor *Alexandru T. Balaban* on the occasion of his 60th birthday.

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