

Electronic Structure of Three-Membered Rings Containing P Atoms—PE Spectroscopic Investigations and Model Calculations

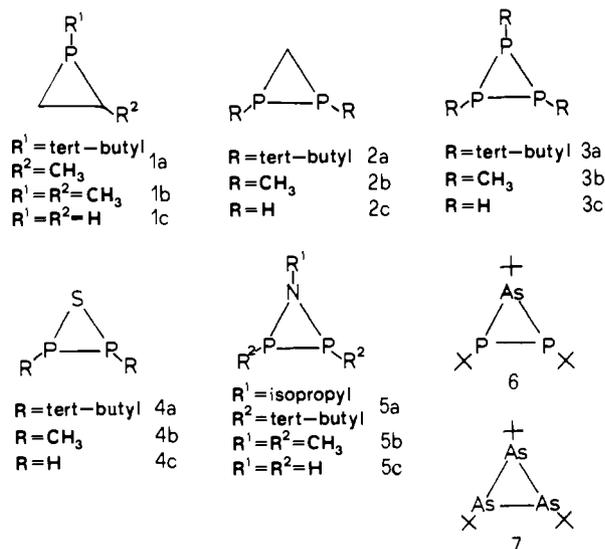
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Abstract: The He I photoelectron (PE) spectra of three-membered rings with one to three phosphorus atoms have been measured. The assignment of the first bands is based on empirical correlations and on calculations using semiempirical models (MNDO, MINDO/3) as well as the Hartree-Fock SCF method. These investigations permit deductions at the sequence of the highest occupied MO's of phosphirane, diphosphirane, cyclotriphosphane, thiadiphosphirane, and azadiphosphirane. The PE spectra of a diphospharsirane (*t*-BuP)₂(*t*-BuAs) and of a cyclotriarsane (*t*-BuAs)₃ also have been recorded and their electronic structures are discussed.

Three-membered rings containing phosphorus and arsenic have come into focus due to the recent synthetic success in several laboratories¹⁻⁵ and the recognition that also in larger molecules the three-membered ring moiety serves as a building block.^{1,6-8}

To understand the bonding properties in compounds containing three-membered rings with P atoms we have investigated the He I photoelectron (PE) spectra of a series of model compounds. The compounds are the following: *trans*-1-*tert*-butyl-2-methylphosphirane (**1a**),⁹ 1,2-di-*tert*-butyldiphosphirane (**2a**),¹⁰ tri-*tert*-butylcyclotriphosphane (**3a**),¹¹ 2,3-di-*tert*-butyl-1-thiadiphosphirane (**4a**),¹² 1-isopropyl-2,3-di-*tert*-butyl-1,2,3-azadiphosphirane (**5a**),¹³ tri-*tert*-butyldiphospharsirane (**6**),¹⁴ and tri-*tert*-butylcyclotriarsane (**7**).⁵



PE spectroscopic studies on molecules are especially useful to chemists interested in the electronic structure of molecules if the PE bands can be correlated with the molecular orbitals (MO's) obtained from the corresponding model calculation. Since our argumentation is based on the MO description of molecules **1-7** we shall start our discussion describing the results of the model calculations.

Model Calculations

We have carried out semiempirical (MNDO¹⁵ and MINDO/3¹⁶) and ab initio calculations using a minimal basis (STO-3G¹⁹). The *tert*-butyl groups were not considered explicitly. They

were replaced by methyl groups for the semiempirical calculations (**1b-5b**) or hydrogen atoms (models **1c-5c**). For **4** and **5** the MNDO method has to be used since the MINDO/3 procedure provides no parameters to treat P-S and P-N bonds. Since for most compounds no geometrical parameters have been reported, we have calculated them using the semiempirical procedures by minimizing the heat of formation for the methyl derivatives **1b-5b** as well as the parent compounds **1c-5c** with respect to the bond lengths and bond angles. For the HF-SCF calculation on **1c-3c** we adopted the geometries derived by the MINDO/3 method;¹⁶⁻¹⁸

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Table I. Most Relevant Geometrical Parameters Calculated for **1b** to **5c**. For **1b-3c** We List the MNDO (First Line) and MINDO/3 Parameters. Heat of Formation (ΔH_f°) in kcal/mol, Bond Length in Å

compound	ΔH_f°	1-2	2-3	1-4	4-5	5-6
 1b	-21.27 21.80	1.78 1.90	1.52 1.52	1.76 1.84	4.23 4.52	
 1c	0.79 21.42	1.77 1.87	1.51 1.50	1.34 1.42	2.68 2.95	
 2b	-40.84 2.67	2.05 2.29	1.75 1.84	1.75 1.83	4.54 5.10	
 2c	-2.81 11.20	2.04 2.21	1.75 1.84	1.34 1.43	3.66 4.01	
 3b	-52.99 23.10	2.04 2.16	2.04 2.16	1.74 1.85	3.48 4.15	4.56 5.02
 3c	4.82 17.01	2.04 2.10	2.04 2.12	1.34 1.44	2.65 2.95	3.68 3.99
 4b	-40.24	2.05	1.97	1.75	4.57	
 4c	-1.71	2.04	1.57	1.34	3.69	
 5b	-36.61	2.10	1.64	1.76	4.67	3.76
 5c	5.73	2.10	1.63	1.35	3.81	3.05

Table II. Calculated Orbital Energies and Wave Functions of Phosphirane (**1c**) and *trans*-1,2-Dimethylphosphirane (**1b**) Using the MINDO/3 (a), MNDO (b), and HF-STO 3G (c) Model

compd	Γ	$-\epsilon_j$ (eV)			% P b	% C b	MO type
		a	b	c			
1b	a'	8.95	10.29		56.0	24.6	lone pair
	a''	9.77	10.94		45.1	35.6	Walsh PC
	a'	10.54	11.98		21.7	40.4	Walsh PC
1c	6a'	9.39	10.81	7.57	58.4	33.9	lone pair
	3a''	10.37	11.38	9.05	50.4	41.4	Walsh
	5a'	11.05	12.64	10.99	27.6	44.7	Walsh

^aLocal C_2 symmetry was assumed.

for **4c** and **5c** those by MNDO were used. The most relevant data are listed in Table I.

A comparison between the bond distances obtained for **3b** with those reported for **3a** shows that the MINDO/3 results are closer to the experiment ($P-P = 2.20$ Å, $P-C = 1.90$ Å)²⁰ than those results derived from the MNDO method. Together with the structural parameters our calculations yield the MO's of **1-5**. We will first discuss the energy sequence of the MO's and the form of the wave functions for **1-5**.

As a starting point we will use the occupied valence orbitals of cyclopropane. Numerous calculations have shown that the highest occupied MO's of cyclopropane are the two e' orbitals (e_A , e_S) shown in Figure 1a.²¹ For a qualitative treatment this Walsh

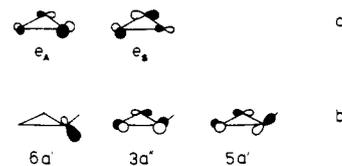


Figure 1. (a) Schematic representation of the highest occupied MO's of a cyclopropane ring as obtained by MNDO. (b) Schematic representation of the highest occupied MO's of **1b** and **1c** as obtained by MNDO.

picture is sufficient while for a more sophisticated treatment some corrections have to be added.²²

Replacing one CH_2 center by a PH group will give the phosphirane **1c**. The introduction of the P atom will reduce the

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Table III. Calculated Orbital Energies and Wave Functions of Diphosphirane (**2c**) and 1,2-Dimethyldiphosphirane (**2b**) Using the MINDO/3 (a), MNDO (b), and HF-STO 3G (c) Model

compd	Γ	$-\epsilon_j$ (eV)			% P b	% C(ring) b
		a	b	c		
<i>cis</i> - 2c (C_s)	6a'	9.17	10.92	7.15	94.4	1.9
	3a''	9.36	11.03	6.96	68.3	23.3
	5a'	10.41	12.55	9.99	58.5	19.0
	2a''	11.69	13.05	11.83	48.0	22.1
<i>trans</i> - 2c (C_2)	5a	9.04	10.77	6.64	93.3	0.1
	4b	9.68	11.30	7.75	69.0	31.4
	4a	10.03	12.09	9.27	65.8	14.1
	3b	11.62	13.40	11.40	35.6	26.3
<i>cis</i> - 2b (C_s)	9a'	8.65	10.30		85.6	1.6
	6a''	8.97	10.39		66.9	17.4
	8a'	9.92	11.39		56.6	15.8
	5a''	11.32	12.30		39.7	23.4
<i>trans</i> - 2b (C_2)	8a	8.56	10.15		86.1	0.2
	7b	9.31	10.82		61.6	26.1
	7a	9.53	11.42		59.5	11.4
	6b	11.35	12.67		36.0	19.6

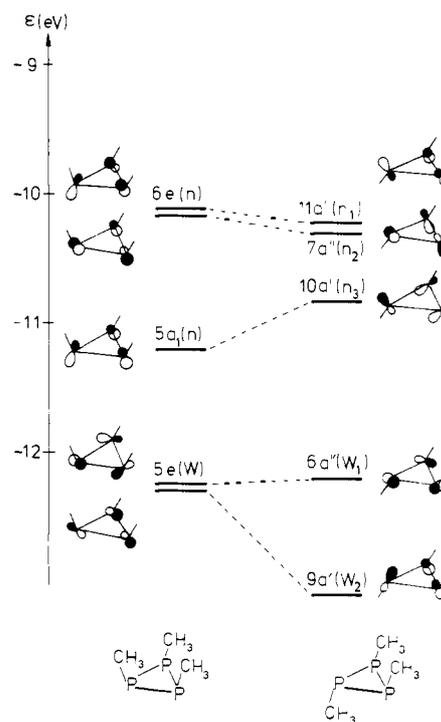
Table IV. Calculated Orbital Energies and Wave Functions of Cyclotriphosphane (**3c**) and Trimethylcyclotriphosphane (**3b**) Using the MINDO/3 (a), MNDO (b), and HF-STO 3G (c) Model

compd	Γ	$-\epsilon_j$ (eV)			MO type
		a	b	c	
<i>cis</i> - 3c (C_{3v})	3e	8.80	11.09	6.07	lone pair
	3a ₁	9.74	12.07	8.54	lone pair
	2e	10.80	13.21	9.94	Walsh
<i>trans</i> - 3c (C_s)	6a'	8.67	11.10	6.12	lone pair
	3a''	8.89	11.13	6.54	lone pair
	5a'	9.37	11.58	7.36	lone pair
	2a''	10.62	13.23	9.95	Walsh
	4a'	12.14	14.49	11.49	Walsh
<i>cis</i> - 3b (C_{3v})	6e	8.26	10.12		lone pair
	5a ₁	9.43	11.22		lone pair
	5e	10.22	12.26		Walsh
<i>trans</i> - 3b (C_s)	11a'	8.14	10.20		lone pair
	7a''	8.35	10.22		lone pair
	10a'	8.99	10.84		lone pair
	6a''	10.15	12.24		Walsh
	9a'	11.31	13.17		Walsh

symmetry from C_{3v} to C_{2v} and add an additional high-lying lone pair on the P atom to the upper valence orbitals.

This qualitative picture is confirmed by the results of SCF calculations with semiempirical (MINDO/3, MNDO) or the Hartree Fock SCF methods. As shown in Table II the lone pair at the P atom is predicted to be the highest occupied molecular orbital (HOMO), followed by two MO's which are related to e_A and e_S of the cyclopropane ring but considerably split in energy. Both MO's, 3a'' and 5a' in Table II can be described in a localized model as the two P-C σ -bonds (see Figure 1b). Replacing two CH_2 units in a cyclopropane ring by PH moieties will likewise lead to diphosphirane **2c**. Since in **2a** both *tert*-butyl groups adopt the anti configuration we will focus on the trans configuration of **2**. All the calculation methods used (see Table III) predict the two lone-pair combinations on P on top of two orbitals of Walsh-type character. The orbital energies predicted for the *cis* and *trans* isomer of either **2b** or **2c** are very close in energy. The energy difference of the two Walsh-type MO's is predicted to be somewhat larger for the *cis* isomer of **2b** and **2c** compared to the *trans* isomer.

In Table IV we have listed the orbital energies calculated for cyclotriphosphane (**3c**)²³⁻²⁵ adopting C_{3v} and C_s symmetry together

**Figure 2.** Correlation between the highest occupied MO's of trimethylcyclotriphosphane (**3b**) assuming C_{3v} and C_s symmetry, according to a MNDO calculation.

with the corresponding trimethyl congeners (**3b**). A comparison between the calculated (MNDO) orbital energies for **3b** assuming C_{3v} and C_s symmetry shows a small split of the former 6e MO's and a slight stabilization if we compare the orbital energy of 6e (10.12 eV) with the center of gravity of 11a' and 7a'' (10.21 eV), a destabilization of 5a₁, and a large split of the former 5e MO's (see Figure 2). If we compare the orbital energy of 5e (12.26 eV) with the center of gravity of 6a'' and 9a' (12.71 eV) we recognize a considerable stabilization of 5e when reducing the symmetry. The reduction of symmetry from C_{3v} to C_s leads furthermore to a strong mixing between the lone pairs $e(n)$, $a_1(n)$ and the Walsh orbitals. This can be seen from the wave function contour diagrams shown in Figure 3. This plot presents those valence MO's of **3b** which are symmetric with respect to the plane of symmetry (xz plane), i.e., 11a'(n₁), 10a'(n₃), and 9a'(n₃). The

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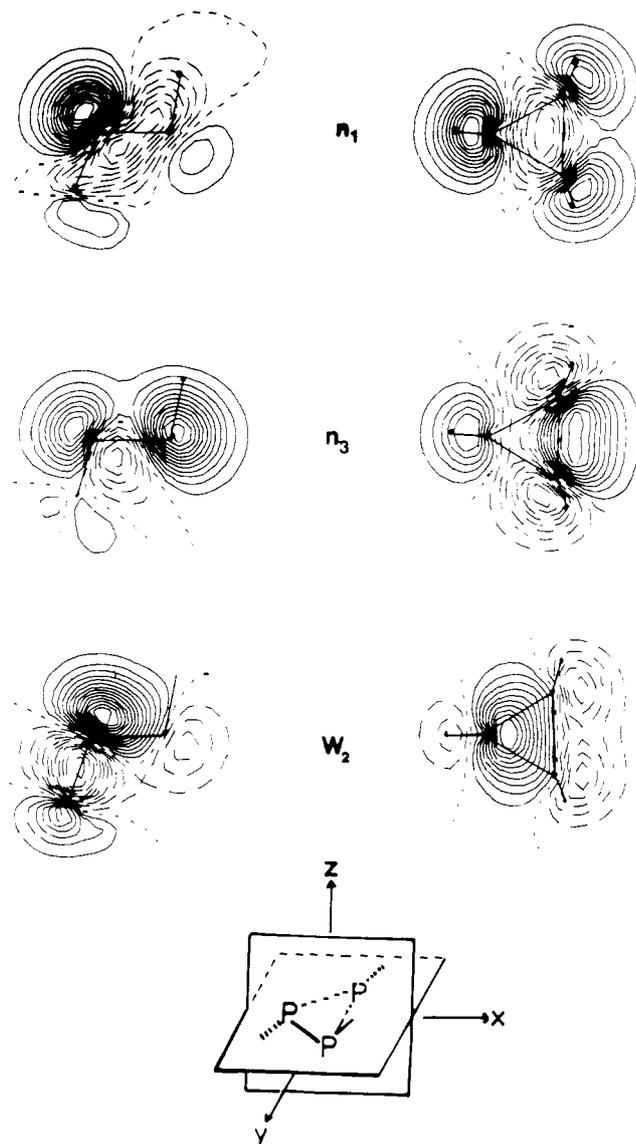


Figure 3. Wave function contour diagrams for $6e(n_1)$, $5e(W_2)$ and $5a_1(n_3)$ of **3b** according to a MINDO/3 calculation. The contours are drawn in the xz plane (left) and in a plane 0.1 \AA above the xy plane (right).

Table V. Calculated Orbital Energies and Wave Functions of Thiadiphosphirane (**4c**) and Dimethylthiadiphosphirane (**4b**) Using the MNDO (a) and the HF-STO 3G Method (b)

compd	Γ	$-\epsilon_j$ (eV)		% P	% S
		a	b		
4b (C_2)	$9a'$	10.12		42.2	48.8
	$6a''$	11.18		62.2	15.6
	$8a'$	11.52		55.9	30.9
	$7a'$	12.54		41.3	45.6
	$5a''$	13.09		32.0	33.6
4b (C_2)	$7b$	10.46		18.6	70.3
	$8a$	10.60		85.6	0.1
	$7a$	11.76		54.6	24.7
	$6b$	12.25		36.9	49.9
4c (C_2)	$6a'$	10.73	6.34	29.1	62.7
	$5a'$	11.94	7.28	74.4	24.0
	$3a''$	13.22	8.19	64.4	21.2
	$4a'$	13.94	10.03	53.2	46.7
4c (C_2)	$4b$	10.87	6.40	13.4	77.2
	$5a$	11.32	7.15	93.0	0.0
	$4a$	12.47	8.65	60.9	30.5
	$3b$	12.81	9.09	46.9	52.6

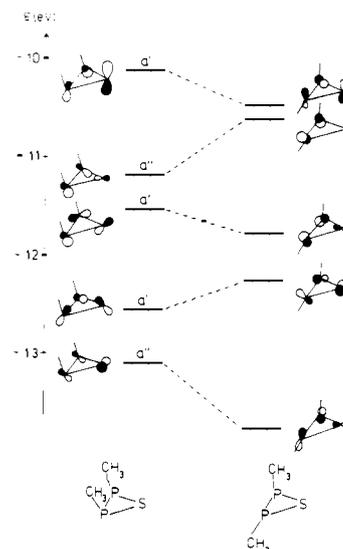


Figure 4. Correlation between the highest occupied MO's of **4b** assuming C_1 and C_2 symmetry, according to a MNDO calculation.

Table VI. Calculated Orbital Energies and Wave Functions of Azadiphosphirane (**5c**) and Trimethylazadiphosphirane (**5b**) Using the MNDO (a) and the HF-STO 3G (b) Method

compd	Γ	$-\epsilon$ (eV)		% P	% N
		a	b		
5b (C_3)	$11a'$	9.24		38.5	38.1
	$10a'$	10.71		54.4	22.1
	$7a''$	10.82		64.5	6.9
	$6a''$	12.71		23.3	15.9
	$9a'$	12.97		40.2	12.9
5b (C_2)	b^a	9.59		20.3	53.3
	a	9.81		87.5	0.3
	a	11.60		54.5	5.2
	b	12.04		38.0	28.8
	b	13.34		26.7	8.3
5c (C_3)	$6a'$	9.99	6.13	44.8	41.7
	$5a'$	11.06	7.46	63.9	25.9
	$3a''$	11.58	8.30	69.7	7.3
	$2a''$	14.40	11.83	42.2	35.1
5c (C_2)	$4b$	10.18	6.30	20.4	60.5
	$5a$	10.37	6.61	94.1	0.5
	$4a$	12.32	9.67	63.6	5.3
	$3b$	13.25	10.28	55.5	44.1

^aThe methyl groups were not considered.

wave functions are calculated by the MINDO/3 method. The contours are plotted in the xz plane (left) and 0.1 \AA above the xy plane, i.e., above the P_3 unit (right). The results of the thiadiphosphirane **4c**, its corresponding dimethyl compound (**4b**), as well as the azadiphosphirane (**5c**) and its trimethyl derivative **5b** are collected in Tables V and VI. In Figure 4 we have shown as an example a correlation between the MO's as predicted by MNDO for **4b** adopting C_3 and C_2 symmetry. As anticipated from the discussion of the P_3 case we find a considerable mixing between P and S lone pairs as well as with the Walsh orbitals. We notice for **4** and **5** pronounced dependence of the energy difference from the conformation of the substituents.

PE Spectra

Figure 5 displays the PE spectra of **1a**, **4a**, **5a**, **6**, and **7**, and the measured vertical ionization energies of **1a**–**5a**, **6**, and **7** are collected in Table VII. The PE spectrum of **1a** shows three bands clearly separated from a region of strongly overlapping bands starting at 11 eV . The PE spectra of **4a** and **5a** are related to that of **2a**²³ in as far as we recognize four bands well separated from strongly overlapping bands. The spectra of **6** and **7** are related to that of **3a** as anticipated.

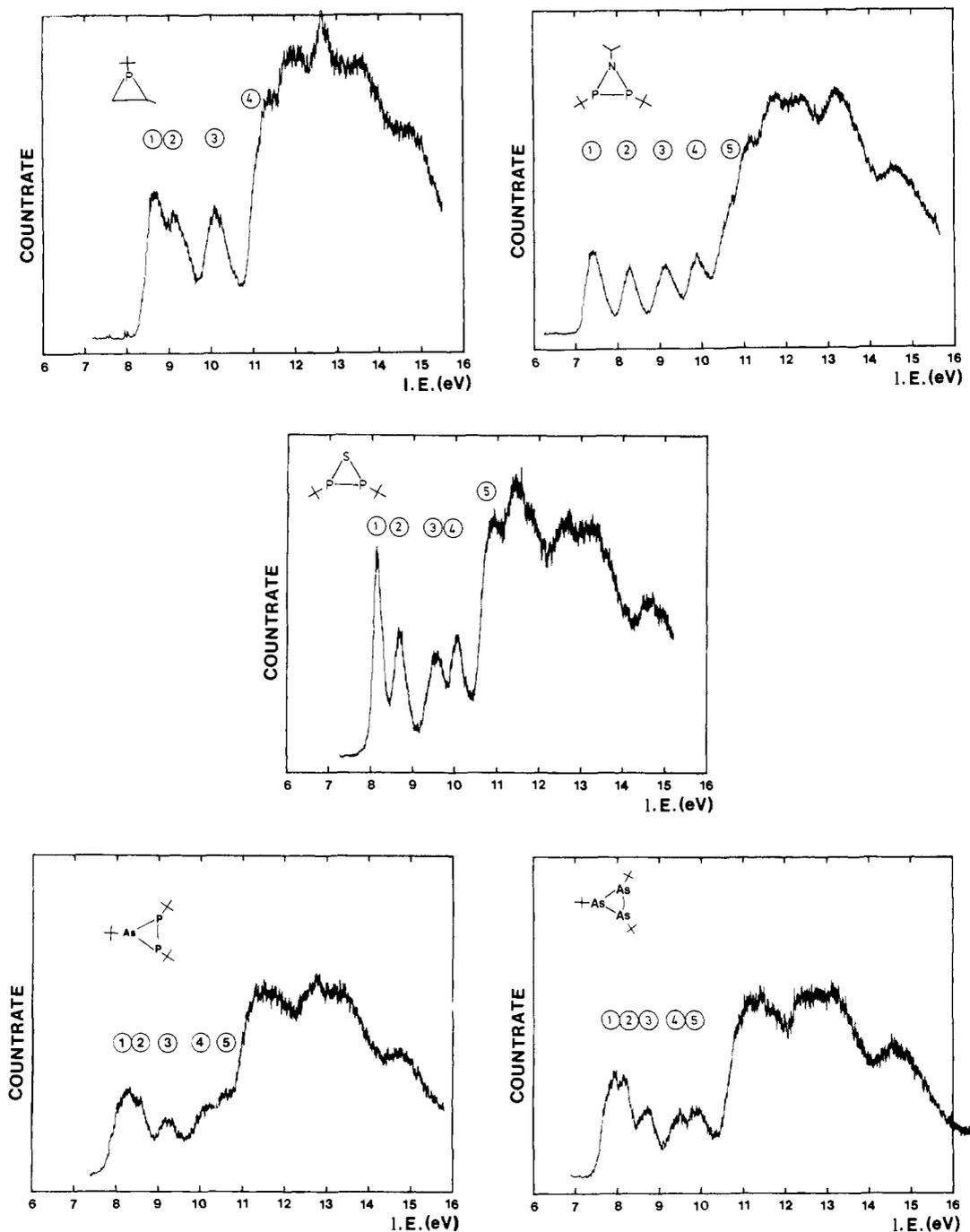


Figure 5. PE spectra of 1a and 4a, 5a, 6, and 7.

Table VII. Ionization Energies of 1a-5a, 6, and 7. All Values in eV

compd	$I_{v,1}$	$I_{v,2}$	$I_{v,3}$	$I_{v,4}$	$I_{v,5}$
1a	8.65	9.1	10.1		
2a	8.38	8.97	9.5	10.14	
3a	8.1	8.2	8.65	9.26	10.08
4a	8.14	8.7	9.6	10.0	10.9
5a	7.44	8.31	9.14	9.9	10.8
6	8.2	8.5	9.2	10.1	10.5
7	7.95	8.2	8.7	9.5	9.9

Interpretation of the PE Spectra

To interpret the PE spectra we rely on the validity of Koopmans' theorem,²⁶ i.e., we assume that the negative value of the calculated orbital energy ($-\epsilon_i$) can be set equal to the measured vertical ionization energy ($I_{v,i}$). This implies that the wave

functions calculated for the ground state can also be used to describe the ionic states. This assumption, although a very crude one, seems to hold for the valence states of most molecules. PE investigations of P compounds have shown that Koopmans' assumption is valid.²⁷ In the following discussion we will rely on the results of MO calculations presented in the previous chapter and we shall try to correlate the bands with those of related species.

PE Spectra of 1a-3a and 6a-7a

To discuss the PE spectra of 1a-3a we will start with the PE results of bicyclo[4.1.0]heptane,²⁸ as a disubstituted cyclopropane. The first two peaks in the PE spectrum of this compound at 9.5

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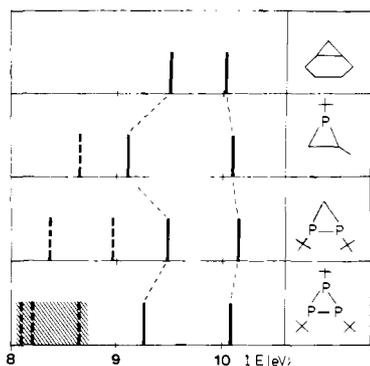


Figure 6. Correlation between the first bands in the PE spectra of bicyclo[4.1.0]heptane and **1a**–**3a**.

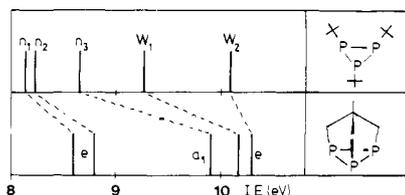
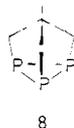


Figure 7. Correlation between the first bands in the PE spectra of **3a** and **8**.

and 10.0 eV correspond to ionizations from the two Walsh-type orbitals shown in Figure 1. As discussed in the previous section we expect an additional MO in the valence region of **1a**: the lone pair on P. From investigations on tertiary phosphines²⁹ an ionization energy around 8.7 eV is anticipated. These empirical considerations are met by the MO calculations (see Table II) and the PE spectrum of **1a** which shows three bands at 8.65, 9.1, and 10.1 eV.

The analysis of the PE spectrum of **2a** reported earlier²³ is congruent with the results shown in Table III. The assignment of the first two bands to the two lone-pair combinations at the phosphorus agrees also with results obtained for diphosphines.³⁰ Bands ③ and ④ at 9.5 and 10.1 eV are ascribed to ionization events from Walsh-type MO's. This assignment is confirmed by the comparison between the PE spectra of **1a** and **2a** shown in Figure 6.

The PE spectrum of **3a** fits very nicely into this picture. As pointed out in the previous chapter the lowering of molecular symmetry from C_{3v} to C_s (see Figures 2 and 3) will cause a considerable mixing between the symmetrical Walsh (e_s) orbital and the a_1 lone-pair combination. This gives rise to a considerable split of the formerly degenerate Walsh pair. The correlation given in Figures 2 and 3 justifies the previous assignment²³ of bands ①–③ to lone-pair combinations and bands ④ and ⑤ to former Walsh MO's. The orbital sequence suggested for **3a** parallels that of $(C_2F_5)_3P$ deduced from its PE spectrum.²⁵ A further confirmation of the assignment of the PE spectra of **3a** is due to Figure 7 which shows the correlation of the PE bands of the phosphorus cage compound **8** (C_{3v})³¹ with the bands of **3a** (C_s). A comparison between the PE bands of **3a** and **8** yields a small shift toward lower



energy for bands ①, ②, and ③ but large shifts for bands ③ and ④. We can rationalize this difference by proceeding in two steps:

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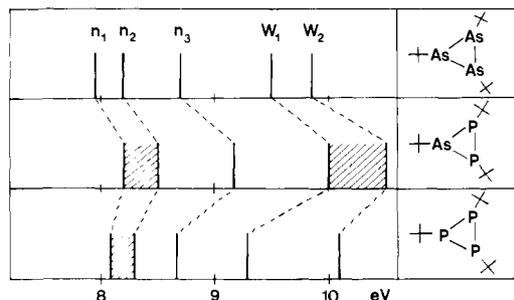


Figure 8. Correlation of the first bands in the PE spectrum of **3a** with those of **6** and **7**.

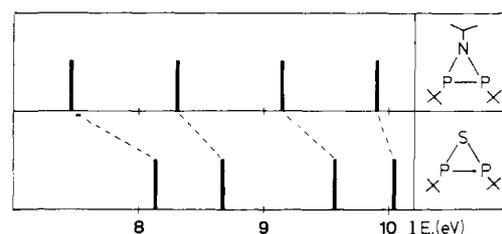


Figure 9. Comparison between the first PE bands of **4a** and **5a**.

(1) by splitting one of the endocyclic C–C bonds of **8** and bending one alkyl group into the anti position of the other alkyl fragments and (2) by replacing the alkyl substituents in the resulting species by *tert*-butyl groups. Carrying out the first operation will stabilize n_1 and n_2 (see Figure 2) while n_3 is destabilized. Exchanging the alkyl groups of the remaining bicyclic compound by *tert*-butyl groups will destabilize n_3 and especially the Walsh-type orbitals because the corresponding wave functions show considerable substituent participation (40–50%). These qualitative considerations imply that *tert*-butyl substitution is mainly responsible for the destabilizations encountered in the comparison between **8** and **3a**, as shown in Figure 7. This argumentation is supported by the observation that the replacement of *one* methyl group in trimethylamine by a *tert*-butyl substituent lowers the ionization energy by 0.5 eV.³² The influence of alkyl substituents on n_1 and n_2 is anticipated to be small since the corresponding wave functions are strongly localized on the P atoms (85%). Both steps taken together yield a strong destabilization of n_3 and W_1 but only a slight one of n_1 , n_2 , and W_2 .

In Figure 8 we have correlated the first five bands of the PE spectrum of **3a** with those of **6** and **7**. A comparison between the bands of **3a** and **7** shows very little change in the ionization energies. A similar close relation is found when comparing the first band in the PE spectra of simple alkyl derivatives $(CH_3)_nX(CF_3)_{3-n}$ ($n = 1-3$; X = P, As).^{29,33} The shift toward higher ionization energy by replacing one P center in **3a** by an As atom we ascribe to the reduced interaction between the 3p atomic orbitals at P with the 4p at As. In **3a** and **7** where the same fragments interfere, interaction is a maximum.

PE Spectra of **4a** and **5a**

The results listed in Tables V and VI together with the correlation diagram shown in Figure 4 suggest the assignment of the first band in the PE spectrum of **4a** to the ionization of a MO which has a large 3p contribution on S. In agreement with this assignment is the observation (Figure 5) that the first band is relatively intense as in the PE spectrum of thiirane.³⁴ Bands ②–④ of **4a** we assign to ionizations from MO's strongly localized on P ($n_{+,n.}$) and Walsh-type MO's.

The correlation shown in Figure 9 between the first PE bands of **4a** and **5a** indicates a parallel assignment of the PE spectrum of **5a** with that of **4a**. The first ionization energy of **5a** is found

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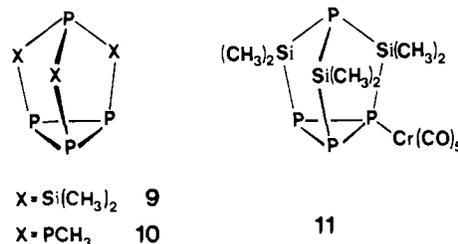
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to be relatively close to that of tertiary amines (7.9 – 8.0 eV)³⁵ thus supporting the assignment of an ionization event out of a N lone pair. Bands ③ and ④ of the PE spectrum of **5a** are relatively close to those of the PE spectrum of **4a** which supports the assignment suggested in Figure 9.

Conclusive Remarks

Our model calculations combined with PE spectroscopic investigations reveal a consistent picture of the electronic structure of three-membered rings containing one to three phosphorus atoms. Due to the low symmetry of the species and the small energy separation between the basis orbital energies of the C–P, P–S, or P–N σ -bonds on one side and the lone pairs on P or the heteroatoms on the other, we encounter a strong mixing for most MO's. Due to this strong mixing the localization properties of the wave function of the HOMO depends on the substituents.

To illustrate this and to point out its consequence for the reactivity of phosphorus compounds, we mention the cage compounds **9** and **10**. While **9** reacts readily with transition-metal carbonyls like $\text{Cr}(\text{CO})_6$ to yield $\text{P}_4[\text{SiMe}_2]_3\text{Cr}(\text{CO})_5$ (**11**),³⁶ it is much more difficult to obtain a similar complex with **10**.³⁷ This difference has been rationalized by recognizing that the HOMO of **9** is a lone-pair combination localized at the basal three-membered ring while for **10** the HOMO is localized at the equatorial P atoms.³⁸



Experimental Section

The syntheses of compounds **1a**,⁹ **4a**,¹² **5a**,¹³ **6**,¹⁴ and **7**⁵ have been reported in the literature. The PE spectra were recorded on a UPS 200 spectrometer of Leybold Heraeus at the following temperatures: **1a**, 25 °C; **4a**, 45 °C; **5a**, 25 °C; **6**, 30 °C; and **7**, 50 °C. The spectra were calibrated with Ar and Xe.

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Registry No. **1a**, 99017-58-0; **1b**, 99017-51-3; **1c**, 6569-82-0; **2a**, 68969-73-3; *cis*-**2b**, 99017-57-9; *trans*-**2b**, 99017-52-4; *cis*-**2c**, 99017-56-8; *trans*-**2c**, 99017-53-5; **3a**, 61695-12-3; *cis*-**3b**, 99095-39-3; *trans*-**3b**, 91121-28-7; *cis*-**3c**, 99095-38-2; *trans*-**3c**, 89254-38-6; **4a**, 79898-83-2; **4b**, 99017-54-6; **4c**, 93109-87-6; **5a**, 82775-02-8; **5b**, 99017-55-7; **5c**, 77680-27-4; **6**, 77614-73-4; **7**, 76173-66-5.

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Kinetic Isotope Effect Associated with the Dissociative Addition of Dihydrogen to *trans*- $\text{Ir}(\text{CO})\text{Cl}(\text{Ph}_3\text{P})_2$ ^{1a}

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Abstract: The temperature dependence of the kinetic isotope effect for the dissociative addition of dihydrogen and dideuterium to *trans*- $\text{Ir}(\text{CO})\text{Cl}(\text{Ph}_3\text{P})_2$ in toluene has been determined between 0 and 30 °C. Model calculations based on these data suggest that the transition state for dissociation is best formulated as triangular with reactant-like character and involves substantial hydrogen tunneling. The weak KIE ($k_{\text{H}}/k_{\text{D}} \approx 1-2$) generally observed for the dissociative addition of dihydrogen to transition-metal complexes is seen to be a consequence of the product of an unusually large MMI factor, a moderately inverse EXC term and a substantially inverse ZPE factor. Only the tunnel correction prevents the overall KIE from being inverse.

The addition of dihydrogen to a transition-metal center is an obligatory step in many catalytic cycles, and a variety of model systems have been investigated in an effort to understand the nature of such processes.² Of these, the addition of dihydrogen to *trans*- $\text{Ir}(\text{CO})\text{Cl}(\text{Ph}_3\text{P})_2$ (**1**) has been examined in greatest detail.

Table I summarizes some of the previously determined kinetic parameters related to the addition of dihydrogen to **1**.³⁻⁵

Kinetic isotope effects afford a powerful technique with which to probe reaction mechanisms.⁶ Despite this fact, there has been little effort to apply it to the dissociative addition of dihydrogen

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