The Electronic Structure of Substituted 1,2,4,5-Tetraphosphaspiro[2.2]pentanes and 1,2,4,5-Tetraphospha-3-silaspiro[2.2]pentanes†

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The sequence of the highest occupied molecular orbitals of 1,2,4,5-tetraphosphaspiro[2.2]pentane, its 1,2,4,5-tetramethyl substituted derivative, and the corresponding 3-sila analogues is derived by means of molecular orbital (m.o.) calculations. The calculations (MNDO, STO-3G) reveal a small split of the valence orbitals due to spiro-interaction. The results of the model calculations are in accord with photoelectron (p.e.) spectroscopic investigations on 1,2,4,5-tetra-t-butyl-1,2,4,5-tetraphosphaspiro[2.2]pentane (**1a**) and its 3-sila congener (**2a**) assuming S_4 symmetry. The assignment of the p.e. bands is based on the comparison between the p.e. spectra of (**1a**) and (**2a**) those of 1,2-di-t-butyl-3,3-diphenyl-1,2-diphospha-3-silacyclopropane and 1,2-di-t-butyl-3,3-dimethyl-1,2-diphosphirane and on the results of m.o. calculations. Essentially no spiro-interaction could be detected.

1,2,4,5-Tetra-t-butyl-1,2,4,5-tetraphosphaspiro[2.2]pentane, (**1a**),[1] and 1,2,4,5-tetra-t-butyl-1,2,4,5-tetraphospha-3-silaspiro-[2.2]pentane (**2a**)[2] are the only known spiro[2.2]pentanes capable of spiro-interaction.[3] In connection with our interest in the bonding properties of diphosphiranes[4,5] and heterospiro compounds[6,7] we have investigated the He I photoelectron (p.e.) spectra of (**1a**) and (**2a**) together with that of 1,2-di-t-butyl-3,3-diphenyl-1,2-diphospha-3-silacyclopropane (**3a**).[8] The p.e. spectrum of 1,2-di-t-butyl-3,3-dimethyl-1,2-diphosphirane (**4**) has been discussed elsewhere.[4]

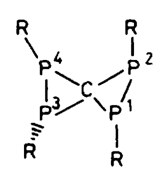
Since our interpretation of the p.e. results is based on a molecular orbital (m.o.) representation of the valence electrons of compounds (**1**) and (**2**) we first discuss the results of model calculations.

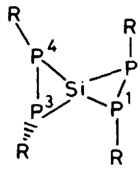
Results and Discussion

Model Calculations.—To derive the valence orbitals of (**1a**)—(**3a**) we have carried out m.o. calculations by replacing the large t-butyl groups by methyl, (**1b**), (**2b**), and (**3b**), or hydrogen groups, (**1c**), (**2c**), and (**3c**). Since the geometries of (**1a**) and all the model compounds just mentioned are unknown we have optimized the geometrical parameters of (**1b**), (**2b**), and (**3b**) as well as (**1c**), (**2c**), and (**3c**) using the MNDO method[9] (MOPN program[10]). Single point STO-3G[11] calculations on (**1c**), (**2c**), and (**3c**) based on the MNDO geometries were then carried out. The most relevant geometrical parameters derived with the MNDO procedure for (**1b**), (**2b**), and (**3b**), as well as for (**1c**), (**2c**), and (**3c**), are listed in Table 1. The corresponding model calculations on the derivatives of (**4**) have been published elsewhere.[4,5]

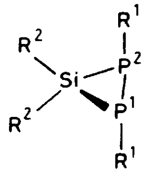
A comparison between the calculated geometrical parameters of (**2b**) and (**3b**) and those found for (**2a**)[12] and (**3a**)[13] shows that the calculated bond lengths are underestimated by 5—10%.

To understand the interactions prevailing in (**1**) and (**2**) we will discuss first the electronic structure of (**1b**) assuming an idealized D_{2d} conformation. In a planar 1,2,4,5-tetraphosphaspiro[2.2]pentane skeleton each phosphorus atom provides one $2p$ orbital. From all four $3p$ orbitals ($\varphi_1,\varphi_2,\varphi_3,\varphi_4$) we can construct the four symmetry-adapted linear combinations given below. All four of them are shown assuming D_{2d} symmetry. Two of the linear combinations (Ψ_1,Ψ_2) belong to the

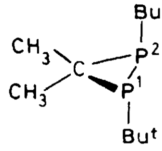




R = Bu^t	(**1a**)	(**2a**)
R = CH$_3$	(**1b**)	(**2b**)
R = H	(**1c**)	(**2c**)



R^1 = Bu^t R^2 = Ph (**3a**)
R^1 = CH$_3$ R^2 = H (**3b**)
R^1 = R^2 = H (**3c**)



(**4**)

$$\Psi_1 = \frac{1}{\sqrt{2}}\left(\varphi_1 + \varphi_2\right)$$

$$\Psi_2 = \frac{1}{\sqrt{2}}\left(\varphi_3 + \varphi_4\right)$$

$$\Psi_3 = \frac{1}{2}\left(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4\right)$$

$$\Psi_4 = \frac{1}{2}\left(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4\right)$$

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

irreducible representation E and are of π type (bonding between φ_1,φ_2 or φ_3,φ_4). The remaining two (Ψ_3,Ψ_4) transform according to B_1 and A_2 (D_{2d}) and are of π^* type (antibonding between φ_1,φ_2 and φ_3,φ_4). The latter ones are split in energy due to spiro-interaction.

The two highest occupied (h.o.) m.o.s of (**1b**) are the two linear combinations with π^* character which are separated by a large gap from the two π m.o.s. These m.o.s are followed by four m.o.s which are linear combinations of the two symmetric (a_2,b_1) and antisymmetric (e) Walsh type orbitals as discussed in the 1,2-diphosphirane series.[4] A schematic drawing of all eight valence orbitals of (**1b**) is shown on the left of Figure 1.

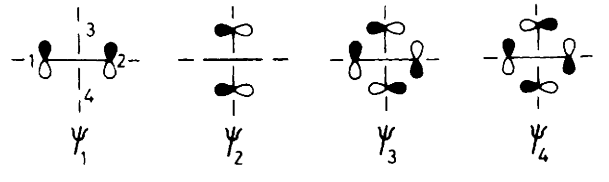
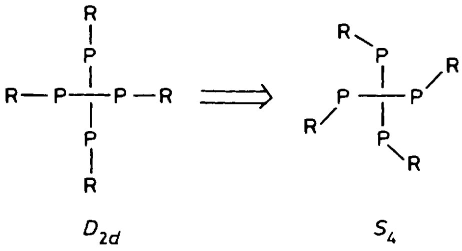


Table 1. Predicted bond lengths (Å) for (**1b**), (**1c**), (**2b**), (**2c**), (**3b**), and (**3c**)

Compound	P¹–C(Si)	P¹–P²	P¹–CH₃	P¹–H
(**1b**)	1.72	2.05	1.76	
(**1c**)	1.73	2.05		1.34
(**2b**)	2.12	2.06	1.74	
(**2c**)	2.12	2.06		1.34
(**3b**)*	2.13	2.08	1.78	
(**3c**)*	2.13	2.06		1.35

* The Si–H distance was found to be 1.43 Å for (**3b**) and 1.44 Å for (**3c**).

The antibonding interaction between the π^* type m.o.s ($2a_2$ and $2b_1$ in Figure 1) is reduced if we bend the substituents of the D_{2d} conformation in such a way (see below) that S_4 symmetry is preserved. It should be mentioned that for (**2a**) S_4 symmetry is found in the solid state.[12] This reduction of the antibonding interaction leads to a strong stabilization of $2a_2$ and $2b_1$ as



shown in Figure 1. For $6e$ and $5e$ an additional stabilization is observed due to the interaction with the lowest unoccupied molecular orbital (l.u.m.o.). This interaction increases the $3s$ character at the P centres and thus a stabilization follows. For $5b_2$ and $5a_1$ the bending of the substituents leads to a bending of the p-type m.o.s out of the plane of the three-membered ring. This reduces the bonding and thus a destabilization is expected and predicted for $5a_1 \rightarrow 6a$. In the case of $5b_2$, the destabilization is approximately compensated for by mixing in $3s$ character from $6b_2$ as outlined above. The strong stabilization of the two h.o.m.o.s of (**1**) and the destabilization of $5a_1$ upon the reduction of symmetry yields six close lying valence orbitals as shown on the right of Figure 1.

For (**2**) a similar sequence is anticipated. Due to the fact that the ionization energy of a Si atom (8.15 eV)[14] is lower than that

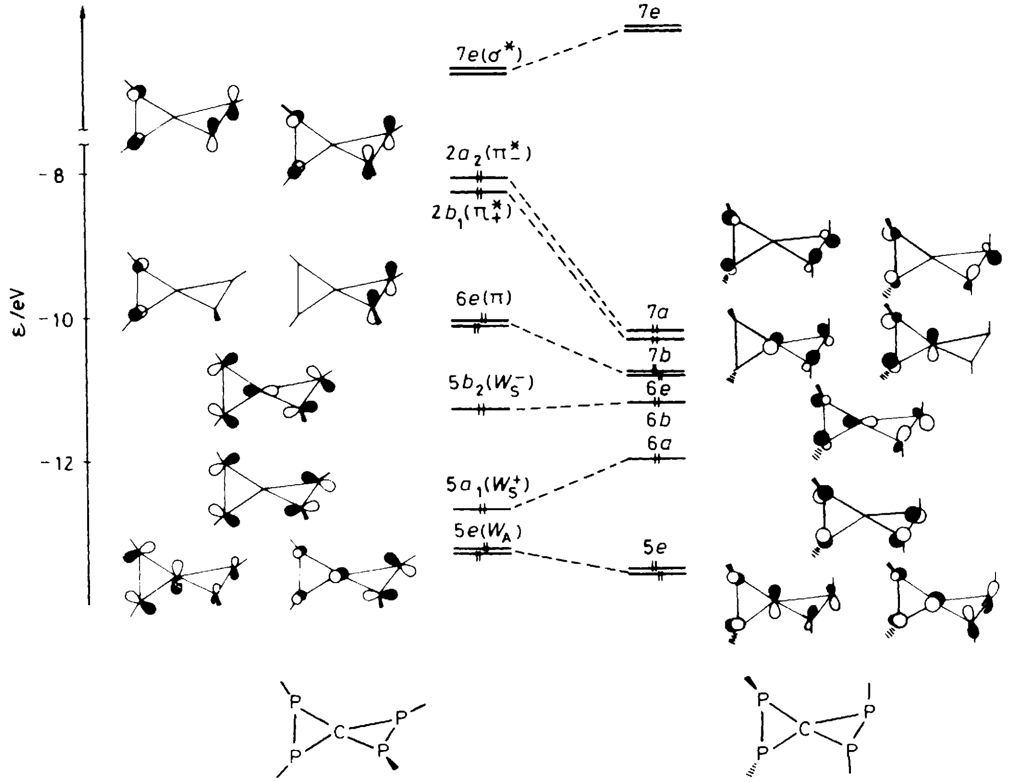


Figure 1. Correlation between the highest occupied m.o.s of (**1b**) assuming D_{2d} symmetry with those of (**1b**) assuming S_4 symmetry. A schematic representation of the m.o.s is presented at the left and right

Table 2. Calculated orbital energies (eV) for (**1b**), (**2b**), (**1c**), (**2c**), and (**3b**)

Compound (geometry)	$-\varepsilon_j$(MNDO)	Compound (geometry)	$-\varepsilon_j$(MNDO)	$-\varepsilon_j$(STO-3G)
(**1b**) (S_4)[a]	10.20 (7*a*)	(**1c**)[a]	10.89 (4*a*)	6.22 (4*a*)
	10.30 (7*b*)		10.95 (4*b*)	6.35 (4*b*)
	10.87 (6*e*)		11.53 (3*e*)	7.34 (3*e*)
	11.19 (6*b*)		12.03 (3*b*)	8.39 (3*b*)
	12.04 (6*a*)		13.10 (3*a*)	10.81 (3*a*)
	13.61 (5*e*)		15.04 (2*e*)	12.81 (2*e*)
(**2b**) (S_4)[a]	9.81 (6*e*)	(**2c**)[a]	10.31 (3*e*)	6.22 (3*e*)
	9.90 (7*b*)		10.96 (4*b*)	6.43 (4*b*)
	10.22 (7*a*)		11.00 (4*a*)	6.56 (4*a*)
	10.90 (6*b*)		11.65 (3*b*)	8.06 (3*b*)
	12.40 (6*a*)		13.51 (3*a*)	10.47 (3*a*)
	13.10 (5*e*)		14.41 (2*e*)	11.56 (2*e*)
(**2b**) (S_4)[b]	9.67 (6*e*)	(**2c**)[b]	10.15 (3*e*)	5.99 (3*e*)
	10.22 (7*a*)		10.72 (4*a*)	6.15 (4*a*)
	10.27 (7*b*)		10.79 (4*b*)	6.23 (4*b*)
	10.44 (6*b*)		11.06 (3*b*)	7.35 (3*b*)
	11.81 (6*a*)		13.25 (3*a*)	10.02 (3*a*)
	12.56 (5*e*)		13.99 (2*e*)	10.98 (2*e*)
(**3b**) (C_2)[a]	9.63 (7*b*)	(**3c**) (C_2)[a]	9.96 (4*b*)	6.18 (4*b*)
	9.88 (8*a*)		10.54 (5*a*)	6.24 (5*a*)
	11.11 (7*a*)		11.75 (4*a*)	8.69 (4*a*)
	12.16 (6*b*)		13.80 (3*b*)	10.49 (3*b*)
(**3b**)[c]	9.54 (7*b*)	(**3c**) (C_2)[c]	9.77 (4*b*)	5.87 (5*a*)
	9.88 (8*a*)		10.30 (5*a*)	5.91 (4*b*)
	10.69 (7*a*)		11.20 (4*a*)	7.91 (4*a*)
	11.71 (6*b*)		12.68 (3*b*)	10.18 (3*b*)

[a] MNDO geometry. [b] Adopting the experimental geometry for the tetraphosphasilaspiro[2.2]pentane (ref. 12). [c] Adopting the experimental geometry for (**3a**) (ref. 13).

Table 3. Ionization energies (eV) and band assignments (Figure 2) of (**1a**), (**2a**), and (**3a**)

Compound	Band	$I_{v,j}$	Assignment
(**1a**)	1—4	7.8—8.3	7*a*, 7*b*, 6*e*
	5	8.7	6*b*
	6	9.4	6*a*
(**2a**)	1—4	7.6—8.4	7*a*, 7*b*, 6*e*
	5	8.6	6*b*
	6	9.4	6*a*
	7	9.8	5*e* (?)
(**3a**)	1	7.65—7.85	n_1, n_2
	2	8.8	W_1
	3—7	8.9—9.4	π(Ph), W_2

of a C atom (11.26 eV)[14] we anticipate a shift of those bands towards lower ionization energies whose m.o.s show large coefficients at the Si, *i.e.* the bands in the σ region at energies > 10 eV. The MNDO calculations predict for (**2**) 6*e* on top of 7*a* and 7*b*. The results derived by the model calculations on (**1b**), (**1c**), (**2b**), and (**2c**) are listed in Table 2. It is found that the sequence of the valence orbitals calculated with the minimal basis set for (**1c**), (**2c**), and (**3c**) parallels that obtained with the MNDO method for (**1b**), (**2b**), and (**3c**).

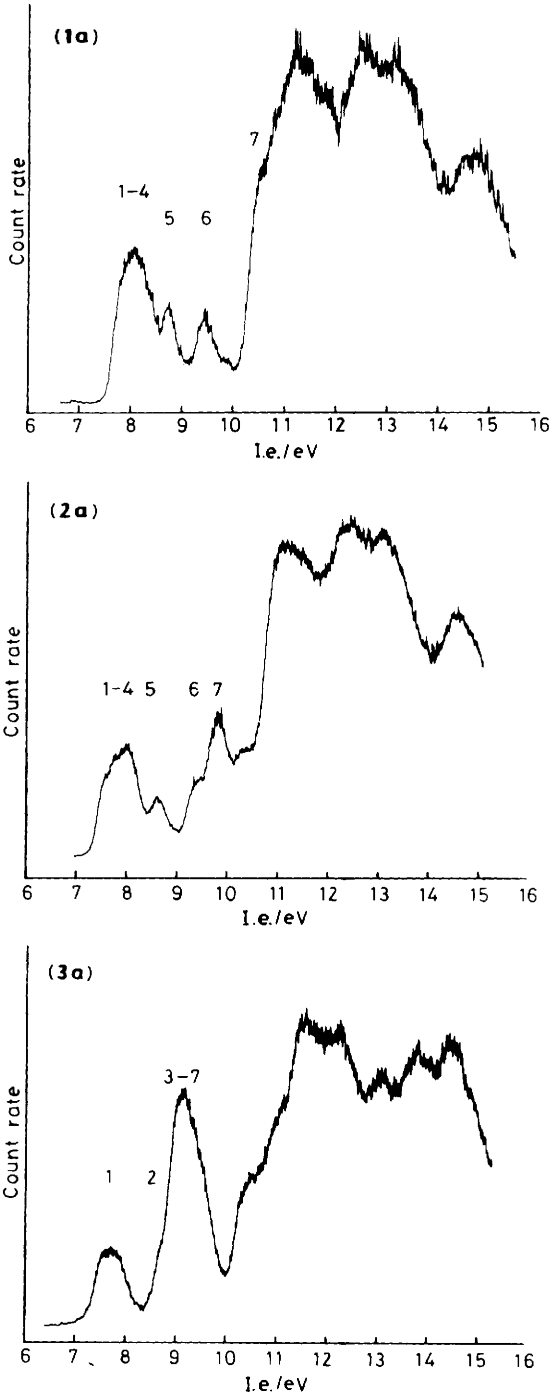


Figure 2. He I$_\alpha$ p.e. spectra of (**1a**), (**2a**), and (**3a**)

Photoelectron Spectroscopic Investigations.—The p.e. spectra of (**1a**), (**2a**), and (**3a**) are shown in Figure 2; the first ionization potentials of (**1a**), (**2a**), and (**3a**) are collected in Table 3. The p.e. spectra of (**1a**) and (**2a**) are similar in as far as they exhibit one broad Gaussian peak (bands 1—4) around 8 eV separated from two smaller peaks at higher energy (bands 5 and 6). If we assign one ionic state to each of the latter bands, the first broad peak corresponds to about four states, using intensity criteria.

To assign the first ionic states we proceed in two ways: (*i*) we correlate the first bands of (**1a**) and (**2a**) with related compounds, like (**3a**) and (**4**) respectively, and (*ii*) we compare the first bands with results of m.o. calculations. In both cases we rely on Koopmans' theorem which states that we can correlate the vertical ionization energies $I_{v,j}$ with the calculated orbital energies ε_j as follows: $I_{v,j} = -\varepsilon_j$.[15]

To carry out our empirical correlation we will first discuss briefly the p.e. spectra of (**3a**) and (**4**). As discussed elsewhere,

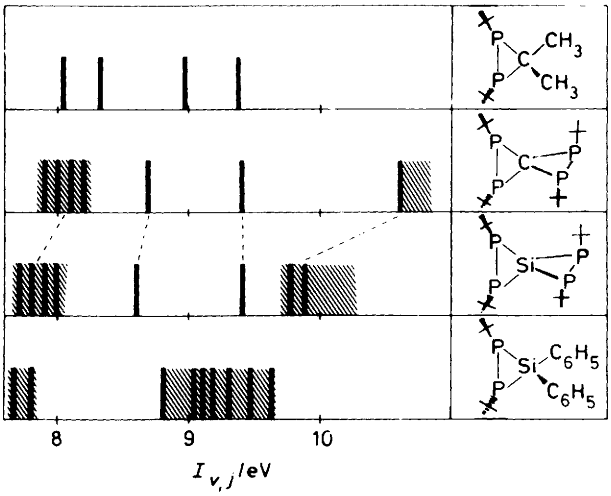
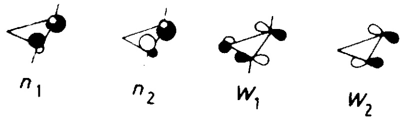


Figure 3. Comparison between the first bands of the p.e. spectra of (**1a**) and (**2a**), with (**3a**) and (**4**)

the first four bands of the p.e. spectrum of (**4**)[4,5] have been assigned to ionizations from the lone-pair linear combinations n_1 and n_2 and two Walsh type m.o.s (W_1 and W_2) shown below. Molecular calculations on (**3b**) suggest assignment of the first



band in the p.e. spectrum of (**3a**) to ionizations out of n_1 and n_2. The second peak (bands 2—7) we assign to six ionic states, two of which arise from ionizations from W_1 and W_2 and four from π orbitals on the C_6H_5 units. In line with this assignment are (apart from intensity arguments) the comparison between the p.e. spectra of (**4**) and (**3a**) and diphenylmethane, (**5**).[16] For (**3a**) the Walsh type ionizations are found at 8.98 and 9.36 eV. The π m.o.s in (**5**) are reported at 8.80 and 9.25 eV.[16]

In Figure 3 are compared the first p.e. bands of (**1a**) and (**2a**) with the p.e. data of (**3a**) and (**4**).[4] The comparison of (**1a**) with (**4**) suggests assignment of the first peak (bands 1—4) in the p.e. spectrum of (**1a**) to four ionizations from the lone-pair combinations *7a*, *7b*, and *6e*. Bands 5 and 6 in the p.e. spectrum of (**1a**) are due to two ionizations from *6b* and *6a*. The similarity between the spectra of (**1a**) and (**2a**) suggests the same sequence of the first six bands for both compounds. This empirical assignment is further corroborated by the comparison between the p.e. bands of (**2a**) and (**3a**) (Figure 3).

The same conclusion is reached if the first p.e. bands of (**1a**) and (**2a**) are compared with the results of m.o. calculations (Tables 2 and 3). Due to the strong overlap of the first four bands it is not possible to make any statement on the relative ordering in (**1a**) and (**2a**) as well as on the split caused by spiro-interaction. The similarity of the splitting pattern obtained in the p.e. spectra of (**1a**) and (**2a**) (Figures 1 and 3) suggests for both compounds the same conformation in the gas phase. A comparison between the orbital energies calculated for (**1b**) assuming D_{2d} and S_4 symmetry and its p.e. bands (Figures 1 and 3) suggests S_4 symmetry in the gas phase as found in the solid state for (**2a**).[12]

Experimental

The syntheses of (**1a**),[1] (**2a**),[2] and (**3a**)[8] have been reported in the literature. The p.e. spectra of the analytically pure compounds were recorded on a Leybold-Heraeus UPG 200 spectrometer. The recording temperatures were 95 °C for (**1a**) and (**2a**) and 85 °C for (**3a**). The spectra were calibrated with Ar and Xe; a resolution of 25 meV of the $^2P_{3/2}$ Ar line was obtained.

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