Organophosphorus Compounds. Part 93.[1] Aromaticity of Thia- and Selenaphospholes: A Photoelectron Spectroscopic and Quantum Chemical Study

László Nyulászi,*[a] Péter Várnai,[a] Steffen Krill[b] and Manfred Regitz*[b]
[a] *Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Gellért tér 4, Hungary*
[b] *Fachbereich Chemie der Universität Kaiserslautern, D-67663 Kaiserslautern, Erwin-Schrödinger-Strasse, Germany*

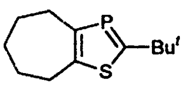
The HeI photoelectron spectra of 2-*tert*-butyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]-1,3-thiaphosphole, 2-*tert*-butyl-4,5,6,7-tetrahydrocyclohexa[*d*]-1,3-selenaphosphole and 3,5-di-*tert*-butyl-1,2,4-selenadiphosphole were recorded and interpreted by using Koopmans' theorem and correlations with the respective spectral data of similar compounds. The positions of the π-ionization energies have been found to be similar to those of the corresponding carbon-containing compounds.

The MP2/6-31G* optimized geometries of the investigated unsubstituted parent compounds are planar and exhibit significant bond length equalization, thus indicating that the systems are aromatic. Since the bonding angles at the ring carbon atoms are nearest to 120° for the systems containing two heavy atoms (*i.e.* the thia- and selena-phospholes), the ring strain should be the smallest in these compounds.

The stabilization of the ring compounds may also be concluded from appropriate isodesmic reactions. Although, at the correlated level used in the present work, the stabilization is considerably larger for all the compounds investigated than at the HF level of the theory, the corresponding compounds containing P=C and C=C bonds exhibit similar stabilization, reflecting the similarities of the P=C and C=C bonds. The slightly higher stabilization of the P=C bond-containing compounds at the correlated levels is likely to be attributed to the overall stability of the ring system and not to the different conjugation of the P=C and C=C units.

The aromaticity of some compounds containing σ^2,λ^3-phosphorus atoms (P=C unit), such as phosphabenzene,[2–8] hexaphosphabenzene[9] and azaphospholes[5–7] has recently been investigated by quantum chemical means, using such measures as bond length equalization and isodesmic reaction energies. In these reports it was pointed out that, on the basis of the similarities of the π-ionization energies (E_i) in the photoelectron spectra[7–8] and the appropriate isodesmic reaction energies as calculated by *ab initio* quantum-chemical methods,[2–9] the aromaticities of these compounds are similar to those of the carbon-containing analogues. All these observations are in complete agreement with the observed similarities in the chemical reactivities of compounds containing P=C and C=C double bonds.[10] It has been found for some types of azaphosphole that the aromaticity increases with the increasing number of nitrogen atoms in the ring.[6]

The aim of the present work was to extend the earlier investigations directed at other ring systems. The effect of different heteroatoms (sulfur and selenium) incorporated into a five-membered ring system was investigated together with the influence of more than one double-bonded phosphorus atom in the ring. In order to enhance the chemical stability of the ring systems, bulky *tert*-butyl groups and other (cyclic) alkyl moieties were introduced. The photoelectron spectroscopic investigations, therefore, were performed for the following compounds: 2-*tert*-butyl-5,6,7,8-tetrahydrocyclohepta-4*H*-[*d*]-1,3-thiaphosphole (**1**), 2-*tert*-butyl-4,5,6,7-tetrahydrocyclohexa[*d*]-1,3-selenaphosphole (**2**) and 3,5-di-*tert*-butyl-1,2,4-selenadiphosphole (**3**).



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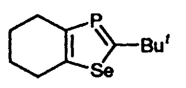

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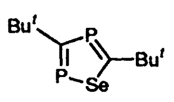

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Experimental and Calculations

The photoelectron spectrometer has been described elsewhere.[11] The spectra were recorded at the 21.22 eV HeI resonance line with a resolution of 35–40 meV at the Ar $^2P_{3/2}$ line. Calibration was carried out by introducing methyl iodide simultaneously with the sample. The syntheses of compounds **1**–**3** have been described previously.[12]

Quantum-chemical calculations were carried out by means of the GAUSSIAN 92 package[13] at the MP2 level of the theory, using the standard 6-31G* basis set. For selenium a basis set of (14s,11p,6d) ⟶ (6s,4p,2d) was used.[14] In order to obtain results comparable with our earlier calculations[5–7] for the sulfur-containing molecules, the HF/4-31G(*) (δ^D = 0.57 on phosphorus) level was used as well with the MICROMOL program package.[15] In order to save computer time, geometry optimizations were carried out only for the unsubstituted ring systems. The stationary points obtained were characterized by second-derivative calculations. The structures discussed here are real minima, since no imaginary frequencies were detected.

For the interpretation of the photoelectron spectra, the effect of the substituent groups were simulated by attaching alkyl groups (with standard geometrical features) to the (optimized) ring systems. The fused rings were simulated by attaching methyl groups at the proper places. HF/6-31G* Calculations were carried out upon these structures.

Results and Discussion

The photoelectron spectra of the investigated compounds **1**–**3** are shown in Fig. 1, while the observed and calculated (Koopmans' HF/6-31G*, see calculations section) vertical ionization energies are listed in Table 1. Based on the calculations, the first two ionizations of the 1,3-thiaphosphole **1**

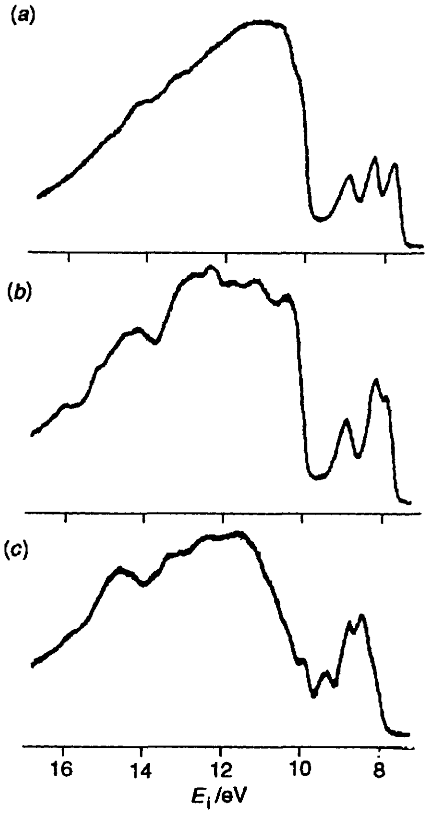

Fig. 1 HeI photoelectron spectra of the investigated compounds: (*a*) **1**; (*b*) **2**; (*c*) **3**

Table 1 Measured and calculated[a] ionization energies (eV) of the investigated compounds

1		**2**		**3**	
Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
8.01 (7.88)[b]	7.98 π	8.07	7.93 π	8.2 (sh)	8.05 π
8.55 (8.78)[b]	8.81 π	8.32	8.55 π	8.49	8.79 π
9.17	10.24 n_p	9.04	10.04 n_p	8.86	9.64 n_p^-
10.4	12.21	10.6	12.15	9.43	11.20 n_p^+
				10.02	11.66

[a] Calculated results refer to the substituted molecules as discussed in the calculations section. [b] 2,5-Di-*tert*-butylthiophene, measured.[16]

(8.01 eV, 8.55 eV) should be assigned to ionizations from the two highest occupied MOs (π_1 and π_2). These values are similar to those for a heavily alkylated 2,5-di-*tert*-butylthiophene[16] (given in brackets in Table 1). The HF/6-31G*//MP2/6-31G* π-orbital energies of the parent 1,3-thiaphosphole (8.66, 9.56 eV) are likewise close to those obtained for thiophene (8.72, 9.30 eV). In the case of the 1,3-selenaphosphole **2**, the splitting of the first two bands is somewhat smaller (Fig. 1) than in the sulfur derivative, **1**. The same trend can be observed upon comparing the first two ionization energies of thiophene and selenophene,[17] or the calculated orbital energies of 1,3-thia- and 1,3-selena-phospholes (Table 1).

These observations suggest that the first two ionization energies of both ring compounds containing one phosphorus atom should be assigned to two π-orbitals. Similarities of this type between P=C and C=C bonded systems have been pointed out before[7] and this behaviour would appear to be a useful tool in the assignment of the photoelectron spectra of phosphorus compounds.

The third bands of both **1** and **2** have been assigned to an ionization from the lone pair of phosphorus in agreement with calculations. These ionization energies are close to each other (9.17 and 9.04 eV for **1** and **2**, respectively) in accordance with their assignment to the n_p orbital. The n_p ionization energy for the heavily alkylated 2,4,6-tris-*tert*-butylphosphinine has been assigned to the high-energy side of a broad band centred at 8.6 eV,[18] providing further support to the present assignment.

The spectrum of 1,2,4-selenadiphosphole **3** is somewhat more complicated in the low ionization energy region where three distinct bands are observed. The first peak, with a maximum at 8.49 eV, is considerably more intense than the one at 9.43 eV, suggesting that two ionizations are hidden in the former band. According to the calculations, the first two π-orbital energies of the unsubstituted 1,3,5-selenadiphosphole (8.60 and 9.45 eV) are only slightly changed in comparison to those of the 1,3-selenaphosphole (8.51 and 9.32 eV) which is in accord with the above-mentioned similarities in the ionization energies of C=C and P=C bonded systems. The calculated π-orbital energies of the alkylated derivatives of the two compounds (Table 1) are likewise similar. Taking all these facts into consideration, the assignment of the 8.86 eV band to the second π-ionization is very unlikely. A more reasonable assignment for the second π-ionization is the band maximum at 8.49, while the first π-ionization is at 8.2 eV where a weak shoulder can be seen (Fig. 1). This assignment is substantiated by the relative intensities of the bands.

The 8.86 and 9.43 eV bands of **3**, therefore, should be attributed to the two combinations of the phosphorus lone electron pairs, in harmony with the calculations. Since the n_p ionization of the 1,3-selenaphosphole derivative at 9.04 eV (Table 1) lies between the above two values, it is indicative of some interaction between the two in-plane orbitals and the assignment seems reasonable. The band at 10.02 eV should be attributed to an ionization from the σ-orbital localized mainly on selenium, however, calculations indicate interaction with the phosphorus lone pair orbitals (the corresponding ionization energy of selenophene is at 11.0 eV; note that the effect of *tert*-butyl groups is to lower the ionization energies).

The spectra discussed above showed no major changes in π-ionizations as compared with the spectra of the corresponding thiophene and selenophene species. This demonstrates that the replacement of carbon by σ^2,λ^3-phosphorus has only a slight effect on the π system and this is valid not only in the case of azaphospholes[5-7] but also in cases of rings containing additional second or third row heteroatoms such as sulfur or selenium as well; furthermore, the same holds when more than one C=C bond is replaced by a P=C unit.

In order to study the energy of the conjugative interaction between the P=C unit and the rest of the ring, isodesmic reactions have been investigated. While the bond-separation (BS) reactions (1) and the semi-homodesmic (SH) † reactions (2) are characteristic for the aromaticity of the ring, reaction (3) is called a ring fragmentation (RF)[6,7] reaction and is designed to measure the effect of the C=C (or P=C) bond in the build-up of the conjugated aromatic system.

The energies of the reactions (obtained at MP2/6-31G*//MP2/6-31G* + ZPE level of the theory) for the investigated (unsubstituted) ring systems (**4**–**9**) are listed in Table 2. The values in brackets correspond to results of calculations at the HF/4-31G(*)//HF/4-31G(*) level of the theory (for the sulfur derivatives only).

The energies are similar for the corresponding sulfur and

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† Note that this reaction is not homodesmic. However, as it compares the stability of the ring to systems with four π-electrons (see the compounds on the right side of the equation), it is analogous with the homodesmic reactions written for the six-membered rings (see, *e.g.*, ref. 1). This reaction is called a semi-homodesmic (SH) reaction in this work.

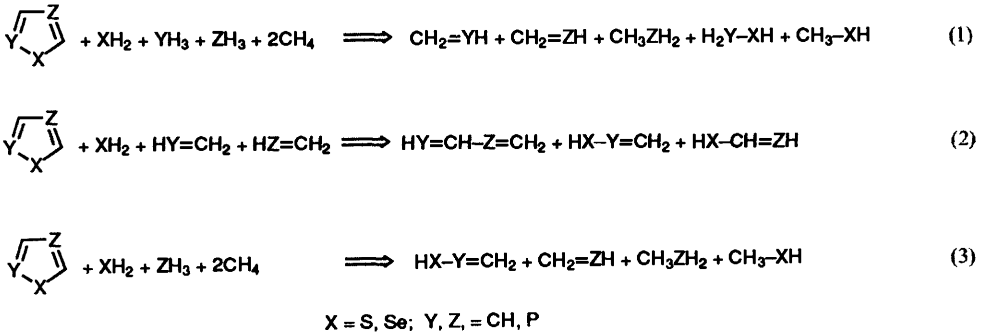
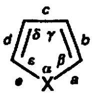


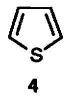
Table 2 Total energies (in atomic units), energies of bond-separation reaction (1) (BS), semi-homodesmic reaction (2) (SH) and ring fragmentation reaction (3) (RF) in kcal mol^{-1} at the MP2/6-31G* + ZPE level of the theory[a]

	4	5	6	7	8	9
$-E_{\mathrm{tot}}$	551.955 97	854.212 72	1156.482 93	2552.026 39	2854.283 73	3156.568 97
E_{BS}	51.99 (35.22)	55.29 (34.89)	58.98 (39.37)	46.13	49.95	56.21
E_{SH}	24.52 (14.82)	29.70 (20.97)	32.56 (21.19)	22.28	27.33	31.06
E_{RF}	44.54 (30.83)	47.84 (30.50)	53.22 (33.19)	40.49	44.31	50.55

[a] The numbers in parentheses refer to values at HF 4-31G(*)//HF 4-31G(*).

Table 3 MP2/6-31G* Bond lengths (Å) and bond angles (°) for compounds 4–9

		a	b	c	d	e	α	β	γ	δ	ε
	4	1.715	1.375	1.418	1.375	1.715	92.0	111.6	112.4	112.4	111.6
	5	1.705	1.722	1.764	1.372	1.708	95.9	117.7	92.9	117.4	116.0
	6	1.705	1.721	1.751	1.719	2.071	101.0	122.1	96.2	124.4	96.2
	7	1.849	1.372	1.421	1.372	1.849	88.0	111.3	114.7	114.7	111.3
	8	1.838	1.717	1.767	1.370	1.841	92.0	117.7	95.0	119.6	115.6
	9	1.841	1.717	1.751	1.722	2.200	97.2	121.8	98.1	126.8	96.2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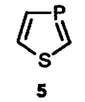
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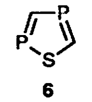
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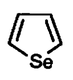
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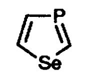
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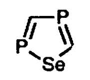
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selenium derivatives, but are somewhat smaller for the selenium compounds in accordance with earlier results obtained for thiophene and selenophene[2] (*cf.* the known small differences between aromaticities of thiophene and selenophene[19]). As the sizes of the molecules on the right side of the equations increase, the reaction energies become smaller, reflecting the conjugative stabilization already present in the molecules used for comparison. The inclusion of the electron correlation increases the reaction energies significantly. However, if the corresponding P=C and C=C bond-containing compounds are compared, the reaction energies are close to each other at any level of the theory (*cf.*, *e.g.*, thiophene with 1,3-thiaphosphole and 1,3,5-thiadiphosphole).

There is a small, but steady increase (3–4 kcal mol^{-1}) in the reaction energies at correlated levels when one C=C unit is replaced by a P=C unit; this trend is, however, much less apparent at the HF level of the theory. Since the increase is similar in all the reactions (1)–(3), irrespective of the size of the conjugated system on the right side of the equation, this increase should not be attributed to differences between the conjugative abilities of the P=C and C=C units, but rather to some overall stabilization of the ring. In the case of phosphinine, a reversed effect was observed: its homodesmic reaction energy is slightly less than that of benzene (27.24 and 28.16 kcal mol^{-1}, respectively, at the MP2/6-31G* level of the theory[20]). A possible explanation for this effect can be the ring strain. P, S and Se prefer bond angles at *ca.* 90°, as interpreted by the inert pair effect which is operational for the second (and third) row atoms.[21] In case of the six-membered ring compound phosphinine, the small bonding angle at phosphorus results in some ring strain (angles at the sp^2 carbon atoms are larger than the ideal 120°, while the bonding angle at phosphorus[4] is somewhat larger than 100°). For the five-membered ring compounds, the strain present in the carbon-containing parent compounds (thiophene and selenophene, with bonding angles at carbon being near 110°) is alleviated by the incorporation of the heavy atom with small bonding angles. Indeed, the bonding angles at carbon atoms are near to 120° for 1,3-thiaphosphole and 1,3,5-thiadiphosphole as well (Table 3). Since in the case of the diphospholes the bond angles at the heavy atoms also show some increase compared to the corresponding phospholes, the above reasoning cannot be considered as the sole explanation for the observed 'extra' stabilization of the rings containing a P=C moiety.

Conjugation and aromatic stabilization are also reflected in the alternation of bond lengths. The calculated geometries of the heteroaromatic rings (at the MP2/6-31G* level of the theory) are shown in Table 3. Thiophene and selenophene were also considered in order to get comparison of the conjugative ability of P=C unit and C=C units. The bond lengths exhibit significant equalization in each of the compounds and the replacement of a C=C group by a P=C unit has only minor effects on the rest of the ring. [See, *e.g.*, the length of the *d* C=C bond in case of the thiophene, 1,3-thiaphosphole or selenophene, 1,3-selenaphosphole pairs (Table 3). Bond length *a* is again similar for all the sulfur- and selenium-containing rings.]

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