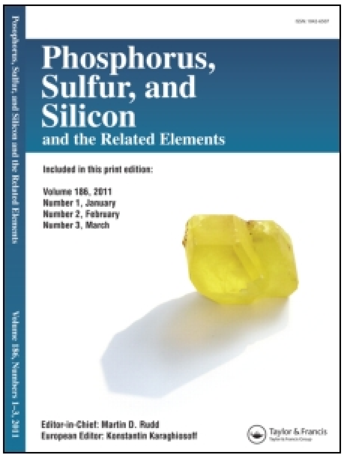

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nyulászi, László and Veszprémi, Tamás(1996) 'The Aromaticity of Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 109 — 112

To link to this Article: DOI: 10.1080/10426509608545102

URL: http://dx.doi.org/10.1080/10426509608545102

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 109–112
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THE AROMATICITY OF PHOSPHORUS COMPOUNDS

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Abstract By using photoelectron spectroscopy and ab initio quantum-chemical methods it has been revealed that phosphorus is capable to build cyclic, stabilized, conjugated systems in any of its oxidation state, including σ^2,λ^3-, σ^3,λ^3-, σ^3,λ^5- as well as σ^4,λ^5-P. The conjugative ability of phosphorus - as shown on π-ionization energies and stabilization energies in isodesmic reactions - is similar to that of carbon.

Key words: σ^2,λ^3-phosphorus, σ^3,λ^3-phosphorus, σ^3,λ^5-phosphorus, σ^4,λ^5-phosphorus, aromaticity, photoelectron spectroscopy, ab inito calculations

INTRODUCTION

The chemistry of π-bonded phosphorus compounds remained nearly intact till the eighties. Apart from the experimental difficulties, the main reason of that was not the lack of interest, but the psychological effect of the "double bond rule" [1]. The great number of phosphinines, aza-, thia- and selenaphospholes synthesized in the eighties, however, showed that π-bonded phosphorus compounds do exist and presumably benefit from aromatic stabilization. Phosphole, on the other hand, is a non-planar, non aromatic molecule [2], as explained by the large inversion barrier about phosphorus, which cannot be compensated by the aromatic stabilization (if any) in the planar system.

In the present work a brief summary is given about the extent of aromaticity in compounds containing phosphorus in different bonding situations, characterizable by basic "bond types" shown in Scheme 1. The methods used were ultraviolet photoelectron spectroscopy and ab initio quantum chemical calculations. More details can be found in the references.

Scheme 1

RESULTS, DISCUSSION

For the comparison of σ^2,λ^3- and σ^3,λ^3-phosphorus containig systems azaphospholes provide an excellent opportunity, as the aromaticity of an isomeric pair can be investigated. Comparing the photoelectron spectra of two alkylated 1,3-benzazaphospholes (**1** and **2**, Fig. 1) [3,4], it is apparent that their electronic structure should be completely different. Since the splitting of the ionization energies is much larger for the 1H-derivative **1**, this compound (containing σ^2,λ^3-phosphorus) seems to be the only aromatic molecule of the investigated pair.

Ab initio quantum chemical calculations on the similar azaphospholes (**3** and **4**) [5-7] revealed that only the 1H-derivative is planar in accordance with the photoelectron spectroscopic results. Furthermore, the alternation of the MP2/6-31G* bond length in the

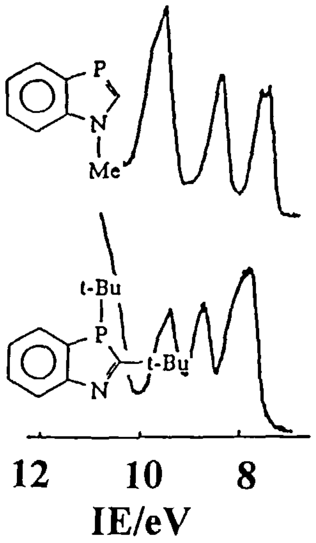


Fig. 1
Photoelectron spectra of alkylated 1H- and 3H-benzazaphospholes

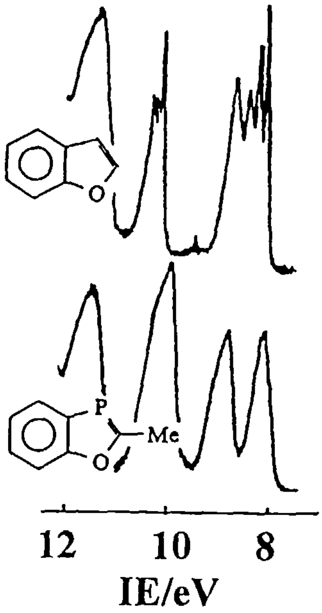
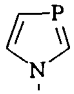


Fig. 2
Photoelectron spectra of benzoxazol and 1,3-benzoxaphosphole

ring is much smaller in this case [7], and the average double bond character (an aromaticity index introduced to measure the bond length shortening [8]) is considerably larger for **3** than for **4** (0.61 vs. 0.52, respectively; confer with the 0.68 for benzene). Semihomodesmic reaction [9] energies for 1H-1,3-azaphosphole indicate 25.45 kcal/mol aromatic stabilization (at the MP2/6-31G* level) [8].



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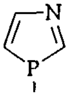

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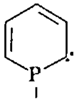

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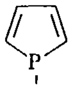

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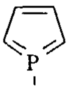

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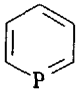

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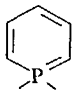

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Comparing the assigned photoelectron spectra of compounds built with C=C and σ^2,λ^3-P=C units, the difference of the π-ionization energies has always been found less than a few tenth of an eV, while for the corresponding derivatives with N=C bond the difference is much larger [10]. As an illustration, the photoelectron spectra of benzoxazole (**5**) [11] and 2-methyl-1,3-oxaphosphole (**6**) [3] are shown in Fig. 2. Comparison of ring fragmentation rection energies of di- and triazaphospholes [10] resulted in similar conclusion.

Considering the abovementioned large conjugative ability of the σ^2,λ^3-P=C bond, it seems reasonable, that σ^3,λ^3-phosphorus is capable to take part in aromatic systems if planarized. Indeed, phosphinine-2-ylidene (**7**) has been shown to be planar [12] at all the levels of theories investigated. In case of this compound the carbenic centre (next to phosphorus) stabilizes the planar σ^3,λ^3-phosphorus atom. By the use of theoretical calculations phosphole (**8**) can be investigated in its planar form as well. The calculated NMR shifts [13], as well as the small alternation of the bond lengths [14] for the (artificially) planarized phosphole have shown the high aromatic character of this system. Furthermore, from the bond length distribution a significant contribution of a resonance form with σ^3,λ^5-phosphorus (**8b**) could have been concluded. By attaching different substituents on the phosphole ring the bond length distribution could be shifted towards the **8a** or **8b** structures. The attachment of the BH_2-substituent not only shifts the structure towards the **8a** form (if attached at phosphorus), or towards the **8b** form (if attached at the α-carbon atom), but lowers the inversion barrier in phosphole significantly (to 1.5 kcal/mol in case of 1-BH_2-phosphole [14]). It is of interest to note that by changing the substituents on the ring the σ^3,λ^3-phosphorus containing structure smoothly transforms to the σ^3,λ^5-phosphorus containing one, thus formally changing the valency of phosphorus.

Pentavalent phosphorus can exist in the σ^4,λ^5- form as well, this structure is considered as ylidic [15]. However, ylides can form formally aromatic structures, and their aromaticity according to Bird [16] is just slightly smaller, than that of their σ^2,λ^3-phosphorus containing counterparts. Indeed, the CC and CP bond lengths in σ^2,λ^3-phosphinine (**9**) are nearly identical to those in σ^4,λ^5-phosphinine (**10**) [17]. The homodesmic reaction (1) energies are of similar values for benzene (28.16 kcal/mol), σ^2,λ^3-phosphinine (27.24 kcal/mol) and σ^4,λ^5-phosphinine (20.55 kcal/mol) [17]. These facts show that although the behavior of σ^4,λ^5-phosphorus containing compounds is different from the "normal" double bonds in many respect, their conjugative ability is similar.

$$C_5H_5X + 2CH_2{=}CH_2 + CH_2{=}XH \Rightarrow CH_2{=}CH\text{-}CH{=}CH_2 + CH_2{=}CH\text{-}CH{=}XH + CH_2{=}CH\text{-}X{=}CH_2 \quad (1)$$

ACKNOWLEDGMENT

Financial support from OTKA T014955 is gratefully acknowledged. The support of Soros foundation for L. Ny. to take part at ICPC is acknowledged too.

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