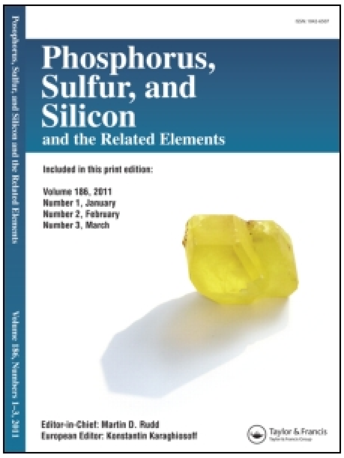

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Are Phosphorins and Phospholes Aromatic?

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ARE PHOSPHORINS AND PHOSPHOLES AROMATIC?

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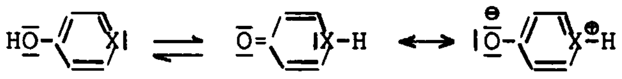
Abstract Aromaticity has been claimed for phosphorins, arsorins, phospholes and arsoles, but the facts brought forward to support this view are easily rationalized without recourse to this concept.

INTRODUCTION

During the last 10 or 15 years, an impressive number of compounds was prepared in which phosphorus has a coordination number smaller than 3. Their existence is at variance with the so-called double bond rule, and they call therefore for an unbiased interpretation. Part of the problem is the type of bonding in five-membered phosphorus-heterocycles which have been claimed to be aromatic systems. It has been argued[1] that, with respect of their open chain counterparts, such heterocycles benefit from the possibility of forming an aromatic 6π-electron system, but that this gain is barely sufficient to overcompensate the inherent instability of low coordination at phosphorus so that the net result is close to "no stabilization". The point of view is then from the "unstable" open chain systems which experience a stabilization by ring closure. One may look at the problem from the other side: Phosphorus-free heterocycles are stable because of aromaticity, but the incorporation of phosphorus occurs at the expense of at least a large part of that stabilization, hence, of their aromaticity. Though less unstable than their open-chain cousins due to cyclic 6π-electron conjugation, these heterocycles, then, may not exhibit "aromatic" properties. Obviously, only experimental criteria can tell us whether they are aromatic or not.

"ARSA- AND PHOSPHA-PHENOLS"

Aromaticity has been claimed to account for the existence of so-called arsa- and phospha-phenols (the mere name implying an analogy with phenol = hydroxy-benzene and hence, aromaticity). In the tautomeric system **Ac** $\rightleftharpoons$ **Bc**, only **Ac** could be detected.[2] In a rationalization, it was argued that γ-pyridone (**Ba** $\longleftrightarrow$ **Ca**), a vinylogous amide, experiences stabilization due to a contribution of the "aromatic" formula **Ca**, and hence competes favourably with its tautomer **Aa** which is aromatic anyway. Arsa-cyclohexadienone, on the other hand, is not planar at As; hence, the canonical structure **Cc** cannot contribute significantly, and because of the lack of such stabilization, the arsa-dienone is incapable of competing with the "arsaphenol". The reason for the prevalence of the latter, then,would be aromaticity.



A **B** **C**

	a	**b**	**c**
X:	N	P	As

There is, however, a simpler rationalization at hand which does not take recourse to aromaticity. **A** and **B**, being tautomers, have a common anion which will preferentially be protonated at the more basic site. Within the realm of aliphatic chemistry, nitrogen of amines is more basic than oxygen of carboxylate anions, and as a consequence, the anion common to the α-amino acids and their zwitterionic tautomers are preferentially protonated at N. This changes if either $-\overline{N}H_2$ is replaced by a less basic group or $-COO^{\ominus}$ is substituted by a more basic group. Hence, the anions of hydroxy-carboxylic acids will be protonated at $-COO^{\ominus}$ rather than at $-\overline{O}H$, whereas amino-alcoholates will be protonated at $-\overline{O}|^{\ominus}$ rather than at $-\overline{N}H_2$. Since phosphines and arsines[3] quite generally are weaker bases than isostructural amines (a generalization which includes arsa- and phospha-benzene compared with pyridine), it is in agreement with expectation that aliphatic phosphino-carboxylic acids exist as such rather than as their $^{\oplus}\mathrm{P}\sim\!\sim\mathrm{COO}^{\ominus}$ dipolar tautomers.[4] Similarly, the common anion of **Ac** and **Bc** is either a phenolate or an enolate anion (depending on whether arsa-benzene is aromatic or not) which, because of the very low basicity of arsines, can be expected to be protonated exclusively at oxygen, giving raise to the hydroxy-arsabenzene (as observed). Since "aromaticity" is not involved in the argument, the fact cannot be taken as evidence for an aromatic character of the ring system.

It has further been reported that 4-hydroxy-1,3λ^3-azaphospholes and -arsoles as well as 5-hydroxy-1,2,4-diazaphospholo- and -arsolo[2,3-a]pyridines exist as such and not in any of their conceivable tautomeric forms.[5] The compounds have been termed "phenolic tautomers" and their hydroxyl substituents "phenolic OH groups" and the prevalence of the HO-tautomers considered plausible, because the "keto-tautomers" are not aromatic. Again, the argument implies that the HO-tautomers are. However, there is no need to take recourse to aromatic stabilization. The anion common to all tautomers may be protonated at O and C-5, as considered by the authors[5], as well as at any other ring center. Protonation at P, As should be taken into consideration in view of the reasoning advanced for the **Ac**/**Bc** equilibrium, and that at N should not a priori be ruled out as long as participation of the electron pair at N in an aromatic 6π-electron system is not taken for granted. In view of the complexity of the system, it is hard to predict which is the most basic center, but regardless whether the anion and its O- and P/As-protonated derivatives are aromatic or not, this may well be the oxygen and certainly will not be P, As.

As an alternative of the five-membered ring being part of an aromatic system, the diazaphospholo(arsolo)pyridine structure can be described as an amide function linked to the (aromatic) pyridine ring, the anion then being an analogon of N-deprotonated oxindole, and the P(As) conceivably acting as a +M-substituent upon the pyridine ring similar to $-\bar{N}H_2$ in 2-amino-pyridine. The published data[5] (high melting points, low solubility in "organic" solvents and broad IR bands in the OH/NH region) do not exclude the N-protonated form, hence the ordinary lactam, but whether N- or O-protonation prevails, has no bearing for the question of aromaticity, and the proton affinity of P, As would be expected to be lower even in the absence of cyclic conjugation in the five-membered ring.

SPECTRAL CRITERIA

One of the accepted criteria for aromaticity is a downfield shift of ^1H-NMR signals caused by ring currents. In organo-P/As chemistry, the effect is blurred by large anisotropy effects. In addition, the azaphospholes and related systems are usually highly substituted so that appropriate compounds are scarce. The few existing data are not in favour of an "aromatic" ring current, nor do ^{31}P and ^{13}C data support the concept of aromaticity. After all, whether these ring systems exhibit any aromaticity, and if so, to what extent, remains an unanswered question which calls for further studies.

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