Aromatic Phosphorus Heterocycles

L. Nyulászi and Z. Benkő

Abstract Phosphorus an element with an electronegativity somewhat less than that of carbon and is an excellent and versatile building block of aromatic systems. Thus, in many systems carbon can be replaced efficiently by phosphorus. The versatility is a consequence of the many different bonding modes available for the pnicogen element. The extent of the aromaticity is different with the different bonding modes, and can also be fine tuned by utilizing various substituents that have inductive or steric effects. It is noteworthy that even small effects can have a large impact on the chemistry of these compounds. Thus, the analysis of subtle changes in aromaticity can be of importance in the future.

Keywords Aromaticity, Delocalization, Phosphorus heterocycles, Structure

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Abbreviations

AIM Atoms in molecules
ARCS Aromatic ring current shielding
ASE Aromatic stabilization energy

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1 Introduction

The chemistry of phosphorus compounds has shown a steady development in the last 30 years. The most interesting results can be related to those systems having \( \pi \)-electrons in the broadest sense. Recent books [1–3] and review papers [4, 5] have appeared on the topic. Particularly noteworthy is the statement summarized by the title of the Mathey–Nixon–Dillon book *Phosphorus: The Carbon Copy* [2], which emphasizes the analogy between compounds of multiply bonded dicoordinate phosphorus (\( \sigma^2, \lambda^3 \)-P, this notation has been used in [1]) and the unsaturated carbon (see Scheme 1).

This analogy is in fact an extension of the well established diagonal relationships (Li–Mg, Be–Al, B–Si) in the periodic table. The analogous behavior can be traced back to the similar energies of the \( p_z \)-orbitals of carbon and phosphorus as represented by the ionization energies of the \( \mathrm{CH}_3 \) and \( \mathrm{PH}_2 \) radicals (9.843 eV [6] and 9.824 eV [7], respectively), invoking Koopmans’ theorem [8]. Not only is the ionization energy of the two radicals of similar value, but also the \( \pi \) ionization energies of ethene and phosphaethene are close to each other (10.51 eV [9] and 10.3 eV [10], respectively). Furthermore, in conjugated systems all the known \( \pi_{\text{C=C}} \) and \( \pi_{\text{P=C}} \) ionizations...
zation energies have similar values exhibiting an excellent linear correlation [11]. As seen in Fig. 1 the similar energies of the occupied orbitals can be interpreted in terms of simple Hückel MO theory. For the C=C and P=C double bonds $\beta/(S + 1)$ should be of similar values, where $\beta$ stands for resonance and $S$ for the overlap parameter. Accordingly, in spite of the similar ionization energies (IE) the strength of the P=C double bond (43 kcal mol$^{-1}$) can be less than that of the C=C bond (65 kcal mol$^{-1}$), as estimated by computing the rotational barriers about the bond axis [12] or using different thermochemical cycles [12, 13]. A further important aspect from the comparison of the two double bonds is also apparent from Fig. 1. While the energies of the occupied orbitals are similar, the unoccupied orbital energies can differ (if the resonance and overlap values are smaller, the unoccupied levels are of lower values). Accordingly, the electron affinities of the systems with P=C bonds are much larger (less negative) than those of the corresponding C=C bonds [14].

It is also worth noting that the phosphorus–carbon analogy is not only restricted to the low valent phosphorus, which forms double bonded compounds. With the recent advances [15–20] in the chemistry of nucleophilic carbenes [21] it turned out that N-heterocyclic carbenes (NHC) can effectively substitute phosphine ligands in different catalysts [22], indicating the similar bonding ability of the lone pairs of tricoordinate phosphorus and (singlet) carbene. The first known NHCs, imidazole-2-ylidenes, possess six $\pi$-electrons and exhibit some aromaticity with the involvement of the empty orbital of the dicoordinate carbon [23–25]. N-heterocyclic phosphonium cations [26–28] are likewise stabilized by $\pi$-interaction from the neighboring nitrogen lone pair and exhibit a certain extent of aromaticity [29, 30]. Not only can

![Fig. 1](image_url)
phosphenium cations (with their empty p-orbital) participate in \( \pi \)-systems, but also phosphide anions (being isoelectronic with sulfur) are excellent \( \pi \)-donor building blocks (Scheme 2). Accordingly, the cyclopentadienyl analogue phospholide (and polyphospholide) anions are known to have high aromaticity [31–33].

Phosphorus also bears a significant (positive) partial charge in neutral compounds. By expanding formally its valence shell, hypervalent bonding structures are formed, which can conveniently be described by the 3c–4e model [34, 35]. (Note that there is no need to consider the involvement of \( d \)-orbitals in the bonding for the hypervalent phosphorus compounds [36, 37].)

While even the saturated compounds have a significant positive partial charge at the pentacoordinate phosphorus (\( \sigma^5\lambda^3\)-P), the unsaturated systems (with tetracoordinate phosphorus: \( \sigma^4\lambda^5\)-P) are usually termed ylides (IA in Scheme 3) [38, 39] to account for the high charge separation within the molecule. Nevertheless, ylide orbitals having \( \pi \)-symmetry are available (ylene structure IB in Scheme 3) [40, 41], and the possibility for conjugation and formation of aromatic \( \pi \)-systems does exist [42]. The ylides can be built in a \( \pi \)-system with their ylidic bond (for C- and N-ylides), or by forming an exocyclic bond with the bridgehead \( \sigma^4\lambda^5\)-P atom in the ring (Scheme 4).

The bonding in certain tricoordinate phosphorus compounds (\( \sigma^3\lambda^5\)-P) is also termed hypervalent (IIA Scheme 5). In these structures the lone pair of the planar phosphorus is effectively involved in the delocalization (IIB Scheme 5). Bis-methylene-phosphorane (and its N, O, and S analogues) are typical examples for such bonding (Scheme 5). Like in the case of the ylides, no \( d \)-orbital participation is needed to describe the bonding in these compounds. Rather, the delocalized 3c–4e model can again be used [33], which also accounts for the positive charge at the central phosphorus atom, in accordance with the ylidic resonance structure (IIC Scheme 5).

![Scheme 2](image)

Scheme 2  Phosphenium cations (a) and phosphide ions (b)

![Scheme 3](image)

Scheme 3  Ylide and ylene bonding description with \( \sigma^4\lambda^5\)-P
Like ylides, bis-methylene-phosphoranes can also be built into π-systems in different ways (see Scheme 6), with one of the \( P=E \) bonds in an exocyclic position, or with the entire 3c–4e \( \pi \)-system incorporated into the cyclic delocalization.

The lone pair of planar tricoordinate phosphorus in \( \text{II} \) is an excellent building block for \( \pi \)-systems. However, the phosphorus environment is usually strongly pyramidal (the inversion barrier in phosphine is about 35 kcal mol\(^{-1}\) [43]) and the lone pair has a considerable “\( s\)”-character. Accordingly, its interaction with \( \pi \)-systems is small. If planarized, however, the interaction becomes effective [44, 45]. It was Schleyer who first made the explicit statement: “the \( \pi \)-donor ability of planar tricoordinate phosphorus rivals that of nitrogen” [45]. Planarizing effects on the tricoordinate phosphorus