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The Important Role of the Phosphorus Lone Pair in Phosphole Aromaticity

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ABSTRACT: *Calculations on phosphole systems using the G3MP2B3 model chemistry show that the phosphorus lone pair is critical to the system's aromaticity. Protonation of the lone pair results in antiaromatic molecules as measured by homomolecular homodesmotic reactions. Attempts to separate out effects of hyperconjugation on the butadiene portion of the system are unsuccessful with current practices. Because these hyperconjugation effects will tend to cancel each other in the phosphole systems, analyses using the unmodified homomolecular homodesmotic reactions are considered reasonable measures of their aromaticity.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:754–758, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20364

INTRODUCTION

Phosphole Aromaticity

The case of aromaticity in the five-membered phosphole ring and its substituted compounds is well known and has long been of interest to chemists because of its borderline behavior. Whereas pyrrole is planar and strongly aromatic, phosphole is not, the phosphorus atom is slightly out of the remaining four-membered carbon ring (by about 10°) and its electronic arrangement basically tetrahedral with the phosphorus lone pair bent away from the ring, greatly reducing its interaction with the carbon π system.

Pyrrole and phosphole differ significantly in their equilibrium geometries because the barriers to achieving planarity from the normal pyramidal configurations of nitrogen and phosphorus are quite different. Using the B3LYP approach [1,2] with a 6-31+G(d,p) basis, the electronic energy barrier to planarity of NH_3 is 4.0 kcal/mol whereas that for PH_3 is 33.8 kcal/mol. For pyrrole, this barrier is easily overcome by the enhanced resonance stabilization of the flat five-membered ring, but such is not the case for phosphole where the energy difference in the electronic energy of the planar and nonplanar forms is some 18.2 kcal/mol. Accordingly, although pyrrole shows a large cyclic stabilization energy and is considered strongly aromatic, the energy for phosphole is small and the system is considered only slightly aromatic.

Although it has generally been assumed by many chemists that the aromaticity of phosphole is primarily due to the finite coupling of the phosphorus lone pair with the carbon π system, it has recently been stated [3,4] that phosphole's aromaticity is due *only* to hyperconjugation with substituents on the phosphorus. Actually, the work cited in support of this conclusion [5] states that *both* substituent hyperconjugation and the phosphorus lone pair contribute to the system's aromaticity.

In this paper, we do not address any of the experimental work accumulated over the years that is believed to be relevant to the presence or absence of conjugation or hyperconjugation in the phosphole ring. Recent reviews can be consulted for discussions of this work [6–8]. Rather, we will consider

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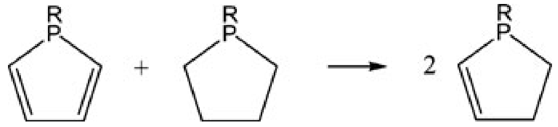
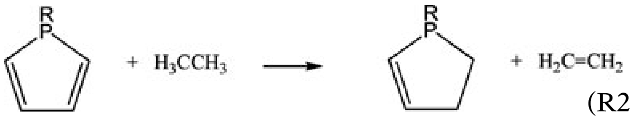
the phosphole system solely from the computational energy point of view.

Conjugative stabilization, including aromaticity, is not a physical observable but rather it is defined by the energetics of a set of reactions. A brief review of many of the older approaches deemed to measure cyclic stabilization has been given [9], whereas Schleyer and coworkers [10,11] have proposed some new approaches. One of the more popular reactions providing a measure of aromaticity is the energy of the homodesmotic reaction R1 [12], in which one reduces the conjugated polyene to its monoene, balancing the reaction with the unsaturated species. Chemically more meaningful, this reaction may be viewed as the difference in the hydrogenation reactions of the polyene and monoene, a procedure first employed by Kistiakowski et al. [13] in 1936 in an attempt to measure the resonance energy of benzene. Schleyer et al. [14] have used this approach to study a number of five-membered ring compounds. Note that while the homomolecular homodesmotic reaction R1 has been written for the five-membered phosphole system, similar equations can be written for acyclic systems.

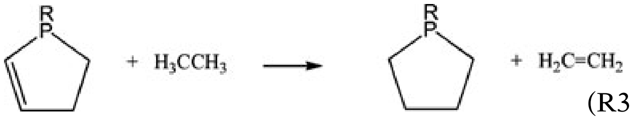


(R1)

One can also look at bond separation reactions [15], more specifically the difference in bond separation reactions shown in reactions R2 and R3 that we have called differential bond separation reactions [9]. These reactions, like R1, may be viewed as the difference of hydrogenation reactions involving the diene or monoene and ethylene. Key to part of our analysis, one can readily see that the difference of reactions R2 and R3 is identically reaction R1. In the present paper, we shall employ all three of these reactions in analyzing the aromatic behavior of phosphole and its substituted derivatives. Note again that equations similar to R2 and R3 can be written for acyclic systems.



(R2)



(R3)

We do not dispute the important role of substituent hyperconjugation in these systems. Rather, by illustrating the enhanced antiaromatic behavior of lone-pair–protonated systems, we show that the phosphorus lone pair is most important to the system's cyclic conjugation stabilization.

Conjugation and Hyperconjugation

Resonance stabilization generally and perhaps too simply is put into two categories: conjugation and hyperconjugation. Conjugation is usually thought of as representing the energy lowering interaction of two or more multiple bonds separated by formally single bonds, such as in 1,3-butadiene or butadiyne. Hyperconjugation is a generally smaller stabilizing effect and is considered to arise from the interaction of a formally non-π system with one or more multiple bonds, such as the interaction of the ethyl fragment in butene-1 with the double bond, or the methyl fragment in 1,3-pentadiene with the 1,3 conjugated double bonds. Conjugation as so defined tends to occur in planar π systems with a σ–π separation, whereas hyperconjugation, almost by definition, results when a noncoplanar part of a molecule interacts with a nearby π system.

Jarowski et al. [16] have introduced the idea that one must subtract out any hyperconjugative stabilization in a system in order to properly determine the conjugative component. Thus, for example, they argue that to properly determine the conjugative stabilization in 1,3-butadiene or butadiyne using the approach in reaction R1, one must subtract the hyperconjugation stabilization of butene-1 or butyne-1 by reference to a suitable nonhyperconjugated system, in these two cases ethylene and acetylene, respectively. We shall return to this issue in our later discussion.

But, as a rose by any other name, conjugation and hyperconjugation both lead to an extra stabilization over the representation of a molecule with completely localized bonds, multiple or single, and attempts to separate them may lie more in semantics rather than chemistry. In this regard, pyrrole is a conjugated system as is 1,3-butadiene, whereas phosphole and its substituted derivatives are both conjugated in the 1,3-butadiene portion of the ring and hyperconjugated by the —PR(lone pair) fragment. However, this unusual molecule has often been viewed as a lone pair partially conjugated to the carbon subring with hyperconjugation from the R substituent. The statement that the overall resonance stabilization of phosphole is due primarily to hyperconjugation of the R portion of the fragment rather than the lone pair is what we take issue with here.

DETAILS OF THE CALCULATIONS

Geometries were optimized at the B3LYP/6-31+G(d,p) level with frequency calculations confirming the minimum energy nature of each structure. Energies including zero-point vibrational corrections at 0 K were then determined using the G3MP2B3 model chemistry [17], a method shown to be good to approximately 1–2 kcal/mol. Energy differences, however, are likely better than this, particularly for molecules with similar molecular structure. All the calculations were carried out employing Gaussian 03 [18].

RESULTS AND DISCUSSION

Homomolecular Homodesmotic Reaction Energies

The G3MP2B3 energies discussed in this paper are shown in Table 1, where data for a number of different phospholes (different substituent R) are shown along with that for several two-multiple bond reference systems. HH refers to the energy change for the homomolecular homodesmotic reaction R1, whereas D and M correspond to the energy changes for the reactions involving the diene converting to the monoene (R2) and the monoene converting to the saturated species (R3). As pointed out earlier, because the difference of reactions R2 and R3 is reaction R1, the energy equality HH = $D - M$ obtains. The HH energies (without any hyperconjugation corrections; vide infra) are normally taken to be a measure of aromaticity in cyclic systems. Positive HH are taken to correspond to aromaticity and negative values to antiaromaticity.

For the phospholes studied here, two data immediately stand out and are readily understood. The P- molecule is the phosphole anion, the phosphorus hydrogen being removed as the cation (proton). It is planar with one phosphorus lone pair in the plane and the other residing in a P pπ orbital resonating with the carbon pπ orbitals, a total of six π electrons forming the very stable $2n + 2$, highly aromatic system, similar to that found for pyrrole. Generally speaking, it has been shown that reduced pyramidal character from steric crowding leads to increased aromaticity [19,20]. On the other hand, if one removes the phosphorus hydrogen as an anion, the P+ molecular cation results. It, too, is planar, but in this case the single remaining phosphorus lone pair is in the molecular plane and only two pπ orbitals are occupied; a highly antiaromatic $2n$ system results. In carbon systems, the highly antiaromatic cyclobutadiene molecule resembles the behavior of the P+ molecule.

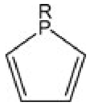
The R = H, CH_3 phosphole systems show the typical small HH indicative of weak aromaticity, similar in magnitude to the stabilization energies of cyclopentadiene and 1,3-butadiene. Although the R = CH_2CH_3 system did not finish in a G3MP2B3 run, the HH, D, and M values obtained at the B3LYP/6-31+G(d,p) level are similar to those for the methyl group, being 5.08, 12,85, and 7.77 kcal/mol, respectively. In all these cases, involvement of both the lone pair and hyperconjugation occurs.

Not all simply substituted phospholes are aromatic as illustrated here in the table by fluorophosphole whose HH value is −3.20 kcal/mol. Generally speaking, systems like those we study show a decreased aromaticity as the phosphorus substituent is made more electronegative. This is more extensively shown by Mattmann et al. for phosphole [21] and by Nyulászi and Schleyer for the cyclopentadienes [22].

The key results here, however, are those in which the lone pair is tied up and unavailable for direct resonance stabilization with the ring system, best illustrated by the R = H_2+ and HCH_3+ cases. In both these cases, hyperconjugative interactions must be present, yet clearly removal of the phosphorus lone pair results in significantly reduced HH values, indicative of weak antiaromatic character. This would seem to us to pinpoint the phosphorus lone pair as critical to the aromaticity of phosphole systems. Note that protonating the lone pair in R = H or

TABLE 1 The G3MP2B3 HH, D, and M Energies for the R1, R2, and R3 reactions

Some phosphole systems



PR	HH	D	M
P−[a]	23.28	39.45	16.16
PH	5.89	10.90	5.00
PCH_3	4.88	9.98	5.09
PF	−3.20	1.56	4.77
$PHCH_3$+	−5.08	−1.03	4.05
PH_2+	−5.12	−1.57	3.55
PHF+	−12.30	−6.60	5.70
P+[b]	−36.53	−18.93	17.60
Some examples of molecules with two multiple bonds			
	HH	D	M
Pyrrole	20.52	29.03	8.51
1,3-Butadiene	3.64	5.80	2.16
Cyclopentadiene	2.83	8.62	5.79
1,3 Butadiyne	−0.52	6.41	6.93
Cyclobutadiene	−31.17	−31.05	0.12

[a] The planar anion resulting from removal of the phosphorus hydrogen as H+.

[b] The planar cation resulting from removal of the phosphorus hydrogen as H−.

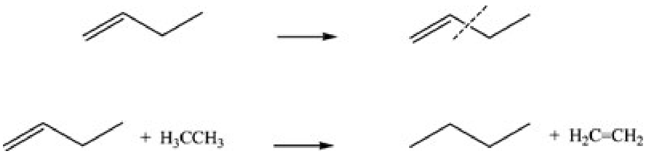
R = CH_3 results in about the same reduction in the HH energy. Fluorophosphole, weakly antiaromatic to begin with, becomes more strongly antiaromatic when the lone pair is protonated, with a decrease in HH comparable to that seen for the protonated R = H and R = CH_3 systems.

We have tried to be careful when emphasizing the importance of the phosphorus lone pair in the phospholes to not at the same time downplay the importance of hyperconjugation in these systems. As Schafer et al. [5] have pointed out, that both effects are important. In some systems, there is no phosphorus lone pair and hyperconjugation is the main determinator of the cyclic stabilization or destabilization. Good examples are the λ^5-phosphorins $(CH)_5PX_2$ [23] where for the electronegative substituents X = F, OH, Cl, and Br aromatic behavior is observed, whereas the electropositive substituents X = H, CH_3, and SiH_2 are nonaromatic or weakly antiaromatic. Stabilization by electronegative substituents also occurs as the σ^*-aromatic effect in gem-disubstituted 1*H*-phosphirenium cations [24]. In both cases, the more electronegative the substituents the more aromatic the system, in contrast to the behavior found for the five-membered ring phospholes [21] and cyclopentadienes [22]. The bonding in the λ^5-phosphorins and gem-disubstituted 1*H*-phosphirenium cations is also clearly different from that in the phospholes.

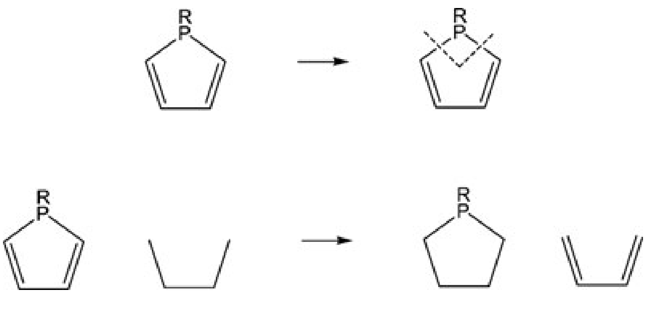
We note in passing that the newer measure of aromaticity proposed for five-membered rings [10] turns out for the phosphole systems we study to be simply the difference of the HH energies for the phosphole system in question and that for cyclopentadiene. Accordingly, a simple shift of stability energies is obtained, here 2.83 kcal/mol, and our general observations above are unaffected.

Hyperconjugation Balance

Jarowski et al. [16] argue that in order to properly characterize the conjugation stabilization in a system, one must correct for hyperconjugation. They argue that the HH values for butadiene and butadiyne, for example, are too small because the monoene and monoyne are stabilized by hyperconjugation. Their method is to determine a hyperconjugation energy correction by taking the difference of hydrogenation energies of the monoene and an appropriate reference system, that part of the monoene where the hyperconjugating part is removed. Thus, in 1,3-butadiene, the reference system is ethylene, in the fully extended 1,3-hexadiene it would be s-*trans* 1,3-butadiene. Scheme 1 illustrates their approach using 1,3-butadiene as an example. The conjugation-free virtual molecule is indicated on the right-hand side of the first line of Scheme 1, and the appropriate energy correction is that energy of the reaction in the second line. It is clear from the R1 reaction that the hyperconjugation correction from the monoenes is the energy 2*M*. Accordingly, $HH^{m.mod}$, the HH energy corrected for monoene hyperconjugation is $HH^{m.mod} = D - M + 2M = D + M$. So, using the data in Table 1, Jarowski et al. would conclude that the true conjugation energy for 1,3-butadiene is 7.96 kcal/mol whereas that for butadiyne is 13.34, a chemically satisfying result in that one might well expect the conjugation energy of the latter to be about twice that of the former. The corrected conjugation energy for cyclobutadiene is insignificantly modified since *M* is so small for that molecule.



SCHEME 1



SCHEME 2

But what does one do for cases such as pyrrole or cyclopentadiene or all the phospholes where hyperconjugation is present not only in the monoene but also in the diene? Consider the general phosphole system, as shown in Scheme 2. One wants a virtual state that removes the PR fragment that is hyperconjugating, which in this case would seem to be s-*cis* 1,3-butadiene, an unstable conformation. But, as we shall see, the choice of reference structure in this case is not key to demonstrating that the approach in Scheme 2 is flawed. It is not difficult to show that, for *any* reference molecular system, the indicated correction for the diene hyperconjugation is given by putting together a series of reactions whose energy is given by $(D_{ref} + M_{ref}) - (D + M)$, where D_{ref} and M_{ref} are the appropriate energies for the reference system. Now, $HH^{d.m.mod}$, HH modified for hyperconjugation in both the diene and monoene, is given by $HH^{d.m.mod} = D - M + 2M + (D_{ref} + M_{ref}) - (D + M) = D_{ref} + M_{ref}$, a value independent of the parent system being studied! Obviously, the approach in Scheme 2 is not correct.

CONCLUSIONS

Calculations with the G3MP2B3 model chemistry show that the phosphorus lone pair is critical to the phosphole systems' aromaticity. Protonation of the lone pair results in antiaromatic systems as measured by homomolecular homodesmotic reactions. Attempts to include effects of hyperconjugation in both the monoene and diene are unsuccessful with current approaches. It seems reasonable to expect these hyperconjugation effects to at least partially cancel each other in these five-membered ring systems, so that analyses using the unmodified homomolecular homodesmotic reactions are reasonable measures of their aromatic character.

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