On the Aromaticity of Phospholes and Arsoles

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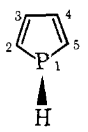
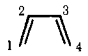
Abstract: A one-electron MO analysis, aided by explicit SCF-MO-CNDO/2 calculations indicates that a well-recognized MO interaction pattern can explain the recent photoelectron spectroscopic results of Schafer et al. and is also responsible for aromaticity in phospholes and arsoles.

In a recent publication, Mislow and his collaborators[1] have argued that the low barrier to pyramidal inversion in phospholes and arsoles is an unmistakable indication of heteroaromaticity in the planar conformation and that the pyrimidal ground state of these systems partakes in cyclic delocalization as well. Mislow et al. have also pointed out that x-ray[2] as well as nuclear magnetic resonance[3] data are also consistent with aromaticity of the aforementioned heterocycles. On the other hand, Schafer et al.[4] have recently reported photoelectron (PE) spectroscopy data on substituted phospholes and arsoles which allegedly constitute "direct proof of the nonaromaticity of phospholes and arsoles". In this paper, we wish to point out that the reported results of photoelectron spectroscopy are, in fact, entirely consistent with aromaticity in phospholes and arsoles and that further PE spectroscopy studies could provide an estimate of the degree of aromaticity.

We shall illustrate the key theoretical ideas by reference to the model systems I–III. One-electron perturbation theory[5] with neglect of overlap provides the simplest theoretical framework for discussing orbital interactions. The π MO's of I can be constructed from the π MO's of II and the p_z "lone pair" AO of III. The net stabilization which accompanies the union of the π systems of II and III to form the π system of I has been variously termed delocalization energy, resonance energy, etc. For example, union of the π systems of butadiene and ethylene to form the π system of benzene is accompanied by substantial stabilization. Accordingly, one says that benzene is aromatic, a statement which can be generalized to encompass all planar cyclic systems with $4N + 2$ π electrons (Hückel's rule).[6] PE spectroscopy is an excellent tool for studying aromaticity because it can yield information about MO energies of the composite molecule (for example, I) and the isolated components (for example, II and III). A comparison of these quantities can lead to qualitative insights regarding whether the composite system is stabilized or destabilized relative to the component fragments and the magnitude of this relative stabilization (aromaticity) or destabilization (antiaromaticity).



I



II

PH_3

III

The interaction diagram of Figure 1 depicts the orbital interactions which obtain in the union of the π systems of II and III to form the π system of I. If the lone pair of PH_3 and the π system of butadiene do not interact, the PE spectrum of phosphole should reveal three ionization potentials, the values of which will be roughly equal to $\epsilon(n)$, $\epsilon(\pi_2)$, and $\epsilon(\pi_1)$.[7] This situation will obtain only when there is near zero overlap between the phosphorus "lone pair" AO and the $2p_z$ AO of C(2) and will result in zero net stabilization of I relative to II + III; e.g., phosphole will be a nonaromatic molecule. However, this possibility is ruled out by the fact that the overlap integral between the hybrid sp^3 phosphorus "lone pair" AO and the sp_z AO of C(2) in pyramidal phosphole is 0.1413, which is a very significant quantity. On the other hand, *if there is interaction and the absolute magnitudes of the $n-\pi_1$ and $n-\pi_3$ orbital interactions are the same,* the PE spectrum should reveal three ionization potentials with values roughly equal to $\epsilon(\phi_3)$, $\epsilon(\phi_2)$, and $\epsilon(\phi_1)$. In such a case, there will be net stabilization amounting to twice the energy difference $\epsilon(\phi_1) - \epsilon(\pi_1)$ and I would be an aromatic molecule. As we shall see later, the magnitude of the aromaticity can be estimated on the basis of the one-electron perturbation approach.

The analysis presented above leads directly to the conclusion that *identification of only the two lowest ionization potentials of I provides absolutely no information about the potential "aromaticity" of I,* simply because $\epsilon(\pi_2) \simeq \epsilon(\phi_2)$ and $\epsilon(n) \simeq \epsilon(\phi_3)$; e.g., whether an interaction between the phosphorus lone pair and the butadiene system fragment is present or absent, the energies of the two highest occupied MO's of I remain unchanged. In such a situation, the energy change of π_1 of the butadiene fragment is the important observable which can provide information about aromaticity. These conclusions are based on the assumption that the orbital interactions $n-\pi_1$ and $n-\pi_3$ are equally strong. Why is that a reasonable expectation in the case of phosphole?

The energy change of an orbital ϕ_i upon interaction with another orbital ϕ_j (nondegenerate case) is given by the expressions shown below.

$$\Delta\epsilon_i = H_{ij}^2/(\epsilon_i - \epsilon_j) \tag{1}$$

$$\Delta\epsilon_i = k^2S_{ij}^2/(\epsilon_i - \epsilon_j) \tag{2}$$

Here, H_{ij} and S_{ij} are MO interaction matrix elements and overlap integrals, respectively, ϵ_i and ϵ_j are one-electron MO energies and k is an energy constant. Equation 1 is a well-known result of perturbation theory and eq 2 is obtained from eq 1 by making the usual assumption that the interaction matrix element is a linear function of the corresponding overlap integral.[8]

$$H_{ij} = kS_{ij} \tag{3}$$

Now, an examination of the interaction diagram of Figure 1 reveals the following relationships:

$$|\epsilon(\pi_1) - \epsilon(n)| < |\epsilon(n) - \epsilon(\pi_3)| \tag{4}$$

$$H_{n\pi_3}{}^2 > H_{n\pi_1}{}^2 \tag{5}$$

The calculation of the interaction matrix elements $H_{n\pi_3}$ and $H_{n\pi_1}$ is illustrated. The circles on the carbon atoms of the butadiene fragment represent the relative magnitude of the carbon $2p_z$ AO coefficients in the π_1 and π_3 MO's of butadiene. In eq 6 and 7, $S(C(2)-P)$ is the overlap integral between the hybrid "lone pair" AO of phosphorus and the $2p_z$ AO of the adjacent carbon atom and the numbers in parentheses are the appropriate π eigenvectors of C(1) in butadiene. Thus, we see that the numerator of eq 2 favors a greater $n-\pi_3$ interaction,

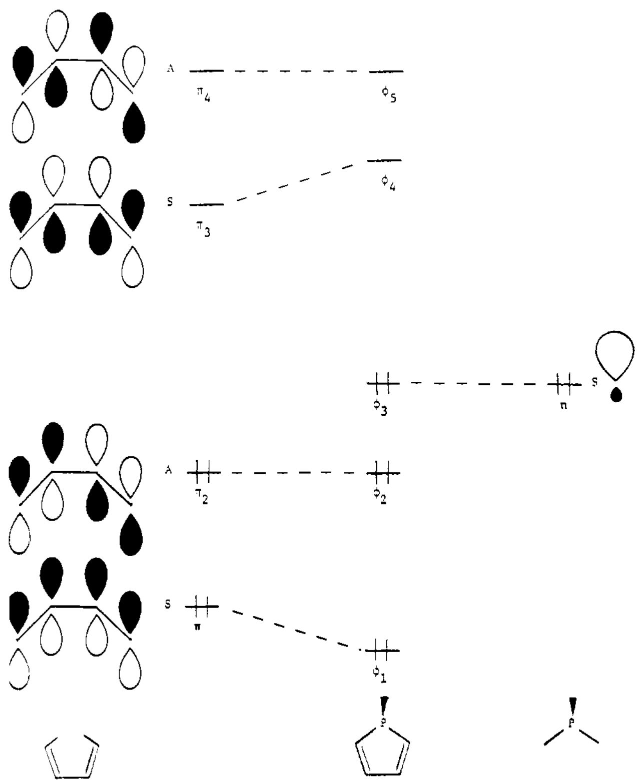
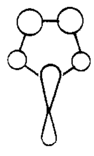
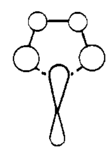


Figure 1. The interaction diagram for phosphole, assuming that the interactions of the phosphorus lone pair with π_1 and π_3 are equal in absolute magnitude.



$$H_{n\pi_1} \simeq 2(0.425)\ S(\mathrm{C1{-}P})k \qquad (6)$$



$$H_{n\pi_3} \simeq 2(0.565)\ S(\mathrm{C1{-}P})k \qquad (7)$$

while the denominator favors a greater n-π_1 interaction. In the situation where the two opposing effects approximately cancel each other, we are led to the interaction diagram of Figure 1. It can be seen that π_1 is depressed and π_3 is raised in energy via their interaction with n. On the other hand, n is raised in energy via its interaction with π_1 and depressed in energy via its interaction with π_3, the two effects cancelling each other when the n-π_1 and n-π_3 interactions are equally strong and leading to a zero $\delta\epsilon(\mathrm{n})$.

In the above discussion, we have focused on the special case of phosphole, where the n-π_1 and n-π_3 orbital interactions tend to become equal in absolute magnitude. In most other heterocycles of the same type as I, the two orbital interactions are not equally strong and lead to $\delta\epsilon(\mathrm{n})$ which depends upon the nature of the heteroatom as well as the nature of any substituents attached on the heteroatom. Indeed, a study of the variation of $\delta\epsilon(\mathrm{n})$, $\delta\epsilon(\pi_2)$, and $\delta\epsilon(\pi_1)$ as a function of the nature of the heteroatom leads to a very clear understanding of why phosphole is a special heterocycle, where the n-π_1 and n-π_3 interactions tend to become equal. Such a study, aided by semiempirical SCF-MO calculations of the CNDO/2 variety,[9] is detailed below.

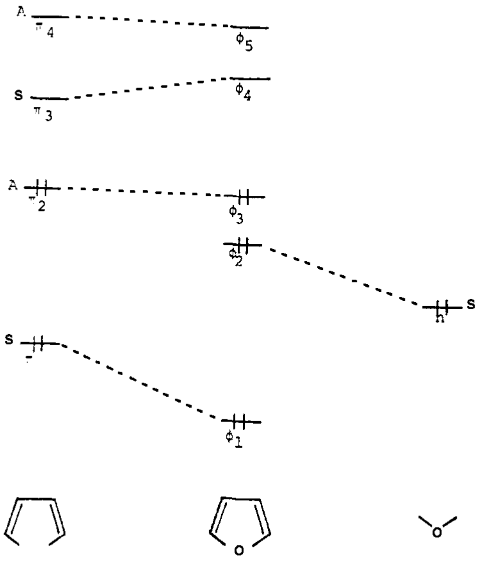


Figure 2. The interaction diagram for furan based on CNDO/2 calculations. The MO energies are drawn to scale.

The potentially heteroaromatic systems furan, thiophene, pyrrole, and phosphole, as well as their model component systems, have been calculated by the CNDO/2 method. In these calculations, we have used the experimentally determined geometries of furan,[10] thiophene,[11] pyrrole,[12] and a phosphole derivative.[13] Furthermore, the geometries of the component systems were assumed to be identical with those which obtain in the heterocycles with the additional saturation by hydrogens. The four interaction diagrams resulting from these CNDO/2 calculations are displayed in Figures 2, 3, 4, and 5. The quantities of interest, $\delta\epsilon(\mathrm{n})$, $\delta\epsilon(\pi_2)$, and $\delta\epsilon(\pi_1)$, are collected in Table I. These quantities are defined with respect to the interaction diagrams of Figures 2, 3, 4, and 5 as follows:

$$\delta\epsilon(\mathrm{n}) = \epsilon(\mathrm{n}) - \epsilon(\phi_3),\ \mathrm{X} = \mathrm{S, P} \qquad (8)$$

$$\epsilon(\mathrm{n}) - \epsilon(\phi_2),\ \mathrm{X} = \mathrm{N, O} \qquad (9)$$

$$\delta\epsilon(\pi_2) = \epsilon(\pi_2) - \epsilon(\phi_2),\ \mathrm{X} = \mathrm{S, P} \qquad (10)$$

$$\epsilon(\pi_2) - \epsilon(\phi_3),\ \mathrm{X} = \mathrm{N, O} \qquad (11)$$

$$\delta\epsilon(\pi_1) = \epsilon(\pi_1) - \epsilon(\phi_1),\ \mathrm{X} = \mathrm{N, O, S, P} \qquad (12)$$

Comparisons can be made between heterocycles of the molecular formula C_4H_4X or C_4H_4XR, where X can be a first or a second period element, e.g., furan vs. thiophene and pyrrole vs. phosphole. On the basis of the interaction diagrams and the data of Table I,[14] one is led to the following conclusions.

(a) As the electronegativity of the heteroatom decreases and the ionization potential of the lone pair also decreases, $\delta\epsilon(\mathrm{n})$ decreases because the n-π_1 and n-π_3 interactions tend to be equalized.

(b) In the cases of furan and pyrrole $\delta\epsilon(\pi_2)$ is very small, as expected. However, in the cases of thiophene and phosphole it becomes much larger. This is only an apparent anomaly, since CNDO/2 calculations treat first row and second row elements differently; i.e., d functions are included in the basis set for second row, but not first row elements. Accordingly, in the case of thiophene and phosphole, there are high lying d orbitals of appropriate symmetry that can mix with π_2 and lead to a greater value for $\delta\epsilon(\pi_2)$ than one would expect by completely disregarding the d orbitals. However, it is well recognized that CNDO/2 calculations exaggerate the importance of d orbitals and one anticipates that ab initio calculations with

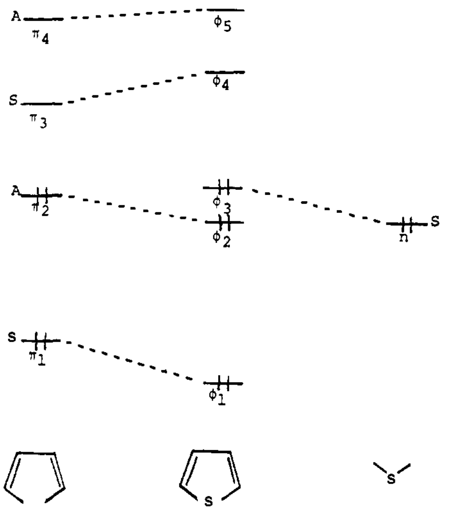


Figure 3. The interaction diagram for thiophene based on CNDO/2 calculations. The MO energies are drawn to scale.

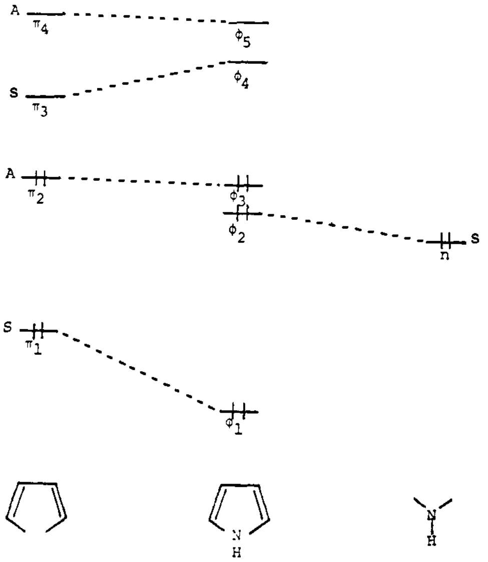


Figure 4. The interaction diagram for pyrrole based on CNDO/2 calculations. The MO energies are drawn to scale.

extended basis sets will lead to uniformly small values for $\delta\epsilon(\pi_2)$ in the case of all the four heterocycles. We note here that the d-orbital electron density of π_2 is 0.0820 in the case of thiophene and 0.0500 in the case of phosphole, indicating that π_2 can interact with the d orbitals *as featured in the CNDO/2 calculation* to an appreciable extent. Furthermore, the role of d orbitals in determining the abnormal $\delta\epsilon(n)$ values in thiophene and phosphole can be understood by reference to some published theoretical work. Specifically, ab initio calculations of the individual heterocycles furan, pyrrole, and thiophene are available. In the cases of furan and pyrrole, the CNDO/2 and ab initio calculations[15a,b] agree in the prediction of the relative energies of the three occupied π MO's, the order being $S^2S^2A^2$. On the other hand, in the case of thiophene, the CNDO/2 calculations predict an $S^2A^2S^2$ order (Figure 3), while the ab initio calculations[16] predict an $S^2S^2A^2$ order. The discrepancy in this latter case may arise from the fact that the CNDO/2 calculations exaggerate the importance of d orbitals, which can mix and lower the energy of the A butadienic MO, while the ab initio calculations employ a much more adequate s and p basis set and the contribution of the d orbitals is found to be unimportant.

(c) The energy of π_1 of the butadiene fragment is depressed significantly in all cases, the absolute magnitude of $\delta\epsilon(\pi_1)$ increasing as the ionization potential of the heteroatom lone pair increases. Once more, in the cases of thiophene and phosphole, the energy change of π_1 is partly due to the presence of d orbitals on sulfur and phosphorus, which have appropriate symmetry to interact with π_1. However, this interaction is very small, as indicated by the d-orbital electron density of π_1 in thiophene and phosphole, 0.0220 and 0.0219, respectively

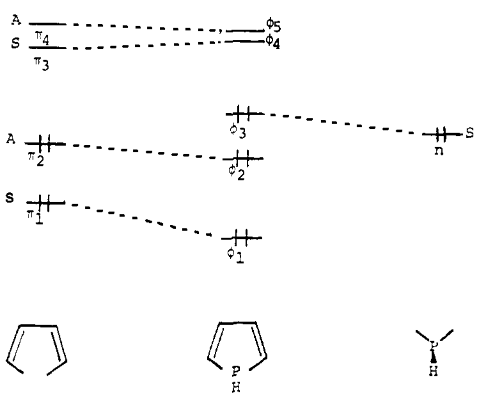


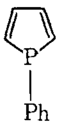
Figure 5. The interaction diagram for phosphole based on CNDO/2 calculations. The MO energies are drawn to scale.

Table I. Orbital Energy Changes in C_4H_4X Heterocycles

X	$\delta\epsilon(n)$	$\delta\epsilon(\pi_2)$	$\delta\epsilon(\pi_1)$
O	−0.1075	0.0132	0.1505
S	−0.0540	0.0343	0.0660
NH	−0.0553	0.0011	0.1517
PH	−0.0188	0.0204	0.0641

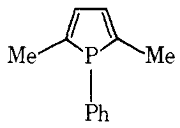
(d) In the case of phosphole and pyrrole, substitution of the hydrogen attached to the heteroatom by a π-donor group will tend to raise the energy of n and lead to a progressive decrease and eventual reversal of the sign of $\delta\epsilon(n)$. Everything else being equal, such a substitution should also result in greater resonance stabilization of the heterocycle.

In the light of the results presented above, we can now re-evaluate the data of Schafer et al. These workers examined the systems IV–VII and in the case of IV they identified two ionizations close to those of the $a_2(\pi)$ of VIII and the lone pair of V. In terms of the interaction diagram of Figure 1, these results amount to saying that $\epsilon(n) \simeq \epsilon(\phi_3)$ and $\epsilon(\pi_2) \simeq \epsilon(\phi_2)$, a situation compatible with aromaticity, as we have seen before. We suggest that a measure of the aromaticity of IV can be obtained from a comparison of the ionizations assigned to the lowest occupied π MO's of IV and VIII. According to our analysis, we expect the lowest occupied MO of IV (ϕ_1 in Figure 1) to have lower energy than that of VIII (π_1 in Figure 1). Unfortunately, Schafer et al. did not look for these key assignments in IV and VIII.

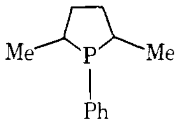


IV

V



VI



VII

VIII

In addition to the PE spectroscopy results discussed above, it was observed that the degenerate $e_{1g}(\pi)$ MO's of the phenyl ring remain unsplit in IV, a piece of evidence which suggests that the five-membered heterocycle does not interact with the benzene ring, since it is known that any substituent splits the degeneracy of the $e_{1g}(\pi)$ MO's of the benzene ring. In this connection, it was further noted that these benzenoid MO's

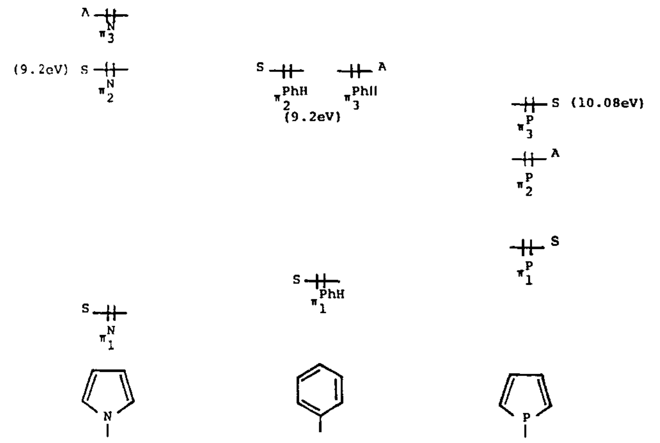


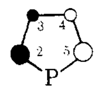
Figure 6. The occupied π MO's of pyrrole, phosphole, and benzene. The degeneracy of the π_2^{PhH} and π_3^{PhH} benzenoid MO's is lifted via the interaction of π_2^{PhH}(S) with π_2^{N}(S) (in 1-phenylpyrrole) or π_3^{P}(S) (in 1-phenylphosphole).

are split by 0.6 eV in 1-phenylpyrrole. The lack of splitting in the case of IV can be due to the following two possibilities.

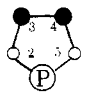
(a) The phosphorus lone pair does not overlap to any perceptible extent with the π system of the phenyl ring. As we have seen, calculations rule out this possibility, yet this is the only possibility considered by Schafer et al.

(b) The phenyl ring is twisted substantially out of the plane of the five-membered heterocyclic ring, thus preventing any appreciable overlap between the phosphorus lone pair and the π system of the phenyl group. This twisting of the phenyl substituent out of conjugation with an adjacent π system is a conformational effect with ample precedent,[17] but was not considered by Schafer et al.

Another interesting result displayed by the data of Schafer et al. is the effect of substitution on the C(2) and C(5) positions upon the ionization potentials of the ϕ_2 and ϕ_3 MO's of phosphole. These MO's are depicted below. Due to the small



ϕ_2



ϕ_3

coefficients at C(2) and C(5), substituents at these positions will have almost no effect on the energy of ϕ_3. On the other hand, ϕ_2 will be strongly influenced by substitution at C(2) or C(5). This is indeed observed experimentally. The ionization potentials corresponding to ϕ_2 and ϕ_3 in IV are 8.45 and 8.45 eV. Those corresponding to ϕ_2 and ϕ_3 in VI are 8.00 and 8.50 eV, respectively.

The factors which influence the magnitude of the splitting of the degenerate benzenoid MO's in 1-phenylphosphole and 1-phenylpyrrole can be understood by reference to the interaction diagram of Figure 6. If we make the reasonable assumption that the π_2^{N}, π_3^{P}, π_2^{Ph}, and π_3^{Ph} MO's are nearly degenerate, then the energy splitting of the degenerate π_2^{Ph} and π_3^{Ph} benzenoid MO's of the phenyl ring will be given by a first-order (in energy) perturbation expression.[18] For example, in the case of 1-phenylpyrrole, we can write

$$\Delta E^{N} = H(\pi_2^{N},\pi_3^{Ph}) = kS(\pi_2^{N},\pi_3^{Ph}) = (k/\sqrt{3})m_{N}S(\mathrm{C(6)}\text{–}\mathrm{N}) \qquad (13)$$

Similarly, in the case of 1-phenylphosphole, we can write

$$\Delta E^{P} = (k/\sqrt{3})m_{P}S(\mathrm{C(6)}\text{–}\mathrm{P})$$

where m_X is the eigenvector of the p_z AO of the heteroatom X and S(C–X) is the overlap integral between the p_z AO's of X and C(6). Since calculations show that the coefficients m_P and m_N are comparable, we can write

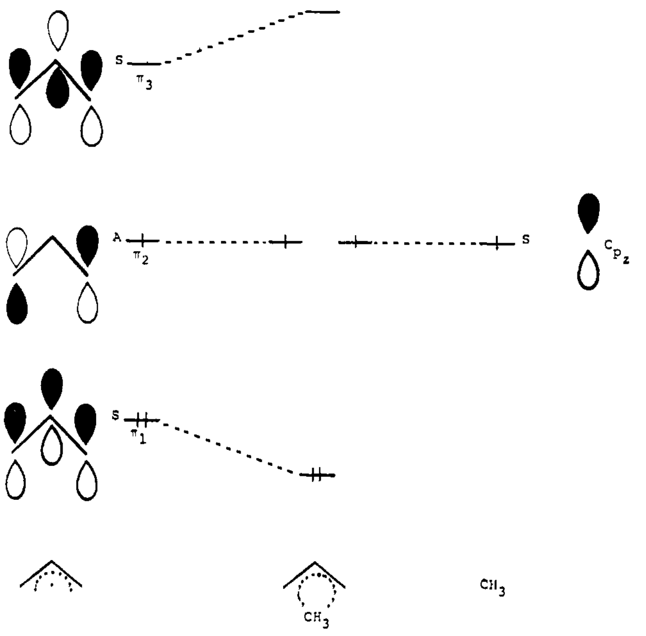


Figure 7. Interaction diagram for a suprafacial 1,3 sigmatropic shift of a methyl group with retention of configuration.

$$\frac{\Delta E^{P}}{\Delta E^{N}} \simeq \frac{S(\mathrm{C(6)}\text{–}\mathrm{P})}{S(\mathrm{C(6)}\text{–}\mathrm{N})}$$

By substituting actual numbers,[19] we obtain 0.787; e.g., we predict a splitting in phenylphosphole which is smaller than that in phenylpyrrole, assuming that the angle of twist of the phenyl ring with respect to the five-membered heterocycle is zero. However, *twisting is expected to be less likely in 1-phenylpyrrole than in 1-phenylphosphole* because there is a weaker stabilizing interaction between the lone pair of the heteroatom and one of the e_{2u} vacant benzenoid orbitals of S symmetry in the case of 1-phenylphosphole. These stabilizing interactions are calculated by means of eq 2 and are found to be $31 \times 10^{-4}k^2$ for 1-phenylpyrrole and $14 \times 10^{-4}k^2$ for 1-phenylphosphole.[20] We suggest that the absence of splitting in the phosphorus compounds IV–VII studied by Schäfer et al. is due to a weak interaction of the phosphorus lone pair with the π system of the phenyl substituent due to a conformational effect.

In summary, we conclude that the PE spectroscopy data of Schafer et al. are consistent with:

(a) An interaction between the phosphorus lone pair and the butadiene system, leading to aromatic stabilization of phosphole in both the planar and pyramidal geometries consonant with the conclusions of Mislow, Quinn, and co-workers.[1-3]

(b) A small interaction between the phosphorus lone pair and the adjacent π system of the phenyl ring due to twisting.

The conclusions of Schäfer et al. imply that the overlap integrals between the phosphorus lone pair AO and the $2p_z$ AO's of both the C(2) in the phosphole ring and C(6) in the phenyl ring are zero, while we have seen that the PE spectroscopy data are compatible with a substantial C(2)–X overlap integral and a small C(6)–X overlap integral, due to a conformational effect.

The analysis we have presented can be extended to arsoles. Since the ionization potential of the lone pair of As is equal to that of P, 10.59 ± 0.02 for PH_3 and 10.58 ± 0.02 for AsH_3,[21] we expect that the aromaticities of phospholes and arsoles will be comparable, in agreement with the conclusions of Mislow

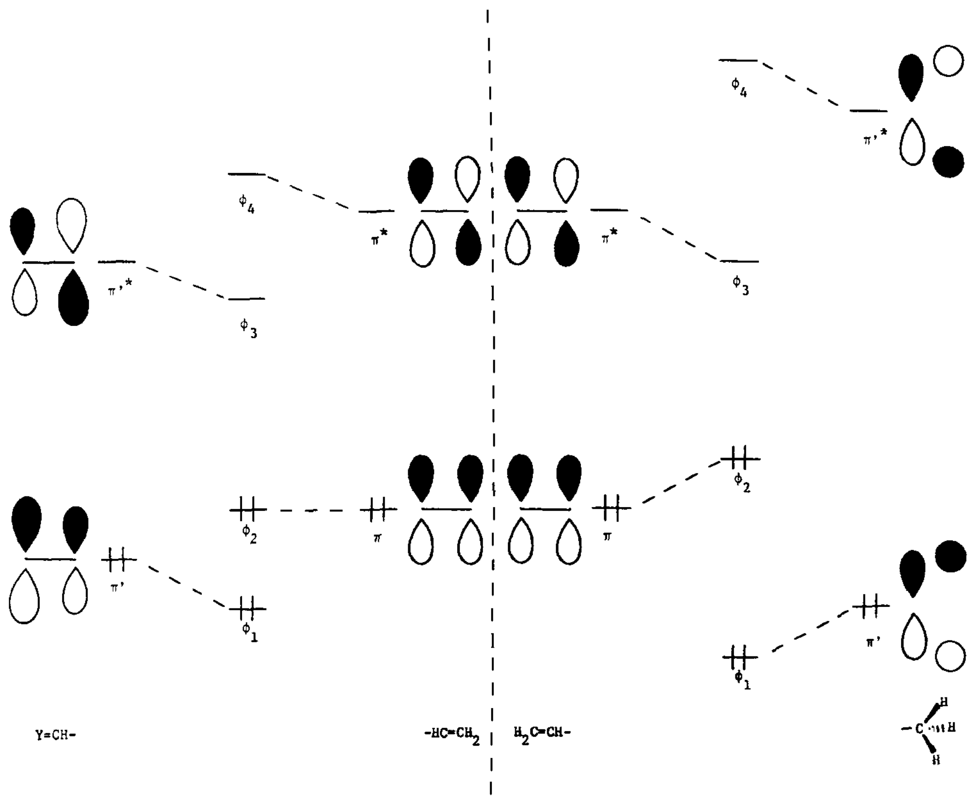


Figure 8. Orbital interactions in CH_2=CHCH=Y and CH_3CH=CH_2.

and co-workers.[1]

As we have seen already, misinterpretations of PE spectroscopic results may occur whenever the energy of an orbital of a fragment remains unaltered within the composite system, e.g., the energy of n in III remains relatively unaltered in I, which is the result of union of II and III. This particular situation arises when the orbital in question is "pushed up" roughly as much as it is "pushed down" through its interaction with other orbitals. Are such orbital interaction patterns common? The answer is affirmative and we proceed to give two illustrative examples.

A. The "Subjacent Orbital Control" in Sigmatropic 1,3 Shifts.[22] The interaction diagram of Figure 7 depicts the orbital interactions which obtain at the transition state of a sigmatropic shift of a methyl group across an allyl framework, with retention of configuration in the migrating group. As it can be seen, the energy of Cp_z does not change upon union of the methyl and allyl fragments to form the transition state complex. This arises because the energy separation between Cp_z and π_1 is equal to that between Cp_z and π_3 and the corresponding interaction matrix elements are equal as well. Hence, the Cp_z-π_1 and Cp_z-π_3 interactions are equally strong and the energy of Cp_z remains unaltered. Furthermore, the union of the methyl and allyl fragments results in stabilization which equals twice $\epsilon(\phi_1) - \epsilon(\pi_1)$; e.g., the situation is completely analogous to the one we have already dealt with in Figure 1. The consequences of this type of orbital interaction are removal of the forbiddenness of the suprafacial 1,3 sigmatropic shift with retention of configuration in the migrating group. Pertinent experimental evidence has been discussed by Berson[23] and calculations of various levels of sophistication support these ideas.[24]

B. The Ionization Potential of Certain Monosubstituted Ethylenes. The ionization potential of ethylene is expected to be modified upon introduction of a substituent X. Nonetheless, when X is -CN and -CHO the change in the ionization potential is small relative to the change in energy observed when X is $-CH_3$, for instance. This observation might have led someone to conclude that there is much less interaction between the substittent and the double bond in CH_2=CHCN and CH_2=CHCHO as compared with CH_2=$CHCH_3$. Once again, this inference is not necessarily correct. Figure 8 shows how the interaction of π of the ethylenic double bond with π′ and π*′ of an unsaturated substituent -CH=Y may lead to no energy change of π_1 and a net stabilization energy equaling twice $\epsilon(\phi_1) - \epsilon(\pi')$. In this case, the energy separation factor favors a greater π-π' interaction, while the matrix element factor favors a greater π-$\pi^{*\prime}$ interaction. These two factors tend to cancel and, hence, the two orbital interactions can become equally strong. On the other hand, when the ethylenic substituent does not have a low-lying vacant orbital, e.g., X is F, OR, NH_2, CH_3, etc., the change in the ionization potential of ethylene upon substitution can be very large. For example, when the substituent is methyl, the π ethylenic MO is mainly "pushed up" in energy due to its principal interaction with the π type HOMO of the substituent, as shown in Figure 8. In this case, the stabilization energy is equal to twice $\epsilon(\phi_1) + \epsilon(\phi_2) - \epsilon(\pi) - \epsilon(\pi')$ *and can be much smaller than the stabilization energy which obtains when the substituent is -CN or -CHO.*

	Ionization potential (eV)[25]
CH_2=CH_2	10.52
CH_2=CHCN	10.91
CH_2=CHCHO	10.90
CH_2=$CHCH_3$	9.73

In short, the energy of the π ethylenic MO may or may not be altered in energy upon substitution and there is no connection between such an energy change and the degree of interaction between the double bond and the substituent. The proper criterion for interaction between any two systems is the overall change in energy, not the change in energy of an isolated orbital.

Finally, we may inquire as to why phosphole is nonplanar,[13] while pyrrole is planar.[12] In addition to the aromaticity of the

π system, there are also interactions present in the σ system which favor a pyramidal heteroatom, i.e., a nonplanar geometry. In pyrrole, these σ interactions are small and the geometry is determined by the aromaticity in the π system. However, in phosphole these σ interactions are larger and dictate a nonplanar geometry as a compromise.[26] We conclude that the nonplanar geometry of phosphole is due to σ interactions and not to a lack of aromaticity of the π system, as has been suggested by Palmer.[27,28]

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(19) The values of S(C(6)–P) and S(C(6)–N) have been calculated for the optimized geometries of $^+CH_2PH_2$ and $^+CH_2NH_2$, respectively. F. Bernardi and N. D. Epiotis, submitted for publication.

(20) The AO overlap integrals have been obtained for the optimized geometries of $^+CH_2PH_2$ and $^+CH_2NH_2$ (see ref 19). The orbital energies of the "lone pair" AO's were taken from photoelectron spectroscopy data of the model compounds NH_3 and PH_3. Finally, the oribtal energy of the e_{2u} MO of benzene was set equal to $-\epsilon_{1g} + \Delta E$, where ΔE is the HOMO − LUMO energy gap of benzene as calculated by the INDO method. The PE spectroscopic results were taken from the following references: (a) NH_3; G. R. Branton, D. C. Frost, F. G. Herring, CA. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **3**, 581 (1969); (b) PH_3; G. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *ibid.*, **5**, 1 (1970); (c) benzene; L. Asbrink, E. Lindholm, and O. Edquist, *ibid.*, **5**, 609 (1970).

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Theoretical Approaches to Rearrangements in Carbocations. 3. The Homocyclopropenyl Cation[1]

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Abstract: The geometrical structures and relative energies of several isomeric forms of $C_4H_5^+$ have been investigated using single determinant ab initio molecular orbital theory. Of lowest energy is the methyl-substituted cyclopropenyl cation, which displays the enhanced stability of the aromatic 2π electron cyclic on which it is based. The homocyclopropenyl cation is much better depicted in terms of a cyclobutenyl-like geometry rather than that corresponding to a true bicyclic arrangement. As was the case for the related homoaromatic systems, the bicyclo[3.1.0]hexenyl and homotropylium ions, the homocyclopropenyl cation is predicted by the calculations to readily undergo degenerate circumambulatory rearrangement. Only this time does rearrangement proceed in a Woodward–Hoffmann forbidden manner, the explanation for which is given in terms of the control of the migration process by an orbital subjacent to the highest occupied. The effects of substituents, both on the geometrical structure of the homocyclopropenyl cation and the energetics of its degenerate rearrangement are briefly considered.

Introduction

There has been intense interest in recent years in detecting and, if possible, characterizing molecules which are expected to show either exceptional stability because of aromatic conjugation or lability due to their incorporation of cyclic antiaromatic arrays. The characterization of the aromatic 2π electron cyclopropenyl cation is an example of the former;[3] the quest for cyclobutadiene, the latter.[4] One set of molecular species which are especially fascinating in this regard are those in which the cyclic aromatic array has been interrupted in one or more places by alkyl chains. A number of these so termed homoaromatic and homoantiaromatic arrangements have already been observed experimentally.[5] Among the better characterized are included the 6π electron homotropylium ion