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# Electronic Structure and Aromaticity of Azaphospholes

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**Abstract:** The electronic structure of 1,3-azaphospholes, 1,2,4-diazaphospholes, and 1,2,3,4-triazaphospholes has been investigated by means of ab initio quantum chemical calculations and He I ultraviolet photoelectron spectroscopy. According to the 4-31G(*) geometry optimized calculations, the total energy of the tautomers containing $\sigma^3,\lambda^3$-phosphorus is significantly higher (by 25–35 kcal/mol) than the total energy of those containing $\sigma^2,\lambda^3$-phosphorus. The aromatic stabilization—as measured by the heats of bond separation reactions—changes in a similar way. The investigation of the calculated optimized geometries revealed that the rings containing $\sigma^2,\lambda^3$-phosphorus can be characterized by bond lengths between those of isolated single and double bonds. In the case of the tautomers containing $\sigma^3,\lambda^3$-phosphorus, however, C–P (N–P) bond lengths are much closer to the single-bond value, indicating that conjugation is in force only on the rest of the molecule. In order to assess the conjugative interaction between the C=P moiety and the rest of the molecule, ring fragmentation reactions have been investigated. The heats of these reactions indicate that the conjugation of the P=C moiety (and thus the aromatic stability) increases with the increasing number of nitrogen atoms in the ring. The photoelectron spectra of the investigated compounds are in accordance with the electronic structure of the compounds containing $\sigma^2,\lambda^3$-phosphorus. Ionization energies when the electron was removed from $\pi$-orbitals are similar to those of the corresponding azoles.

## Introduction

According to the empirical "double-bond rule[1]", second and higher row elements should not form stable compounds in which they are involved in double bonding of the $p\pi$–$p\pi$ type. This rule was derived on the basis of the limited overlap of the bulky orbitals involved in the new bond.[2,3] Recent developments, however, have necessitated a revision of this concept, and in the case of trivalent phosphorus, a large number of compounds containing a P=C double bond have been synthesized.[1,3,4] The stability of these compounds toward dimerization (polymerization) has been explained in terms of kinetic factors (bulky substituents hinder the formation of dimers[3]). Other compounds containing a P=C bond were assumed to be stabilized by delocalization of the electrons in a coupled $\pi$ system.[3] In the case of the $\sigma^2,\lambda^3$-azaphospholes, there is chemical and spectroscopic evidence that this class of compounds exhibits a certain degree of aromaticity and possesses a delocalized electronic structure. With regard to their chemical reactions, addition reactions on the P=C double bond, for example, are much less common than in the case of analogous open-chain compounds.[5] In certain cases, an ionic HCl adduct can even be formed.[6] These ring systems are inert toward sulfur—that reaction would be characteristic for the P=C bond. In comparison with the case of acyclic phosphaalkanes, a reduced nucleophilicity at phosphorus was observed as well.[7] All the structural investigations carried out so far agree that $\sigma^2,\lambda^3$-heterophospholes are planar, and the bond distances are averaged in accordance with a delocalized bond structure.[8,9] The P–C bond lengths in heterophospholes are between 1.70 and 1.75 Å[8,9] (localized double- and single-bond lengths are 1.67 and 1.85 Å, respectively[10]); P–N bonds are between 1.62 and 1.70 Å[8,9] (1.56 and 1.67 Å for localized double- and single-bond lengths, respectively[11]). In $^{31}$P-NMR investigations, a low-field chemical shift was observed.[9] In a recent study, however, it was pointed out that neither $^{31}$P- nor $^{13}$C-NMR data can give an unambiguous answer to the question of aromaticity.[12] According to $^{1}$H-NMR investigations, a low-field shift is observed for the substituents when a conjugated cyclic system is compared to a nonconjugated analogue.[13] This latter fact can be rationalized on the basis of ring currents due to the aromaticity of the conjugated compound. In view of the limited overlap of bulky orbitals of heavy atoms, however, the occurrence of aromaticity in this class of compounds seems to be somewhat controversial. Consequently, the kinetic and thermodynamic stabilities of azaphospholes were considered to be much lower than those of azoles,[5] and the question of the aromaticity for these compounds was recently reported as being unexplained.[12] In our recent work, however, the aromaticity of 1*H*-1,3-azaphosphole was found to be similar to that of imidazole.[14] On the other hand, $\sigma^3,\lambda^3$-azaphospholes are generally considered to be nonaromatic, nonconjugated systems,[14,15,16] although some authors have assumed a certain degree of conjugation even for this class of compounds.[17–19] These molecules are nonplanar, and the arrangement around the phosphorus atom is pyramidal. It is generally agreed that the aromatic stabilization (which might exist in the case of the planar structure) is much less than the energy of the inversion barrier at phosphorus.[20]

In spite of the experimental evidence concerning the aromaticity, only a few investigations have dealt with the electronic structure of this intriguing class of compounds and detailed theoretical investigations were published only recently.[14,21–25]

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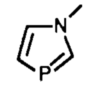
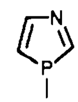
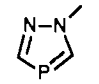
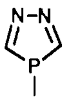
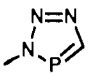
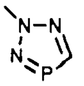
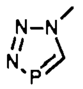
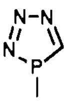
**Table I.** Calculated Structural Data (Å and deg)[a]

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| *a* | 1.698 | 1.837 | 1.708 (1.734) | 1.828 | 1.685 | 1.761 | 1.703 | 1.833 |
| *b* | 1.361 | 1.275 | 1.341 | 1.271 | 1.368 | 1.312 | 1.343 | 1.266 |
| *c* | 1.365 | 1.424 | 1.346 (1.340) | 1.445 | 1.272 | 1.324 | 1.353 | 1.509 |
| *d* | 1.353 | 1.329 | 1.304 | 1.271 | 1.348 | 1.308 | 1.265 | 1.221 |
| *e* | 1.772 | 1.814 | 1.771 (1.734) | 1.828 | 1.681 | 1.632 | 1.700 | 1.761 |
| α | 88.9 | 86.4 | 86.1 (87.5) | 83.7 | 86.0 | 86.6 | 88.2 | 85.5 |
| β | 113.1 | 114.3 | 112.3 | 115.0 | 113.6 | 112.5 | 109.9 | 113.8 |
| γ | 114.8 | 112.1 | 116.6 | 113.0 | 113.4 | 108.6 | 115.3 | 110.4 |
| δ | 112.1 | 116.6 | 109.2 | 113.0 | 110.9 | 118.6 | 110.4 | 113.6 |
| ε | 111.7 | 110.2 | 115.9 | 115.0 | 116.6 | 111.6 | 116.2 | 116.3 |

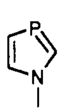
[a] Data in parentheses were obtained by X-ray diffraction.[8,9] The values *a* and *e* are averaged distances in the case of 1*H*-1,2,4-diazaphosphole.[8,9]

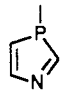
In an investigation of the photoelectron spectrum of 1,2,3-diazaphosphole, the breakdown of Koopmans' theorem was reported. The orbital energies differed significantly in magnitude from the observed ionization energies.[24] In the case of 1,2,4,3-triazaphospholes as well, the photoelectron spectroscopic investigation showed the failure of Koopmans' theorem.[25] In this case, however, the changes in the ordering of the orbitals were restricted to close-lying (ca. 0.5 eV) ionic states only, and in their recent work on azoles, the same authors stated that "some of the criticism of Koopmans' theorem has been excessive".[26]

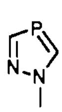
In our recent work, however, the photoelectron spectra of 1,3-azaphosphole and 1,3-azarsole,[14] as well as their benzo derivatives,[27] were successfully interpreted using Koopmans' theorem. In the case of 1*H*-1,3-benzazaphospholes, the photoelectron spectra showed a large splitting of the energy levels (compared to those of the nonconjugated building blocks[27]), and for 1*H*-1,3-azaphosphole, the π-system showed a close resemblance to that of pyrrole.[14] From the calculated molecular structures and the bond separation reactions, a high degree of aromaticity was concluded for 1*H*-1,3-azaphosphole and 1*H*-1,3-azarsole. The aromaticity was much smaller (if any) in the case of the 3*H*-tautomers.[14]

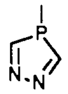
In continuation of our recent study,[14] the aim of the present work is to investigate the electronic structure of several, possibly aromatic, ring systems containing a P=C or P=N double bond in order to study the delocalization and aromatic stabilization of the rings as well as the participation of the P=C subunit in the aromatic system. The effects of incorporating other heteroatoms into the ring will also be considered.

The target molecules of the present study are 1,3-azaphosphole (**1**), 1,2,4-diazaphosphole (**2**), and 1,2,3,4-triazaphosphole (**3**).

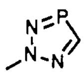

**1a**


**1b**


**2a**


**2b**


**3a**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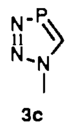
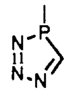
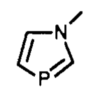
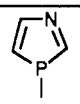
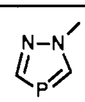
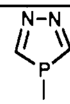
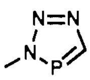
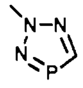
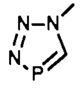
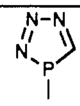

**3c**


**3d**

The electronic structures (of their alkyl-substituted derivatives) have been studied by photoelectron spectroscopy. In order to obtain an estimation of the aromaticity, bond separation reactions[28,29] will be considered. For estimating the involvement of the P=C subunit in the aromatic stabilization, ring fragmentation reactions (see below) have also been discussed.

**Table II.** Calculated Total Energies (au)

| |  |  | |
|---|---|---|---|
| 4-31G(*) | −510.477 958 | −510.438 644 | |
| 6-31G**//4-31G(*) | −511.086 560 | −511.059 395 | |
| MP2/6-31G**/4-31G(*) | −511.797 855 | −511.755 861 | |
| |  |  |  |
| 4-31G(*) | −526.415 254 | −526.364 141 | −542.361 670 |
| |  |  |  |
| 4-31G(*) | −542.357 176 | −542.352 796 | −542.299 967 |

## Experimental Details and Calculations

The syntheses of the compounds investigated have been described earlier.[30] Their purity was checked by NMR spectroscopy.

Photoelectron spectra were recorded on the instrument described earlier[31] using the He I resonance line. The resolution of the spectrometer was 40 meV (fwhm) at the Ar $^{2}P_{3/2}$ line. The spectrum of 5-*tert*-butyl-1,2,3,4-triazaphosphole was recorded at below 55 °C in order to avoid decomposition of the substance. Decomposition at higher temperatures was indicated by the presence of $N_2$ in the photoelectron spectrum.

Ab initio quantum chemical calculations were carried out using the CADPAC program package.[32] The basis set used was split valence 4-31G augmented by polarization functions for phosphorus ($\delta^{d} = 0.57$).[33]

Since only few structural data on the compounds investigated were available, the geometries were optimized. As no imaginary value appeared among the calculated vibrational frequencies at the equilibrium geometries obtained, we consider these structures as real minima on the potential energy surface. In the case of 1,3-azaphospholes, single-point 6-31G**/MP2 calculations at the 4-31G(*) optimum geometry have been carried out as well.

In the case of **3c**, the SCF procedure converged to an excited state, resulting in extremely high orbital energies. After swapping the HOMO and LUMO with respect to the initial guess, the SCF procedure converged to the ground state, as proved by the lower total energy and the "normal" orbital energies.

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Table III. Calculated Bond Lengths for Isolated Single and Double Bonds (Å)

| bond | estimated from covalent radii | estimated from X-ray data[8,9] | calc 4-31G(*) data for the compd listed | |
|---|---|---|---|---|
| C—C | 1.54 | | 1.546 | $CH_3$—$CH_3$ |
| C=C | 1.33 | | 1.316 | $CH_2$=$CH_2$ |
| C—N | 1.47 | | 1.450 | $CH_3$—$NH_2$ |
| C=N | 1.26 | | 1.256 | $CH_2$=NH |
| N—N | 1.40 | | 1.416 | $NH_2$—$NH_2$ |
| N=N | 1.20 | | 1.224 | NH—NH (cis) |
| C—P | 1.87 | 1.85 | 1.860 | $CH_3$—$PH_2$ |
| C=P | 1.66 | 1.67 | 1.640 | $CH_2$=PH |
| N—P | 1.80 | 1.67 | 1.695 | $NH_2$—$PH_2$ |
| N=P | 1.60 | 1.56 | 1.529 | NH=PH (cis) |

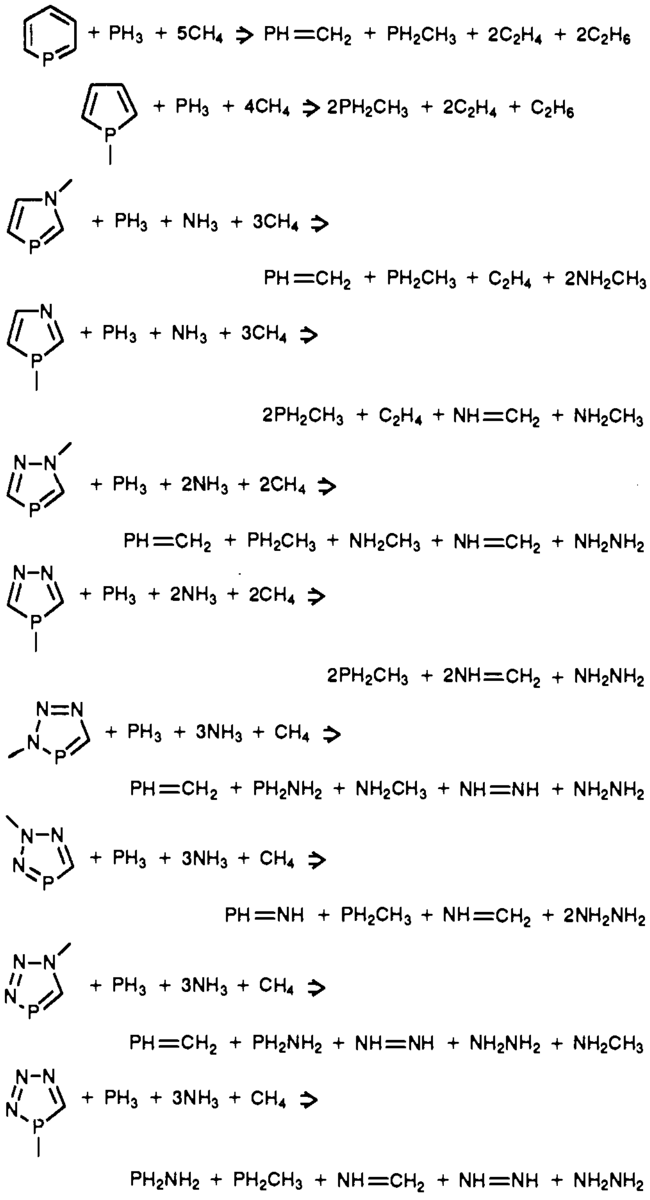
## Results and Discussion

The calculated geometries of the diazaphospholes and triazaphospholes are compiled in Table I together with the available experimental data. Calculations using the same basis set have previously been shown to be in good agreement with experimental data.[14] (The structure of the 1,3-azaphospholes was published elsewhere.[14]) When substitution takes place at the phosphorus atom, the molecule is not planar. The phosphorus atom is slightly (by 4–5°) out of the plane formed by the other ring atoms, and the P–H bond is nearly perpendicular to the C–P–C (N–P–C) plane. This geometrical arrangement is very similar to those of phosphole[17,29] and 3*H*-1,3-azaphosphole.[14] The compounds containing a P=C unit are planar. The planar compounds are calculated to be more stable by about 25–35 kcal/mol in each case (Table II).

In order to estimate the effect of the electron correlation on the relative energies of the two tautomers, single-point 6-31G**/MP2 calculations were carried out at the 4-31G(*) optimum geometries of 1*H*-1,3-azaphosphole and 3*H*-1,3-azaphosphole. These values are given in Table II and show that inclusion of the correlation energy increases the energy difference between the two tautomeric forms. In the case of 1,2,3,4-triazaphosphole, four different tautomeric forms may exist. According to the calculations, **3a** is the most stable molecule. From NMR measurements, however, **3b** was observed in solution as the dominant tautomer.[30] This phenomenon is very similar to the case of 1,2,3-triazole where the 1*H*-form was found to be the most stable one in the condensed phase,[34] while the 2*H*-form was the most stable in the gas phase,[35,36] in agreement with the results of the quantum chemical calculations.[26,37,38] Taking the similarities between 1,2,3,4-triazaphosphole and 1,2,3-triazole into consideration, we believe that the gas-phase stability of the tautomers is predicted well by the calculations.

The calculated bond lengths can be compared to isolated single- and double-bond lengths. These values are collected in Table III and were obtained by optimizing the geometries of the simplest hydrogenated compound that contains the relevant bond. For these calculations, the same basis set was used as for the ring compounds. Although the "classical" structures might be recognized from the calculated geometries (formal single bonds are longer than formal double bonds), the bond distances are between those for single and double bonds, in agreement with previous results obtained for $\sigma^2,\lambda^3$-azaphospholes.[8,23] In the case of compound **3c**, however, the P–N "single" bond is even longer than the calculated single-bond distance. A similar situation was observed in investigations of the X-ray structure of some other triazaphospholes.[8,9] The effect can probably be attributed to repulsion of the phosphorus and nitrogen lone pairs present only in the cis form predetermined by the geometry of the ring.

Scheme I



In the case of $\sigma^3,\lambda^3$-azaphospholes, the C–P (N–P) bond lengths are much closer to the single-bond value than to the double-bond value.

The bond angles around phosphorus are about 90° for each tautomeric form, regardless of the position of the hydrogen (on P or on N). No systematic change in this bond angle could be observed when the number of nitrogen atoms in the ring was changed.

The aromaticity of the compounds can be discussed in terms of bond separation reactions.[14,28,29] The energy of this type of reaction is a measure of the stability of the ring system relative to its isolated prototypical bonds. The bond separation reactions for the investigated compounds can be imagined as shown in Scheme I. The heats of the bond separation reactions are given in Table IV.

As can be seen from the data, compounds substituted at phosphorus possess about $^1/_3$ of the stabilization energy of their isomers; this is in agreement with our earlier observations on 1,3-azaphospholes.[14] The compounds can be classified into two groups: the phosphabenzene type (with $\sigma^2,\lambda^3$-phosphorus) and the phosphole type (with $\sigma^3,\lambda^3$-phosphorus) structures. The bond separation reaction energy values reflect the above classification irrespective of the nature and the connection of the atoms in the

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**Table IV.** Heats of Bond Separation and Ring Fragmentation Reactions (kcal/mol)

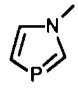
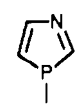
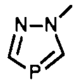
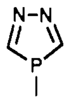
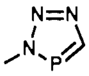
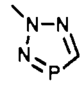
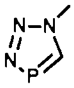
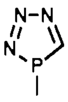
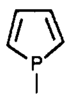
| |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| bond separation | 49.43 | 18.15 | 55.46 | 16.22 | 68.19 | 57.65 | 62.62 | 22.86 | 63.74 | 18.74 |
| ring fragmentation | 36.17 | | 42.88 | | 44.26 | 45.62 | 38.66 | | 52.12 | |

**Table V.** Differences of Total Energies ($\Delta E$) and Bond Separation Reaction Heats ($\Delta 4E_{BS}$) (kcal/mol)

| | **1a,b** | **2a,b** | **3a,d** | **3b,d** | **3c,d** | **4a,b**[a] |
|---|---|---|---|---|---|---|
| $\Delta E$ | 24.65 | 32.05 | 38.69 | 35.87 | 33.12 | |
| $\Delta E_{BS}$ | 31.28 | 39.23 | 68.19 | 57.65 | 62.62 | 45.00 |

[a] **4a** and **4b** are phosphabenzene and phosphole, respectively.

ring. A tendency for increasing aromaticity as CH groups are replaced by N can be observed for the phosphabenzene type compounds as well. For phosphole type compounds, however, no clear trend is observable with regard to the aromaticity as the number of nitrogen atoms increases. The difference between phosphabenzene and 1,3-azaphosphole (77%) is very similar to the reported reduction in aromaticity between benzene and pyrrole (71%).[29] In both cases, a C=C moiety has been replaced by an NH unit. It should be mentioned that a similar increase in bond separation reaction heats is observable by increasing the number of nitrogens in the case of azoles also.[39]

In order to determine whether the increased aromaticity with the increased number of nitrogen atoms is due to a greater delocalization of the C–N moiety or to an increase in the conjugative ability of the P=C subunit, ring fragmentation reactions were considered. This type of reaction reflects the energy lowering when the energy of the ring is compared to the sums of energy for the separated P=C bond and the rest of the ring fragments. The investigated ring fragmentation reactions are illustrated in Scheme II.

The heats of these reactions are compiled with the bond separation reaction data in Table IV. As the number of nitrogen atoms in the ring increases, the heat of the ring fragmentation reactions rises, suggesting that the conjugation of the P=C subunit is increasing, presumably as a result of the electron-withdrawal effect of the nitrogens. (The increasing positive charge contracts the orbitals of the heavy atom, thus allowing a larger overlap and consequently an increased conjugation.) It should be noted, however, that the energy decrease in the studied ring fragmentation reactions accounts for 60–80% of the reaction heat of the bond separation reactions, suggesting that conjugation with the P=C (P=N) subunit plays an important role in the construction of the aromatic system.

The energy difference between the derivatives substituted on phosphorus and on nitrogen, respectively, changes similarly to the difference in the aromaticity (concluded from the bond separation reactions) of the corresponding compounds (Table V), indicating a correlation between the stability and aromaticity of the molecules investigated.

The He I photoelectron spectra of 5-*tert*-butyl-1,2,3,4-triazaphosphole and 5-*tert*-butyl-1,2,4-diazaphosphole are presented in Figure 1 together with the previously reported spectrum[14] of 2-methyl-3*H*-1,3-azaphosphole. The observed and calculated ionization energies are compiled in Table VI. As the failure of Koopmans' theorem in the interpretation of the photoelectron spectrum of 1,2,4,3-triazaphospholes[25] has been reported, the calculated orbital ordering should be used with great care in the assignment of the spectra, especially in the case of close-lying states. For a more reliable assignment, the spectral data were correlated with those of other related compounds, 1*H*-1,3-azaphosphole[14] and azoles.[26,40–42] As can be seen in Table VI, there is little agreement between the measured IE values and the IE values calculated for the derivatives substituted at phosphorus. For the other tautomers, however, there is not too much difference between the measured and calculated values in the case of 1,2,3,4-triazaphosphole,[25] thus no decisive argument is given by the calculations for the selection of the dominant tautomeric form.

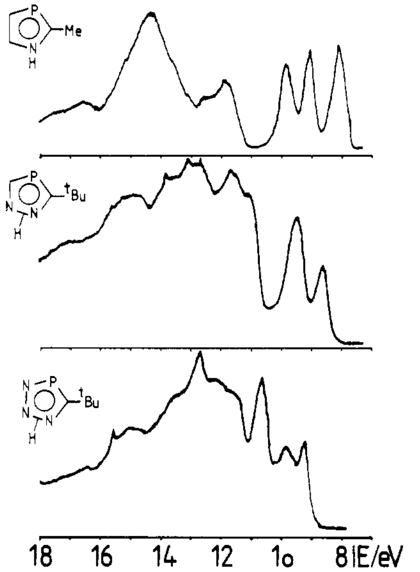


**Figure 1.** He I photoelectron spectra of 2-methyl-1*H*-1,3-azaphosphole, 5-*tert*-butyl-1*H*-1,2,4-diazaphosphole, and 5-*tert*-butyl-1*H*-1,2,3,4-triazaphosphole.

**Scheme II**

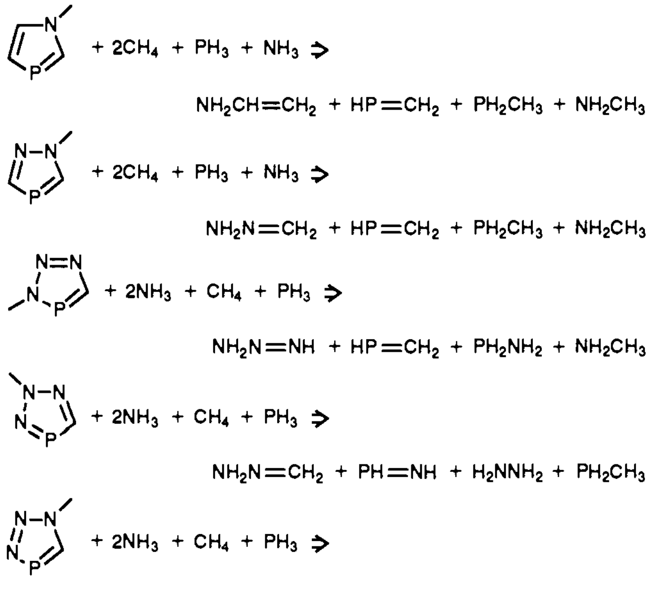


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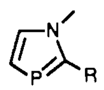
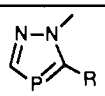
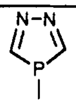
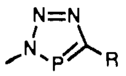
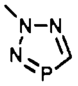
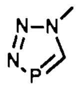
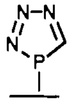
**Table VI.** Observed and Calculated Ionization Energies for Azaphospholes (eV)

|  | | |  | | |  |
|---|---|---|---|---|---|---|
| obs[b] | calc[a] | assgnt | obs[c] | calc[a] | assgnt | calc |
| 8.04 | 7.97 | $\pi$ | 8.69 | 8.71 | $\pi$ | 10.77 |
| 9.07 | 9.17 | $\pi$ | 9.52 | 10.42 | $\pi$ | 11.13 |
| 9.73 | 10.23 | $n_P$ | | 10.63 | $n_P - n_N$ | 12.57 |
| 11.68 | 13.14 | $\delta_{CPC}$ | 11.1 | 12.57 | $n_P + n_N$ | 12.49 |
| 12.4 | 15.40 | $\pi$ | 11.7 | 14.78 | | 15.29 |
| | | | | 16.68 | | |

|  | | |  | |  | |  |
|---|---|---|---|---|---|---|---|
| obs[c] | calc[a] | assgnt | calc | assgnt | calc | assgnt | calc |
| 9.25 | 9.77 | $\pi$ | 9.78 | $\pi$ | 9.37 | $\pi$ | 10.70 |
| 9.81 | 11.48 | $\pi$ | 11.36 | $\pi$ | 10.93 | n | 11.93 |
| 10.63 | 11.89 | $n_{N1} - n_{N3}$ | 11.48 | n | 11.97 | $\pi$ | 12.51 |
| | 12.30 | $n_P$ | 12.59 | n | 12.01 | n | 12.94 |
| 11.7 | 14.97 | $n_{N1} + n_{N3}$ | 13.67 | n | 14.87 | n | 14.97 |
| | 17.39 | $\pi$ | 17.88 | $\pi$ | 17.59 | $\pi$ | 16.49 |

[a] R = H. [b] R = Me. [c] R = tBu.

Due to the slight broadening of the second band (as compared to the first one), the possibility of observing a mixture of tautomers cannot be safely excluded.

The spectra can be divided into two parts. At higher IE values above 11.5 eV, the spectra are masked by ionizations from the tBu groups (judged from the known spectra of *tert*-butylbenzene,[43] *tert*-butylthiophene,[44] and *tert*-butylfuran[45]). The bands observed in the low IE region shift toward higher IE values as the number of nitrogen atoms in the ring increases. This phenomenon was observed earlier for the azoles.[41]

In the case of 1*H*-1,3-azaphospholes, the first two ionizations were assigned to two $\pi$-levels, while the third band was attributed to the in-plane $n_P$ orbital. The ionization energy of the $n_P$ orbital depends mainly on the bond angle around the phosphorus atom, and has an IE value of approximately 10 eV at about 90° (Table VI), provided that no interaction with other orbitals occurs. In the case of azaphospholes, the bond angles are near to 90° (Table I).

According to the calculation, however, a considerable mixing between the $n_N$ and $n_P$ levels occurs in the case of 1*H*-1,2,4-diazaphosphole, which compensates the stabilization with the increasing number of nitrogens. As the $\pi$-levels are affected by the stabilizing effect only, the second and the third bands of 3*H*-1,3-azaphosphole coalesce in the case of 1,2,4-diazaphosphole, in agreement with the calculated orbital energies.

By comparing the $\pi$-ionizations of 1*H*-1,3-azaphosphole and pyrrole, it can be established that replacement of the C=C unit by a P=C unit in the molecule affects the energies of the $\pi$-levels only slightly. Similarly, the $\pi$-ionizations of 1,2,4-diazaphosphole and pyrazole[26,36,41] are close to each other (taking the effect of the substituent alkyl group into consideration).

## Conclusions

In the investigation of the electronic structure and aromatic stability of the different tautomeric forms of 1,3-azaphosphole, 1,2,4-diazaphosphole, and 1,2,3,4-triazaphosphole, the compounds investigated could be divided into two distinct groups. One of these groups consists of compounds containing $\sigma^2,\lambda^3$-phosphorus atoms, while the ring systems containing $\sigma^3,\lambda^3$-phosphorus atoms form the other group. While azaphospholes belonging to the first group have a conjugated system with a high degree of aromaticity, the aromatic character of compounds belonging to the second group is much smaller, in accordance with our earlier conclusions.[14]

According to the 4-31G(*) geometry optimized calculations, bond lengths for the compounds containing $\sigma^2,\lambda^3$-phosphorus atoms are between those of the isolated single and double bond, while C–P bond lengths for the other group of compounds are just slightly shorter than the isolated C–P bond length.

Bond separation reaction heats for compounds belonging to the first group are considerably larger than those for the second group. The aromatic stability in the first group of compounds increases with an increasing number of nitrogen atoms, while no significant effect of the number of nitrogen atoms in the ring can be observed in the case of the second group of compounds. The conjugative ability of the P=C bond has been measured by ring fragmentation reactions as well, by fragmenting the ring into the P=C bond and the rest of the molecule. The increase in the heats of these reactions by increasing the number of nitrogen atoms in the ring has been observed here as well. The greater aromatic stability of the rings containing $\sigma^2,\lambda^3$-phosphorus atoms is reflected in the total energy of the rings too; thus compounds belonging to the second group can safely be excluded as the most stable tautomeric forms. This conclusion is supported by MP2/6-31G**//4-31G(*) calculations for the 1,3-azaphospholes as well.

The He I photoelectron spectra can be interpreted using Koopmans' ionization energies for the most stable tautomeric forms. Ionization energies of $\pi$-orbitals are similar to those of the corresponding azoles, indicating the similar electronic structure of the corresponding azaphospholes and azoles.

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