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Pentaphosphole: An Aromatic Ring with a Planar σ^3-Phosphorus

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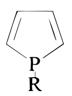
Correlated ab initio calculations show that pentaphosphole (P_5H) is a planar five-membered heterocycle at all levels of theory investigated here. The HP out of plane bending potential, however, is rather shallow. All the PP bond lengths are nearly equal, indicating significant aromatic character. The Bird index is 77, a value that is among the largest for the five membered heterocycles. The average of the double bond characters is 59.6% that is smaller than the 67% for benzene. The stabilization as measured by an isodesmic reaction is comparable to the value for thiophene. In spite of the aromatic stabilization the inherent instability of the P═P−P═P linkage indicates that the ring is rather unstable. Several dimeric products ($P_{10}H_2$) were found, however, which were more stable than two P_5H molecules by 28−35 kcal/mol. Since in case of P_5R there is no possibility for kinetic stabilization by bulky substituents, it is questionable that the compound can be synthesized.

Introduction

The nonplanar arrangement of the substituent (R) on phosphorus in phosphole (**1**) makes the interaction of the phosphorus lone pair orbital and the π-system difficult. As a consequence, phosphole is claimed to be nonaromatic[1] or slightly aromatic.[2] It has recently been shown, however, that if planarized then phosphole would be aromatic.[3,4] Furthermore, several substituent groups have been shown to reduce the inversion barrier about phosphorus in phospholes.[3] Replacement of CH groups in phosphole by σ^2,λ^3-phosphorus atoms results a release in the ring strain of the planar form with respect to the nonplanar one. As a consequence the inversion barrier in di- and triphospholes decreases.[5]



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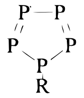

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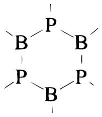

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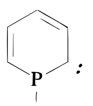

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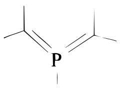

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The aim of the present work is to investigate, by theoretical means, if the five membered ring could entirely be planarized by replacing all the CH groups by σ^2,λ^3-phosphorus atoms, resulting in P_5H (**2**). P_5^- as well as planar P_5 decks in complexes are known.[6] These systems are planar, similarly to the aromatic[4,7] phospholide ion ($PC_5H_5^-$), which is isoelectronic with thiophene. In the ab initio studies[8] of P_5^- it was shown that the ring is nearly strain free, in accordance with the present expectations on HP_5. There are some known molecules containing planar σ^3-phosphorus atoms, such as the six-membered ring $(MesPBC_6H_{11})_3$ (**3**)[9] as well as $PhB(PMes_2)_2$,[10] and phosphinine-2-ylidene (**4**) calculated at several levels of theory[11] and (properly substituted) bis(methylene)phosphorane (**5**).[12] Despite significant efforts to planarize phospholes with bulky substituents,[13] among the five-membered ring phospholes no entirely planar system has been reported.

Since there is a note in the literarture about the failed synthesis of an alkyl-substituted P_5 ring from the corresponding pentaphospholide ion,[14] the stability and the effect of an alkyl substituent on the RP_5 ring will be considered as well. Nevertheless, the recent successful synthesis of the first alkyl-substituted 1,2,4-triphosphole[15] indicates that rings with even more than one phosphorus atoms are synthesizable.

Calculations

Ab initio calculations were carried out by the GAUSSIAN 92/DFT suite of program.[16] The structure of P_5H has been optimized at the HF and MP2 (frozen core) levels of theory using the 6-31G*, 6-311G*, and 6-311+G(2D) basis sets, under planarity constraint. At the optimized structures analytical second derivatives were calculated, while numerical second derivatives were calculated at the MP2/6-311G* and MP2/6-311+G(2D) levels. Since no imaginary frequencies were found,

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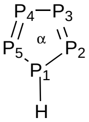
Table 1. Bond Distances in Å, α (the $P_2P_1P_5$ Angle) in deg, and the Lowest Calculated Harmonic Frequency ν_7 in cm^{-1} for Pentaphosphole at Several Levels of the Theory



	HF			MP2			BLYP			B3LYP		
	1^a	**2**^{b}	**3**^{c}	**1**^{a}	**2**^{b}	**3**^{c}	**1**^{a}	**2**^{b}	**3**^{c}	**1**^{a}	**2**^{b}	**3**^{c}
P_1P_2	2.068	2.061	2.054	2.076	2.071	2.081	2.119	2.117	2.107	2.093	2.090	2.081
P_2P_3	2.085	2.083	2.093	2.118	2.114	2.131	2.143	2.148	2.140	2.12	2.120	2.117
P_3P_4	2.111	2.110	2.103	2.119	2.113	2.130	2.168	2.167	2.158	2.141	2.140	2.131
α	120.6	120.9	122.5	123.0	123.2	124.4	122	122.3	123.0	122.2	122.1	123.0
ν_7	95	96	116	128	105	110	104	92	76	98	105	95
$-E_{tot}$	4.17277^d	4.25915^d	4.29877^d	4.72488	4.82712^d	4.93260^d	7.30076^d	7.42127^d	7.45034^d	7.37849^d	7.48631^d	7.51841^d

^{a} **1** denotes 6-31G* basis set. ^{b} **2** denotes 6-311G* basis set. ^{c} **3** denotes 6-311+G(2D) basis set. ^{d} Add 1700 au.

the planar structures are real minima at the corresponding potential energy surfaces. Density functional calculations with the B3LYP and BLYP functions of Becke[17] and the abovementioned three basis sets were carried out too. Second derivative calculations again proved that the planar structure is a real minimum on these potential energy surfaces.

To assess the effect of higher level of electron correlation on the planarity of the system CCSD(T)/6-311+G(2D)//MP2/6-311+G(2D) calculations were carried out, placing the substituting hydrogen at different out of plane angles.

Results and Discussion

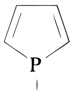
The calculated total energies, optimized structural parameters and the lowest harmonic frequencies for pentaphosphole are shown in Table 1 at different levels of the theory.

The lowest calculated harmonic frequency (ν_7) is the out of plane movement of the substituent hydrogen group. This frequency is about 100 cm^{-1} at all the levels investigated here. At the HF level the increase of the basis set raises this frequency slightly. At the MP2 level or by using density functional theory, however, some decrease of this frequency can be observed when the basis set is increased or augmented by further polarization and diffuse functions. Nevertheless, the change in ν_7 is not too large; thus it seems that pentaphosphole remains planar (ν_7 remains positive) at the investigated levels even by using an infinitely large basis set.

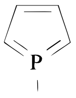
It was shown before that the barrier to planarization is larger at the HF than at the MP2 level for phosphole[3] as well as for di- and triphospholes.[5] The use of higher levels of electron correlation placed the barrier between the MP2 and the HF results. Since in the present case the planar structure was proved as a minimum even by using the HF method, it seems fairly safe to assume that pentaphosphole is planar at any level of the theory. Nevertheless, to consider a higher level of electron correlation, the CCSD(T)/6-311+G(2D)//MP2/6-311+G(2D) out of plane bending potential was investigated. The planar structure was found even at this level to be the lowest energy one. The structure with the hydrogen out of plane angle of 15° was higher by 0.07 kcal/mol while that at 30° was 0.33 kcal/mol higher in energy than the planar one. The corresponding energy differences at the MP2/6-311+G(2D) level were 0.15 and 0.74 kcal/mol, respectively. Therefore, although the planar structure was found to be the lowest energy one at all levels considered here, the potential surface for the HP out of plane bending is quite shallow and the ring is rather flexible. It should be noted that other aromatic rings containing third row heavy atoms only are flexible as well.[18]

To undertsand why σ^3-phosphorus is planar in contrast to the usual pyramidal arrangement, the effect of ring strain should be considered. A D_{5h} pentagon requires 107° angles. This is much smaller than the 120° bonding angle for a sp^2 carbon. Thus, in case of phosphole the pyramidal phosphorus with a nearly 90° CPC angle suffers less ring strain than the planar structure, which should have a nearly 120° CPC angle. The replacement of a CH unit by a σ^2,λ^3-phosphorus (nearly 95° in $HP{=}CH_2$), thus alleviates the ring strain in case of the planar form. Indeed, it was shown[5] in case of di- and triphospholes that the bonding angle about the σ^3-phosphorus gradually opens up by increasing the number of σ^2,λ^3-phosphorus atoms, with a simultaneous decrease of the inversion barrier. In case of tetraphospholes, however, one P=P unit in cis form should be considered, instead of $HP{=}CH_2$. The bonding angle here is opening up toward 100°. The PPP angle in cis P=P—P=P is about 104° (MP2/6-31G*). As a result of these effects tetraphospholes are still pyramidal at the HF/6-31G* and the MP2/6-31G* levels, while pentaphosphole is the first planar five-membered aromatic system, containing σ^3-phosphorus. The α angle in the pentaphosphole (for the notation see Table 1) is somewhat larger than 120° at any level of the theory. The $P_1P_2P_3$ and the $P_2P_3P_4$ angles are about 100 and 110°, respectively.

There are three different PP bonds in the molecule. The shortest among them is the P_1P_2 bond, a formal single bond according to the classical structure **1a**. This indicates that a significant weight should be devoted to the **1b** type structure, as was shown before in case of planarized phosphole[3] as well as di- and triphospholes.[5] The other two bond lengths are nearly identical and their equalization is larger at the MP2 than at the HF level or than in case of the density functional results. It has recently been shown[19] that the MP2 level calculations are superior to the density functional (using the BLYP functional) and HF results in predicting structural data for aromatic ring systems, thus as the "best" geometry in the following discussion the MP2/6-311+G(2D) results will be considered. It is worthy to note that these results are quite close to the B3LYP/6-311+G(2D) results too.



1a



1b

It is likely that the planar P_5H ring has a significant aromatic character. The delocalized electronic structure can be seen on

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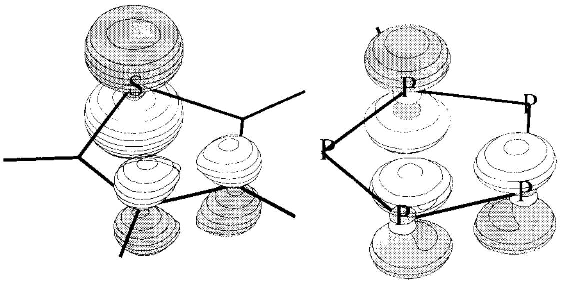


Figure 1. Shape of the highest occupied MO of pentaphosphole and thiophene at their MP2/6-31G* optimum geometries as plotted by the MOLDEN program[26] Density contour was given at 0.1.

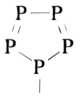
Table 2. Electron Density (ρ), Ellipticity (ϵ) and Laplacian (∇^2) at the Bond Critical Points and Bond Lengths (r_{PP}) in Å at the MP2/6-31G* Level of the Theory

	ρ	ϵ	∇^2	r_{PP}
P_1P_2 (in **2**)	0.136	0.212	−0.130	2.074
P_2P_3 (in **2**)	0.136	0.192	−0.231	2.116
P_3P_4 (in **2**)	0.136	0.183	−0.224	2.116
P—P[a]	0.118	0.080	−0.181	2.183
$P{=}P_{cis}$[b]	0.153	0.350	−0.298	2.049
$P{=}P_{trans}$[c]	0.154	0.362	−0.300	2.039
$P{=}P({=}P)_{cis}$[d]	0.133	0.735	+0.004	2.058
$P{=}P({=}P)_{trans}$[e]	0.132	0.802	+0.015	2.053

[a] In $H_2P—PH_2$. [b] In *cis*-HP═PH. [c] In *trans*-HP═PH, which is the more stable form. [d] HP═P(H)═PH. The vicinal hydrogens are in cis position. [e] HP═P(H)═PH. The vicinal hydrogens are in trans position; thus this is the ringlike conformation. This conformation is more stable than the one with cis hydrogens by 5.16 kcal/mol (MP2/6-31G*).

the MO-s. In Figure 1 the uppermost occupied b_1 orbitals of thiophene and pentaphosphole are shown. The involvments of the "lone pair" orbitals of those atoms which contribute by an electron pair to the π-system (sulfur and σ^3-phosphorus, respectively) are quite similar, indicating that the aromatic π-system indeed has been formed in case of pentaphosphole.

It was shown[20] that the isodesmic reaction[21] of the type shown in eq 1 is a useful measure of aromatic stabilization in five-membered heterocycles. At the MP2/6-31G* level the stabilization energy of this reaction is 28.94 kcal/mol, a value comparable to the 21.13 kcal/mol result obtained in the corresponding reaction for thiophene,[20] at the same level of theory.



$$+ PH_3 \quad + 2HP{=}PH \quad \Rightarrow \quad HP{=}P\text{-}P{=}PH \quad + 2\ PH_2\text{-}P{=}PH \qquad (1)$$

To assess the aromaticity, geometrical criteria can be used as well, among them the widely acknowledged[22] criterion, the Bird index.[23] This is based on the statistical evaluation of the peripheral bond lengths in the ring. Following the original procedure of Bird,[23] the bond order was defined from the bond lengths of $H_2P—PH_2$ and HP═PH, calculated at the MP2/6-311+G(2D) level, by the help of the Gordy relationship.[24] Using these values 77 was obtained for the Bird index, which is in the range of most aromatic five-membered rings (pyrazole 73, 1*H*-1,2,3-triazole, 73).[23] For thiophene and pyrrole, somewhat smaller values, 66 and 59, were reported.[23] It should be noted, however, that according to the **1b** structure the P_1P_2 bond cannot be simply considered as an intermediate between the classical single and double bonds, but the bonding in HP═P(H)═PH can be considered instead of the normal double bond. The length of this PP bond is only slightly larger than in HP═PH (Table 2). Using the method for analysis of the electron density developed by Bader,[25] the electron density at the bond critical points correlates with the bond order, and can be used as an alternative measure of the bond order instead of the bond length. The density at the critical point is 0.136 for each PP bond (Table 2), including the P_1P_2 bond. Uniform bond orders result in a Bird index of 100, equal to that in benzene. It should be noted, however, that the density at the critical point of the HP═PH(═PH) bond is 0.133 and thus less than for the double bond of HP═PH (Table 2). Nevertheless, the ellipticities indicate that the electron distribution in the ring is rather asymmetric about the PP bond; furthermore, the ellipticities are between those of the single and double bonds for all the PP bonds as usual for the delocalized systems.

The recently introduced[20] index, which measures the average double bond character in the ring, is 59.6%. The corresponding index was 55.3% for furane, 62.7% for thiophene and 61.6% for pyrrole, while 67% for benzene (all at the MP2/6-31G* level). This index reflects the general shortening of the bonds in the ring which is related to the aromatic stabilization. While the energetic measure of aromaticity, as well as the Bird index, indicates a higher degree of aromaticity in P_5H than in case of pyrrole or thiophene, the bond shortening is smaller. It should be considered, however, that the P—P bond length in HP═P—P═PH is already longer (2.196 Å) than in case of the normal single bond (2.183 Å, Table 1) and this bond length shows further increase in case of the cis structure (2.228 Å). Since in the isodesmic reaction 1 the energy of HP═P—P═PH is considered, the stability of the ring is related to that of this conjugated four-membered chain. The apparent destabilization due to the weak P—P bond has already been accounted for in HP═P—P═PH. Thus, the relatively small average double bond character is conform with the large isodesmic reaction energy. The value of the average double bond character on the other hand indicates that the ring is only moderately stable despite the rather large aromatic stabilization.

Alkyl substitution on the σ^3-phosphorus atom does not affect the planarity. Optimization of P_5CH_3 resulted in a planar structure similar to the case of P_5H at the MP2/6-31G* level of theory. A bicyclic isomer, bicyclo[2.1.0]pentaphosphane, which on basis of the general bonding pattern in polyphospholes[8] is likely to be a stable structure, is less stable by 17 kcal/mol at the MP2/6-31G* level of theory with respect to **2**.

It has been reported in an attempted synthesis of P_5R[14] that only polymeric products were obtained. Indeed, unlike the case of N_5H,[27] no dissociation toward fragments (N_2 is very stable) should be considered, but formation of dimeric products is likely. Investigating different dimerization possibilities, all of them resulted in structures more stable than two P_5H, by 28−35 kcal/mol at the HF/6-31G* level of the theory. The most stable dimer is shown in Figure 2. Similar bonding patterns were reported in investigations on phosphorus clusters.[8] In an attempted search for a transition state at the MNDO level (which gave an energy difference of 42 kcal/mol between the two monomers and the dimer, cf. the ab initio value) no transition structure could be located with the rings fixed between 2.5 and

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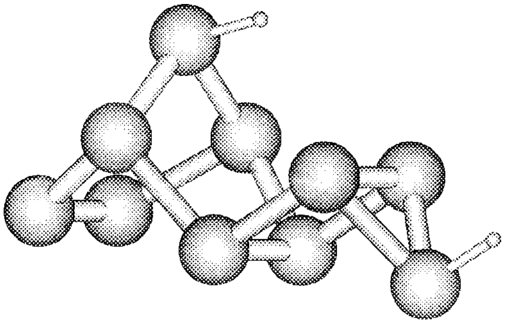

Figure 2. Most stable dimeric structure ($P_{10}H_2$) obtained at the HF/6-31G* level of theory. The structure was plotted by the MOLDEN program.[26]

4 Å distances. Since there is no substituent on four of the phosphorus atoms, shielding substituent groups are of little help in the stabilization of that ring. In the dimeric structure—shown in Figure 2—the lengths of the single bonds are between 2.206 and 2.257 Å at the HF/6-31G* level, while that of the double bond is 2.020 Å. Since this double bond is capable for further dimerization (or polymerization), the unidentified mixture of polymers in the attempted synthesis of P_5R can be explained.

Conclusions

On the basis of ab initio calculations carried out at different levels of the theory including CCSD(T)/6-311+G(2D)//MP2/6-311+G(2D), pentaphosphole P_5H (**2**) is a planar molecule. This finding is in contrast with the nonplanarity of phosphole $PH(CH)_4$ (**1**). The ring itself is rather flexible. The energy cost of the 30° HP out of plane bending is only 0.33 kcal/mol. The molecule has a considerable aromatic character, similar to the hypothetical planar phosphole. To achieve planarization, however, the decrease of the ring strain, with small (nearly 95°) bonding angles about the σ^2,λ^3-phosphorus atoms, should be taken into account apart from the effect of aromaticity.

Alkyl substitution does not change the planarity of P_5H. A bicyclic structure was found less stable than the planar ring. However, several dimeric structures are more stable than the monomer by 28−35 kcal/mol. Since in these dimers further unshielded P═P double bonds are present, it is likely that further polymerization occurs, in agreement with the observation of Baudler et al.[14]

Note Added in Proof. While this paper was being processed, the author refereed the paper of M. N. Glukhovtsev, A. Dransfeld, and P. v. R. Schleyer entitled “Why Pentaphosphole, P_5H, is Planar in Contrast to Phosphole, $(CH)_4PH$”, which is now accepted for publication in *J. Phys. Chem.* It turns out from this paper that the planarity of P_5H, which was discovered computationally at Erlangen in 1992, has already been mentioned in: Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, 1995.

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