Phosphinin-2-ylidene: An Isomer of Phosphinine with a Phosphinocarbene Unit[†]

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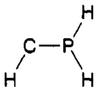
Received November 29, 1994[®]

Phosphinin-2-ylidene, an isomer of the stable aromatic phosphinine, has been shown to be a minimum by ab initio calculations, at all levels of theory investigated. Similar to phosphinocarbene, the ground state of phosphinin-2-ylidene is singlet at correlated levels of theory, as well as by density functional studies. The bond length alternation in the ring is small, and homodesmic reaction energies indicate significant aromatic stabilization; both "measures" of aromaticity, however, provide somewhat smaller values than in the case of phosphinine. Although phosphinine is more stable by about 75 kcal/mol, the two structures are separated by a barrier of 25.96 kcal/mol at the MP2/6-31G* level of theory. The dimerization of phosphinin-2-ylidene is exothermic by about 106 kcal/mol. This dimerization, however, can be prevented by the presence of bulky protecting groups at phosphorus and the carbon adjacent to the carbenic carbon atom. On the basis of the present calculations, phosphinin-2-ylidene (protected with a bulky group) is a likely example of a synthesizeable carbene with a planar σ^3,λ^3-phosphorus atom.

Introduction

Carbenes are generally considered to be short-lived, reactive intermediates having a triplet ground state.[1] It has been shown, however, that π-donor substituents can stabilize the singlet state relative to the triplet, by saturating the carbenic LUMO.[2] Such stabilizing factors made possible the preparation of the two "bottle-able", ground state singlet compounds, the Bertrand type carbene (**1**)[3] and the Arduengo type carbene (**2**).[4] Phosphorus, being a good electron donor was able to stabilize carbene **1** by a single PH_2 group (although it has been considered whether this compound might be better described as a λ^5-phosphaacetylidene[5]). This stabilization was great enough to overcome the barrier to planarization of the phosphorus, resulting in a planar PH_2 group. In the case of **2**, the two nitrogen atoms and the aromaticity are thought to provide the stabilization of the compounds.[6]



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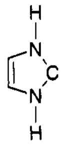

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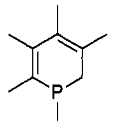
The aim of the present work was to show that the phosphorus-stabilized (Bertrand type) carbene **1** can be incorporated into an aromatic ring system (**3**), which is an isomer of phosphinine (**4**). The stability and aromaticity of a ring containing the analogous −Si(II)−N< unit has recently been demonstrated by us.[7]

The electronic and steric structures of **1** have been thoroughly investigated in recent works.[5,8] According to Nguyen et al.,[5] calculations at correlated levels predict a singlet ground state with a bent structure (having a PCH angle of 123.5°) and a planar PH_2 group. The lowest triplet state has been calculated to lie only 3 kcal/mol higher than the lowest singlet. The importance of the incorporation of electron correlation in the calculations was shown by the fact that, at the HF level, the ground state was determined to be a triplet. CISD and CEPA calculations[8] have also been carried out for **1**, predicting the singlet to be more stable by 6.4 kcal/mol than the triplet, but no data about the importance of using multiconfiguration wave functions have been published yet.

Phosphinine **4**, the structural isomer of **3**, is a well-known molecule. Its aromaticity has been indicated by both experimental and theoretical investigations.[9] No compound, however, has ever been reported with a planar σ^3,λ^3-phosphorus in an aromatic ring. Phospholes[9b] and azaphospholes[10] have nonplanar ground states, due to the large inversional barrier about phosphorus. Although this barrier can be reduced significantly by proper



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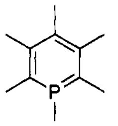

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[†] Dedicated to Professor Manfred Regitz on the occasion of his 60th birthday.

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1995.

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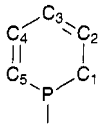
Table 1. Total Energies (in au), Relative Energies to Phosphinine (ΔE in kcal/mol), Lowest Calculated Harmonic Frequencies (δ_{Ph} in cm^{-1}), and Selected Geometrical Data (in Å and deg) for Phosphinin-2-ylidene at Different Levels of Theory[a]

	ΔE	δ(PH)	CPC	PC1C2	PC1	C1C2	C2C3	C3C4	C4C5	C5P	$-E_{tot}$
					Singlet State						
HF/6-31G*	74.24	146	118.6	109.9	1.666	1.427	1.380	1.412	1.371	1.715	532.83642
MP2/6-31G*	74.56	221	120.7	108.3	1.673	1.422	1.408	1.403	1.399	1.708	533.61326
HF/6-311G*	66.00	191	118.6	110.0	1.664	1.426	1.381	1.410	1.371	1.710	532.90352
CCD/6-31G*	75.51		120.1	108.5	1.676	1.431	1.398	1.413	1.389	1.718	533.60487
CAS(6,6)	73.34		119.1	109.9	1.666	1.434	1.394	1.418	1.386	1.723	532.90412
CAS(8,8)			119.5	109.0	1.685	1.440	1.390	1.422	1.383	1.729	532.92828
DFT/6-31G*	65.98	147	120.3	108.1	1.702	1.437	1.413	1.420	1.405	1.740	534.65723
DFT/6-311G*	65.13	160	120.0	108.4	1.697	1.433	1.411	1.416	1.402	1.734	534.73127
					Triplet State						
ROHF/6-31G*			96.9	128.1	1.797	1.424	1.342	1.466	1.331	1.831	532.84269
DFT/6-31G*			96.6	129.8	1.788	1.363	1.433	1.425	1.384	1.843	534.63922

[a] MP2 and CCD calculations were carried out using the full and frozen core approximations, respectively.

substitution to 1.5 kcal/mol,[11] complete planarization of phospholes have been hitherto unsuccessful.

Calculations

Quantum chemical calculations have been carried out with the GAUSSIAN 92 program package.[12] The 6-31G* basis set has been used throughout at the HF and MP2 levels of theory. All the structures have been fully optimized, and the nature of the stationary points was characterized by second derivative calculations. Since the structural differences are only minor at the higher levels in the case of singlet **3** (see later), further frequency calculations were not carried out for economic reasons. Reoptimization of the obtained structures was performed for **3** and **4** using the 6-311G* basis set at the HF and MP2, as well as at the CCD/6-31G* levels of theory. Density functional optimizations and second derivative calculations as implemented in the GAUSSIAN 92 suite of programs[13] were carried out too, using Becke's correlated functional[14] and the 6-31G* as well as the 6-311G* basis set (further referred to as DFT/6-31G* and DFT/6-311G*, respectively).

In order to test the adequacy of the single determinant wave function, CASSCF calculations have been carried out for **3**, both with the active space set on the π-space including 6 electrons and 6 orbitals (6,6) and 8 electrons and 8 orbitals (8,8). In the latter case, the in-plane carbenic lone pair has been included in the active space, too. Although in the CASSCF wave function some configurations besides the reference had non-negligible weight (the second largest coefficient for a π–π^* double excitation was 0.15), a similar wave function was obtained for **4** as well. Such aromatic compounds are generally considered to be well describable by single determinant based perturbation procedures. Inclusion of the carbene in-plane orbital in the active space resulted in only minor changes, and no excitation from this orbital had larger than a 0.03 CI coefficient in the CASSCF wave function.

As for the singlet–triplet splitting, methods based on the UHF wave function were of little use because of the high spin contamination ($s^2 = 2.4$) of the triplet. Optimization of the triplet structure therefore has been carried out using the ROHF method. The effect of electron correlation could be estimated only by single point calculations, projecting out the unwanted spin contaminants. Thus MP2/6-31G*//HF/6-31G* energies were compared to PUMP2/6-31G*//ROHF/6-31G* energies (s^2 after projection was 2.02). In the density functional studies, s^2 was only at about 2.03 for the triplet state; thus the energies of the singlet and the triplet could easily be compared. It should be noted that spin contamination was not so severe in the case of triplet **1** at the UHF level, s^2 being only 2.02.

Results and Discussion

The calculated geometries and energies as well as the lowest calculated (out of plane δ_{PH}) frequency of singlet **3** are shown in Table 1, at different levels of theory. Second derivative calculations at all of the investigated levels (see Calculations section) revealed that the planar structure **3** is a real minimum on the potential energy surface.

The triplet structure on the other side is nonplanar, with a pyramidal phosphorus. At the ROHF/6-31G* level, the triplet (derivable by an excitation from the carbene "lone pair" to the carbene "empty" p orbital) was found to be more stable than the singlet by 3.9 kcal/mol. Inclusion of electron correlation, however, reversed the ordering of the states, and at the PMP2/6-31G*//ROHF/6-31G* level the singlet state was preferred by 22.06 kcal/mol. Although this result might seem suspicious as the energies have not been obtained at the corresponding optimized geometries, at the DFT/6-31G*//DFT/6-31G*+ZPE level of theory, the singlet state was again more stable than the triplet by 10.26 kcal/mol. Since this behavior is similar to the case of the synthesizeable and obviously singlet **1**, in which at the HF level the triplet is predicted, while at correlated levels the singlet state proves to be more stable, it is reasonable to deduce that the ground state of **3** is singlet.

The lowest harmonic frequency of singlet **3** corresponds to the out-of-plane motion of the hydrogen on phosphorus, in accordance with the propensity of phosphorus to be

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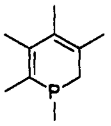
nonplanar. The more involved the phosphorus lone pair is in conjugation, the more fixed the hydrogen should be in the plane, i.e. the corresponding harmonic frequency should increase (cf. with the nonplanarity of the triplet **3**). According to HF/6-31G* calculations, the out-of-plane motion of the hydrogen on the phosphorus atom has a rather low (147 cm^{-1}) harmonic frequency. This value, however, increases significantly, using either a larger basis set (HF/6-311G**; 191 cm^{-1}) or considering electron correlation (MP2/6-31G*; 220 cm^{-1}). This behavior is again similar to the case of **1**, where the out-of-plane frequency was $-320\ \mathrm{cm}^{-1}$ at the HF/6-31G* but 464 cm^{-1} at the MP2/6-31G* level. The out-of-plane frequency obtained from density functional calculations for **3** was 146 cm^{-1}.

The C−C bond lengths for **3**, between the C_2, C_3, C_4, and C_5 atoms, show some alternation (Table 1). The largest deviation from the average was 1.7% at the HF/6-31G*, 1.6% at the HF/6-311G*, and only 0.3% at the MP2/6-31G* and 0.4% at the DFT/6-31G* levels of theory. CCD/6-31G* calculations, however, show a somewhat larger alternation (0.9% deviation from the average). CCD calculations for phosphabenzene and phosphole[11] also indicate smaller bond equalization than MP2 calculations. It has been shown, however, for phosphole that while MP4(SD) results are close to the CCD results, inclusion of triples and quadruples (MP4(SDTQ)) provides results nearer to those of MP2.[11] The largest deviation was 0.1% in the case of phosphinine, 5.46% in butadiene, and 2.1% in the aromatic five-membered ring thiophene (each at the MP2/6-31G* level of theory). These data indicate that although phosphinin-2-ylidene is "less aromatic" than its isomer phosphinine, the ring still exhibits significant bond length equalization.

The contribution of aromaticity to the stabilization of **3** can be estimated by homodesmic reaction 1 at the MP2/6-31G* level of theory:



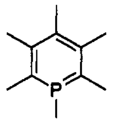
$$+ \ PH_2CH + 2CH_2{=}CH_2 \Longrightarrow$$

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHPHCH + CH_2{=}CHCPH_2 \qquad (1)$$

$$\Delta E = 16.47\ \text{kcal/mol}$$

All possible conformers of the fragments at the right side of the equation have been optimized at the HF/6-31G* level of theory, and those having the lowest energy were reoptimized at the MP2/6-31G* level. The largest difference between the energies of the different conformers did not exceed 2 kcal/mol.

The stabilization indicated by this reaction is smaller than that obtained in homodesmic reaction 2 for phosphinine[9b,15] or in the similar homodesmic reaction[9b,15] for benzene (28.2 kcal/mol), at the MP2/6-31G* level in each case.



$$+ \ PH{=}CH_2 + 2CH_2{=}CH_2 \Longrightarrow$$

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHP{=}CH_2 + CH_2{=}CHCH{=}PH \qquad (2)$$

$$\Delta E = 27.10\ \text{kcal/mol}$$

(At the HF/6-31G* level,[15] somewhat smaller values—24.0 and 24.8 kcal/mol—were obtained for phosphinine and benzene, respectively.) These data indicate that although the aromaticity of phosphinine-2-ylidene is smaller than that of phosphinine, it still has a significant effect on the electronic structure and stabilization of **3**.

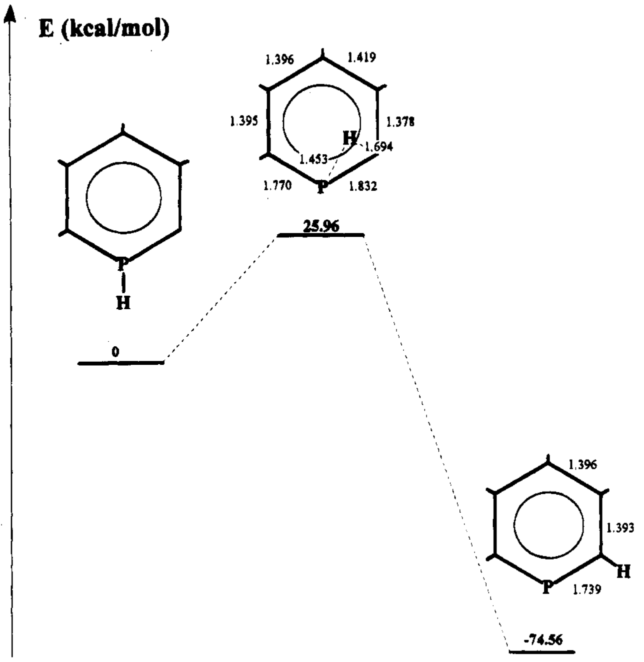
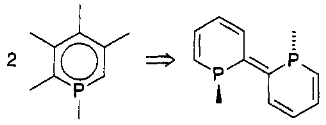


Figure 1. Energies of phosphinine and the transition structure relative to phosphinin-2-ylidene at the MP2/6-31G* level of theory, together with some important geometrical features.

It is apparent from Table 1 that although both **3** and **4** are local minima, phosphinine lies lower on the potential energy surface by about 75 kcal/mol. (Similarly, H_2PCH (**1**) is less stable than $HP{=}CH_2$ (**5**) by 61.17 and 64.45 kcal/mol at the HF/6-31G* and MP2/6-31G* levels of theory, respectively.) In order to get more information about the stability of **3**, calculations for the barrier to the [1,2]sigmatropic hydrogen shift were carried out at different levels of theory (Figure 1). The energy of the first-order saddle point for the motion of the hydrogen atom (**34**) was found to be 25.96, 20.55, 18.78, and 18.69 kcal/mol (MP2/6-31G*+ZPE, HF/6-31G*+ZPE, DFT/6-31G*+ZPE, and DFT/6-311G*+ZPE levels of theory, respectively) higher than **3**. Since the increase of the basis set resulted in some slight change in the activation barrier as calculated by the density functional method, the barrier is likely to be at least 18−19 kcal/mol. Upon replacement of the hydrogen (on phosphorus) by a bulky substituent, an increase of this barrier is likely, thus preventing the isomerization to phosphinine. The possible bimolecular tautomerization of **3** can similarly be blocked by using bulky substituents at the neighboring atoms of the carbenic center. (To model the effect of alkyl substitution on the relative energies of phosphinine (**4**) and carbene (**3**), the energy difference of $HP{=}CHMe$ and HMePCH has been compared to that of $HP{=}CH_2$ and H_2PCH at the HF/6-31G* level of theory. The energy differences remained virtually unchanged, indicating the similar strength of the C−C and P−C bonds.) The arrangement of the ring atoms in the saddle point (**34**) is nearly planar, with the hydrogen lying above the P−C bond almost perpendicular to the ring plane. It is worthy of note that even the equalization of the C−C bond lengths (bonds C_2C_3, C_3C_4, and C_4C_5 according to the notation used in Table 1) has not decreased significantly

Scheme 1



$\Delta E = -105.95$ kcal/mol

(at the MP2/6-31G* level the largest deviation from the average was 1.1%), despite the more significant changes in the P–C bond length (Figure 1). The barrier of the $HPCH_2$ (**1**)–H_2PCH (**5**) isomerization was found to be somewhat smaller, 18.1 kcal/mol at the MP4SDQ/6-31G*//HF/3-21G(*) level of theory.[5]

Another possibility for the decay of **3** would be dimerization. During the dimerization of **3** (Scheme 1), a double bond forms between the two rings, as evidenced by the length of this bond in the dimer. The bond alternation increases significantly. The hydrogens on phosphorus are nearly perpendicular to the CPC planes, the structure resembling the triplet structure of **3** (note that the formation of an ethylenic double bond can be better described from two triplet carbenes, than from two singlet carbenes[16]). This dimer is more stable than the monomer at the HF/6-31G*+ZPE level by 105.95 kcal/mol. Although the stabilization upon dimerization is significant, such reaction can again be avoided by the inclusion of bulky shielding groups on both sides of the carbenic center.

Conclusions

Phosphinin-2-ylidene, an isomer of the well-known aromatic phosphinine, has been predicted by ab initio quantum-chemical calculations carried out at different levels of theory to be a possibly-stable aromatic species.

The compound is a member of the family of nucleophilic carbenes. Furthermore, it contains a planar σ^3,λ^3-phosphorus atom, hitherto unknown in π-systems.

Phosphinin-2-ylidene possesses considerable aromatic character as concluded from the equalization of the different CC bond lengths and homodesmic reaction energies. All these criteria, however, indicate that the degree of aromaticity is somewhat less than in the case of phosphinine.

The barrier leading to isomerization (to the more stable phosphinine) is significant. According to HF-6-31G* calculations, the dimer of phosphinin-2-ylidene is much more stable than two monomers.

Introduction of bulky protecting groups at phosphorus and the carbon nearest to the carbenic center should prevent dimerization, and both mono- and bimolecular isomerization processes, thus making the phosphinin-2-ylidene ring system synthesizable.

Acknowledgment. Financial support from OTKA 642 and T-4097 is gratefully acknowledged.

JO9420073

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