Relative Energies of Methyl- and Vinylphospholes

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The geometries of all isomers of methylphosphole and three isomers of vinylphosphole (1-vinyl-1*H*-phosphole, 2-vinyl-2*H*-phosphole, and 3-vinyl-3*H*-phosphole) were completely optimized at the HF/6-31G* level. The phosphole ring is minimally perturbed by the substituents. The relative energies of these compounds suggest that substitution is preferred upon phosphorus over carbon to minimize steric interactions between the substituent and the phosphole ring.

We recently reported a study of the [1,5] hydrogen migration in phospholes.[1] This study fully supported the mechanistic proposal by Mathey[2-7] that a substituted 1*H*-phosphole rearranges to the 2*H* isomer before undergoing a Diels–Alder reaction, with the phosphole as the diene component. One interesting result we noted is that 2*H*-phosphole (**2**) is lower in energy than 1*H*-phosphole (**1**). At HF/6-31G*, **2** is 1.00 kcal $\mathrm{mol^{-1}}$ more stable than **1**, and this energy difference increases to 7.68 kcal $\mathrm{mol^{-1}}$ at MP2/6-31G*. This is contrary to the relative energies of the pyrroles where 1*H*-pyrrole is significantly more stable than 2*H*-pyrrole, due to aromaticity present only in the former isomer. These calculations are also contrary to experiment where only derivatives of **1** have been isolated, though derivatives of **2** have been postulated as intermediates. Simple analysis of bond energies favors **2** over **1**, if one assumes a reasonable value for the C=P π-bond energy and that aromatic stabilization of **1** is small at best. We speculated that when large substituents are placed on the phosphole ring, steric interactions would favor **1** over **2** or 3*H*-phosphole (**3**), and this accounts for the general isolation of only substituted 1*H*-phospholes.[1] In this paper, we examine the relative energies of all of the methylphosphole isomers (**4**–**14**) and three vinylphospholes (**15**–**17**) at the HF/6-31G* level (see Chart 1) and find that substitution on phosphorus is favored over substitution on carbon.

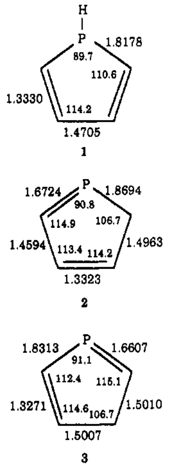
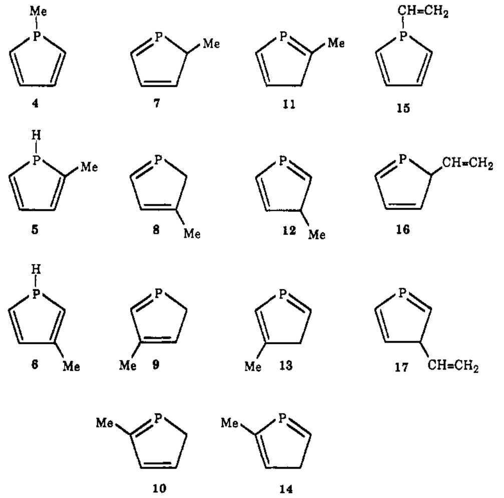


Figure 1. HF/6-31G*-optimized structures of the phospholes **1**–**3** from ref 1. All distances are in angstroms and all angles are in degrees.

Chart 1



Computational Methods

The geometries of all of the substituted phospholes were completely optimized at the HF/6-31G* level using the standard methods incorporated into GAUSSIAN-90.[8] We obtained the lowest energy geometries of all of the methylphospholes: 1-methyl-1*H*-phosphole (**4**), 2-methyl-1*H*-phosphole (**5**), 3-methyl-1*H*-phosphole (**6**), 2-methyl-2*H*-phosphole (**7**), 3-methyl-2*H*-phosphole (**8**), 4-methyl-2*H*-phosphole (**9**), 5-methyl-2*H*-phosphole (**10**), 2-methyl-3*H*-phosphole (**11**), 3-methyl-3*H*-phosphole (**12**), 4-methyl-3*H*-phosphole (**13**), and 5-methyl-3*H*-phosphole (**14**). The structures of **8**–**14** were found to have C_s symmetry, with the phosphole ring lying in the plane of symmetry; **4** is also of C_s symmetry with the symmetry plane perpendicular to the ring. The structures of **5**–**7** were optimized with no symmetry constraints. Optimization of all of the possible isomers of vinylphosphole is prohibitively expensive. Instead, we have examined the isomers where the vinyl group is attached to the saturated center only: 1-vinyl-1*H*-phosphole (**15**), 2-vinyl-2*H*-phosphole (**16**), and

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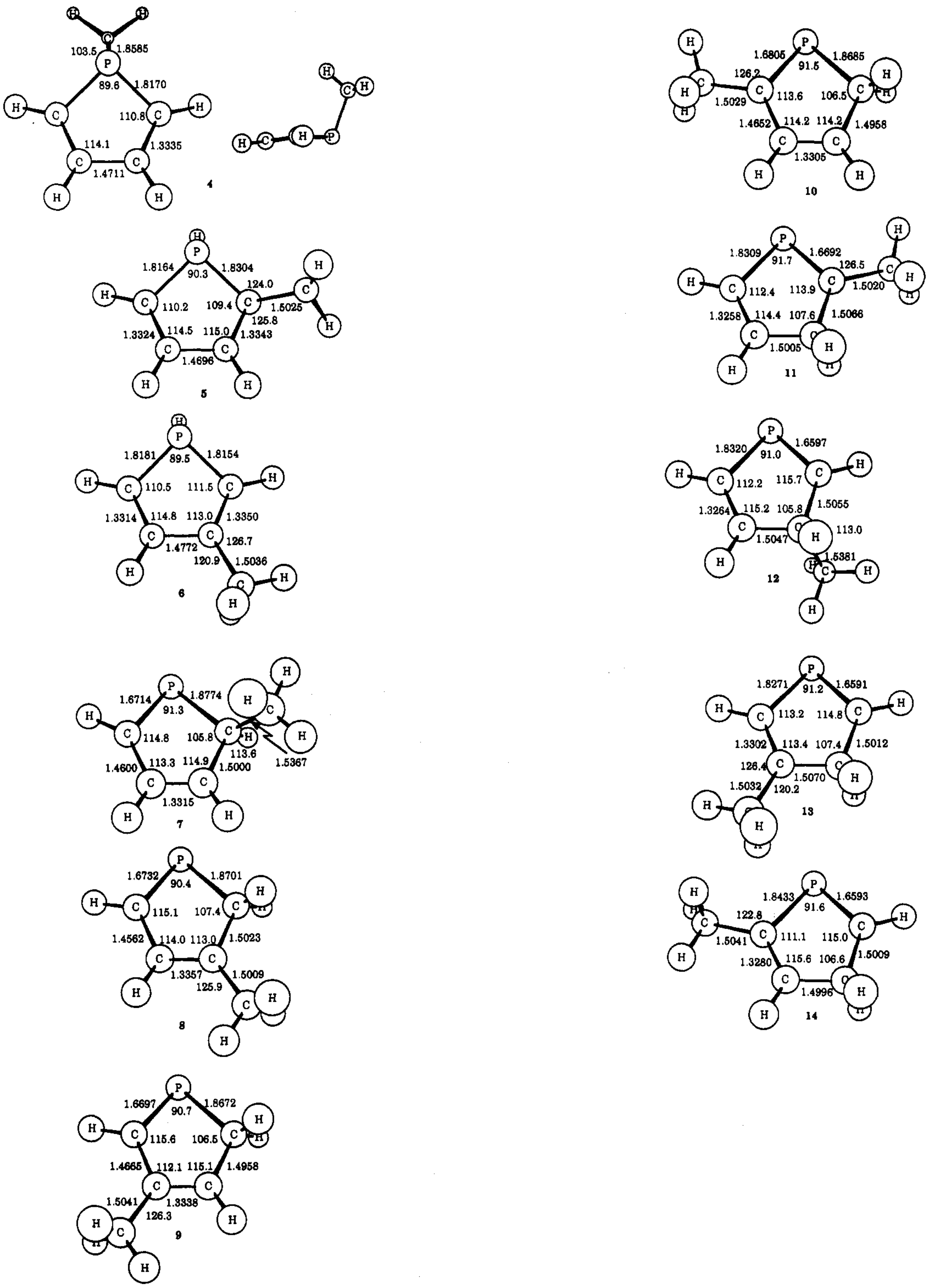

Figure 2. HF/6-31G*-optimized structures of the methylphospholes 3–14. All distances are in angstroms and all angles are in degrees.

3-vinyl-3*H*-phosphole (17). C_s symmetry was invoked for 15 and the other two structures were optimized with no symmetry constraints. All structures were confirmed to be local minima by calculating the analytical frequencies and finding no imaginary frequencies. For comparison purposes, the optimized structures of 1–3 obtained earlier are repeated in Figure 1. The optimized geometries of the methylphospholes 4–14 are drawn in Figure 2 and the geometries of the vinylphospholes 15–17 are drawn in Figure 3. The total and relative energies of 4–17 are listed in Table 1. Zero-point vibrational energies (ZPE) have been scaled by 0.89.

There are no structural data for the methyl- or vinylphospholes with which we could compare our calculated geometries. 1-Methyl-1*H*-phosphole was first prepared in 1967[9] but no structural data are avilable. Vinylphosphole has not been prepared. In our previous paper we compared the geometries of 1–3 with the limited structural data available for a few substituted phospholes and found excellent correspondence among them. Therefore, we believe that the HF/6-31G* computational level is suitable for the study of the methyl- and vinylphospholes.

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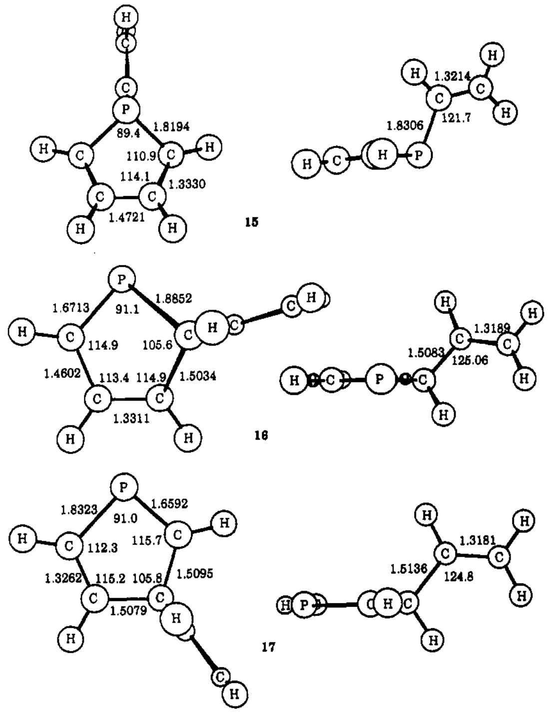

Figure 3. HF/6-31G*-optimized structures of the vinylphospholes 15–17. All distances are in angstroms and all angles are in degrees.

Our previous study[1] of 1–3 indicated that inclusion of electron correlelation through MP2 did not alter the geometries appreciably from the HF/6-31G*-optimized structures. Furthermore, the energy differences between the isomers changed by only a few kcal mol^{-1}. Particularly important is that 1 is higher in energy than 2 at both the HF and MP2 levels. The correlation energy differences brought about by the methyl or vinyl substituents are likely to be small in these closely related isomers. Therefore, since optimization of the geometires of all of the isomers 4–17 at the MP2 level would be extremely time consuming, and would likely not significantly change the relative energy of the isomers, we have restricted our calculations to the HF level.

Results and Discussion

In order to discuss the geometries of the methyl- and vinylphospholes, we reproduce the HF/6-31G*-optimized geometries of 1–3 in Figure 1. The phosphole ring is 1 is not planar, and since 2 and 3 possess C_s symmetry, their rings are planar. Similarly, we find that the substituted analogues of 1, specifically 4–6 and 15, have nonplanar rings and that the substituted analogues of 2 (i.e., 7–10 and 16) and 3 (i.e., 11–14 and 17) have either exactly planar rings due to the molecular symmetry or essentially planar rings.

The fact that the substituted 1*H*-phospholes are nonplanar further disputes the commonly held notion of aromatic character for these systems.[10-14] This is especially apparent in the structure of 15. The vinyl group is perpendicular to the phosphole ring, allowing for no conjugation between the vinyl group and the phosphorus lone pair.

Table 1. Energy (hartrees) and Relative Energies (kcal mol^{-1}) of 1–17

compd	E	E_{rel}	E_{rel} + ZPE[a]
1		1.00[b]	
2		0.00[b]	
3		3.25[b]	
4	−534.100124	0.00	0.00
5	−534.097762	1.48	0.72
6	−534.099316	0.51	−0.30
7	−534.093463	4.18	5.00
8	−534.101154	−0.65	−0.25
9	−534.100301	−0.11	0.27
10	−534.100157	−0.02	0.42
11	−534.094358	3.62	4.12
12	−534.090448	6.07	6.87
13	−534.095670	2.79	3.25
14	−534.094207	3.71	4.19
15	−571.942323	0.00	0.00
16	−571.936347	3.75	4.29
17	−571.932465	6.18	6.71

[a] Relative energies including zero-point vibrational energy scaled by 0.89. [b] See ref 1.

The geometries of the parent 1*H*-phosphole and the substituted analogues 4–6 and 15 are quite similar. Placing a methyl substituent on phosphorus in 1 results in almost no changes in the bond lengths and angles in the phosphole ring (compare 1 and 4). Methyl substitution at the 2 (5) or 3 (6) position or vinyl substitution at the 1 position (15) also causes little change in the geometry of the phosphole ring. The biggest effect of these substitutions is a (slight) lengthening of the bonds to the substituted atom.

This same pattern holds for methyl or vinyl substitution on 2 or 3. The geometries of the phosphole rings are essentially unchanged by the substitution, outside of a small lengthening of the bonds to the substituted center. Therefore, substitution is not significantly changing the phosphole ring. Further, the only significant changes in the rings occur at the site of substitution in an attempt to reduce the steric interactions between the substituent and the phosphole ring.

We now turn our attention to the relative energies of the phospholes. As we previously reported, 2 is 1.00 kcal mol^{-1} more stable than 1.[1] From a bond energy additivity viewpoint, the difference in 1 and 2 is the energy of the P—H bond and the C═C π-bond present in 1 versus the energy of the C—H bond and the C═P π-bond present in 2. If we do this type of comparison between 4 and 7, then the energy difference results from the presence of the P—C bond and the C═C π-bond in the former and the C—C bond and the C═P π-bond in the latter. The energy for the model reaction 1 + 7 → 2 + 4 can be obtained solely by the strength of the P–H (77 kcal mol^{-1}), C–H (98 kcal mol^{-1}), P–C (63 kcal mol^{-1}), and C–C (83 kcal mol^{-1}) bonds.[15] This reaction is exothermic by 1 kcal mol^{-1}, and when combined with our previous study, this simple model predicts that 4 and 7 should have identical energies.

At the HF/6-31G* level we find that 4 is 4.18 kcal mol^{-1} (5.00 with ZPE correction) more stable than 7 and 6.07 kcal mol^{-1} (6.87 with ZPE correction) more stable than 12. Substitution on phosphorus over carbon is more stabilizing

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than predicted by bond additivity alone. This is also found in the series of the vinylphospholes, where **15** is more stable than **16** and **17** by 3.75 (4.29 with ZPE) and 6.18 (6.71 with ZPE) kcal mol^{-1}, respectively. These results support the notion that substitution on phosphorus will be energetically favorable over substitution on carbon due to less steric repulsion, since the C–P bond is much longer than the C–C bond.

Energetic comparison of the series **4**–**6** supports the steric argument. **5** and **6**, which have the methyl group attached to a ring carbon, are higher in energy than **4**, where the methyl group is connected to phosphorus. However, ZPE corrections reduce the energies of **5** and **6** relative to **4** such that **6** is actually lower in energy than **4**.

For the other methylphospholes, two trends can be discerned and rationalized. First, the 2*H*-phospholes are lower in energy than the 3*H*-phospholes. The only bond difference between these isomers is the position of the phosphorus atom in the diene fragment. Thus, the diene fragment of 2*H*-phosphole is analogous to 1-phospha-1,3-butadiene, while the diene fragment of 3*H*-phosphole corresponds to 2-phospha-1,3-butadiene. We have previously examined these dienes.[16] Using the *cis* conformations, which would most closely correspond to the diene geometry in the phospholes, we found that at HF/6-31G* 1-phospha-1,3-butadiene is 2.50 kcal mol^{-1} lower in energy than 2-phospha-1,3-butadiene. This is the result of the poorer ability of phosphorus (relative to carbon) to conjugate across the interior single bond, due to the longer P–C bond and inferior *p*-orbital overlap between C and P. The relative energies of the 2*H*- versus the 3*H*-phospholes simply reflects the energies of the component diene, and fundamentally the ability of phosphorus relative to carbon to participate in conjugation.

Second, **7** and **12** are very destabilized relative to their positional isomers. These two isomers have the methyl group attached to the saturated carbon which allows for a geminal methyl–hydrogen interaction not present in the other isomers, another example of the importance of steric interactions in these systems. An additional component is the somewhat stronger C_{sp^2}–C_{sp^3} bond over the C_{sp^3}–C_{sp^3} bond. We also note that some of the destabilization of **16** and **17** is attributable to this geminal interaction.

The fact that **8**–**10** are slightly more stable than **4** indicates the very similar energetics involved in these systems—the inherent stability of the 2*H* isomer over the 1*H* isomer pitted against the steric interactions that favor P over C substitution.

These calculations are in accord with the mechanistic proposal of Mathey concerning the Diels–Alder reactions of phospholes.[2-7] In this mechanism, the 1*H*-phosphole first rearranges to a 2*H*-phosphole which then acts as the diene component of the Diels–Alder reaction. The relatively small energy differences of the methylphospholes suggests that if the barriers for rearrangements are small enough, the 2*H* isomers will be present along with the more stable 1*H* isomers.

In conclusion, these calculations support our previous contention that for unsubstituted phospholes, the 2*H* isomer is the lowest energy form. However, substituents will preferentially select phosphorus over carbon to minimize steric interactions, due to the long C–P bond. These results further refute any significant aromatic character in 1*H*-phosphole. In addition, the proposed mechanism for the Diels–Alder reactions of the phospholes is supported by our calculations.

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Supplementary Material Available: Optimized geometries in the form of Z matrices for structures 4–17 at the HF/6-31G* level (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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