

# Ab Initio Calculations on the Diphosphine Radical Cation ( $P_2H_4^+$ )

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**Abstract:** Ab initio calculations on the title compound find it to have an optimal geometry in which the two phosphorus atoms are both pyramidalized and electronically nonequivalent. The energy required to planarize both phosphorus atoms is high, but twisting about the P-P bond has a much lower barrier than twisting about the N-N bond in the hydrazine radical cation. Electron delocalization in  $P_2H_4^+$  is predicted to require only a small activation energy, but the computational results suggest that electronically localized structures may be detectable in diphosphine radical cations and in the isoelectronic disilene radical anions.

Several years ago one of us offered a theoretical interpretation of the observation that tricoordinate atoms in the second row of the periodic table are more highly pyramidalized than their first row counterparts.<sup>1</sup> It was also pointed out that the tendency of tricoordinate atoms in the second row to pyramidalize should serve to weaken the  $\pi$  bonds in molecules such as disilenes<sup>2</sup> and silabenzene.<sup>3</sup> However, this effect would not act to destabilize molecules like diphosphenes<sup>4</sup> or phosphabenzene,<sup>5</sup> where the phosphorus is coordinated to only two other atoms, because in these molecules phosphorus pyramidalization is undefined. The apparently greater stability of such phosphorus compounds, compared to their silicon analogues can thus be explained.

Nevertheless, when phosphorus is covalently bonded to three atoms, the tendency of the tricoordinate element to pyramidalize should serve to weaken  $\pi$  bonds involving phosphorus. This provides one rationale for the high reactivity of metaphosphate,<sup>6</sup> compared to its first row analogue nitrate.<sup>1</sup>

In order to test the hypothesis that pyramidalization should serve to destabilize  $\pi$  bonds involving tricoordinate phosphorus, we have carried out ab initio calculations on the radical cation of diphosphine,  $P_2H_4^+$ . This molecule, like its nitrogen analogue, hydrazine radical cation, contains a three-electron  $\pi$  bond. In this paper we report our computational results, which predict substantial differences between diphosphine and hydrazine radical cations.

Tetraalkylhydrazine radical cations have been extensively studied by Nelsen and co-workers.<sup>7</sup> These radical cations prefer planar, olefin-like geometries, although pyramidalization at ni-

Table I. Relative Energies of  $P_2H_4^+$  Geometries

| geometry   | RHF energy <sup>a</sup> | SDQ-CI energy <sup>b</sup> |
|------------|-------------------------|----------------------------|
| $C_s$      | 0                       | 0                          |
| $D_{2h}^c$ | 36.7                    | 33.3                       |
| $C_1$      | 5.5                     | 8.8                        |
| $D_{2d}^d$ | 48.6                    | 50.8                       |
| $C_{2h}$   | 2.1                     | 0.6                        |

<sup>a</sup>Energy in kcal/mol relative to -683.4534 hartrees. <sup>b</sup>Energy in kcal/mol relative to -683.805 hartrees. <sup>c</sup>Only the symmetry plane bisecting the H-P-H angles was imposed on the wave function, but the wave function did emerge with the full  $D_{2h}$  symmetry of the molecule. <sup>d</sup>Only  $C_{2v}$  symmetry was imposed on the wave function, in order to allow for localization, which did in fact occur.

trogen is relatively facile. Twisting about the partial N-N bond has an appreciable barrier. A recent measurement of the isomerization rate in the radical cation derived from 8,8'-bis(azabicyclo[3.2.1]octane) gave a free energy barrier of about 22 kcal/mol.<sup>8</sup> Ab initio calculations predict a barrier of around 30 kcal/mol for the parent hydrazine radical cation.<sup>8</sup>

In contrast to  $N_2H_4^+$ ,  $P_2H_4^+$  is predicted by our calculations to prefer a nonplanar geometry and to have a low barrier to twisting about the P-P bond. The geometry was optimized with the 3-21G\* basis set<sup>9</sup> and an RHF wave function.<sup>10</sup> As shown in Figure 1, the optimal geometry corresponds to a localized electronic structure, with the phosphorus that bears the pair of nonbonding electrons being more highly pyramidalized than the phosphorus on which the radical cation resides. Although the geometry is nonplanar, its  $C_s$  symmetry places the orbitals containing these electrons in the same plane, thus giving evidence of some three-electron bonding.

A planar ( $D_{2h}$ ) geometry, which allows for maximal three-electron  $\pi$  bonding, was optimized too. As shown in Figure 1, its P-P bond length is nearly 0.1 Å shorter than that of the optimal  $C_s$  geometry. Nevertheless, the energy of the  $D_{2h}$  structure was higher by more than 30 kcal/mol. Obviously, the increased three-electron bonding in the  $D_{2h}$  structure is more than compensated for by the energy lowering on allowing phosphorus pyramidalization, as in the  $C_s$  structure.

For calculating energy differences between the optimized geometries, the Dunning-Hay double- $\zeta$  basis set was used, augmented by a set of d functions on phosphorus.<sup>11</sup> The relative energies are reported in Table I, both at the RHF level of theory and with the inclusion of correlation effects via configuration interaction (CI). The CI calculations included all single and

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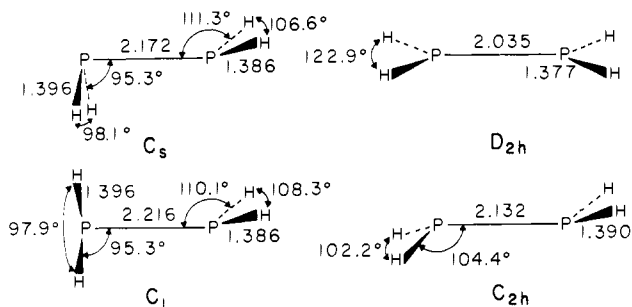


Figure 1. Optimized geometries for  $P_2H_4^{+\bullet}$ .

double excitations from the Hartree-Fock configuration (SD-CI). The SD-CI energy was estimated from perturbation theory, which was used to extrapolate the approximately 90% of the SD-CI correlation energy that was recovered variationally. The Davidson formula<sup>12</sup> was employed to provide an estimate of the effect of including quadruple excitations. From the estimated SDQ-CI energies that are reported in Table I, it is clear that correlation effects are not of great consequence in determining the relative energies.

Although the results in Table I indicate that maximizing three-electron bonding in  $P_2H_4^{+\bullet}$  is less important than allowing pyramidalization at phosphorus, evidence for a stabilizing role for three-electron bonding in  $P_2H_4^{+\bullet}$  comes from calculations carried out at a geometry with no ( $C_1$ ) symmetry imposed but in which the bisectors of the two H-P-H angles were required to lie in orthogonal planes. Overlap between the phosphorus p orbitals comprising the two nonbonding atomic orbitals was thus prohibited. The optimized geometry is shown in Figure 1. As revealed in Table I, an 8.8 kcal/mol barrier to rotation in  $P_2H_4^{+\bullet}$  is predicted by the SDQ-CI calculations. This is considerably smaller than the predicted barrier of 30 kcal/mol in  $N_2H_4^{+\bullet}$ .

How much of this reduction results from phosphorus pyramidalization and how much from an intrinsically weaker three-electron bond between phosphorus atoms was estimated by rigid rotation of the  $D_{2h}$  geometry to  $D_{2d}$  symmetry, where the H-P-H planes are orthogonal.<sup>13</sup> To allow for P-P bond lengthening on loss of  $\pi$  bonding, the P-P distance in the  $C_1$  "orthogonal" structure was employed. Since the  $D_{2d}$  structure was not optimized, the

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(13) Only  $C_{2v}$  symmetry was imposed on the wave function to allow for electronically nonequivalent phosphorus atoms.

SDQ energy difference of 17.5 kcal/mol between it and the  $D_{2h}$  structure is probably an upper limit. Nevertheless, it appears that the three-electron  $\pi$  bond in planar  $P_2H_4^{+\bullet}$  is approximately half as strong as the three-electron bond in  $N_2H_4^{+\bullet}$ . Pyramidalization in  $P_2H_4^{+\bullet}$  reduces the size of the rotational barrier by an additional 50%.

In addition to assessing the effect of pyramidalization and three-electron bonding at the optimal geometry of  $P_2H_4^{+\bullet}$ , we also investigated the role of electron localization. The  $C_1$  structure was reoptimized in  $C_{2h}$  symmetry, which requires that the two phosphorus atoms be identical. The optimized  $C_{2h}$  structure, which also appears in Figure 1, was found to be higher than the  $C_1$  structure but by only 0.6 kcal/mol at the SDQ-CI level of theory.

The present calculations are not of sufficiently high quality to predict with quantitative accuracy the barrier to delocalization. In fact, the energy difference between the localized and delocalized structures is sufficiently small at the SDQ-CI level that geometry reoptimization or basis set expansion could, conceivably, cause the barrier to vanish.<sup>14</sup> Nevertheless, the possibility of detecting nonequivalent phosphorus atoms in diphosphine radical cations, which is suggested by our results, is certainly deserving of experimental investigation.

Disilene radical anions are, of course, isoelectronic with diphosphine radical cations. It is of considerable interest, therefore, that when the disilene prepared by West and Michl<sup>15</sup> undergoes one-electron reduction, the EPR spectrum of the radical anion formed indicates that the odd electron is not delocalized equally over both silicon atoms.<sup>15,16</sup>

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**Registry No.**  $P_2H_4^{+\bullet}$ , 86676-97-3.

(14) UHF calculations, carried out by Professor Timothy Clark, find the delocalized  $C_{2h}$  structure to be an energy minimum, presumably lower in energy than localized  $C_1$  structures. The difference between his UHF results and our RHF and CI findings is a further indication that the localized and delocalized structures are close in energy.

(15) West, R., reported at the 19th Reaction Mechanisms Conference, Salt Lake City, Utah, 1982. We thank Professor West for permission to quote these results.

(16) Given the small energetic cost of twisting about the P-P bond that is calculated for  $P_2H_4^{+\bullet}$  it seems likely that the disilene radical anion prepared by West may be twisted about the Si-Si bond in order to decrease steric interactions between the four bulky mesityl substituents. Such twisting, which further reduces three-electron bonding, would be expected to favor a localized structure.

## The Diphosphine Radical Cation ( $P_2H_4^{+\bullet}$ )

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**Abstract:** UHF/6-31G\* calculations on the title radical cation suggest that, in contrast to the hydrazine radical cation, the phosphorus centers are strongly pyramidal and that the P-P bond is only 3% shorter than in the neutral molecule. The rotation barrier about the P-P bond is calculated (UMP2/6-31G\*) to be only 7.9 kcal mol<sup>-1</sup>. A strong interaction between the singly occupied molecular orbital and the P-P  $\sigma$  bond results in a 0.92-eV stabilization of  $PH_2H_2^{+\bullet}$  relative to  $PH_3^{+\bullet}$  and accounts for the long P-P bond.

The theory of bonds involving an odd number of electrons is not as highly developed as that for closed-shell systems. Investigations into the nature of three-electron  $\sigma$  bonds<sup>1-3</sup> and the

hydrazine radical cation<sup>4</sup> led to calculations on the diphosphine radical cation,  $P_2H_4^{+\bullet}$ . The results not only suggest that the

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