

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 formula¹² 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.¹³ To allow for P-P bond lengthening on loss of π bonding, the P-P distance in the C_1 "orthogonal" structure was employed. Since the D_{2d} structure was not optimized, the

(12) Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1977**, *52*, 403.

(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 π 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_s 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_s 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.¹⁴ 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 Michl¹⁵ 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.^{15,16}

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(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_s 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⁻¹. A strong interaction between the singly occupied molecular orbital and the P-P σ 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 σ bonds¹⁻³ and the

hydrazine radical cation⁴ led to calculations on the diphosphine radical cation, $P_2H_4^{\bullet+}$. The results not only suggest that the

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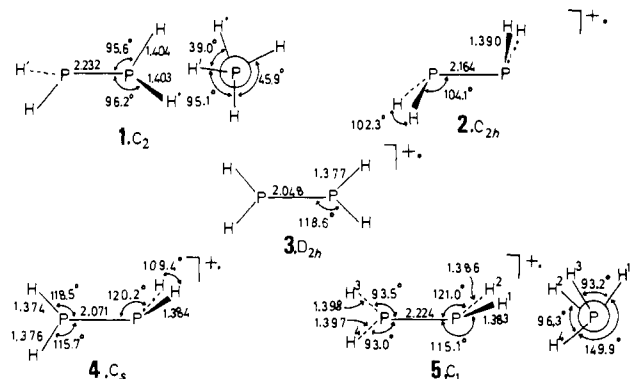
Table I. HF/6-31G* and MP2/6-31G* Total (au) and Relative (kcal mol⁻¹, in Parentheses) Energies for P₂H₄ (1) and P₂H₄⁺ (2-5) (All at the 6-31G* Optimized Geometries)

		RHF/6-31G*	RMP2/6-31G*
P ₂ H ₄	(1)	-683.75029	-683.95341
		UHF/6-31G*	UMP2/6-31G*
P ₂ H ₄ ⁺	(2)	-683.46211 (0.0)	-683.64899 (0.0)
	(3)	-683.40327 (36.9)	-683.59804 (32.0)
	(4)	-683.39682 (41.0)	-683.58329 (41.2)
	(5)	-683.45455 (4.7)	-683.63636 (7.9)

diphosphine radical cation behaves differently than its nitrogen counterpart but also emphasize the problems still to be solved for open-shell calculations. The unrestricted Hartree-Fock calculations reported here give slightly different predictions to the spin-restricted calculations reported in the previous paper.⁵

The hydrazine radical cation is calculated to be planar, or very nearly so, depending on the theoretical level used, with a rotation barrier of 31 kcal mol⁻¹.⁴ The N-N bond in the radical cation (1.292 Å) is calculated to be significantly shorter than that in hydrazine itself (1.413 Å, both values at 6-31G*). NH₂NH₂⁺ therefore behaves as a typical two-center π bond with about half the π bond energy of ethylene.

Optimization⁶ of diphosphine (1) and its radical cation 2 shows completely different behavior, however. The radical cation 2 is found to have C_{2h} symmetry with strongly nonplanar phosphorus centers and a P-P bond which is only slightly shorter (2.164 Å) than that in the neutral diphosphine (2.232 Å). The total of the three bond angles to phosphorus in 2 is 310.5°, about half-way between that for PH₃ (289.2°) and PH₃⁺ (338.3°) at 6-31G*. Constraining P₂H₄⁺ to D_{2h} symmetry results in structure 3, which is found to be 32.0 kcal mol⁻¹ less stable than 2 at MP2/6-31G*. The C_s conformer 4, in which one phosphorus center is held planar and the two phosphorus nonbonding orbitals held perpendicular to each other, is found to be 41.2 kcal mol⁻¹ less stable than 2. Both 3 and 4 have shorter P-P bonds than 2. The transition state for rotation about the P-P bond (5) has a slightly longer (2.224 Å) central bond than 2 but lies only 7.9 kcal mol⁻¹ higher in energy. The UHF/6-31G* and MP2/6-31G* total energies for 1-5 are shown in Table I.

**Figure 1.** ROHF/STO-3G molecular orbital plots showing the interaction of the phosphorus lone pairs with the σ_{pp} and σ_{pp}^* orbitals.

by any three-electron π stabilization. In this context it is important to note that not only the large barrier to planarization of the phosphorus centers but also the long P-P bond render a classical π bond uncompetitive.

P₂H₄⁺ is nevertheless strongly stabilized relative to PH₃⁺, however. The adiabatic ionization potential of diphosphine (8.28 eV, MP2/6-31G*) is calculated to be 0.92 eV lower than that of PH₃ at the same level.

The mechanism of this stabilization should be general for radical cations with long, relatively weak, central bonds and presents an effective alternative to the classical π bonds observed for the elements of the first row of the periodic table. As observed previously¹ for the H₂SSH₂⁺ radical cation, there is strong mixing between the high-lying unsymmetrical lone-pair combination (n^-) and the phosphorus-phosphorus σ bonding orbital (σ_{pp}). In contrast to the situation for H₂SSH₂⁺, however, this interaction is strongly stabilizing in H₂PPH₂⁺ because the n^- orbital is only singly occupied. This through-bond effect results in a net flow of electrons from the σ_{pp} to the n^- orbital, and therefore it results in a longer P-P bond than would normally be expected. The pronounced skewing of the phosphorus contribution to the σ_{pp} orbital away from the P-P vector (see Figure 1) is also a result of this phenomenon, which leads to a non-Koopman's stabilization of P₂H₄⁺ because of the extreme charge dependence of three-electron interactions.^{2,3} This σ stabilization is about half as effective as the π stabilization of N₂H₄⁺, hydrazine having an adiabatic ionization potential 2.12 eV lower than that of NH₃ at MP2/6-31G*. This type of stabilization is, however, largely independent of the torsional angle, so that P₂H₄⁺ has a strikingly low rotational barrier (7.9 kcal mol⁻¹) compared with N₂H₄⁺ (31 kcal mol⁻¹).

Borden et al.⁵ have pointed out that the energy required to make the two phosphorus centers planar is too large to be compensated

(5) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) All calculations used the GAUSSIAN 82 series of programs (Binkley, J. S.; Frisch, M.; Raghavachari, K.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release A, Carnegie-Mellon University, 1983, modified for CDC computers by Dr. A. Sawaryn). P₂H₄ was optimized by using the RHF and the P₂H₄⁺ conformers by using the UHF formalisms within the symmetry constraints given. All calculations used the 6-31G* basis set (Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* 1973, 28, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* 1982, 77, 3654). MP2 calculations (Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* 1976, 10, 1) did not include the phosphorus core orbitals, and used the 6-31G* optimized geometries. The transition state 5 was located by using the standard "BERNY" procedure in GAUSSIAN 82 (Schlegel, H. B. *J. Chem. Phys.* 1982, 77, 3676).

(7) Compare, for instance, UHF results on CH₂OCH₂⁺ (Clark T. J. *Chem. Soc., Chem. Commun.* 1984, 666; Bouma, W. J.; Poppinger, D.; Saebo, S.; Macleod, J. K.; Radom, L. *Chem. Phys. Lett.* 1984, 104, 198) with ROHF calculations on the same system (Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1984, 106, 2513).

Borden et al.⁵ are due to the two different formalisms used to treat open-shell systems.

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Theoretical Electron Deformation Density Studies on Chromium Benzene Tricarbonyl

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Abstract: Theoretical calculations on the electron density distribution of chromium benzene tricarbonyl are reported. A new method of including thermal smearing into static deformation density maps is used to produce theoretical dynamic deformation density maps of chromium benzene tricarbonyl which are directly compared to experimental maps. This comparison shows that a number of problems remain in the experimental electron deformation density of this complex. The changes in the electron distribution around the chromium are inconsistent with the theoretical deformation density maps and seem to be too large to be explained as an effect that would result from thermal smearing. Also the pattern of electron gain and loss around the chromium in one experimental study is difficult to explain in simple chemical terms and suggests that perhaps these peaks may be representative of the "ghost peaks" found by other researchers. This study shows that accurate calculations can aid in the interpretation of experimental deformation densities.

Recently, there has been increasing interest in studying electron density distributions, both experimentally and theoretically. Improved experimental design and low-temperature crystal structures have together increased the accuracy of electron densities determined by X-ray diffraction methods. Electron density distributions determined theoretically have also improved due to faster computers. As a result, the number of studies comparing theoretical and experimental electron density distributions has increased significantly.¹⁻¹¹ The quality of both experiment and theory now provides the opportunity to quantitatively compare the two as a way of checking the reliability of both approaches.

In order to compare directly experimental and theoretical electron density distributions, one must take into account the effect of thermal smearing of the experimental density. A growing number of papers have examined this problem and have proposed ways to incorporate thermal smearing into their theoretical maps.¹²⁻¹⁴ Up to now most of the molecules chosen for comparison have consisted of only light atoms. In this paper we report the first study that compares theoretical static and dynamic deformation densities with experimental electron density distributions for a transition-metal complex. We also report a new and simple

technique for incorporating thermal smearing into the theoretical charge distribution that compares favorably with previously reported techniques. We have verified our thermal smearing technique by comparing our result for the formate ion with calculations reported by Fuess and co-workers.¹⁵ The transition-metal complex we have studied theoretically is chromium benzene tricarbonyl, $Cr(C_6H_6)(CO)_3$. Experimental deformation densities on this compound were first reported in a pioneering study by Rees and Coppens¹⁶ in 1973. This study was the first low-temperature X-ray crystal determination of a transition-metal complex, and in this study deformation densities of the benzene and carbonyl planes were reported. We will be comparing our theoretical results with this experimental study as well as with more recent work done at the Molecular Structure Corp. by Troup and Extine.¹⁷

Although a theoretical electron density distribution study including thermal smearing on a transition-metal complex has not yet been reported, numerous experimental studies of electron density distributions in transition-metal complexes have been reported.¹⁸⁻²⁵ These studies illustrate several problems in experimentally determined electron density distributions. First, the presence of chemically unreasonable electron density features around metal atoms and metal-ligand bonding regions have been

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