is plotted with respect to the same quantity as above in Figure 3. In accord with eq 4, the plot is approximately linear with a negative intercept.

In conclusion, all the features of the phosphorescence and the delayed fluorescence are satisfactorily interpreted in terms of a mechanism in which the annihilation of two triplet states yields the singlet excited state. Delayed fluorescence due to this mechanism has been observed quite extensively for organic molecules,[9] and a few examples exist for metalloporphyrins.[10] However, with regard to pure inorganic complexes, this is the first observation of delayed fluorescence. Another point to be emphasized is that the triplet–triplet annihilation investigated here is significantly more efficient than that found for organic molecules. In the majority of cases studied for organic compounds,

the decay of the delayed fluorescence is nearly exponential and the lifetime is half of that of the phosphorescence. Such behavior is expected only in the low limit of the triplet–triplet annihilation. In the present case we are able to analyze the nonexponential behavior because the annihilation is so efficient. An evaluation of the annihilation rate as well as an analysis focusing attention on the triplet sublevels is in progress and will be discussed elsewhere.

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# Articles

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## π-Bond Strengths in HP=PH, H₂P=P, HP=NH, and HN=NH

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The chemistry of the HP=PH π bond found in the recently isolated diphosphene compounds is considered in several ways. The P=P π-bond strength is found by computing the rotation barrier (36 kcal/mol) and is compared to that found for HN=NH (63.5 kcal/mol) and HP=NH (47 kcal/mol). The structure of the HPPH anion is presented. Various electronic states of the H₂PP isomer are considered and compared to those of HPPH. Dipole moments and PP stretching frequencies are reported. The concerted hydrogenation of diphosphene is also examined.

### Introduction

A major research topic in main-group inorganic chemistry in recent years has been the investigation of multiple bonding by elements in the third and higher rows of the periodic table. Because of the relative weakness of such multiple bonds most of the early work focused on multiple bonds involving only one such element. Such bonds are now commonplace. For example, the multiple bonding of silicon to such second row elements as carbon and oxygen has recently been reviewed.[1]

Molecules containing multiple bonds between two heavy atoms are much less common. Cowley[2,3] has recently reviewed the field of double bonding between two atoms of Si, Ge, Sn, P, or As, as well as a very few mixed double bonds between these elements.

The present work seeks to add to the body of knowledge concerning the –P=P– linkage, found in the class of compounds named diphosphenes. One such compound, phosphobenzene, was proposed over 100 years ago,[4] but was subsequently shown by X-ray diffraction to exist in polymeric form.[5] Therefore the first report of an actual P=P bond was the detection[6,7] in the mid-1960s by mass spectrometry of the parent diphosphene, HPPH, as an intermediate gas-phase species. The first isolable diphosphene was reported in 1981[8] and owed its existence to the bulkiness of its substituents. The numerous diphosphenes reported since then

all share the same bulkiness in their ligands, which are commonly large aryl, amino, or alkyl groups. Cowley[2] has reviewed the very rich chemistry of the P=P bond. It is reactive toward electrophiles, leading to either addition or cleavage products. It is subject to radical attack. Recently[9] the P=P bond has also been shown to be reactive towards nucleophiles. Diphosphenes form thiiranes (containing PSP three-membered rings) and hypervalent oxides (–(P=O)=P–) or sulfides. They also can form coordination complexes with transition metals.

The chemistry of this bond is of course dominated by the presence of its low-lying π* orbital. Evidence for this orbital's accessibility is the red color of the diphosphenes. More quantitatively, the n → π* and π → π* excitation energies[2] are about 2.6–2.9 and 3.5–3.8 eV, respectively. An additional piece of evidence is the ease of electron attachment[10] to the P=P moiety. Finally, theoretical calculations[11] show the low energy of the π* LUMO.

Early theoretical interest[11,12] in HP=PH focused on the cis–trans energy difference and determination of the PP bond length. Both studies reach the same conclusions: the cis form is less stable by 3–4 kcal/mol, and without d orbitals the PP bond distance is overestimated by 0.13 Å. The interaction of N lone pairs with the P=P bond in N—P=P—N compounds has recently been studied.[13] NMR coupling constants for HN=NH, HP=PH,

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HP=NH, and HAs=AsH have been computed.[14] The rotation barrier in HP=PH as well as the H₂PP isomer has been considered.[15]

In spite of all this experimental and theoretical work, some fundamental questions remain about the P=P bond: What is the strength of the π bond? How does this compare to analogous nitrogen compounds? What is the mechanism of cis–trans interconversion? Does the observed mass fragment[6,7] corresponding to P₂H₂ really contain a double bond HP=PH, or is it possibly H₂PP? What are the energetics for the hydrogenation of diphosphene? These and other questions are the subject of the present paper.

Ha et al.[15] have considered some of these questions. However, these authors used a closed-shell SCF wave function to investigate the rotated singlet biradical HP-PH. Even after the subsequent inclusion of configuration interaction, their rotation barrier (60 kcal/mol) is as large as that of HN=NH. These workers also assume that the saddle point for rotation occurs at a dihedral angle of 90° and that the inversion barrier occurs through a linear PPH group. The rigorous saddle point searches described below show these two assumptions were quite reasonable. Finally, many of their structures were obtained from calculations without d orbitals, although these had previously been demonstrated to have a significant impact on the computed PP distances.[11,12]

The stage can be set for the results to be presented below by reviewing what is already known for similar nitrogen-containing species. Diazene, HN=NH, has attracted a great deal of interest, as evidenced by the numerous references given by Parsons and Dykstra.[16] The cis form is about 6–8 kcal/mol above the trans isomer.[16] Winter and Pitzer[17] demonstrated that the inversion barrier of *trans*-diazene is 47 kcal/mol, less than the 60 kcal/mol barrier they find to rotation.

Diazenes have less conventional isodiazene isomers, which have been observed experimentally.[18] The parent isodiazene H₂NN has recently been trapped in a low-temperature matrix.[19] Theoretical calculations predict H₂NN to have a planar singlet ground state about 24–29 kcal/mol above that of *trans*-diazene,[16,20,21] with a bent triplet state about 15 kcal/mol above that.[22] Calculated bond lengths and the planarity of the molecule indicate substantial double-bond character for isodiazene. The activation energy for the 1,2-hydrogen shift converting diazene to isodiazene is calculated to be 80–83 kcal/mol.[16,21] Finally, bimolecular mechanisms have been predicted for both the cis–trans isomerization[20] and the 1,2-hydrogen shift[23] with substantially lower barriers than for the unimolecular processes cited above.

Rather less is known about the mixed compound phosphinimine, HP=NH. A substituted molecule containing the -P=N- group was first reported in 1973.[24] The P=N bond length has been measured,[25] and the chemistry of this bond has been reviewed.[26] Recently, HP=NH has been shown to be capable of serving as a 2-, 4-, or 6-electron donor in transition-metal complexes.[27] The name phosphinimine is also used for a much larger class of compounds, R₃P=NR, containing pentavalent phosphorus. The second PN bond in these compounds is formed with d orbitals on phosphorus, and consequently is a fundamentally different bond.

The rotational barrier in these hypervalent phosphinimines is believed to be less than 8 kcal/mol.[28] Long-chain hypervalent phosphinimines are promising polymers.[29]

The parent HP=NH has been the subject to a modest amount of theoretical interest.[14,30–32] Two studies[30,31] show the trans form of HP=NH is less than 1 kcal/mol below the cis form. The pi bond strength is estimated to be about 40–48 kcal/mol.[30,31] These estimates are based on SCF + CI calculations and so are probably less reliable than the MCSCF results for the HN=NH value cited above.

Trinquier[30] has also considered the possible isomers of HP=NH, which are aminophosphinidene, H₂N=P, and phosphinonitrene, H₂P=N. The latter compound may well possess some triple bond character[30] and accordingly is perhaps better named phosphonitrile. This molecule (with the hydrogens substituted) has recently been generated, and trapped as its cyclic dimer.[33] However, singlet phosphonitrile, in spite of its possible triple PN bond character, is very much less stable than the trans form of phosphinimine, by 41 kcal/mol. In contrast, aminophosphinidene has a singlet state only 7 kcal/mol less stable than that of *trans*-HPNH, and its ground triplet state is nearly degenerate with that of the trans form.[30] The fact that its ground state is a triplet, in contrast to the singlet nature of the all-nitrogen analogue may explain why an aminophosphinidene has never been reported.

## Computational Method

Structures and transition states were computed at the Hartree–Fock (HF) SCF level, using unrestricted wave functions for triplets. In many instances these molecular geometries were also computed at the multiconfigurational SCF (MSCSF) level. MCSCF wave functions are necessary whenever bonds are broken, as in the rotations considered here, and they also facilitate comparison of singlet and triplet energies. The MSCSF wave function used is based on the full optimized reaction space method of Ruedenberg.[34] In this instance the four active orbitals are the $\sigma$, $\pi$, $\pi^*$, and $\sigma^*$ orbitals of diphosphene. The two π orbitals are essential to correctly describe the scission of the π bond upon rotation. The two σ orbitals are included as the PH bond length changes somewhat in the various molecules considered. Four electrons are distributed in these four orbitals in all possible ways, while the lone pairs and PH bonds are held doubly occupied. This same type of wave function is also applied to the various H₂PP isomers. The MCSCF wave functions contain 20 or fewer electron configurations, depending on the symmetry present.

Structures and transition states for all species were found by using the 3-21G atomic basis,[35] supplemented by d polarization orbitals on both phosphorus and nitrogen. *This basis will be referred to throughout this paper as 3-21G\**, even though the usual meaning[35c] of this name implies d orbitals only on P and not on N. Previous studies[11,12] have indicated these d functions are essential for computing accurate P=P distances. Nitrogen bond angles are known to be affected by d orbitals: NH₃ is planar for split-valence sp bases and becomes pyramidal only when a d orbital is used.[35,36] Once these geometries were found, single-point calculations at these geometries with the larger 6-31G* basis[37] were made

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**Table I.** HPPH and H$_2$PP Energies[a]

| molecule | figure | HF/3-21G*[b] | MCSCF/3-21G* | MCSCF/6-31G*[c] | SOCI/6-31G*[c] | HF/6-31G**[d] | MP4/6-31G**[d,e] |
|---|---|---|---|---|---|---|---|
| trans | 1A | −679.1914 | −679.3566 | −682.6170 | −682.7184 | −682.5737 | −682.8283 |
| cis | 1B | −679.1858 | −679.3514 | −682.6119 | −682.7125 | −682.5682 | −682.8224 |
| rotated tripl | 1C | −679.1772 | −679.3014 | −682.5635 | −682.6649 | −682.5633 | −682.7826 |
| planar | 1D | −679.1539 | −679.3088 | −682.5679 | −682.6703 | −682.5351 | −682.7847 |
| bent tripl | 1E | −679.1920 | −679.3189 | −682.5806 | −682.6747 | −682.5768 | −682.7957 |
| bent singl | 1F | −679.1726 | −679.2767 | −682.5382 | −682.6363 | −682.5573 | −682.7765 |
| rotated singl | 2A | | −679.3002 | −682.5625 | −682.6610 | | |
| inv | 2B | −679.0812 | −679.2471 | −682.5009 | −682.6040 | −682.4641 | −682.7221 |
| singl isom | 2C | −679.1006 | | | | −682.4887 | −682.7422 |
| tripl isom | 2D | −679.1265 | | | | −682.5156 | −682.7479 |
| diphosphine | | −680.3700 | | | | −683.7604 | −684.0322 |
| 1,1 elim | 4A | −680.2569 | | | | −683.6506 | −683.9262 |
| 1,2 elim | 4B | −680.2062 | | | | −683.6066 | −683.8933 |
| hydrogen | | −1.1230 | | | | −1.1313 | −1.1646 |

[a] Total energies in hartrees. 1 hartree = 627.5 kcal/mol. [b] For this column only, the 3s contaminant in the d orbitals was excluded. [c] Calculated at the MCSCF/3-21G* geometry. [d] Calculated at the HF/3-21G* geometry. [e] MP4(SDQ) calculation, neglecting triples contribution.
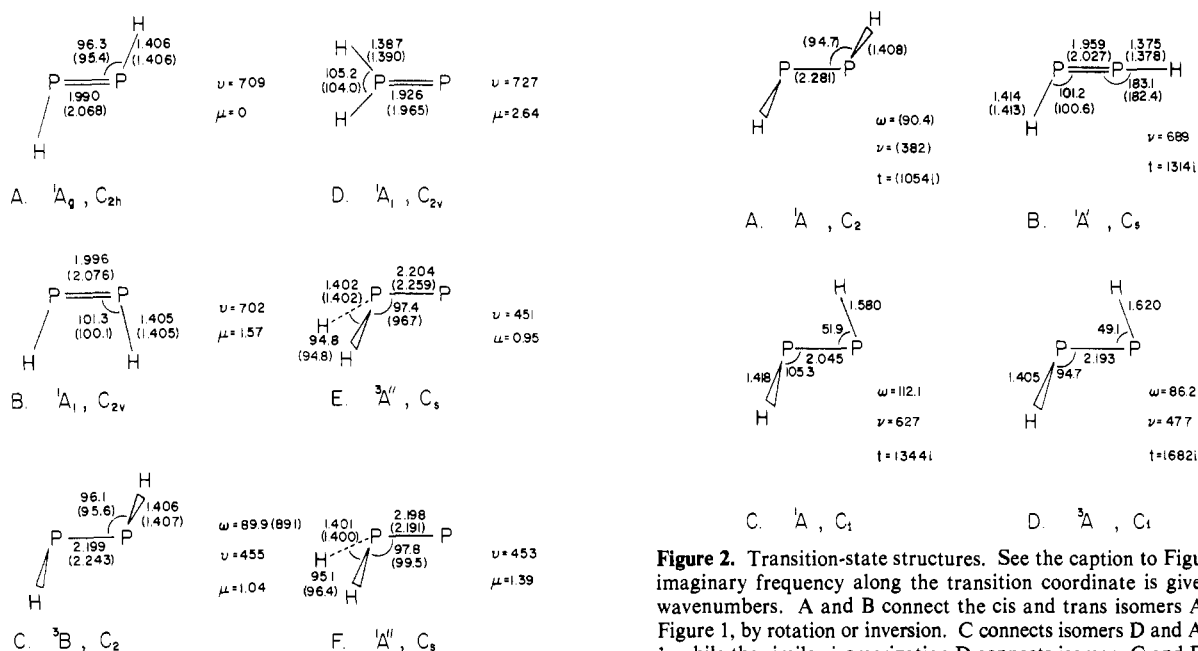


**Figure 1.** HF/3-21G* structures, with MCSCF/3-21G* structures given in parentheses. All bond distances are in angstroms, and angles are in degrees. ω is the HPPH torsion angle. ν gives the HF/3-21G* PP stretching frequencies, in wavenumbers. μ gives the SOCI/6-31G* dipole moments, in debye.

to obtain more accurate energies. This basis contains better s and p functions and the same d orbitals. In some instances the 6-31G** basis,[37] which adds p orbitals to the hydrogens, was used. The same polarization exponents were used for all three bases, namely 0.80 for N,[38] 0.55 for P,[37a] and 1.1 for H.[37b]

Electron correlation effects not included in the HF or simple MSCSF wave functions are taken into account by two different methods. In those cases where HF level wave functions are a reasonable approximation, the simplest method of including electron correlation for all valence electrons is by means of many-body perturbation theory.[39] Such calculations were carried to fourth order in the Moller−Plesset formalism, neglecting triple excitations, and are designated MP4(SDQ).[40] The MCSCF calculations were extended by means of second-order CI calculations. These SOCI calculations contain all single and double excitations from any of the MCSCF configurations, except that the two lowest energy valence orbitals as well as the core orbitals were restricted to double occupancy.[41]



**Figure 2.** Transition-state structures. See the caption to Figure 1. The imaginary frequency along the transition coordinate is given by *t*, in wavenumbers. A and B connect the cis and trans isomers A and B of Figure 1, by rotation or inversion. C connects isomers D and A of Figure 1, while the similar isomerization D connects isomers C and E of Figure 1.

Physically, this approximation is based on the expectation that PH and NH bonds will be less affected by rotation than will be the lone pairs at P or N. The SOCI calculations include 30 000−80 000 configurations. The computational ansatz and the basis set used are conveniently specified together, e.g. SOCI/6-31G*.

Vibrational frequencies have been computed for all species considered at the HF/3-21G* level. These calculations serve two purposes. First, the heavy-atom stretching frequency is an indication of the strength of the heavy-atom bond. Second, valid equilibrium geometries and saddle points must possess 0 and 1 imaginary frequencies, respectively. This guards against the assumption of too high molecular symmetry. For example, H$_2$Si=SiH$_2$ is known to be nonplanar,[42,43] and the same might perhaps be expected for the isoelectronic HP=PH. In fact, vibrational analysis of the structures suffices to prove HP=PH is indeed a planar molecule. All other structures represented below as equilibrium geometries or transition states have been proven to indeed be so by vibrational analysis.

Two programs were used to carry out the calculations. GAMESS[44] was used to do the MCSCF geometry optimizations and the SOCI energy evaluations. GAUSSIAN82[45] was used for the HF level geometry optimi-

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(41) In all cases, the two valence orbitals held doubly occupied had orbital energies less than −0.7 hartree, while the two orbitals opened to partial occupancy had energies of −0.3 to −0.6 hartree. For H$_2$PP, the two orbitals held closed correspond to the symmetric combination of the PH bonds and a σ lone pair at the terminal P atom.
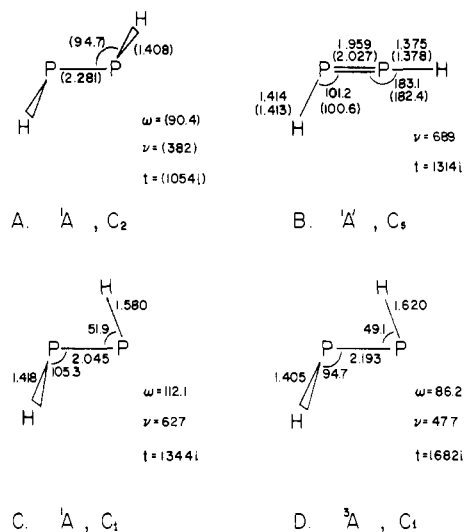
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zations and frequency calculations, using analytically computed energy second derivatives. This program was also used for the MP4(SDQ) calculations.

## Results and Discussion

**P₂H₂ Structures.** HF and MCSCF level equilibrium geometries for H₂P₂ species are shown in Figure 1. Transition states separating some of these species are shown in Figure 2. The greatest difference between the HF and MCSCF structures is a small increase in the PP bond lengths for the latter, since the MCSCF wave function imparts some antibonding character to this bond. The energies of these molecules are gathered in Table I. The figures also include the point group symmetry, electronic states, dipole moments, and PP stretching frequencies.

The PP bond lengths determined by X–ray diffraction[8,46] for substituted *trans*-diphosphenes are 2.00–2.03 Å. The HF and MCSCF bond lengths for *trans*-HPPH are 1.99 and 2.07 Å, respectively. These computed bond lengths narrowly bracket the experimental lengths, as is typical for these two computational methods. Thus we find, as have other workers,[11,12] that PP bond lengths in good agreement with experiment can be obtained provided the basis set contains d orbitals. The double bond is responsible for a significant 0.2 Å shortening compared to the 90° rotated structures shown in Figures 1C and 2A, which contain only a PP single bond.

The computed PP vibrational frequencies for the doubly bonded species are about 710 cm⁻¹. As usual for HF level frequencies, the calculated value is somewhat larger than the experimental Raman stretching frequencies reported[12,47] for substituted diphosphenes, about 610 cm⁻¹. The computed frequencies are useful in that they clearly distinguish the doubly bonded species from the singly bonded molecules, whose computed PP stretches are about 450 cm⁻¹. Note that the vibrational analyses summarized in Figures 1 and 2 show that the rotated singlet and triplet diphosphene are rotational maxima and minima, respectively. However the singlet structure shown in Figure 2A and triplet structure shown in Figure 1C have very similar geometries, as they have exactly the same spatial orbital occupancy. In particular, both the rotational saddle point and the triplet state have very nearly, but not exactly, orthogonal geometries. At the inversion barrier shown in Figure 2B for conversion of *trans*- to *cis*-diphosphene, the PP bond distance and frequency shows this bond retains its double-bond character.

Our MCSCF calculations give the expected elongation from 2.068 Å of the P=P bond to 2.281 Å upon rotation through a singly bonded biradical. Ha et al.[15] find a longer RHF/3-21G bond length of 2.102 Å for *trans*-HP=PH (because of the omission of d orbitals). These workers obtain only a small elongation of the PP bond to 2.191 Å upon rotation (because a RHF wavefunction has only the bonding and not the antibonding portion of a correct biradical wave function).

Because the P=P bond so readily accepts an electron,[10] we have found the structure of its trans anion. To accommodate the negative charge, the 3-21G* basis was supplemented with a diffuse sp shell on P and diffuse s orbitals on H (exponents 0.0348 and 0.0360, respectively). This 3-21++G* basis[48] gives PP and PH bond lengths of 2.125 and 1.417 Å, and an HPP angle of 95.80°. Vibrational analysis proves the anion is planar and has a PP stretching frequency of 553 cm⁻¹. The PP bond length and frequency are entirely consistent with a formal bond order of 1.5 for the anion.

The remaining species in Figures 1 and 2 relate to the phosphinophosphinidene isomer H₂PP. Consider first the planar form, shown in Figure 1D. After the four orbitals of the σ skeleton (2 PH and 1 PP bonds, and a mostly s lone pair at the terminal P)
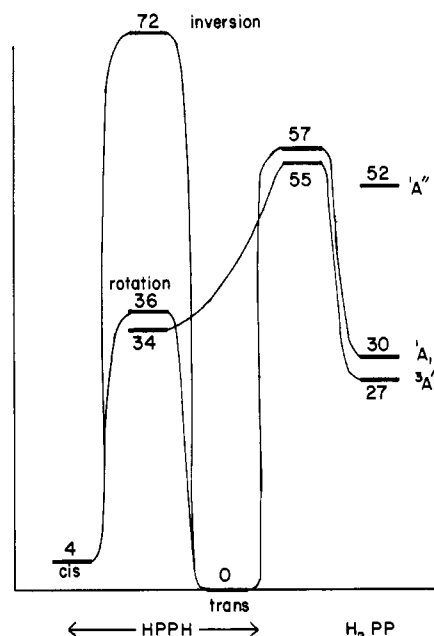


**Figure 3.** Relative energies of HPPH and H₂PP species, in kcal/mol. The isomer labels refer to the first two figures.

are filled in, there are four electrons left. If the molecular plane is defined as *xz*, two of these electrons occupy a p_y orbital at the central P, and the other two occupy a p_x orbital at the terminal P atom. This permits substantial donation of the central atom's pair to a vacant p_y orbital on the terminal atom. The p_x lone pair on the terminal atom can also delocalize, into the vacant d_{xz} orbital of the central atom. If both the in-plane and out-of-plane delocalizations occur to a significant extent, the PP bond order in the structure shown in Figure 1D could be as high as 3.

In fact, both these multiple-bonding interactions in H₂PP do occur, at least to some extent. The PP bond length is even shorter and the stretching frequency greater than in the conventional isomers HPPH. Electronic evidence for these additional bonding interactions comes from Mulliken population analysis[49] of the HF/6-31G** wave functions. For the valence π orbital, the nominal lone pair on the central atom gives up 0.55 e to the "vacant" p orbital of the terminal P atom. It is this strong π interaction that forces this molecule to be planar. The in-plane backdonation can be assessed by looking at the central P atom's d orbital population. The total d orbital population of 0.19 is due almost entirely to the 0.12-e population in the d_{xz} orbital, the orbital that acts as the acceptor for the in-plane delocalization. (The residual d population on the central atom is similar to the 0.08 total d population of the terminal P atom.) Although this in-plane multiple bonding is present, it is much weaker than the out-of-plane interaction. The bond length, frequency, and electronic distributions show that the two types of π interaction, together with the σ bond, give a net bond order slightly more than 2, but not nearly as much as 3. For this reason, the structure shown in Figure 1D is shown as possessing a double bond.

If one of the electrons in the in-plane lone pair at the terminal P atom is instead placed in the vacant, low-energy, out-of-plane orbital of that atom, the strong π interaction with the central atom is lost. As a result the structures shown in Figure 1, parts E and F, are bent molecules. They also have PP distances and vibrational frequencies characteristic of single bonds. However, even though the multiple binding is lost, there is now one less electron intrapair repulsion present. Because of this, bent triplet phosphinophosphinidene is the calculated ground state of H₂PP, by a narrow margin.

**P₂H₂ Energetics.** The various energy results given in Table I are shown as relative energies in Figure 3. This figure was distilled from Table I by taking the most reliable energy computed for each

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particular molecule. In most cases these are the SOCI energy differences, but for the $H_2PP$ isomerization barrier to HPPH they are MP4(SDQ). Both types of calculations incorporate extensive treatments of electron correlation, within ample bases. In general, then, there is little difference between these two calculations. The SOCI relative energies for triplets are usually 3–7 kcal/mol above the MP4(SDQ) results, since the latter are based on spin-unrestricted HF orbitals. This problem is even more acute for the open-shell singlet structure shown in Figure 1F, whose unrestricted HF wave function is heavily contaminated by the triplet structure shown in Figure 1E. We have taken the SOCI results for the open-shell species as being more reliable.

Figure 3 shows the cis isomer to be less stable than the trans isomer, by about 4 kcal/mol, in agreement with other workers[11,12] who have considered these isomers. There are two unimolecular mechanisms, rotation and inversion, that interconvert the cis and trans isomers. The rotational barrier is 36 kcal/mol, half the inversion barrier of 72 kcal/mol. As mentioned by the Introduction, cis–trans isomerization in diazene occurs by inversion, rather than rotation. Diphosphene is different for two reasons: the $\pi$ bond is weaker, making rotation easier, and phosphorus inversion barriers are usually substantially larger than those for nitrogen.[50] Triplet HPPH is slightly more stable than the rotated singlet, in accord with Hund's rules.

The ground state of phosphinophosphinidene is calculated to be a triplet. This state is about 27 kcal/mol above the trans form, and only about 2.7 kcal/mol below the doubly bonded closed-shell singlet state. Our result for $H_2PP$ is consistent with the finding[30] that $H_2NP$ also has a triplet ground state. However, the triplet and planar singlet are predicted to be so close that the ground state cannot be stated unambiguously to be the triplet. Substitution would probably also affect the order of these two states. Note that the near degeneracy of singlet and triplet $H_2PP$ differs from the results of Ha et al.[15] These workers incorrectly assume the triplet to have a planar geometry. Hence they find the triplet to lie at 47 kcal/mol relative to the trans form, in contrast to our result of 27 kcal/mol.

The barriers to unimolecular isomerization from $H_2PP$ to singlet and triplet HPPH are about 25–30 kcal/mol for both states. It is quite likely that a bimolecular process, such as is known for $H_2NN$,[23] would have a lower barrier than do these 1,2-hydrogen migrations.

**$P_2H_2$ Hydrogenation.** Hydrogenation of either isomer, HP=PH or singlet $H_2P$=P leads to diphosphine, $P_2H_4$. The inverse reactions are therefore either 1,1- or 1,2-elimination reactions. The gauche equilibrium structure of diphosphine is used.[35c] The transition states for both elimination reactions are shown in Figure 4. The energies for these species are included in Table I.

First, consider the endothermicities of the two elimination reactions. The zero of energy is taken to be $P_2H_4$. At the MP4(SDQ)/6-31G** level, hydrogen plus HP=PH is at 24.6 kcal/mol, while hydrogen plus singlet $H_2P$=P is at 52.0 kcal/mol. (Elimination to the triplet state of $H_2PP$ is of course spin forbidden, but would require about the same energy.) The mass spectrometry experiment that detected a mass fragment of empirical formula $P_2H_2$ also gave an experimental value[7] of 21 ± 8 kcal/mol for the endothermicity of this hydrogen elimination. Therefore, this experiment undoubtedly saw one of the conventional isomers HP=PH, as indeed was assumed to be the case.

Next, consider the barriers to the hydrogen eliminations. Even though the 1,2-elimination is much less endothermic, it has a higher barrier (87.1) than does the 1,1-elimination (66.5 kcal/mol). This means the reverse reaction, hydrogenation of trans-HP=PH, has a large barrier, 62.5 kcal/mol. At the transition state, both hydrogens are attacking the same phosphorus atom. The "bridging" hydrogen in Figure 4B is 1.586 Å away from the left phosphorus atom, and much farther (2.13 Å) from the right P atom. However the transition vector at the saddle point reveals this hydrogen is moving rapidly toward the right P atom, where it will ultimately be attached.
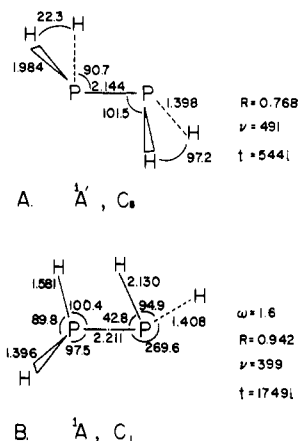


**Figure 4.** HF/3-21G* transition states for the 1,1- (A) and 1,2-elimination (B) of molecular hydrogen from diphosphine. $R$ is the HH distance, which is 0.735 Å in $H_2$. The remaining symbols have the same meaning as in Figures 1 and 2.

The saddle point for hydrogenation of diphosphene, including the reaction's one-sided initial attack, is very similar to that recently found[51] for the hydrogenation of the isoelectronic $H_2Si$=SiH$_2$. The disilene hydrogenation reaction was found to have an exothermicity of 52 kcal/mol and a barrier of 30 kcal/mol). The smaller exothermicity (25 kcal/mol) and larger barrier (63 kcal/mol) for the hydrogenation of diphosphene are an indication that the $\pi$ bond for P=P is significantly stronger than for Si=Si.

As a technical note, the energetics for hydrogen elimination converge at low orders of perturbation theory. For example, the barriers to 1,2-elimination (using the 6-31G** basis) are 96.5, 85.8, 86.9, and 87.1 kcal/mol at the RHF, MP2, MP3, and MP4(SDQ) levels of theory. The overall endothermicities of the 1,2-elimination at the same levels are 34.7, 23.8, 24.8, and 24.6 kcal/mol. Thus only second-order perturbation theory is required here for accurate energetic predictions. The energetics of the 1,1-elimination show a similar behavior.

Hydrogenation of a diphosphene has been observed experimentally[9]. Treatment of a substituted diphosphene with a borohydride complex causes hydrogenation to proceed presumably via sequential attack of H$^-$ and H$^+$.

**$\pi$-Bond Strengths.** The strength of P=P $\pi$ bonding may be put in perspective by comparing it with the N=N and mixed P=N bonds. Accordingly we have carried out MCSCF/3-21G* structure determinations for trans, cis, and rotated-triplet HN=NH and HP=NH. The MCSCF PN bond lengths are about 0.08 Å longer than the 1.544 X-ray bond length reported[25] for a bulkily substituted phosphinimine. We have also located the saddle point for the singlet rotational barriers separating the cis and trans isomers. All these structures are shown in Figure 5. Once again, the singlet rotational maxima and triplet minima have very similar geometries.

The energies of these species are given in Table II. This table also includes the results of calculations with larger atomic bases, and more extensive electron correlation treatments. Unfortunately, the complete lack of symmetry at the HPNH rotational barrier causes the SOCI wave function analogous to those used above for HPPH to contain over 700 000 configurations, making such calculations impossible. The SOCI calculations described above for HPPH and $H_2PP$ species correlated the top two valence orbitals (lone pairs) in addition to the $\sigma$- and $\pi$-bonding electrons. Thus these will be denoted as SOCI-2 calculations. If no lone-pair orbital excitations are allowed, the wave functions contain fewer than 10 000 configurations, and are denoted SOCI-0. Table II contains the results of SOCI-0, and (where possible) SOCI-2 calculations.

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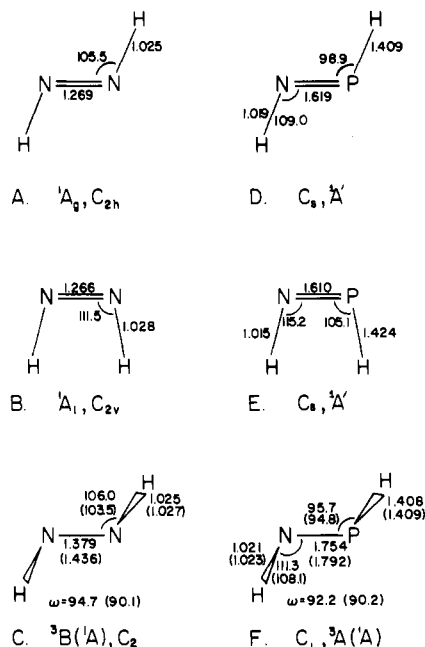
**Figure 5.** MCSCF/3-21G* HNNH and HPNH structures. All bond distances are in angstroms, and angles are in degrees. ω is the HXYH torsion angle. For the rotated forms, both the triplet equilibrium geometry and singlet rotational saddle point (in parentheses) are given.

**Table II.** Energies of Nitrogenous Molecules[a]

| molecule | MCSCF/ 3-21G* | MCSCF/ 6-31G* | SOCI-0/ 6-31G* | SOCI-2/ 6-31G* |
|---|---|---|---|---|
| trans-NH=NH | -109.5412 | -110.0728 | -110.1018 | -110.2116 |
| cis-HN=NH | -109.5310 | -110.0615 | -110.0905 | -110.2021 |
| tripl HN—NH | -109.4397 | -109.9694 | -110.0029 | |
| rotated HN—NH | -109.4324 | -109.9612 | -109.9934 | -110.1104 |
| trans-HP=NH | -394.4505 | -396.3449 | -396.3731 | |
| cis-HP=NH | -394.4481 | -396.3424 | -396.3705 | |
| tripl HP—NH | -394.3758 | -396.2667 | -396.2992 | |
| rotated HP—NH | -394.3712 | -396.2655 | -396.2944 | |

[a] Energies in hartrees. The SOCI-0/6-31G* energies for trans, cis, and rotated singlet HPPH are -682.6423, -682.6372, and -682.5849. All other HPPH energies are given in Table I.

The MCSCF/3-21G* rotational barriers for trans HN=NH, HP=NH, and HP=PH are 68.3, 49.8, and 35.4 kcal/mol, respectively. Improving the atomic basis changes little, as the MCSCF/6-31G* barriers are 70.0, 49.8, and 34.2 kcal/mol. The extended correlation treatment of only the σ and π electrons also has little effect, as the SOCI-0/6-31G* barriers are 68.1, 49.4, and 36.0 kcal/mol. At this point the results are similar to those we found recently[52] for the rotational barrier of Si=C, which changes little in going to the SOCI-0 level. Finally, however, inclusion of electron correlation effects within N lone pairs does have a significant effect on the HN=NH rotational barrier. The SOCI-2/6-31G* barriers are 63.5 and 36.0 kcal/mol for N=N and P=P. It is possible to estimate the SOCI-2 barrier for P=N by noting that the SOCI-2 barrier drops 2.3 kcal/mol per N lone pair from the SOCI-0 barrier for N=N but that correlating P lone pairs does not affect the barrier in HP=PH. Therefore we can estimate the P=N SOCI-2 rotational barrier as about 47 kcal/mol.

The best values for the N=N, P=N, and P=P π-bond strengths, defined as the rotational barrier about these bonds, are 63.5, 47, and 36 kcal/mol, respectively. As shown, these numbers are quite stable with respect to both basis set and level of electron correlation. We have recently used similar methodology to compute the Si=C π-bond strength[52] within 2 kcal/mol of ex-

perimental estimates. Accordingly we assign an uncertainty of no more than 5 kcal/mol to the π-bond strengths presented here.

There are apparently no definitive experimental estimates for any of these π-bond strengths, even for HN=NH. Recent determination[53] of the heat of formation of HNNH yielded estimates for the NN bond strengths in $H_2N-NH_2$ (63.9 ± 2.2 kcal/mol) and HN=NH (128 ± 9 kcal/mol). Subtraction affords a π-bond strength of 64 ± 11. Hydrogenation energies can also be used to estimate a π-bond strength. Using a typical NH bond strength of 92 ± 2 kcal/mol,[54] with a HH bond energy of 103 kcal/mol[55] the consecutive loss of two hydrogens from $N_2H_4$ to form $H_2$ and the hypothetical HN-NH without a π bond requires 92 + 92 - 103 = 81 ± 4 kcal/mol. Comparison to the actual $\Delta H$ of 26 ± 2 kcal/mol for $N_2H_4 \rightarrow$ HNNH + $H_2$ yields a NN π-bond strength of 55 ± 6 kcal/mol. Our computed rotation barrier is consistent with both these rather uncertain estimates.

Very recently, the photochemical cis–trans isomerization of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene was reported.[56] This experiment achieved trans to cis isomerization by irradiation with a photon energy of 55 kcal/mol, more than sufficient to surmount our computed rotation barrier of 36 kcal/mol. The activation energy ($\Delta G^{\ddagger}$) for reversion from the cis form was determined to be 20.3 kcal/mol. Since this activation energy probably has only small entropic contributions, it may be taken as approximately the enthalpy of activation. This experimental activation energy is considerably smaller than our $\Delta E$ value of 32 kcal/mol for the rotation of *cis*-HPPH, which is not surprising. There must be a much larger energy penalty for forcing these bulky ligands into a cis arrangement than for H atoms.

Ha et al.[15] have reviewed the previous theoretical π-bond strengths for the compounds HN=NH, HP=NH, and HP=PH. Note the extreme contrast between the 47 kcal/mol rotation barrier for the $p_\pi-p_\pi$ bond in HP=NH, and the less than 8 kcal/mol rotation barrier[28] for the $d_\pi-p_\pi$ bond in hypervalent phosphinimines. The rigidity of these two types of bonds is so different that these compounds should perhaps not be thought of in the same class, as is implied by their common name of phosphinimine.[26]

The cis forms of HNNH, HPNH, and HPPH are less stable than the trans forms by 6.0, 1.6, and 3.7 kcal/mol. The smaller value for the mixed compound could be rationalized as due to the favorable alignment of the $N^-H^+$ and $P^+H^-$ bond dipoles in the cis form. The triplet states of HNNH, HPNH, and HPPH lie 6.0, 3.0, and 2.4 kcal/mol below the barriers to rotation on the ground singlet surfaces of these molecules. As has already been noted, the structures of the triplets are quite similar to these singlet saddle points, whose spatial orbital occupancy they share.

**Conclusions**

A major conclusion of this work is that phosphorus forms π bonds having appreciable strength, albeit less than those for nitrogen. The π-bond strengths for HN=NH, HP=NH, and HP=PH were found to be 63.5, 47, and 36 kcal/mol. It is interesting to compare these results to the best available data for the isoelectronic group 14 compounds. The experimental C=C and Si=C and theoretical Si=Si π-bond strengths are 65,[57] 38,[58,59] and 22[60] kcal/mol, respectively. Thus phosphorus forms significantly stronger π bonds than does silicon. Because of this the P=P group is planar, while the Si=Si group is not. This planarity persists in the P=P anion, where the bond order is only 1.5. In

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fact, the P=P $\pi$ bond is about as strong as the Si=C bond, in spite of the fact that silaethylene contains only one third-row atom.

Borden and co-workers[61] have offered a simple explanation of the difference between P and Si multiple bonding, in terms of so-called "inert-pair effect". Atoms in the third row are reluctant to form sp hybrids, leading to preferred bond angles near 90°. To form a $\pi$ bond Si must hybridize, giving up its predominantly s lone pair, whereas P need not.

*trans*-HPPH is found to be more stable than the $H_2PP$ isomers by around 27 kcal/mol. The lowest energy unimolecular process converting *trans*- to *cis*-HPPH is rotation about the $\pi$ bond, in contrast to the inversion mechanism for HNNH.[17] $H_2PP$ has two quite closely spaced states, a bent triplet and a planar, doubly

bonded singlet. Confident prediction of the ground state of phosphinophosphinidene must therefore await the experimental demonstration of such a compound.

The hydrogenation of diphosphene to diphosphine is computed to be exothermic by 25 kcal/mol, in good agreement with the experimental estimate of 21 ± 8 kcal/mol.[7] The concerted hydrogenation has a quite substantial barrier (about 63 kcal/mol) and proceeds via an initially one-sided attack. Pyrolysis of the saturated diphosphine has a lower barrier for 1,1-elimination to $H_2PP$ than 1,2-elimination to HP=PH (67 vs. 87 kcal/mol). (We have not considered other possible channels, such as H + $HPPH_2$, or PH + $PH_3$.)

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# Structure and Properties of the Sulfur Dinitride Dianion

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The properties of the $N_2S^{2-}$ dianion are calculated by using Hartree–Fock–Slater and MNDO methods and are related to those of $N_2S$ and experimental results. A locally stable $NSN^{2-}$ species with an NSN angle of 135° is characterized, and a decomposition channel to $N_2 + S^{2-}$ is identified.

## I. Introduction

A $C_{2v}$ form of the sulfur dinitride fragment, NSN, appears to be transferred in various reactions encountered in sulfur nitride chemistry.[1,2] This motivated us recently to report a Hartree–Fock–Slater (HFS) MO–LCAO[3] calculation for the $N_2S$ species.[1] While the linear NNS form appeared to be the ground state of the molecule, we were abe to detect a local minimum for a symmetric species with an NSN angle of 90° (NSN-90), with a barrier of some 9–15 kcal/mol toward decomposition into $N_2 + S$. However, the symmetrical NSN species has not been isolated so far. Nevertheless, the $N_2S^{2-}$ dianion has been obtained recently by two different routes.[4,5]

The crystal structure of $N_2S^{2-}$ is not known, but on the basis of vibrational spectra[4] there seems to be no doubt that it has a symmetrical NSN form. It seems interesting to complete our calculations on the NSN fragment by reporting features for the dianion of this species. We focus on the geometrical structure, the UV spectrum, and the electronic structure and relate our findings to the neutral NSN fragment and to experimental results.

## II. The NSN Fragment

It is useful to start by recalling briefly the main features of the electronic structure of NSN and relate them to the $NSN^{2-}$ anion. The NSN-90 fragment single determinant valence orbital configuration is $a_1^8 a_2^2 b_1^2 b_2^4$ with four $\pi$ electrons ($a_2$ and $b_1$). The lowest unoccupied MO (LUMO), $3b_2$, is a $\sigma$ orbital with moderate SN bonding character and very strong NN antibonding behavior. Thus, the occupancy of this orbital to form a dianion should strengthen somewhat the SN bonds and open the NSN angle. At NSN angles of ≤60° there is a decomposition channel leading to the formation of $N_2$ and S. The configuration of the wave function for this species is $a_1^8 a_2^0 b_1^4 b_2^4$ where the $a_2$ orbital, which is NS bonding and NN antibonding, is now empty while $2b_1$, an antibonding, $\pi^*_{NS}$ orbital, is occupied with the result that the NS

bond is weakened and the NN linkage strengthened through the $1a_2 \rightarrow 2b_1$ electron transfer.

As remarked earlier, the absolute minimum for the $N_2S$ species is a linear NNS form, and this too can be analyzed as to the effect of adding two electrons. The LUMO of linear NNS is a $\pi$ orbital with antibonding NN character and little NS bonding. The addition of two electrons to this orbital would certainly weaken the overall bonding. Furthermore, since this orbital is degenerate, the linear $NNS^{2-}$ anion is unlikely to be stable.

## III. The $NSN^{2-}$ Anion

**III.1. Geometry.** As a first step for the geometry optimization of the $NSN^{2-}$ anion we employed the MNDO program, which is well suited for this purpose.[6,7] Keeping the SN distance fixed at 1.6 Å and letting the NSN angle vary up to 180°, one can locate a minimum for the standard heat of formation, $\Delta H_f°$, between 110 and 120° (Figure 1). A full optimization in this region leads to an NSN angle of 118° and a SN distance of 1.53 Å. At low angles $\Delta H_f°$ decreases steadily indicating a decomposition channel just as in NSN and leading, in this case, to $N_2 + S^{2-}$ with a barrier toward decomposition of ca. 25 kcal/mol.

As for the HFS method, the total statistical energy, $E_T$, indicates a very flat minimum for an NSN angle around 135°, NSN-135(2–) (Figure 2), with the NS distance fixed at 1.6 Å. Further variation of the NS distance indicates a minimum for 1.60 Å. Again, for small angles, there appears to be a decomposition channel (cf. Figure 2).

**III.2. Electronic Structure of the NSN-135(2–) Anion.** In the following sections we provide a description of the electronic structure of NSN(2–) based on the HFS results for an NSN angle

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