234 nm (ϵ 1080). Anal. Calcd for $C_9H_{14}O_2$: C, 70.01; H, 9.15. Found: C, 70.00; H, 8.79.

1-Methoxy-1,4-cyclohexadiene was prepared by the Birch reduction of anisole.

4,4-Dimethoxycyclohexene (3). 1-Methoxy-1,4-cyclohexadiene (2.0 g, 0.018 mol) was dissolved in 50 mL of anhydrous ether (distilled from Na/benzophenone) and placed in a 100-mL round-bottomed flask. Methanol (6 mL, 0.148 mol) was added along with several crystals of *p*-toluenesulfonic acid. The mixture was stirred overnight under N_2. The mixture was neutralized with NaOMe and washed once with 50 mL of H_2O. The ether solution was dried (Na_2CO_3), filtered, and distilled. The product was a colorless liquid: bp 48-50 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.62 (q, 2, alkene), 3.24 (s, 6, OCH_3), 2.27 (br s, 2, allylic CH_2), 2.10 (br s, 2, allylic CH_2), 1.81 (t, 2, CH_2).

1,4-Dioxaspiro[4.5]dec-7-ene (4).[18] 1-Methoxy-1,4-cyclohexadiene (3.0 g, 0.0272 mol) was dissolved in 50 mL of anhydrous toluene (distilled from Na/benzophenone) and placed in a 100-mL round-bottomed flask fitted with a Dean-Stark trap. Ethylene glycol (1.70 g, 0.0272 mol) was then added along with several crystals of *p*-toluenesulfonic acid. The solution was heated to 110 °C, and H_2O was taken off via the trap. The organic solution was washed twice with 50 mL of saturated $NaHCO_3$ and 30 mL of H_2O, dried ($MgSO_4$ and K_2CO_3), filtered, and concentrated. The resulting solution was distilled: bp 62-64 °C (7 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.64 (m, 2, alkene), 3.93 (s, 4, OCH_2CH_2O), 1.5-2.3 (m, 6, CH_2).

Methylenecyclohexane (5) was prepared by a standard Wittig reaction of cyclohexanone.

1,1-Dimethoxycyclohexane (7) was prepared by the reaction of cyclohexanone with trimethylsilyl trifluoromethanesulfonate and trimethylmethoxysilane.

1,4-Dioxaspiro[4.5]decane (8) was prepared by the reaction of cyclohexanone with ethylene glycol.

3-Methoxy-1-methylenecyclohexane (9) was prepared by the method of Clikeman:[2] UV(pentane) λ_{max} 229 nm (ϵ 1410).

4-Methoxycyclohexene (10) was prepared by the method of Marko.[5]

Calculations. Semiempirical and ab initio calculations were carried out on an IBM 2700 computer at the University of Illinois at Chicago. CHEMGRAPH and MM2 calculations were carried out on a Harris H1000 computer, Department of Chemistry, Northwestern University.

Registry No. 1, 104598-80-3; **2**, 104598-81-4; **3**, 16831-48-4; **4**, 7092-24-2; **5**, 1192-37-6; **6**, 110-83-8; **7**, 933-40-4; **8**, 177-10-6; **9**, 59627-58-6; **10**, 15766-93-5; **11**, 931-56-6; Ph_3PCH_3Br, 27200-84-6; 3-hydroxy-1-methylenecyclohexane, 6749-63-9; 7-oxo-1,4-dioxaspiro[4.5]decane, 4969-01-1; 1-methoxy-1,4-cyclohexadiene, 2886-59-1; cyclohexanone, 108-94-1; anisole, 100-66-3.

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Theoretical Studies of Diphosphene and Diphosphinylidene in Their Closed-Shell States, Low-Lying Open-Shell Singlet and Triplet States, and Transition States. Search for a Stable Bridged Structure[†]

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Abstract: We have undertaken a systematic study of the various low-lying electronic states of the H_2P_2 system, about which little is known experimentally, using the methods of ab initio molecular electronic structure theory. For each state we have predicted its molecular geometry, energy, dipole moment, vibrational frequencies, and their associated normal modes. The ground state is *trans*-HP=PH, 3.5 kcal/mol below *cis*-HP=PH. The $H_2P{=}P$ isomer lies at a relative energy of 28 kcal/mol above the ground state. For the ground state the highest occupied molecular orbital (HOMO) is n_+, a symmetric lone-pair combination; the second HOMO is the P-P π bond. In $H_2P{=}P$ a lone pair n_y is the HOMO, and the P-P π bond is the second HOMO. For both isomers the lowest unoccupied molecular orbital (LUMO) is the antibonding P-P π^* orbital. A variety of states involving $n-\pi^*$ and $\pi-\pi^*$ excitations have been studied for various molecular geometries. The lowest energy open-shell singlet is a pyramidal H_2PP $^1A''$ state (out-of-plane angle 77°) at a relative energy of 46 kcal/mol. A skewed HPPH ^1B state (torsion angle 109°) is at 64 kcal/mol. Highly distorted geometries are also characteristic of the triplet states. A pyramidal H_2PP $^3A''$ state (out-of-plane angle 79°) has a relative energy of only 21 kcal/mol, and thus it is predicted to lie below the closed-shell planar H_2PP state. A skewed HPPH ^3B state (torsion angle 90°) is at 29 kcal/mol. An unsuccessful search has been made for a stable doubly bridged PH_2P structure, analogous to SiH_2Si. Studies of transition states between the various structures show the following. (1) Closed-shell cis-trans isomerization occurs more readily by internal rotation (barrier 34 kcal/mol) than by inversion (barrier 66 kcal/mol). From this calculated rotation barrier and experimental data in the literature, it is estimated that the cis isomer of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene lies approximately 14 kcal/mol above the trans isomer. (2) Between closed-shell *trans*-HPPH and H_2PP, both planar, the transition state is nonplanar (torsion angle 112°) at 53 kcal/mol. Evidence is presented showing that the unusual structure of this transition state is caused by attraction of the transiting proton to the P-P π bond. (3) Between triplet skewed HPPH and pyramidal H_2PP, both nonplanar, the transition state is also nonplanar (torsion angle 87°) at 49 kcal/mol. (4) Other internal rotation barriers in the HPPH system, and inversion barriers in the H_2PP system, are also examined. Finally, it is shown that in many cases polarization functions (phosphorus d orbitals and hydrogen p orbitals) play an important role in predicting the chemistry of the H_2P_2 system.

The double-bonded nitrogen structure, -N=N-, has been well known for many years in the form of diazene (also called diimide or diimine), HN=NH, and substituted diazenes (also called azo compounds), RN=NR. However, it was long thought that if phosphorus, the next member of group 15, did form the analogous diphosphene configuration, -P=P-, then it was of only fleeting significance. The only experimental evidence for its existence was the observation of H_2P_2, by means of its mass spectrum, in the thermal decomposition products of diphosphine, H_4P_2.[1-3] The

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H_2P_2 rapidly decomposed to form elemental phosphorus, P_4, and another product, possibly phosphine, PH_3.

This situation changed dramatically in 1981 with the discovery by Yoshifuji and co-workers[4] of a substituted diphosphene, RP=PR, where R is the 2,4,6-tri-*tert*-butylphenyl group. Since then many substituted diphosphenes have been synthesized, either alone or as metal complexes.[5-7] In all of these substances the use of a large, bulky R group has been essential to a successful synthesis. X-ray crystallographic studies have shown that the diphosphene's central X—P=P—X moiety is typically in the planar trans configuration (although Yoshifuji's original product has a slight out-of-plane twist, with a dihedral angle of 172.2°). In some metal complexes the diphosphene is in the planar or nearly planar cis form.[8-10]

Like their nitrogen analogues, the solid substituted diphosphenes have intense colors at the red end of the spectrum, being variously described as orange, orange-red, intense red, ruby red, yellow-orange, etc. Their absorption spectra show a strong band in the near-ultraviolet, assigned to a $\pi-\pi^*$ transition, and a weaker band in the blue, indigo, or violet, assigned to an $n_+-\pi^*$ transition.[5] Because these absorption bands indicate the presence of low-lying excited states, and because of the new importance of the diphosphene structure, we have undertaken a systematic theoretical investigation of the "parent" diphosphene molecule, HP=PH, and its isomer diphosphinylidene, H_2P=P, in their closed-shell states, low-lying open-shell singlet and triplet states, and transition states, using a basis set of high quality and including the energetic effects of electron correlation by the configuration interaction method. (A preliminary report of some of the triplet state results has been published.[11])

Silicon, phosphorus's neighbor in the periodic table, forms a hydride, H_2Si_2, with an unusual doubly bridged structure,[12,13] and therefore we have also examined similar bridged structures, both planar and nonplanar, for H_2P_2.

There have been several other theoretical studies of diphosphene.[5,10,14-23] Most are confined to the closed-shell structures, but several include transition states,[10,19,23] triplets,[19,23] and an open-shell singlet state.[23] There has also been a theoretical study of the conformations of substituted diphosphenes in which the substituents are amino groups.[24]

Method

Except for the two-configuration studies described below, each of our studies began with the restricted self-consistent-field (SCF) method, using the contracted double-ζ (DZ) Gaussian basis set of Huzinaga, Dunning, and Hay.[25-27] An analytic gradient method[28] was then used to optimize the molecular geometry, constrained to the appropriate symmetry point group, until the magnitudes of all forces were less than 1×10^{-7} hartree/bohr.

Table I. Energy of the *trans*-HPPH Closed-Shell Structure

method	energy, hartrees
DZ basis, SCF	−682.483 44
CI	−682.628 50
corrected[a]	−682.643 77
DZ basis, TCSCF	−682.519 15
CI	−682.639 42
corrected[b]	−682.649 05
DZ + P basis, SCF	−682.574 70
CI	−682.820 08
corrected[a]	−682.849 58
DZ + P basis, TCSCF	−682.601 50
CI	−682.830 44
corrected[b]	−682.854 93

[a] With the Davidson correction.[32] [b] With the generalized Davidson correction.[35]

The basis set was then expanded by adding polarization functions. For each phosphorus atom we added six functions of d type, with orbital exponents of 0.5. For each hydrogen atom we added three functions of p type, with orbital exponents of 0.75. This basis set is designated P(11s7p1d/6s4p1d), H(4s1p/2s1p), and abbreviated DZ+P. In the DZ set there are 40 contracted Gaussian functions, in the DZ+P set 58. The molecular geometry was then reoptimized with this expanded basis set, still at the SCF level of theory.

The vibrational frequencies and corresponding normal modes for each electronic state were then determined, for both the DZ SCF and DZ+P SCF structures, from analytic second derivatives.[29-31]

The final step was the determination of configuration interaction (CI) wave functions for both the DZ SCF and DZ+P SCF geometries. In so doing we froze the 10 inner-shell molecular orbitals, i.e., 1s, 2s, and 2p atomic-like orbitals on each phosphorus atom. Otherwise the CI wave functions included all singly and doubly excited configurations. The effect on the molecular energy of quadruple excitations was included in an approximate way be means of the Davidson correction.[32] The number of configurations varied from 3108 for the cis or trans closed-shell structure with the DZ basis to 41 923 for the triplet skew-to-pyramid transition state with the DZ+P basis.

For several structures (e.g., the internal rotation transition state) it was necessary to carry out a two-configuration SCF (TCSCF) calculation. The basis sets employed in this work were the same as those described above. A TCSCF analytic gradient method[33] was used to optimize the molecular geometry, and a TCSCF analytic energy second-derivative method[34] was used to determine the vibrational frequencies of the normal modes. Again the 10 inner-shell MO's were frozen when determining the CI wave function; apart from this the CI procedure included all single and double excitations relative to the two reference configurations. The effect of quadruple excitations was estimated by the Davidson formula in a generalized form.[35] The number of configurations

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Table II. Properties of HPPH and H_2PP Closed-Shell Structures[a]

	trans-HPPH ^1A_g	*cis*-HPPH $^1A_1$	planar H_2PP $^1A_1$
r_e(PP)	2.004 (2.055)	2.010 (2.064)	1.943
r_e(PH)	1.413 (1.413)	1.412 (1.411)	1.394
θ_e(PPH)	96.0 (95.6)	100.9 (100.2)	127.3
energy, SCF	0.0 (0.0)	3.5 (3.2)	24.7
energy, CI	0.0 (0.0)	3.7 (3.5)	27.2
energy, Davidson cor	0.0 (0.0)	3.6 (3.5)	28.1
no. of config	8949 (17 435)	8949 (17 435)	9084
dipole moment	0.00 (0.00)	1.50 (1.46)	2.28
vibrational frequency, ν_e			
asym PH stretch	2526 (2525), B_u	2510 (2511), B_2	2619, B_2
sym PH stretch	2512 (2512), A_g	2534 (2534), A_1	2613, A_1
sym bend	1065 (1056), A_g	823 (812), A_1	1255, A_1
torsion (col 3, wagging)	864 (781), A_u	780 (692), A_2	354, B_1
asym bend	754 (749), B_u	961 (959), B_2	715, B_2
PP stretch	699 (606), A_g	693 (597), A_1	706, A_1

[a] All results were obtained with the DZ+P basis set. SCF results are listed first, with TCSCF results in parentheses. Energies are in kcal/mol relative to the *trans*-HPPH closed-shell structure. Bond lengths are in Å, angles are in deg, vibrational frequencies are in cm^{-1} for ^{31}P and ^1H isotopes, and dipole moments are in D. For C_{2v} symmetry, the molecular plane is taken as the *yz* plane (σ_v').

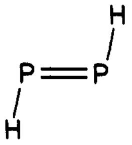
varied from 5999 for the cis or trans closed-shell structure with the DZ basis to 31 556 for the internal rotation transition state with the DZ+P basis.

Closed-Shell Molecular Structures

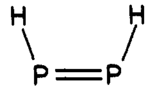
We find that the closed-shell structure of planar trans configuration, **1**, is the ground state, in agreement with all previous studies.[10,14,15,17,19,21-23] Its orbital occupation is

$$1a_g^2 1b_u^2 2a_g^2 2b_u^2 3a_g^2 3b_u^2 1a_u^2 1b_g^2 4a_g^2 4b_u^2 \times 5a_g^2 5b_u^2 6a_g^2 6b_u^2 7a_g^2 2a_u^2$$

As this structure becomes the reference point for all others, its energies for various methods and basis sets are listed in Table I. From a variational point of view these are the most accurate results yet obtained for diphosphene.



1



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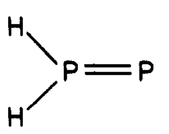

3

Other closed-shell structures that we have examined are the cis (**2**) and the planar H_2PP structure (**3**). Table II summarizes the properties of the closed-shell structures. For each structure the first set of results was obtained with a single configuration wave function; TCSCF results are listed in parentheses for the trans and cis structures. In each case all six vibrational frequencies are real, showing that these are true minima on the potential energy surface. The relative energies of the closed-shell structures are shown in Figure 1.

With the SCF method the lowest unoccupied molecular orbital (LUMO) of the trans structure is the $2b_g$ antibonding π^* orbital. With the TCSCF method its occupation is 0.154 electron, and there is a corresponding decrease in the occupation of the $2a_u$ orbital to 1.846 electrons. (For the cis structure the occupations change to 0.159 electron in the $2a_2$ orbital and 1.841 electrons in the $2b_1$ orbital.) The antibonding character of the $2b_g$ orbital leads to some substantial changes: an increase in the PP bond length from 2.004 to 2.055 Å, and decreases in the vibrational frequency for torsion from 864 to 781 cm^{-1} and for PP stretch from 699 to 606 cm^{-1}. These changes are all in the direction to be expected when adding a π^* orbital. Similar changes are observed for the cis structure. The other properties are not greatly affected by addition of the second SCF configuration.

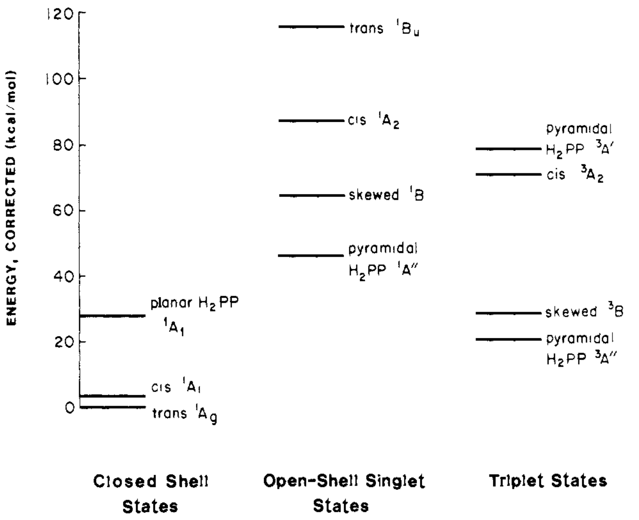

Figure 1. Davidson corrected energies of closed-shell, open-shell singlet, and triplet states that are minima on the potential energy surface.

As noted above, little is known experimentally about diphosphene. We may, however, compare some of our results with those obtained for substituted diphosphenes. For example, our "best" DZ+P SCF (TCSCF) value for the PP bond length in the trans structure, 2.004 (2.055 Å), is about the same as experimental values for substituted diphosphenes, which range from 2.001[36-38] to 2.034 Å.[4,39] Our PPH bond angle of 96.0° (95.6°) is considerably smaller than the range of 102.2[39] to 108.9°[36-38] observed for PPC and PPN bond angles in substituted diphosphenes. It has previously been suggested that steric interactions may cause substituted diphosphenes to have larger bond angles than diphosphene itself.[15,17] Our best PP stretching frequency of 699 (606) cm^{-1} compares favorably with the experimental frequencies of 595 and 610 cm^{-1} observed by Raman spectroscopy on two substituted diphosphenes.[40,41]

The SCF orbital energies of the valence electrons are shown in Table III for the closed-shell structures. For both *trans*- and *cis*-HPPH we find that the π orbital has the highest energy, the n_+ combination being next highest. This result for the trans structure is in agreement with the findings of previous molecular orbital studies.[5,16,17]

To obtain further evidence regarding the relative energies of the π and n_+ MO's in *trans*-diphosphene, we studied the vertical ionization energies to form the $H_2P_2^+$ cation. When an electron is removed from the $2a_u$ (π) MO to form the cation in a ^2A_u state, then the SCF, CI, and Davidson corrected ionization energies are 9.03, 9.72, and 9.88 eV, respectively. The corresponding energies for removal of an electron from the $7a_g$ (n_+) MO, to form the cation in a ^2A_g state, are 9.29, 9.38, and 9.35 eV. (In each case the DZ+P basis set was used with the DZ+P geometry of *trans*-HPPH.) Thus the π MO is the HOMO according to both the SCF ionization energies and the SCF orbital energies, whereas the n_+ MO is the HOMO according to the presumably more accurate CI and Davidson corrected energies. The latter result agrees with the order of ionization energies calculated by Galasso[18]

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Table III. Valence Electron Molecular Orbital Symmetries, Energies, and Assignments for Closed-Shell Structures[a]

	trans-HPPH	*cis*-HPPH	planar H_2PP
LUMO	$2b_g$, –, π^*	$2a_2$, –, π^*	$4b_1$, –, π^*
HOMO	$2a_u$, –9.69, π	$2b_1$, –9.65, π	$4b_2$, –8.31, n_y
2HOMO	$7a_g$, –9.86, n_+	$7a_1$, –10.80, n_+	$3b_1$, –9.99, π
3HOMO	$6b_u$, –13.33, n_-	$6b_2$, –10.85, n_-	$9a_1$, –12.28, n_z
4HOMO	$6a_g$, –13.40, $\sigma(PH)_+$	$6a_1$, –15.11, $\sigma(PH)_+$	$3b_2$, –15.84, $\sigma(PH)_-$
5HOMO	$5b_u$, –19.65, $\sigma(PH)_-$	$5b_2$, –19.55, $\sigma(PH)_-$	$8a_1$, –19.67, $\sigma(PH)_+$
6HOMO	$5a_g$, –25.02, $\sigma(PP)$	$5a_1$, –24.96, $\sigma(PP)$	$7a_1$, –25.21, $\sigma(PP)$

[a] All results were obtained by the SCF method with the DZ+P basis set. Energies are in eV.

Table IV. Properties of Cis, Trans, and Skewed Open-Shell Singlet Structures[a]

	trans-HPPH $n-\pi^*$ ^1B_g	*cis*-HPPH $n-\pi^*$ $^1A_2$	*trans*-HPPH $\pi-\pi^*$ ^1B_u	*cis*-HPPH $\pi-\pi^*$ $^1B_2$	skewed HPPH ^1B
r_e(PP)	2.111	2.256	2.149	2.156	2.028
r_e(PH)	1.404	1.412	1.411	1.409	1.409
θ_e(PPH)	106.3	101.4	94.9	99.2	109.4
θ_e(torsion)[b]	180.0	0.0	180.0	0.0	109.2
energy, SCF	69.5	83.7	135.6	138.1	63.6
energy, CI	71.0	87.8	122.0	125.2	64.2
energy, Davidson cor	70.8	87.5	114.9	118.6	64.4
dipole moment	0.00	1.22	0.00	1.54	0.99
vibrational frequency, ν_e					
asym PH stretch	2575, B_u	2524, B_2	2546, B_u	2535, B_2	2532, B
sym PH stretch	2565, A_g	2538, A_1	2534, A_g	2555, A_1	2525, A
sym bend	898, A_g	610, A_1	1041, A_g	793, A_1	832, A
torsion	456i, A_u	613, A_2	710, A_u	204i, A_2	554, A
asym bend	702, B_u	1053, B_2	742, B_u	957, B_2	467, B
PP stretch	516, A_g	417, A_1	578, A_g	572, A_1	663, A

[a] All properties were obtained with the DZ+P basis set. See Table II footnote for units, etc. [b] The torsion angle is defined as the angle between the two PPH planes.

and with the results of Xα studies of diphosphene.[5,20] It thus appears that Koopmans' theorem does not give the correct order of the SCF molecular orbitals in *trans*-diphosphene. This conclusion may be relevant to the question of the assignment of bands in the photoelectron spectra of substituted diphosphenes.[16,42–44] Incidentally, for the cis structure Galasso has previously deduced on theoretical grounds that the n_+ and n_- ionization energies are nearly identical.[18] Similarly, Table III shows that the n_+ and n_- orbital energies in the cis isomer are nearly identical.

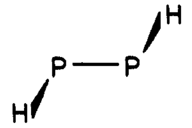
The order of the orbital energies shown in Table III for *trans*-diphosphene differs from that found in *trans*-diazene. There n_+ lies above π, σ(NN) lies above the two σ(NH) MO's, and σ(NH) of b_u symmetry lies above σ(NH) of a_g symmetry.[45,46] (These assignments are based on the simple molecular orbital considerations of Walsh[47] and on more recent calculations.[48–50])

Diphosphinylidene, H_2PP, has a somewhat different ordering of the SCF molecular orbital energies. As shown in Table III the π MO is sandwiched between the two lone-pair MO's. These lone-pair orbitals are largely associated with the terminal phosphorus atom. If the z axis is taken along the P–P bond, and the y axis is taken in the molecular plane, then one of these MO's (designated n_y) has major contributions from the p_y functions on this phosphorus atom, and the other (designated n_z) has major contributions from the p_z functions on this phosphorus atom. (Our MO assignments differ from those of Schmidt and Gordon,[23] who state that the top two valence orbitals in both HPPH and H_2PP are lone pairs. They also find that in H_2PP one of the two lowest energy valence orbitals is a σ lone pair at the terminal P atom.)

Open-Shell Singlet Structures

In this study we have examined open-shell singlet structures with both $n-\pi^*$ and $\pi-\pi^*$ excitations. The results are shown in Table IV for states with trans and cis geometry. (For C_{2h} symmetry, the $n-\pi^*$ excitation is designated $7a_g \rightarrow 2b_g$, and the $\pi-\pi^*$ excitation is designated $2a_u \rightarrow 2b_g$.)

Two structures have imaginary torsion frequencies: the trans $n-\pi^*$ singlet, and the cis $\pi-\pi^*$ singlet. This implies that a skewed structure (or structures) will have lower energy, and in fact a skewed ^1B structure, **4**, of lower energy is found, with a torsion angle of 109.2° (see Table IV). It turns out that this structure indeed correlates with both the trans $n-\pi^*$ singlet and the cis $\pi-\pi^*$ singlet. (In view of this correlation, it is clear that the terms $n-\pi^*$ and $\pi-\pi^*$ have no meaning when applied to the skewed structure.) The fact that its torsion angle is significantly larger than 90°, closer to trans (180°) than cis (0°), no doubt is a reflection of the much lower energy of the trans $n-\pi^*$ singlet as compared to the cis $\pi-\pi^*$ singlet. Figure 1 shows the relative energies of those structures that represent local minima on the potential energy surface (six real vibrational frequencies).



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For the planar H_2PP structure we have studied $n-\pi^*$ excitation to an open-shell singlet state, and the results are shown in Table V. (The $\pi-\pi^*$ excitation was not examined because both singly occupied orbitals would have the same symmetry.)

The imaginary wagging frequency of the planar H_2PP $n-\pi^*$ singlet of course implies the existence of a lower energy pyramidal structure, **5**. Its properties are listed in Table V. (Note the very large out-of-plane angle, 76.5°.) Of the various open-shell singlets we have studied, this one has the lowest energy (see Figure 1).

Diazene, HN=NH, also has an open-shell singlet with skewed geometry.[51,52] Its torsion angle differs from that of the trans

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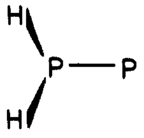

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conformer by only 28° (i.e., its torsion angle is 152° using our convention). Formaldehyde, $H_2C{=}O$, which is isovalent with diphosphinylidene, also has a pyramidal n–π* singlet (out-of-plane angle 34°),[53] but thioformaldehyde, $H_2C{=}S$, has a planar n–π* singlet.[54]

Comparing the energies of the various structures in Table IV, we see that, for both *trans*-HPPH and *cis*-HPPH, n–π* excitation is much lower in energy than π–π* excitation, as had been deduced previously from the absorption spectra of substituted diphosphenes.[5] This is consistent with our CI studies on the positive ion states.

At this point, we must consider to what extent our results are consistent with the experimental electronic absorption spectra, recognizing that the experimental data are for substituted diphosphenes, while these results are for diphosphene itself.

The visible and UV absorption peaks of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene lie at 460 and 340 nm, respectively.[4] (With other substituents there are small changes in the positions of the absorption peaks; see Table 3 of ref 5.) These wavelengths correspond to excitation energies of 62 and 84 kcal/mol, respectively, and they have been assigned to n–π* and π–π* excitations, respectively.[5] Thus we may compare these data with the results shown in Table IV for the n–π* and π–π* open-shell singlets of trans geometry, for which the relative energies (Davidson corrected) are 70.8 and 114.9 kcal/mol, respectively. Our results for diphosphene are substantially higher than the experimental data for substituted diphosphenes, the differences being 9 and 31 kcal/mol, respectively, for the n–π* and π–π* transitions.

To obtain more accurate energy data, we expanded the basis set beyond the DZ+P level by adding diffuse functions on the phosphorus atoms. Three different sets of diffuse functions were tried, and the results are shown in Table VI. The energy changes were relatively small, with the largest change in Davidson corrected energies being a decrease of 4.1 kcal/mol for the π–π* singlet with basis set 2 (DZ plus two sets of d functions, with orbital exponents of 0.75 and 0.25).

It is conceivable that we are dealing here with excitation to triplet rather than open-shell singlet states, but as such transitions are spin-forbidden this possibility seems extremely unlikely.

The final question that remains is: Do these differences between diphosphene and substituted diphosphenes represent a red shift induced by the substituents? Diazene provides a precedent for such a conclusion. Gaseous diazene is colorless; the strongest absorption peak lies at about 344 nm, and there is only very weak absorption at wavelengths above 400 nm.[46] (In liquid ammonia and certain other condensed systems diazene has a yellow color, which is ascribed to strong hydrogen bonding.) In contrast, substituted diazenes have colors similar to substituted diphosphenes.[4] Where the substituent is 2,4,6-tri-*tert*-butylphenyl, the compound is orange, with λ_{max} values of 465 and 307 nm.[55] A shift from 344 to 465 nm corresponds to an energy change from 83 to 61 kcal/mol, and thus the substituent induces a very large red shift in the case of the nitrogen compounds. We do not know to what extent this phenomenon is caused by a shift in the 0,0 band, and to what extent it is caused by a change in the absorption intensity profile. In view of these data for nitrogen compounds, we conclude that the energy differences betwen theoretical results for H_2P_2 and experimental results for R_2P_2 are likely to be, at least in part, due to substituent effects.

Table V. Properties of Planar and Pyramidal H_2PP Open-Shell Singlet Structures[a]

	planar n–π* $^1A_2$	pyramidal n–π* $^1A''$
r_e(PP)	2.081	2.195
r_e(PH)	1.385	1.409
θ_e(PPH)	124.6	99.0
θ_e(out-of-plane)[b]	0.0	76.5
energy, SCF	49.3	30.1
energy, CI	58.7	42.8
energy, Davidson cor	61.7	46.4
dipole moment	2.20	1.02
vibrational frequency, ν_e		
asym PH stretch	2705, B_2	2540, A″
sym PH stretch	2671, A_1	2536, A′
sym bend	1149, A_1	1202, A′
wagging	791i, B_1	726, A′
asym bend	574, B_2	767, A″
PP stretch	579, A_1	478, A′

[a] All properties were obtained with the DZ+P basis set. See Table II footnote for units, etc. [b] The out-of-plane angle is defined as the angle between the PP axis and the H_2P plane.

Table VI. Effect of Diffuse Functions on Calculated Energies for *trans*-HPPH Open-Shell Singlet Structures

basis set[a]	SCF energy[b]	CI energy[b]	Davidson corrected energy[b]
	n–π* Singlet		
DZ+P	69.5	71.0	70.8
set 1 (DZ+2d)	70.6	71.9	71.7
set 2 (DZ+2d′)	72.4	71.6	70.8
set 3 (DZ+P+s+p)	68.9	70.1	69.8
	π–π* Singlet		
DZ+P	135.6	122.0	114.9
set 1 (DZ+2d)	135.8	122.3	115.3
set 2 (DZ+2d′)	128.7	117.3	110.8
set 3 (DZ+P+s+p)	130.2	119.0	112.4

[a] Basis set 1 has the DZ basis set for phosphorus plus two sets of d functions, with orbital exponents of 2.5 and 0.5. Basis set 2 is similar but with orbital exponents of 0.75 and 0.25. Basis set 3 has the DZ+P basis set for phosphorus plus one s function (orbital exponent = 0.035) and one set of p functions (orbital exponent = 0.035). In all cases hydrogen has the DZ+P basis set. [b] Energies are in kcal/mol relative to the closed shell trans structure with the same basis set, for which the SCF energies are: DZ+P, −682.57470; basis set 1, −682.58063; basis set 2, −682.58559; basis set 3, −682.57727.

Triplet Structures

Both n–π* and π–π* excitations to states with triplet spin coupling have been examined. The properties of states with cis and trans geometry are shown in Table VII. In contrast to what is observed with open-shell singlets, here it is the π–π* excitation that is lower in energy, consistent with the SCF orbital energies in the closed-shell structures (Table III) but not with our CI studies on the positive ion states. Both the cis and trans π–π* triplets have imaginary torsion frequencies, indicating that a structure with skewed geometry, **4**, will have lower energy. This is indeed the case, as shown in the last column of Table VII. The skewed ^3B state correlates with the cis and trans π–π* triplets; in terms of torsion angle (89.8°) it is almost exactly halfway between them.

The cis n–π* triplet has six real vibrational frequencies, and thus it is a true minimum on the potential energy surface, but the trans n–π* triplet has an imaginary asymmetric bending frequency. This indicates that motion toward the H_2PP structure lowers its energy, and in fact the planar H_2PP n–π* triplet is lower in energy. Its properties as well as those of the corresponding π–π* triplet are shown in Table VIII. Each has an imaginary wagging frequency, and thus the triplets with pyramidal structure, **5**, have lower energy. They are also listed in Table VIII. Figure 1

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Table VII. Properties of Cis, Trans, and Skewed Triplet Structures[a]

	trans-HPPH n–π^* ^3B_g	*cis*-HPPH n–π^* $^3A_2$	*trans*-HPPH π–π^* ^3B_u	*cis*-HPPH π–π^* $^3B_2$	skewed HPPH ^3B
r_e(PP)	2.084	2.214	2.282	2.293	2.209
r_e(PH)	1.403	1.412	1.412	1.411	1.414
θ_e(PPH)	105.6	100.6	93.9	97.3	96.0
θ_e(torsion)	180.0	0.0	180.0	0.0	89.8
energy, SCF	45.9	64.4	18.4	20.4	11.9
energy, CI	50.9	69.9	32.9	35.1	25.3
energy, Davidson cor	52.6	71.1	36.7	38.9	28.9
dipole moment	0.00	1.06	0.00	1.37	0.98
vibrational frequency, ν_e					
asym PH stretch	2540, B_u	2527, B_2	2530, B_u	2520, B_2	2506, B
sym PH stretch	2574, A_g	2533, A_1	2520, A_g	2539, A_1	2508, A
sym bend	920, A_g	676, A_1	1006, A_g	759, A_1	783, A
torsion	486, A_u	373, A_2	395i, A_u	474i, A_2	421, A
asym bend	2306i, B_u	1524, B_2	714, B_u	926, B_2	784, B
PP stretch	561, A_g	458, A_1	464, A_g	457, A_1	479, A

[a] All properties were obtained with the DZ+P basis set. See Table II footnote for units, etc.

Table VIII. Properties of Planar and Pyramidal H_2PP Triplet Structures[a]

	planar n–π^* $^3A_2$	pyramidal n–π^* $^3A''$	planar π–π^* $^3A_1$	pyramidal π–π^* $^3A'$
r_e(PP)	2.117	2.218	2.211	2.186
r_e(PH)	1.382	1.409	1.397	1.404
θ_e(PPH)	123.0	97.6	128.6	121.6
θ_e(out-of-plane)	0.0	78.6	0.0	35.9
energy, SCF	29.5	2.5	61.7	58.3
energy, Cl	41.7	17.0	77.1	74.6
energy, Davidson cor	45.2	20.9	80.9	78.7
dipole moment	0.94	0.91	4.13	4.17
vibrational frequency, ν_e				
asym PH stretch	2733, B_2	2540, A''	2600, B_2	2547, A''
sym PH stretch	2691, A_1	2538, A'	2598, A_1	2551, A'
sym bend	1128, A_1	1210, A'	1268, A_1	1261, A'
wagging	887i, B_1	758, A'	624i, B_1	595, A'
asym bend	562, B_2	772, A''	567, B_2	658, A''
PP stretch	550, A_1	477, A'	380, A_1	409, A'

[a] All properties were obtained with the DZ+P basis set. See Table 11 footnote for units, etc.

illustrates the relative energies of the various triplet structures that are secondary minima on the potential energy surface.

For H_2PP linkage the n–π^* triplets fall below the π–π^* triplets of comparable structure. This is consistent with the SCF orbital energies in the closed-shell structures (Table III). The pyramidal n–π^* triplet lies so low that it actually falls below the closed-shell planar H_2PP structure, the difference in DZ+P Davidson corrected CI energies being 7.2 kcal/mol. Thus it appears that diphosphinylidene has a triplet ground state.

For diazene, the existence of a skewed ^3B state has been predicted in previous theoretical studies. Its torsion angle has been reported as 96.2[56] and 94.7°.[23] The pyramidal $^3A''$ state of H_2NN is also known. Its out-of-plane angle has been calculated to be 43.7° (decreasing to 21° when correlation effects are included)[57] and 50.8°.[56] Thus the corresponding H_2PP state has a much larger out-of-plane angle (78.6°). In contrast to H_2PP, the triplet state of H_2NN lies above the closed-shell planar singlet; different calculations place the energy difference at 14.8[57] and 10.5 kcal/mol.[56]

Other isovalent molecules with which diphosphinylidene may be compared include formaldehyde, H_2CO, and thioformaldehyde, H_2CS. Formaldehyde also has pyramidal structures for its n–π^* and π–π^* triplets, with out-of-plane angles of about 41 and 35°, respectively.[53,29] On the other hand, thioformaldehyde has an n–π^* triplet that is either planar or nearly so.[54]

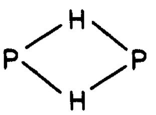
Table IX. Properties of Some Doubly Bridged Structures[a]

	rhombus, DZ basis	rhombus, DZ+P basis	boat, DZ+P basis
r_e(PP)	2.678	2.457	2.221
r_e(PH)	1.668	1.581	1.616
θ_e(PHP)	106.8	102.0	86.8
θ_e(out-of-plane)	0.0	0.0	101.1
energy, SCF	89.0	106.6	96.7
energy, CI	102.3	109.7	93.5
energy, Davidson cor	105.0	110.5	92.8
dipole moment	0.00	0.00	0.29
vibrational frequency, ν_e			
sym ring stretch	1627, A_g	1895, A_g	1886, A_1
asym HPH bend	1212, B_{3u}	1530, B_{3u}	954i, B_1
asym PHP bend	1137, B_{2u}	1526, B_{2u}	1456, B_2
sym bend	412, A_g	451, A_g	1094, A_1
asym ring stretch	391, B_{1g}	1337, B_{1g}	397i, A_2
ring puckering	174, B_{1u}	597i, B_{1u}	467, A_1

[a] For units, etc., see the footnote to Table I1.

Bridged Structures

By analogy with the unusual doubly bridged SiH_2Si molecule,[12,13] one might expect to find a stable PH_2P structure. We have examined this possibility by studying both the planar rhombus (**6**) and nonplanar boat (**7**) forms. This work had a promising start; with a DZ basis set, a closed-shell rhombic structure (constrained to D_{2h} symmetry) is found that has only real vibrational frequencies. However, when polarization functions are added, the ring-puckering frequency becomes imaginary, indicating the existence of a boat form of lower energy. When the geometry of that structure (constrained to C_{2v} symmetry) is optimized, its ring-puckering frequency is real, but now two other frequencies are imaginary. The properties of these three structures are listed in Table IX.



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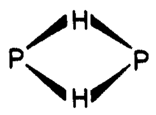

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We also considered a variety of other structures (closed shell with different orbital occupations, triplets, open-shell singlets) and methods (TCSCF, adding an additional set of polarization functions), but all of the rhombic and boat forms thus examined have at least one imaginary frequency. We are forced to conclude that, presumably because of the additional pair of electrons in the H_2P_2 molecule, phosphorus is distinctly dissimilar to silicon with respect to formation of a doubly bridged structure of formula H_2X_2.

In the course of this work we noticed a curious feature of the molecular orbital occupations in some of the triplet states. For the closed-shell rhombus the orbital energies are in the order $2b_{1g}$

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Table X. Transition States between Cis and Trans Closed-Shell Structures[a]

	rotation ^1A	inversion $^1A'$
r_e(PP)	2.232	1.974
r_e(PH)	1.414	P_1H_1, 1.421; P_2H_2, 1.379
θ_e(PPH)	95.1	$P_2P_1H_1$, 100.8; $P_1P_2H_2$, 177.0[b]
θ_e(torsion)	90.6	180.0
energy, SCF	31.0	68.7
energy, Cl	33.6	67.1
energy, Davidson cor	33.8	66.2
dipole moment	0.95	1.03
vibrational frequency, ν_e		
ν_1	2502, A (sym PH stretch)	2726, A′ (P_2H_2 stretch)
ν_2	2501, B (asym PH stretch)	2441, A′ (P_1H_1 stretch)
ν_3	805, B (asym bend)	982, A′ ($P_2P_1H_1$ bend)
ν_4	802, A (sym bend)	676, A′ (PP stretch)
ν_5	474, A (PP stretch)	64, A″ (torsion)
ν_6	951i, A (torsion)	1325i, A′ ($P_1P_2H_2$ bend)

[a] All properties were obtained with the DZ+P basis set. TCSCF was used for the rotation transition state. Its energy is given relative to the energy of the *trans*-HPPH closed-shell structure obtained by the same method. See Table II footnote for units, etc. [b] Note that H_1 and H_2 lie on opposite sides of the PP axis.

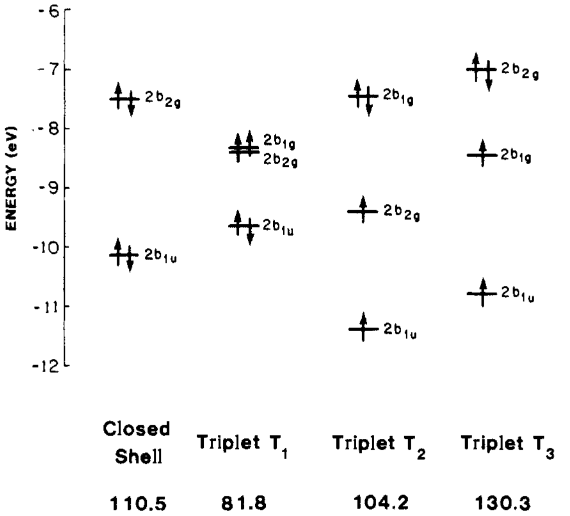


Figure 2. Molecular orbital energies of PH_2P with rhombic structures in closed-shell and triplet states, all with a DZ+P basis set. Davidson corrected energies for each state in kcal/mol relative to the *trans*-HPPH closed-shell ground state are listed at the bottom.

(LUMO) > $2b_{2g}$ (HOMO) > $2b_{1u}$ (2HOMO).[58] The lowest triplet state (T_1) has, as expected, singly occupied $2b_{1g}$ and $2b_{2g}$ orbitals. But the next triplet (T_2) has a double excitation to a doubly occupied $2b_{1g}$ orbital, leaving the $2b_{2g}$ and $2b_{1u}$ orbitals singly occupied. The third triplet (T_3) has the occupancy expected for T_2. Figure 2 illustrates the orbital occupancy of these states. This same pattern occurred with both the DZ and DZ+P basis sets. (The open-shell singlet states show a normal energy pattern, with well-spaced relative Davidson corrected energies of 97.7, 143.7, and 174.2 kcal/mol.)

As an extenuating circumstance we note that, in the closed-shell rhombus structure, the $2b_{1g}$ LUMO must not lie very far above the $2b_{2g}$ HOMO. With the TCSCF method their occupations are 0.421 and 1.579 electrons, respectively.

Transition States

For each pair of closely related structures, we have studied the transition state between them. Each transition state is characterized by zero energy gradients, and thus the same methods used to find potential minima suffice to determine the transition-state structures. Of course, each transition state must have an imaginary vibrational frequency for motion along the reaction coordinate. Where there are symmetry constraints, additional imaginary frequencies may occur; one such case is described below.

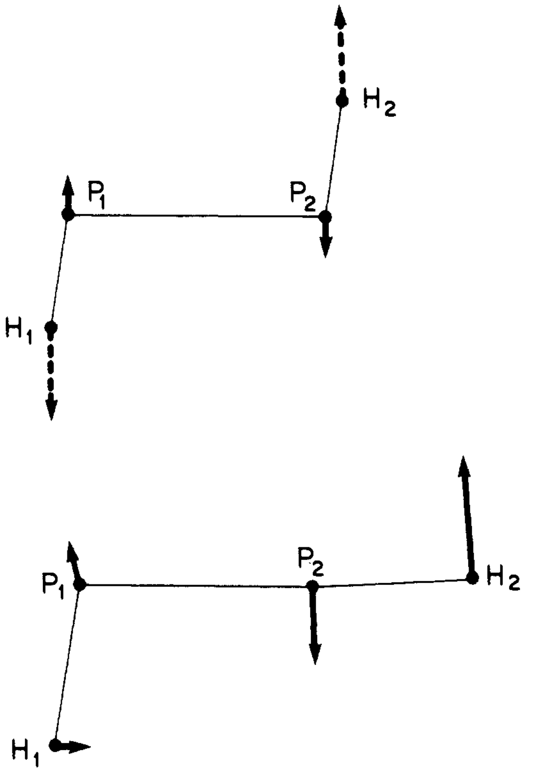
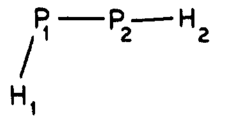


Figure 3. Normal modes for motion along the reaction coordinates of the rotation (top) and inversion (bottom) transition states. For clarity, vectors representing motion of the phosphorus atoms have been magnified 10-fold. The rotation transition state is projected onto the plane perpendicular to the twofold symmetry axis. In the phase shown here, P_1 and P_2 are moving up, while H_1 and H_2 are moving down.

Closed-Shell *cis*-HPPH-*trans*-HPPH Isomerization. Conversion between the closed-shell cis and trans structures may occur either by internal rotation about the P–P bond, or by a planar reaction path ("inversion") where one hydrogen atom revolves around its phosphorus neighbor from one stable position to the other. The rotation transition state has a skewed structure, **4**. The inversion transition state has a planar structure, **8**. Table



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X lists the geometries and other properties of these transition states,

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(58) If the phosphorus nuclei lie along the *z* axis and the hydrogen nuclei lie along the *y* axis, then the orbitals may be described as follows: LUMO, π_y^*; HOMO, π_x^*; 2 HOMO, π_x.

Table XI. Stationary Points between Closed-Shell H_2PP and *trans*-HPPH Structures[a]

	nonplanar ^1A	planar $^1A'$
r_e(PP)	2.062	1.978
r_e(PH)	P_1H_1, 1.427; P_2H_2, 1.590	P_1H_1, 1.429; P_1H_2, 1.472
θ_e(PPH)	$P_2P_1H_1$, 105.1; $P_1P_2H_2$, 51.6	$P_2P_1H_1$, 126.7; $P_2P_1H_2$, 67.4
θ_e(torsion)	112.1	180.0
energy, SCF	52.3	88.3
energy, CI	52.6	78.1
energy, Davidson cor	52.7	74.2
dipole moment	1.51	1.48
vibrational frequency, ν_e[b]		
ν_1	2393, A, 11	2345, A′, 11−12
ν_2	1780, A, 22+122	2161, A′, 12+11
ν_3	1115, A, T−122+22	849, A′, 211−PP
ν_4	909, A, 211	710, A′, PP
ν_5	625, A, PP	1133i, A″, T
ν_6	1229i, A, T+122−22	2276i, A′, 212

[a] All properties were obtained with the DZ+P basis set. See Table II footnote for units, etc. [b] Symbols for changes in internal coordinates: PP stretch, PP; P_1H_1 stretch, 11; P_1H_2 stretch, 12; P_2H_2 stretch, 22; $P_2P_1H_1$ bend, 211; $P_1P_2H_2$ bend, 122; $P_2P_1H_2$ bend, 212; torsion, T. Where motion of more than one internal coordinate makes a significant contribution to the normal mode, they are listed in order of decreasing importance. Plus and minus signs indicate relative phases. (The sign of a phase is taken as positive when the internal coordinate increases.)

and Figure 3 illustrates each transition state's normal mode (motion along the reaction coordinate) for the imaginary vibrational frequency.

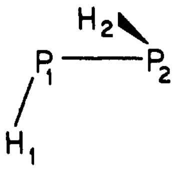
Because the cis and trans structures correlate with skewed structures having different orbital occupations (trans → $9a^27b^2$, cis → $8a^28b^2$), it is necessary to apply the TCSCF method to the rotation transition state. The resulting occupation numbers for the two orbitals involved, 9a and 8b, are almost equal (1.004 and 0.996 electron, respectively), consistent with the torsion angle (90.6°) and the "biradical" character expected for this transition state.

For diphosphene, internal rotation presents a much lower energy barrier than inversion, a conclusion also reached in other investigations.[10,21,23] We find a rotation barrier that is only about half the inversion barrier, the Davidson corrected energies being 33.8 vs. 66.2 kcal/mol. In spite of its higher energy, the inversion transition state has a torsion frequency that is real, though barely so (64 cm^{-1}). This result implies that the inversion transition state lies in a shallow potential well, separated from the rotation transition state by a region of higher potential energy.

An experimental study by laser irradiation of a substituted diphosphene, R_2P_2, where R is the very bulky 2,4,6-tri-*tert*-butylphenyl group, has shown that the activation free energy for the cis to trans conversion is only 20.3 kcal/mol at 0 °C.[59] It is not surprising that this result is much smaller than our calculated diphosphene barrier height from the cis side, which is 33.8 − 3.5 = 30.3 kcal/mol (using Davidson corrected energies in Tables X and II). One would expect a large steric strain in the cis isomer of the substituted compound, as pointed out by Schmidt and Gordon.[23] With the aid of two assumptions one can, in fact, combine these two results to obtain an estimate for the energy difference between the cis and trans isomers of the substituted diphosphene. These assumptions are that: (a) the activation free energy is approximately equal to the energy difference between the cis isomer and the rotation transition state, i.e., entropy effects are negligible; and (b) steric effects and other substitutional effects are negligible in the trans isomer and in the rotation transition state. The energy differences in R_2P_2 are then: barrier − trans, 33.8; barrier − cis, 20.3; cis − trans, 33.8 − 20.3 = 13.5 kcal/mol. While the assumptions involved are admittedly rather simplistic, this result does not seem unreasonable.

Diazene, HN=NH, shows very different behavior from diphosphene; the inversion barrier is significantly lower than the rotation barrier.[23,50,56,60–64] Schmidt and Gordon have made the very reasonable suggestion that this difference between diazene and diphosphene is caused by the relative weakness of the P–P π bond compared to the N–N π bond, combined with the tendency of phosphorus to have larger inversion barriers than nitrogen.[23]

Closed-Shell H_2PP–*trans*-HPPH Isomerization. Between the closed-shell H_2PP and trans structures, both planar, one might well expect to have a planar transition state, but in fact the transition state of lowest energy, **9**, is nonplanar with a torsion angle of 112.1°. If the transition state is constrained to planar symmetry, **10**, then the energy is much higher (DZ+P Davidson corrected CI, 74.2 kcal/mol, compared to 52.7 kcal/mol for the nonplanar transition state) and the torsion frequency is imaginary, giving this structure two imaginary frequencies. Furthermore, this stationary point occurs closer to the H_2PP structure, so much so that the P_1H_2 bond length is much shorter than the P_2H_2 bond length (1.472 vs. 1.961 Å). For comparison, in the nonplanar transition state the bond lengths are: P_1H_2, 1.645; P_2H_2, 1.590 Å.



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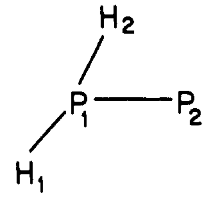

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Table XI lists the properties of the two stationary points. Where motion of more than one internal coordinate makes a significant contribution to the normal mode, they are listed in order of decreasing importance; plus and minus signs indicate relative phases. Figure 4 shows the normal modes for the imaginary vibrational frequencies (in the case of the planar structure, the higher imaginary frequency).

As the reason for the unusual (nonplanar) geometry of transition state **9**, we suggest attraction of the transiting proton to the high electron density of the P–P π bond. In support of this explanation, we note that in going from the planar to the nonplanar transition state, the main effect on the valence MO energies is a large change in the energy of the π MO. In the constrained planar transition state this molecular orbital is the second HOMO, lying at −9.85 eV. In the nonplanar transition state (C_1 symmetry) there is no π MO per se, but the third HOMO at −12.26 eV exhibits three-center bonding which involves the p_z orbitals of both phosphorus atoms and the s orbital of the H_2 hydrogen atom; it includes P_1–H_1 bonding as well. (The x axis is taken along the PP bond, and the z axis is taken perpendicular to the $H_1P_1P_2$

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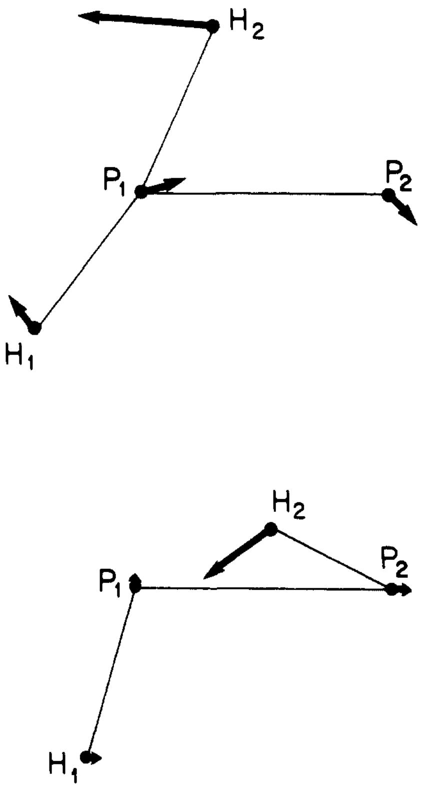
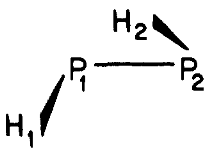


Figure 4. Normal modes for motion along the reaction coordinates of the planar (top) and nonplanar (bottom) H_2PP-*trans*-HPPH stationary points. For clarity, vectors representing motion of the phosphorus atoms have been magnified 10-fold. The nonplanar transition state is projected onto the $H_1P_1P_2$ plane. In the phase shown here, H_1 and H_2 are moving up, while P_1 and P_2 are moving down.

plane.) Thus we see that there is very strong stabilization of this MO (by 2.41 eV) in the nonplanar transition state.

Another curious feature of the nonplanar transition state is the direction in which the transiting proton is headed as it moves toward its equilibrium position in the H_2PP structure. As shown in Figure 4, its y coordinate is decreasing, even though it is already much smaller than in the H_2PP structure (0.469 Å in the transition state compared to 1.108 Å in H_2PP), and therefore it must eventually increase. Also, the dihedral angle is decreasing, even though eventually it must increase from the transition state value of 112.1 to 180° in H_2PP. In undergoing this motion the H_2 proton acts as though it is attracted toward a region directly above the P_1 phosphorus atom, and this is a region in which the P–P π bond has high electron density.

Triplet Skewed HPPH–Pyramidal H_2PP Isomerization. The lowest triplet HPPH structure is skewed (torsion angle 89.8°), and the lowest triplet H_2PP structure is pyramidal (out-of-plane angle 78.6°), so it is not surprising that the transition state between these structures, **11**, is nonplanar (torsion angle 86.7°). Its



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properties are listed in Table XII, and the normal mode for the imaginary vibrational frequency is shown in Figure 5. It is of interest that its relative energy is lower than that of the closed-shell transition state of similar geometry. (The Davidson corrected relative energies are 49.2 and 52.7 kcal/mol, respectively.)

Internal Rotation about P–P Bond of Triplet and Open-Shell Singlet HPPH. Some other transition states are implicit in the structures described in earlier sections. For triplet and open-shell singlet HPPH, where the skewed structure has the lowest energy (Tables IV and VII), one may argue on the basis of symmetry considerations that the planar cis and trans structures represent transition states between the two equivalent skewed forms (left and right rotation about the P–P bond).

Table XII. Transition State between Triplet Skewed HPPH and Pyramidal H_2PP Structures[a]

	nonplanar ^3A
r_e(PP)	2.197
r_e(PH)	P_1H_1, 1.412; P_2H_2, 1.594
θ_e(PPH)	$P_2P_1H_1$, 94.6; $P_1P_2H_2$, 48.5
θ_e(torsion)	86.7
energy, SCF	43.6
energy, CI	47.8
energy, Davidson cor	49.2
dipole moment	0.72
vibrational frequency, ν_e[b]	
ν_1	2518, A, 11
ν_2	1764, A, 22+122
ν_3	928, A, T+211
ν_4	746, A, 211–T
ν_5	506, A, PP
ν_6	2310i, A, 122–22

[a] All properties were obtained with the DZ+P basis set. See Table II footnote for units, etc. [b] See Table XI footnote for symbols.

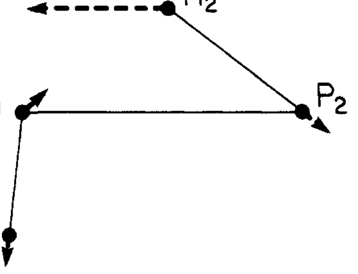

Figure 5. Normal mode for motion along the reaction coordinate of the triplet skewed HPPH–pyramidal H_2PP transition state. The structure is projected onto the xy plane, where the phosphorus atoms lie on the x axis, and the z axis bisects the dihedral angle. For clarity, vectors representing motion of the phosphorus atoms and H_1 have been magnified 10-fold. In the phase shown here, P_1 is moving up, while P_2, H_1, and H_2 are moving down.

For example, the lowest triplet energy surface for HPPH linkage has two minima of the same energy (the two equivalent skewed ^3B structures) at torsion angles of 89.8° left and right from the cis structure. It also has two maxima, one at 0° (cis π–π^* triplet) and one at 180° (trans π–π^* triplet). The data in Table VII show that, using Davidson corrected energies, the trans maximum lies 7.8 kcal/mol above the minima, and the cis maximum is slightly higher, at 10.0 kcal/mol above the minima.

For the open-shell singlet structures of HPPH linkage, we recall that the skewed ^1B structure correlates with the trans n–π^* singlet and with the cis π–π^* singlet (see Table IV). Therefore, there are two minima of the same energy (the two equivalent skewed ^1B structures) at torsion angles of 109.2° left and right from the cis structure. Between these minima there is a trans maximum (torsion angle 180°) at 6.4 kcal/mol, and a cis maximum (torsion angle 0°) at 54.2 kcal/mol (using the Davidson corrected energies in Table IV).

Inversion of Triplet and Open-Shell Singlet H_2PP. Following a similar line of reasoning, the planar triplet and open-shell singlet H_2PP structures are transition states between two equivalent pyramidal forms. Using the Davidson corrected energies in Table VIII, we see that the planar n–π^* triplet lies 24.3 kcal/mol above two equivalent pyramidal $^3A''$ forms, while the planar π–π^* triplet lies only 2.2 kcal/mol above two equivalent pyramidal $^3A'$ forms. In the open-shell singlet case, the planar n–π^* singlet is 15.3 kcal/mol above two equivalent pyramidal $^1A''$ forms (Davidson corrected energies from Table V).

Comparing the two n–π^* inversion barriers, singlet and triplet, we see that the triplet barrier is much higher than the singlet (24.3 vs. 15.3 kcal/mol). A somewhat similar situation occurs with the n–π^* singlet and triplet inversion barriers of formaldehyde, H_2CO. Although there both energy barriers are much lower, the triplet barrier of 762 cm^{-1} or 2.18 kcal/mol is again higher than the singlet barrier of 316 cm^{-1} or 0.90 kcal/mol.[53]

Comparison of Results with Different Basis Sets

A controversy of long standing surrounds the question of the extent to which d orbitals influence the chemistry of phosphorus.[65] As we have used both DZ and DZ+P basis sets for each structure, it is of interest to compare our results to see if any generalizations can be made.

When polarization functions (phosphorus d orbitals and hydrogen p orbitals) are added to the DZ basis set, with one exception[66] the optimum bond lengths always decrease, but in general bond lengths and bond angles do not change very much. Taking the closed-shell trans ground state as an example, the PP bond length decreases ~4% (2.094 to 2.004 Å), the PH bond length decreases ~1% (1.425 to 1.413 Å), and the PPH bond angle decreases ~1% (97.0 to 96.0°).

Other properties tend to be somewhat more sensitive to the basis set. For example, the dipole moment of the closed-shell cis state decreases from 2.03 to 1.50 D on going from a DZ to a DZ+P basis. With one exception[67] the relative energies (SCF, CI, and Davidson corrected) of the various excited states always increase when polarization functions are added. As examples, consider the closed-shell cis state, where the relative energy (Davidson corrected) increases from 2.7 to 3.6 kcal/mol, and the trans n–π^* triplet, where the increase is from 44.0 to 52.6 kcal/mol.

Vibrational frequencies often do not change very much on going from the DZ to DZ+P basis sets, but in some cases the changes are large enough to give a qualitatively different picture of the state. We have already seen one example of this sort in Table IX, where the ring-puckering frequency of the doubly bridged rhombic structure changes from real to imaginary (174 to 597i cm^{-1}). Other examples include the trans n–π^* singlet, where the torsion frequency changes from 107 to 456i cm^{-1}, and the trans π–π^* singlet, where the change in torsion frequency is in the opposite direction (195i to 710 cm^{-1}).

Of course, DZ+P results are not in every known case more accurate than DZ results, and definitive conclusions must await comparisons with experimental data and/or more accurate theoretical work. Nevertheless, we are inclined to the view that in many cases polarization functions play an important quantitative role in the chemistry of the H_2P_2 system.

Concluding Remarks

In view of the paucity of experimental information on the H_2P_2 system, it is our hope that the results presented in this paper will be of use in suggesting experimental conditions under which diphosphene and diphosphinylidene in their various electronic states can be detected and their physical properties measured. This work should also be of assistance to experimentalists working on substituted diphosphenes; in the section on open-shell singlets we endeavored to relate our results to the visible and UV absorption spectra of substituted diphosphenes.

Comparisons with related molecules, such as diazene and formaldehyde, should be helpful in understanding the chemistry of those molecules. Many such comparisons have been included in this paper.

Finally, our study of the unusual nonplanar transition state between closed-shell H_2PP and *trans*-HPPH should be of aid in understanding the nature of 1,2-hydrogen shifts.

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Registry No. Diphosphene, 41916-72-7; diphosphinylidene, 90883-63-9.

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(66) For the planar stationary point, **10**, between closed-shell H_2PP and *trans*-HPPH, the P_1–H_1 bond length increases slightly (1.422 to 1.429 Å).

(67) For the nonplanar transition state, **9**, between closed-shell H_2PP and *trans*-HPPH, the relative energies decrease (SCF, 53.8 to 52.3; CI, 55.4 to 52.6; Davidson corrected, 54.2 to 52.7 kcal/mol).