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Potential energy profiles of the geometric isomerization and the thermal decomposition of diphosphene HP=PH in the ground and excited electronic states

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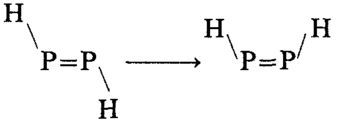
Summary. The geometric isomerization and the dehydrogenation of HP=PH in the ground and some low-lying excited states are investigated by theoretical calculations. The reaction paths are traced by either the CASSCF or UHF-SCF calculations using the 6-31G(d, p) basis functions, and the accompanying energy changes are calculated by the MRD-CI method employing the [5*s*3*p*1*d*]/[2*s*1*p*] basis functions. The barrier heights for the trans-to-cis isomerization, by the planar inversion and the nonplanar twisting, in the ground state are calculated to be 265 and 144 kJ/mol (with the vibrational zero-point energy corrections), respectively. The latter barrier is noticeably lower than the H–P and the P–P bond dissociation energies of *trans*-HP=PH (^1A_g), which are 304 and 271 kJ/mol, respectively. The ground-state HP_2 radical ($^2A'$), which is to be formed by the dehydrogenation of HP=PH, should suffer further decomposition into P_2 ($^1\Sigma_g^+$) and H with an activation energy of 139 kJ/mol. The lowest excited state of HP_2 is found to be a hydrogen-bridged 3π-electron system ($^2A_2$) having an isosceles triangle structure. It has proved to be formed by the dehydrogenation of the lowest excited singlet state (^1B) of HP=PH via a transition state which lies 194 kJ/mol above the ^1B state. The excited HP_2 ($^2A_2$) is state-correlated with P_2 ($^3\Delta_u$) + H.

Key words: Diphosphene – Diphosphenyl radical (HP_2) – Geometric isomerization – Isosceles triangle

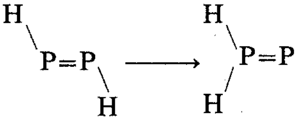
1 Introduction

Diphosphene HP=PH has already received much attention from a number of theoretical chemists [1–7]. It is now well recognized that the closed-shell ground state has two energy minima, the cis and trans-structures, the latter isomer being slightly more stable. In addition, the geometric isomerization of *trans*-HP=PH [2–5]



(1)

has been shown to be energetically more favorable than the 1,2-hydrogen shift isomerization [2, 3, 6, 7]:



(2)

It has also been clarified that the lowest triplet and singlet excited states are both skewed in structure conforming to C_2 symmetry. The existence of energy-minimum planar structures has also been suggested for some higher excited states [1, 2].

The present work is aimed at elucidating two points in a somewhat comprehensive manner. First, we scrutinize the potential energy profiles of a few low-excited states as well as the ground state of HP=PH with respect to the internal twisting angle. A search for energy-minimum structures in a systematic manner would be beneficial for a better understanding of the characteristics of HP=PH. We then consider the dehydrogenation process

$$H_2P_2 \rightarrow HP_2 + H \rightarrow P_2 + 2H \tag{3}$$

also in the ground and low-excited states. A knowledge of the thermal stability of H_2P_2 could serve as a useful guide for experimental studies of the chemistry of H_2P_2. Interestingly, the lowest excited state of the HP_2 radical has proved to be a 3π-electron system, which has an isosceles triangle (C_{2v}) structure. We will discuss the significance of this characteristic structure in relation to various hydrogen-bridged structures reported hitherto.

2 Method of calculations

2.1 *Cis–trans isomerization and the internal rotation*

The course of the cis–trans isomerization of the closed-shell ground state (^{1}A) was followed by the CASSCF procedure, in which six electrons are accommodated in the five active frontier orbitals (n_-, n_+, π, π^*, σ^*). The HONDO program [8] was used for this purpose. The internal rotation paths for the excited state (^{1}B, ^{3}B, ^{3}A) were traced for simplicity by the UHF-SCF procedure with the Gaussian 86 program package [9]. The basis sets used for all these SCF calculations are the conventional 6-31G(d, p) functions [10]. Since the geometries of 2^3B, 2^1A and 2^1B cannot be treated by SCF calculation, special expedience has been invoked. Thus, the optimal structures of the ^{3}A state were used for 2^1A, while for 2^1B and 2^3B their internal coordinates V were assumed to vary linearly from cis to trans with the torsional angle ϕ,

$$V = V_{\text{cis}} + \frac{\phi}{180}(V_{\text{trans}} - V_{\text{cis}}),$$

where V_{cis} and V_{trans} are the UHF-SCF optimized internal coordinates for the relevant excited states of the cis and trans isomers, respectively.

Multi-reference double-excitation configuration-interaction (MRD-CI) calculations were performed for all the SCF optimized geometries and the conventionally assumed structures. The Table MRD-CI program furnished by Buenker [11, 12] was used. Configurations were constructed from the molecular orbitals generated by the restricted Hartree–Fock calculations. The maximal dimension of the configurational space used was ca. 15 000. The MRD-CI energies were all subjected to the Langhoff–Davidson corrections [13] to estimate the full CI energies. The basis sets employed in these CI calculations were the contracted [5*s*3*p*1*d*]/[2*s*1*p*] functions due to McLean and Chandler [14] throughout. The second roots of the MRD-CI calculations were adopted as the CI energies for the 2^3B, 2^1A and 2^1B states.

2.2 Decomposition

Structures of the HP_2 radical were first treated by the UHF-SCF/6-31G(d, p) procedure, and their energies were then evaluated by the MRD-CI calculations employing the [5*s*3*p*1*d*]/[2*s*1*p*] basis functions. Furthermore, for more accuracy of the geometry of the $^2A_2$ state in particular, the energy-minimum point was located by conducting a set of MRD-CI calculations for various structures constrained to the C_{2v} symmetry.

For P_2 in the ground and excited states MRD-CI calculations were carried out by varying the interatomic distance. The P–P bond lengths corresponding to the CI energy minima were adopted as the equilibrium distances.

Decomposition paths were traced by the UHF-SCF procedure. CI computations were performed at several points on the SCF paths.

3 Results

3.1 Cis–trans isomerization of the ground state and the internal rotation of the excited states

3.1.1 Cis–trans isomerization of the ground state. Two distinct paths are conceivable for the cis–trans isomerization of HP=PH in the ground state [2, 3]. One is due to the in-plane inversion (C_s), while the other involves the internal twisting motion (C_2). The transition state geometries located by the present MCSCF procedure for the inversion path (TS1) and the twisting path (TS2) are shown in Fig. 1. Both the TS geometries are essentially in good agreement with previous results obtained by similar MCSCF calculations [2, 3].

The relative energies of the ground states (cis and trans) of HP=PH and the transition states (TS1 and TS2) of the cis–trans isomerization calculated by the present MRD-CI calculations are collected in Table 1. According to the present MRD-CI calculations, *trans*-HP=PH (^1A_g) is predicted to be more stable than *cis*-HP=PH ($^1A_1$) by 11.0 kJ/mol. The energy gap obtained is somewhat smaller than previous results (14.6 [2], 16.7 [3], and 15.1 [4] kJ/mol). The barrier heights obtained here for the two types of the trans–cis isomerization, i.e. inversion (TS1) and internal rotation (TS2), are 274 and 152 kJ/mol, respectively. The results are to be compared with previous results (277 and 141 kJ/mol [2], 301 and 151 kJ/mol [3], 278 and 131 kJ/mol [4, 5], respectively). Upon the vibrational zero-point energy corrections, these TS barrier heights are lowered to 265 and 144 kJ/mol, respectively.

3.1.2 Planar excited structures. The modes of electronic excitation investigated in this work are illustrated in Fig. 2. Geometries of the various excited states, both singlet and triplet, have been optimized by the UHF-SCF procedure under

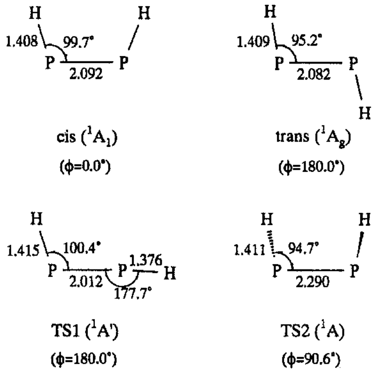


Fig. 1. Geometries of the ground state (cis and trans) of HP=PH and of the transition states (TS1 and TS2) of the cis–trans isomerization. All the geometries were obtained by the 6-electron 5-orbital CASSCF procedure employing the 6-31G(d, p) basis functions. The bond lengths are given in units of Å. The symbol ϕ stands for the torsional angle

Table 1. Relative energies calculated for HP=PH by the MRD-CI/[5*s*3*p*1*d*] method

States	ΔE_{CI}[a]	ΔE_{CI} + vib[b]
trans	(0)	(0)
cis	11.0	10.1
TS1	274	265
TS2	152	144

[a] Relative CI energies given in units of kJ/mol
[b] With the vibrational zero-point energy corrections made by the SCF/6-31G(d, p) calculations

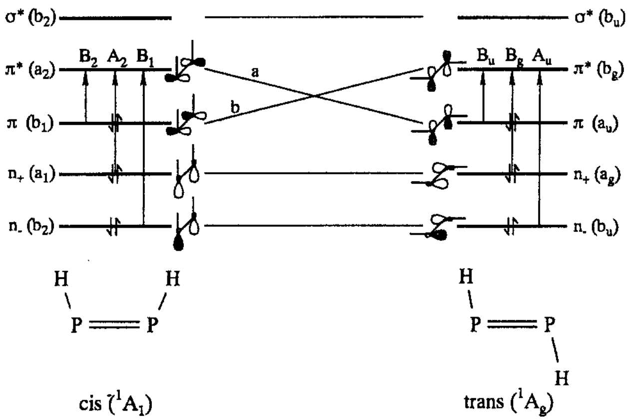


Fig. 2. Modes of the electronic excitations of *cis* and *trans*-HP=PH

a constraint of planarity. Some of them can in reality correspond to the potential energy minima, but others do not. All the planar stationary geometries obtained and the excitation energies thereof are collected in Table 2.

Except for the $^3B_1$, ^3A_u, $^1B_1$, ^1A_u states, which are all caused by the one-electron excitations from the n_-(b_2 and b_u) orbitals, all of the excited states have already been investigated by Allen et al. [1,2]. Compared with the closed-shell ground states ($^1A_1$ and ^1A_g), the P–P bond lengths of the π–π^* excited states (B_2 and B_u) are elongated by ca. 0.15–0.23 Å. Electron excitations from the lone-pair n_+ (a_1 and a_g) orbitals exert greater influence on the cis structure than on the trans. Thus, the P–P bond lengths for the cis structure in the n_+–π^* excited states ($^3A_2$, $^1A_2$) are as long as those in the π–π^* excited states ($^3B_2$ and $^1B_2$), while the lengths in the trans form (^3B_g and ^1B_g) are clearly shorter than those in the cis form. On the contrary, the P–P bond lengths in the n_-–π^* excited states ($^3B_1$ and $^1B_1$) of the cis structure are even shorter than the length in the ground state ($^1A_1$), while those in the corresponding states (^3A_u, ^1A_u) for the trans structure are clearly longer than the length in the ground state (^1A_g). The relatively large HPP angle of the n_-–π^* excited states ($^3B_1$ and $^1B_1$) of the cis form will have some bearing on their uniquely shorter P–P bond lengths.

As far as these planar structures are concerned, the triplet π–π^* states ($^3B_2$, ^3B_u) are the most stable. The second most stable are the triplet n_+–π^* states for both the cis and trans structures ($^3A_2$, ^3B_g). The corresponding singlet n_+–π^* states ($^1A_2$, ^1B_g) are the lowest singlet excited state. It is noteworthy, however, that, although ^1B_g is the third lowest excited state for the trans form, $^1A_2$ is slightly less

Table 2. Excited states of the planar (cis, trans) structures of HP=PH calculated by the UHF-SCF/6-31G(d, p) procedure

States	Extremum[a]	r (P–P)[b]	r (H–P)[b]	θ (HPP)[c]	ΔE_{CI}[d]
Triplet states					
cis					
$^3B_2$ ($^3\pi$–π^*)	1	2.284	1.408	97.8	191
$^3A_2$ ($^3n_+$–π^*)	0	2.228	1.408	99.8	314
$^3B_1$ ($^3n_-$–π^*)	0	1.987	1.397	121.5	354
trans					
^3B_u ($^3\pi$–π^*)	1	2.272	1.408	94.3	182
^3B_g ($^3n_+$–π^*)	0	2.094	1.398	105.6	236
^3A_u ($^3n_-$–π^*)	0	2.123	1.406	104.9	471
Singlet states					
cis					
$^1A_2$ ($^1n_+$–π^*)	0	2.248	1.408	101.0	368
$^1B_1$ ($^1n_-$–π^*)	1	2.000	1.417	117.7	417
$^1B_2$ ($^1\pi$–π^*)	1	2.216	1.406	98.7	486
trans					
^1B_g ($^1n_+$–π^*)	1	2.118	1.401	105.6	298
^1B_u ($^1\pi$–π^*)	1	2.207	1.406	94.7	470
^1A_u ($^1n_-$–π^*)	0	2.130	1.419	105.0	479

[a] The entities 0 and 1 indicate that the states calculated fall on the energy minimum and maximum, respectively

[b] Bond lengths given in units of Å

[c] Bond angles given in units of degree

[d] Relative to *trans*-HPPH (^1A_g), given in units of kJ/mol

stable than the triplet n_-–π* state ($^3B_1$) as the third lowest excited state of the cis structure.

3.1.3 Potential energy profiles of the excited states. In Fig. 3, variations in the CI potential energies for the six excited states as functions of the torsional angle ϕ are illustrated. Curves drawn in full lines indicate the energy variations for the singlet states, while those shown in dotted lines are for the triplet states. For the sake of reference, the potential energy profile for the ground state traversing the already mentioned transition state (TS2) has been included.

As has already been mentioned, the trans structure of closed-shell ground states (^1A_g) is more stable than the cis structure ($^1A_1$) by 11.0 kJ/mol. The barrier height for the cis–trans isomerization is 152 kJ/mol relative to the trans state. The energy minimum of the lowest triplet state (^3B) correlates with the planar cis and trans $^3\pi$–π* excited states ($^3B_2$, ^3B_u). However, the energy minimum of the open-shell singlet state (^1B) is correlated with the trans $^1n_+$–π* excited state (^1B_g) but with the $^1n_-$–π* state ($^1B_1$) of the cis structure. The skewed ^3B and ^1B energy-minimum structures are shown in Fig. 4. The excitation energies ΔE_{CI} are 157 and

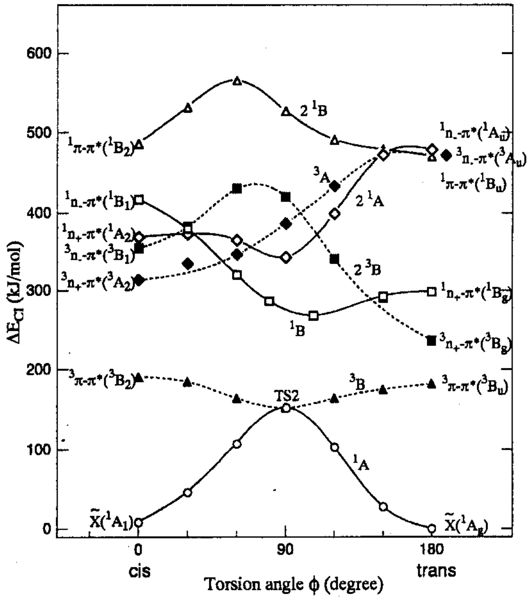


Fig. 3. Potential energy profiles calculated for the nonplanar twisting motion around the P–P bond of HP=PH in the ground and excited states. Calculations were carried out by the MRD-CI method using the [5*s*3*p*1*d*]/[2*s*1*p*] basis functions

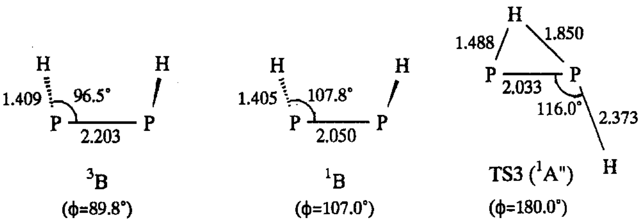


Fig. 4. Geometries of the lowest triplet (^3B) and singlet (^1B) excited states for HP=PH and of the transition state (TS3) for the process H_2P_2 (^1B) → HP_2 ($^2A_2$) + H. All the geometries were optimized by the UHF-SCF procedure using the 6-31G(d, p) basis functions

266 kJ/mol, respectively, which are reduced to 152 and 261 kJ/mol, respectively, upon the vibrational energy corrections.

The second lowest triplet excited state of the cis structure is ${}^3n_+\text{–}\pi^*\,({}^3A_2)$, which is an energy minimum. As the torsional angle ϕ increases, its energy increases monotonically until it reaches the ${}^3n_-\text{–}\pi^*\,({}^3A_u)$ state of the trans form. Likewise, the second lowest triplet state ${}^3n_+\text{–}\pi^*\,({}^3B_g)$ of the trans structure correlates with the triplet third excited state ${}^3n_-\text{–}\pi^*\,({}^3B_1)$ of the cis structure. Both these triplet states are energy minima, and there exists a transition state at the torsional angle of ca. 70°.

The ${}^1\pi\text{–}\pi^*$ excited states (${}^1B_2$, ${}^1B_u$) are comparatively of high energy. Both states, however, appear to be local energy minima against the torsional angle.

3.2 Thermal decomposition

3.2.1 HP_2 radicals. Geometries of the HP_2 radical optimized by the UHF-SCF procedure are shown in Fig. 5. The ground state (${}^2A'$) is a 2π-electron system. Because the geometries are influenced by the electron correlation effects, we further optimized them by MRD-CI calculations. As a result, the P–P bond of the ground state has been elongated to 2.010 Å.

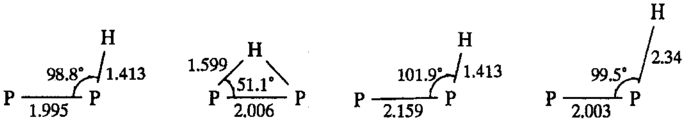
The lowest excited state is found to be a 3π-electron system having the isosceles triangle (C_{2v}) structure, there existing no asymmetric (C_s) energy-minimum structure. Vibrational analysis of the C_{2v} structure showed that all frequencies are real. The HPP bending frequency is 838 cm^{-1}. Reoptimization of the ${}^2A_2$ (C_{2v}) structure by MRD-CI calculations has led to the result such that the P–P bond length is 2.015 Å and the HPP angle is 51.0°. The excitation energy ΔE_{CI} at the CI optimized geometry (${}^2A_2$) was calculated to be 143 kJ/mol.

The second excited state (${}^2A''$) is a 1π-electron system. The P–P bond length in this state is appreciably larger than in the 2π- and 3π-electron systems. The excitation energy ΔE_{CI} is evaluated to be 277 kJ/mol.

3.2.2 P_2. The optimal bond lengths r and the excitation energies ΔE of P_2 in various excited states are shown in Table 3. Agreements of the calculated values of r and ΔE with the experimental data [15] are satisfactory.

To the best of our knowledge, no experimental data for the second lowest excited state (${}^3\Delta_u$) have been reported as yet. Experimental determinations of r and ΔE for this state are eagerly awaited.

3.2.3 Potential energy profiles of decomposition. The potential energy profiles of the thermal dehydrogenation of HP=PH to P_2 + 2H via HP_2 + H are shown in Fig. 6. The binding energies of the H–P and P–P bonds of *trans*-HP=PH (${}^1A_g$) are



${}^2A'$ (2π) ${}^2A_2$ (3π) ${}^2A''$ (1π) TS4 (${}^2A'$)

Fig. 5. Geometries of the HP_2 radicals optimized by the UHF-SCF procedure using the 6-31G(d, p) basis functions

Table 3. Bond length r and excitation energy ΔE of P_2 calculated by the MRD-CI method employing the [$5s3p1d$] basis functions

States	r (Å)[a]	ΔE (kJ/mol)[a]
$^1\Sigma_g^+$	1.918 [1.893]	(0)
$^3\Sigma_u^+$	2.108 [2.085]	207 [225]
$^3\Delta_u$	2.086	301
$^3\Pi_g$	1.994 [1.970]	345 [337]
$^3\Sigma_u^-$	2.077 [2.052]	360 [341]
$^1\Pi_g$	2.013 [1.989]	426 [413]

[a] The data given in brackets are the experimentally obtained values [15]

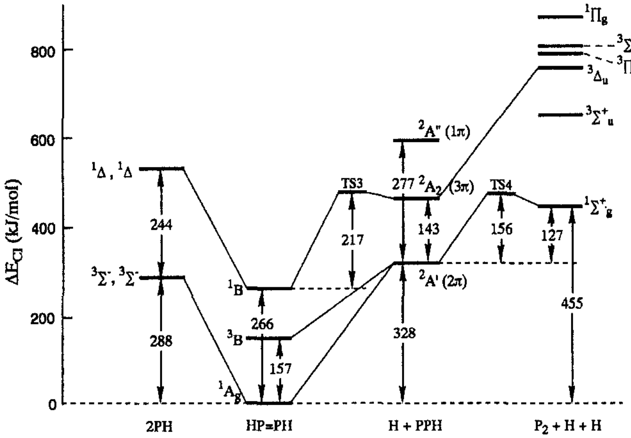


Fig. 6. Potential energy profiles of the decomposition processes of HP=PH calculated by the MRD-CI method employing the [$5s3p1d$]/[$2s1p$] basis functions

evaluated to be 328 and 288 kJ/mol, respectively, which are reduced respectively to 304 and 271 kJ/mol upon vibrational zero-point energy corrections. No doubt, HP=PH in its ground state will be more liable to suffer the P–P bond cleavage than dehydrogenation.

The dehydrogenation of the triplet HPPH (^3B) leads to the HP_2 ($^2A'$) radical with no activation barrier. The dehydrogenation of the open-shell singlet-HPPH (^1B), on the other hand, was found to lead to the excited HP_2 ($^2A_2$), which has the isosceles triangle structure. The transition state (TS3) has been located by the UHF-SCF procedure. It is planar in structure, as is shown in Fig. 4. The imaginary frequency of vibration is calculated to be $629i$ cm^{-1}. MRD-CI calculation has given the activation energy 217 kJ/mol (194 kJ/mol with the vibrational zero-point energy correction). Apparently, the dehydrogenation path via TS3 is energetically more favorable than the P–P bond cleavage giving 2PH ($^1\Delta$).

The H–P bond scission of the HP_2 radical in its ground state ($^2A'$) gives rise to the ground-state P_2 ($^1\Sigma_g^+$). Tracing of the bond breaking process by MRD-CI calculations has given a transition state (TS4) at the H–P distance 2.34 Å, as is shown in Fig. 5. The barrier height obtained was 156 kJ/mol (139 kJ/mol by zero-point energy correction).

The first excitation state ($^2A_2$) of the HP_2 radical leads to P_2 ($^3\Delta_u$) + H with no barrier top, when the dehydrogenation is assumed to proceed maintaining the C_{2v} symmetry all the way. It should be mentioned, however, that the P–P bond breaking process giving rise to HP ($^3\Sigma^-$) + P (^2P) seems to be slightly more favorable than the C_{2v} path; the product system HP ($^3\Sigma^-$) + P (^2P) is calculated to be 18 kJ/mol more stable than the other binary system P_2 ($^3\Delta_u$) + H.

4 Discussion

4.1 Crossings of the potential energy curves

As can be seen in Fig. 3, the potential energy curves for the 2^3B and ^3A states cross each other at $\phi \cong 100°$. A similar crossing is discernible between the ^1B and 2^1A states at $\phi \cong 30°$. The situations are the consequences of the alteration in symmetry type of the π and π^* orbitals for the cis and trans forms of HP=PH. Thus, the π^* orbital is of the a_2 symmetry in cis but is of the b_g symmetry in trans (Fig. 2). Because of this symmetry change, the n_+–π^* excited state has the A_2 symmetry in cis, while it has the B_g symmetry in trans. Likewise, the n_-–π^* excited state has the B_1 symmetry in cis but is of the A_u symmetry in trans. Since the n_+–π^* excited states should generally be more stable than the n_-–π^* excited states, the state energies should necessarily be such that $A_2(n_+–\pi^*) < B_1\ (n_-\pi^*)$ in the cis structure whereas $B_g(n_+–\pi^*) < A_u\,(n_-–\pi^*)$ in the trans counterpart. It is natural, therefore, that the A and B states cross each other at certain torsional angles in the course of the cis–trans isomerization.

Incidentally, the B_1 states in cis correlate with the B_g states in trans. Therefore, the open-shell singlet energy minimum (^1B) should be correlated with the $^1B_g(^1n_+–\pi^*)$ state of the trans structure but is with the far less stable $^1B_1(^1n_-–\pi^*)$ state in the cis structure. We would like to mention this point with some emphasis, particularly because Allen et al. [2] seem to have overlooked the position of the $^1B_1$ ($^1n_-–\pi^*$) state.

One remark seems to be in order in connection with the above issue. That is, the term "crossing" used above should better be understood as meaning the conical crossing. The potential energy profiles shown in Fig. 3 are the curves calculated by assuming that the four-atomic system in question changes its geometry strictly under the constraint of the C_2 symmetry. However, the system may well lose its symmetry in the regions of "crossing" to effect avoided crossings. Because any close examination of this point is out of the scope of this work, we have left it out entirely in the present context.

4.2 Bridged structure of the excited HP_2 radical

As has been described in the foregoing section, the lowest excited state of the HP_2 radical ($^2A_2$) takes on an isosceles triangle structure. This characteristic structure is originated from its electronic structure characterized by the 3π-electron configuration. Since HP_2 ($^2A_2$) is state-correlated with P_2 ($^3\Delta_u$) + H, it can be considered as arising from the addition of a hydrogen atom onto P_2 ($^3\Delta_u$). When the H atom approaches P_2 ($^3\Delta_u$), there would be a stabilizing interaction between the 1*s* orbital of the H atom and the bonding π_{ux} orbital of one of the two component configurations of the $^3\Delta_u$ state of P_2, as is illustrated in Fig. 7. Such an interaction would be most favorable at a geometry of the maximal overlap between them. The result will be that the H atom is imbedded at a position equidistant from the two P atoms of P_2.

The above view could also be applied to P_2^+ ($^2\Pi_u$) in place of P_2 ($^3\Delta_u$). As can be seen in Fig. 7, the π_{ux} orbital in P_2^+ ($^2\Pi_u$) is also singly occupied, so that the cationic species $[HP_2]^+$ as an H atom adduct onto P_2^+ should take an isosceles bridged structure ($^1A_1$). In fact, Nguyen and Fitzpatrick [16] and Busch and Schoeller [17] have confirmed the bridged structure ($^1A_1$) of $[HP_2]^+$ by MP2 and MCSCF calculations, respectively.

The point common between HP_2 ($^2A_2$) and $[HP_2]^+$ ($^1A_1$) is that P_2 ($^3\Delta_u$) and P_2^+ ($^2\Pi_u$) as their components have by necessity only one electron in one of the bonding π_u orbitals. With an H atom added, it should allow the formation of a three-center two-electron bond. The antibonding π_g^* orbitals should remain

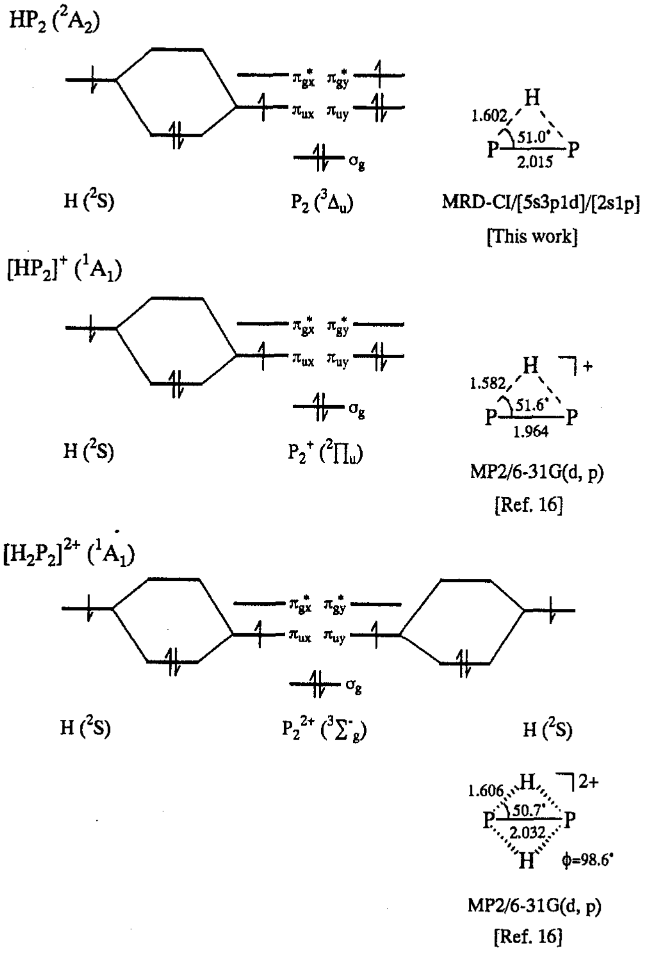


Fig. 7. Schematic orbital-interaction diagrams illustrating the formation of the H–P one-electron bonds

intact, and hence it is not important whether there is an electron in the π_{gy}^* orbital or not. In other words, it is not a general requisite that the compound should be a cation.

One may extend the above view further to $[H_2P_2]^{2+}$. The dication P_2^{2+} ($^3\Sigma_g^-$) has two bonding π_u orbitals, as is shown in Fig. 7. Each of these bonding orbitals will be capable of forming a three-center two-electron bond with one each additional H atom. Because the two bonding π_u orbitals are perpendicular to each other, it is expected that the two PHP planes lie nearly at right angles. Such a bibridged structure of $[H_2P_2]^{2+}$ ($^1A_1$) has been calculationally demonstrated by Nguyen and Fitzpatrick [16]. The important point here is that P_2^{2+} ($^3\Sigma_g^-$) as the component has only one electron in each of the two bonding π_u orbitals. Here again, the situation should not generally be confined to dicationic cases. The notable example of the bibridged structure of Si_2H_2 [18] clearly evidences this last statement.

5 Conclusions

1. The barrier heights for the thermal geometric isomerization of *trans*-HP=PH (^1A_g) are evaluated to be 265 and 144 kJ/mol for the inversion and the internal rotation pathways, respectively.
2. In the course of the internal rotation isomerization of H_2P_2 in excited states, there are crossings of the potential energy profiles between some of the A and B states.
3. The H–P and P–P binding energies of *trans*-HP=PH (^1A_g) are estimated to be 304 and 271 kJ/mol, respectively.
4. The lowest excited state of the HP_2 radical is a 3π-electron system having an isosceles triangle structure ($^2A_2$). It is to be formed by the dehydrogenation of the first excited singlet state (^1B) of HP=PH. The activation energy for the dehydrogenation is calculated to be 194 kJ/mol.

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