Closed-Shell vs Diradical States of Bis(methylene)phosphorane. Is the Phosphirane–Bis(methylene)phosphorane Interconversion a Pericyclic Reaction? A Theoretical Study

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The energy and structure of bis(methylene)phosphorane $HP(CH_2)_2$ have been calculated in its singlet closed shell planar ground state, on the one hand, and its lowest triplet pyramidal diradical state, on the other, using ab initio MP4/6-31G**//MP2/6-31G** method. The singlet–triplet gap (16.9 kcal mol^{-1}) is significantly lower than for the $HN(CH_2)_2$ analogous (22.8 kcal mol^{-1}). The same calculations have been performed on CH_3, NH_2 and BH_2 P-substituted compounds; the latter exhibit a rather low singlet–triplet separation (9.4 kcal mol^{-1}). The phosphirane–bis(methylene)phosphorane interconversion has been studied at the GVB/6-31G** level. The transition state (TS) shows a disrotatory conformation, contrary to Woodward–Hoffmann rules, with, however, weak rotational barriers of the CH_2 groups. Indeed, the TS is strongly pyramidal, with a diradicalar dominent character, and the phosphorus lone pair, having a strong 3s character, does not participate significantly in a homoaromatic system: the reaction is nonpericyclic. When the phosphorus is constrained to a planar structure, a conrotatory TS is found. In contrast, the TS or aziridine ring opening, at the same calculation level, shows a conrotatory conformation and significant flattening of the nitrogen group. The influence of substitution on the conrotatory or disrotatory path of the reaction is briefly discussed.

Introduction

A large variety of bis(methylene)phosphorane derivatives have been synthesized and described over the years.[1] Bulky substituents, such as TMS, Ph, and NR_2, on the P atoms and C atoms are required to ensure the stability of these species. Chemical evidence[2] and X-ray measurements[3] have shown that the phosphorus and its three neighboring atoms are coplanar, and that the P-C bonds are short, and thus that the C–P–C π system is analogous to the allyl anion, with two filled π molecular orbitals (MO). The phosphirane–bis(methylene)phosphorane interconversion has been observed. In most cases, the nature of the substituents precludes knowing the stereochemistry of the process,[4] but in a few cases,[5] it was shown that the ring closure occurs in a conrotatory fashion, according to Woodward–Hoffmann[6] rules.

Calculations are available concerning the structure of the parent bis(methylene)phosphorane compound **1s** and some of its derivatives,[7,8a] which confirm the experimental results obtained with highly substituted systems. In addition, theoretical studies of related imino-, oxo-, and silylenephosphoranes have been published.[8b,c]

According to these studies, these compounds would exhibit, at least qualitatively, a behavior very similar to that of their nitrogen homolog. Nevertheless, the relatively small natural valence angles of PR3 derivatives imply a tendancy for the heteroatom lone pair to have greater s character than in nitrogen compounds, and so to minimize its participation to a conjugated system. We have endeavored to learn to what extent, and in what part of the reaction coordinate (RC) this lone pair is involved during the ring opening/closure process.

First section, we present the results of calculations of singlet planar **1s** and triplet pyramidal **1t** structures and some of their P-substituted derivatives, **2–4**. The CH_3 and NH_2 substituents were studied as models of alkyl and amino substituents frequently present in the molecules studied experimentally, and the BH_2 substituent as a model of a π acceptor exhibiting an interesting effect on the singlet–triplet separation. We will then present our study of the C–C ring opening of phosphirane **5** into **1** and discuss the main differences with aziridine.

Calculation Methods

Molecular geometries of stable species were fully optimized at the 6-31G** [9] second-order Møller–Plesset (MP2) level,[10] followed by a fourth-order MP4/SDTQ . The RHF Hamiltonian was used for closed-shell systems and the UHF Hamiltonian was used for triplet systems. Optimization of the transition states (TS) was carried out

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with the same 6-31G** basis set at a two configuration GVB level, in order to take into account the possible diradical character of these structures. For the sake of consistency, calculations of several points on the RC (structures **7**, **9**, and **9a**–**c**) were performed at the same level of calculation. For these calculations the GAUSSIAN 92 series of programs[11] was used.

Additional MCSCF/6-31G**//SCF/6-31G** calculations, using the HONDO 8 series of programs,[12] are presented for species **1**-**4**.

Exploratory scans affording qualitative reaction coordinates were also carried out, in the following manner. After the 6-31G SCF calculation, a space of about 100 selected configurations was diagonalized. The active space typically included the four highest occupied MOs and the seven lowest unoccupied ones. In this space, we considered all the monoexcitations and, for singlet states, pair excitations. Other diexcited configurations were included in a space restricted to the two highest occupied and the five lowest unoccupied MOs. In this case, the reaction coordinate was simply described by a linear variation, in 10 steps, of the main geometrical parameters between initial and final structures. This method will be referred as QPES (qualitative potential energy surface).

Parent Compounds 1s and 1t, Comparison with Their Nitrogen Analogs 6s and 6t. The MP2/6-31G** optimized structures of 1s and 1t, together with that of phosphirane **5**, are displayed in Figure 1. The geometrical parameters are close to those calculated by Cowley et al. at the MP2/6-31G* level for **1s**[7] and at the SCF 6-31G* level for **5**.[7,13] For the latter compound, the data are in good agreement with microwave determinations.[14] The triplet diradical **1t** has a C_s symmetry with a disrotatory conformation of the CH_2 groups and an almost planar PCH_2 group. Since the frontier MOs of **1s** and **5** have been reported,[7,8a] we only present a schematic drawing of the SOMOs of **1t**, 5a″ and 12a′ (Figure 2). The lowest in energy is the antisymmetrical one, in contrast to homosymmetric diradicals.[15] As a matter of fact, the symmetrical 12a′ SOMO of **1t** is destabilized by a strong out-of-phase contribution by phosphorus. The same result is found in the triplet diradical open form of aziridine **6t**, which also exhibits a disrotatory conformation.

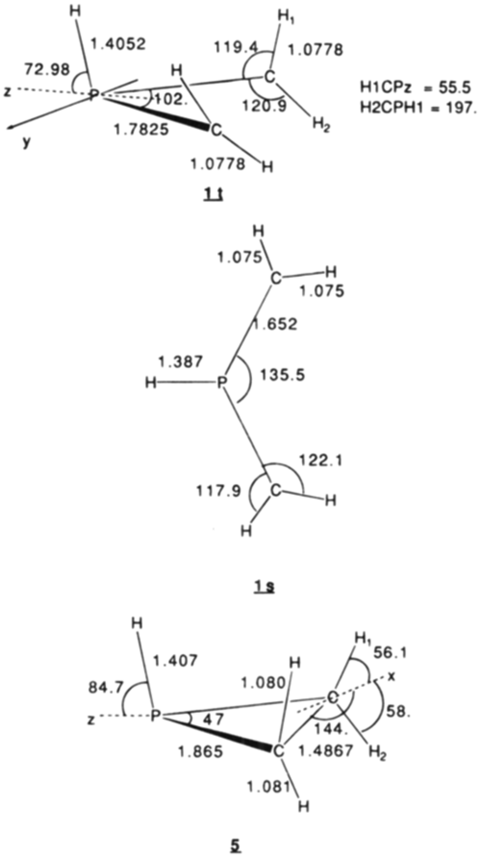

Figure 1. Optimized geometries (MP2/6-31G**) of bis(methylene)phosphorane (**1**) in its GS (**1s**) and its lowest triplet state (**1t**), and of phosphirane **5**.

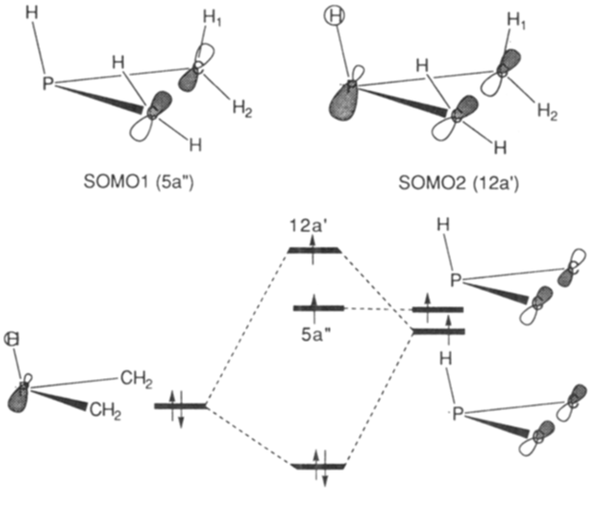

Figure 2. Frontier MO perturbation scheme of **1t**.

A general discussion of the conformations of triplet and singlet open forms of phosphirane will be developed below.

From the data reported in Table 1, one can see that the open form **1s** lies 50.75 (SCF) and 49.70 kcal mol^{-1} (MP2) above phosphirane **5**. This value is very close to that previously reported[7,8c] and remains almost the same at the MP4 level (49.85 kcal mol^{-1}). In contrast, the singlet–triplet separation of the open species **1** is strongly dependent on the calculation level. At the SCF/6-31G** level, the triplet **1t** is found more stable than **1s** by 7.0 kcal mol^{-1}. Their energies become almost equal at a limited MCSCF level including ca. 10 configurations, the

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Table 1. Calculated Energies

	SCF,[a] au	MSCF,[b] au	MP2,[c] au (MP4,[e] au)	$E_t - E_s$,[d] kcal mol^{-1}
1s	−419.25505	−419.28986	−419.67971 (−419.70904)	20.5 (16.9)
1t	−419.26619	−419.29107	−419.64705 (−419.68206)	
2s	−458.30491	−458.34067	−458.85127 (−45891874)	22.5 (19.2)
2t	−458.31014	−458.39967	−458.81540 (−458.88813)	
3s	−474.30656	−474.33241	−474.89893 (−474.93179)	18.2 (13.3)
3t	−474.31481	−474.33625	−474.86997 (−474.910550	
4s	−444.50708	−444.55331	−444.99187 (−445.05911)	10.9 (9.4)
4t	−444.52398	−444.54345	−444.97452 (−445.04409)	
5	−419.33593		−419.75894 (−419.788490	
6s	−132.98693		−133.47369 (−133.50560)	33.1 (22.8)
6t	−132.99876		−133.42089 (−133.42089)	

[a] SCF/6-31G**//SCF/6-31G**. [b] MCSCF/6-31G**//SCF/6-31G**. [c] MP2/6-31G**//MP2/6-31G**. [d] Singlet−triplet energy separation, MP2 (MP4). [e] MP4/6-31G**//MP2/6-31G**.

triplet being only slightly more stable (0.76 kcal mol^{-1}). But, at higher MP2 and MP4 levels of calculation, the singlet **1s** is more stable than the triplet **1t** by 20.5 and 16.9 kcal mol^{-1}, respectively. These data, as compared with the vertical energy gap (66.8 kcal mol^{-1}) previously calculated,[8c] emphasize the importance of structure relaxation.

For comparison, calculations were also performed on **6s** and **6t**, nitrogen homologs of **1s** and **1t**. The optimized geometrical parameters are given in ref 16. The singlet-triplet separation is 22.8 kcal mol^{-1} (MP4/6-31G**//MP2/6-31G**) for those species.

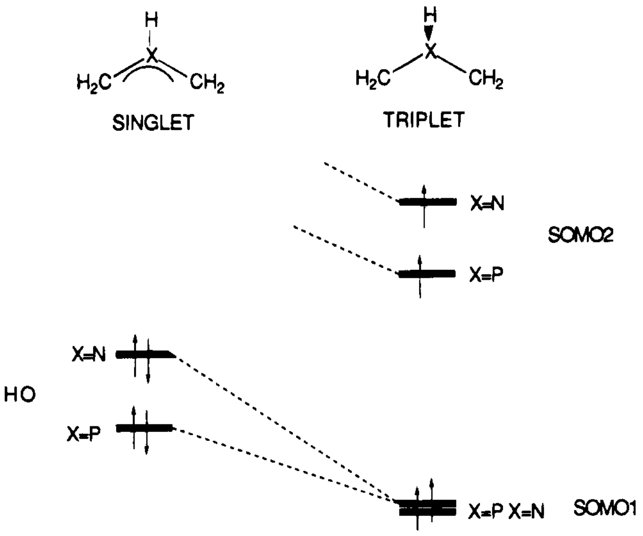

Figure 3. Frontier orbitals diagram of the singlet (**1s** and **6s**) and triplet (**1t** and **6t**) open forms.

The relative singlet−triplet separations for species **1** and **6** appear to result from a compromise between several opposing trends.[17] For the SCF MO level, these trends are summarized in Figure 3. In the singlet species, the HO is the allyl-like π_2 MO. It is purely nonbonding in **6s** and slightly bonding in **1s** due to the participation of the d AO of proper symmetry (coefficient: 0.13), which stabilizes **1s** with respect to **6s**. In the triplet species, the SOMO1 has almost the same energy for the two compounds: it consists of out-of-phase 2p AOs of carbon, with a negligible participation of the d AOs of phosphorus in **1t**. The SOMO2 of **1s** is stabilized with respect to that of **6t** because of a weaker antibonding overlap along P−C bonds. The balance of these effects is nearly zero, since it can be seen from Table 1 that the singlet−triplet separation is almost the same for both pairs of species (−7.4 kcal mol^{-1} for **6** vs −7.0 kcal mol^{-1} for **1**). Indeed, the state separation arises mainly from correlation effects in MP2 and MP4 calculations. The correlation appears to more strongly stabilize the **6s** singlet (−0.518 au) than the **1s** one (−0.454 au). Such effects are difficult to analyze, but one can say that, among others, the angular correlation (participation of d AOs) has a stronger effect in nitrogen compounds since it is already partly taken into account, at the SCF level, in the phosphorus cases, and that this participation more strongly stabilizes singlet species than triplet ones. In addition, the much larger inversion barrier of phosphorus, as compared with that of nitrogen, should favour the nonplanar triplet **1t** over the planar singlet **1s**.

At the GVB 6-31G** level, no energy minimum is found for the singlet counterpart of the diradical **1t**. This entity undergoes a spontaneous evolution, depending on the conformation of the starting structure. When starting from the optimized structure **1t** (a reasonable approximation for the singlet diradical) of Figure 1, a ring closure occurs, yielding phosphirane **5**; when starting from a coplanar $P(CH_2)_2$ group, the fully planar closed-shell **1s** is obtained. The lowest vertical triplet state of **1s**, $^3B_2$, is monotonously correlated with the GS triplet diradical.

Closed-Shell (GS) and Lowest Triplet State of P-Substituted Species 2-4. Optimized geometries (6-31G**/MP2) of species 2−4, in their singlet closed-shell GS (2s−4s) on the one hand, and in their lowest triplet diradical state (2t−4t), on the other hand, are displayed in Figure 4.

The singlet species possess at least a symmetry plane: **2s** is of C_s symmetry while **3s** and **4s** are of C_{2v} symmetry. All the diradicals exhibit a disrotatory conformation of the CH_2 groups, like the parent compound **1t**. Nevertheless, the torsion angle is weaker than in **1t**, since it ranges from ca. 42° for the amino compound **3t** to 16° for the methyl compound **2t**. Triplet states **2t** and **4t** have a C_s symmetry, whereas **3t**, in which the NH_2 group is pyramidal, has no symmetry element. The amino group in **3t** adopts a conformation that minimizes lone pair lone pair repulsion between the phosphorus and nitrogen atoms. Another rotamer has been found, with a H_5NP angle close to 90°, which lies 9.2 kcal mol^{-1} above the absolute minimum.

The singlet−triplet separations of **2**−**4** are reported in Table 1, together with their absolute energies. As previously noted for the parent species **1s**, the singlet-

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(16) Optimized parameters (bond lengths in Å, angles in degrees) for **6s** (C_{2v}) and **6t** (C_s). **6s**: C−N = 1.340; N−H = 1.013; C−H(syn) = 1.074; C−H(anti) = 1.072; CNC = 133.2; NCH(syn) = 118.8; NCH(anti) = 118.1. **6t** (with the same atom labelling as **1t** in Figure 1): C−N = 1.412; C−H1 = 1.077; C−H2 = 1.078; N−H = 1.010; CNC = 113.6; NCH1 = 116.4; NCH2 = 115.1 ; HNz = 56.8 ; H1CNz = 51; H2NCH1 = 214.6.

(17) This point was suggested by one referee.

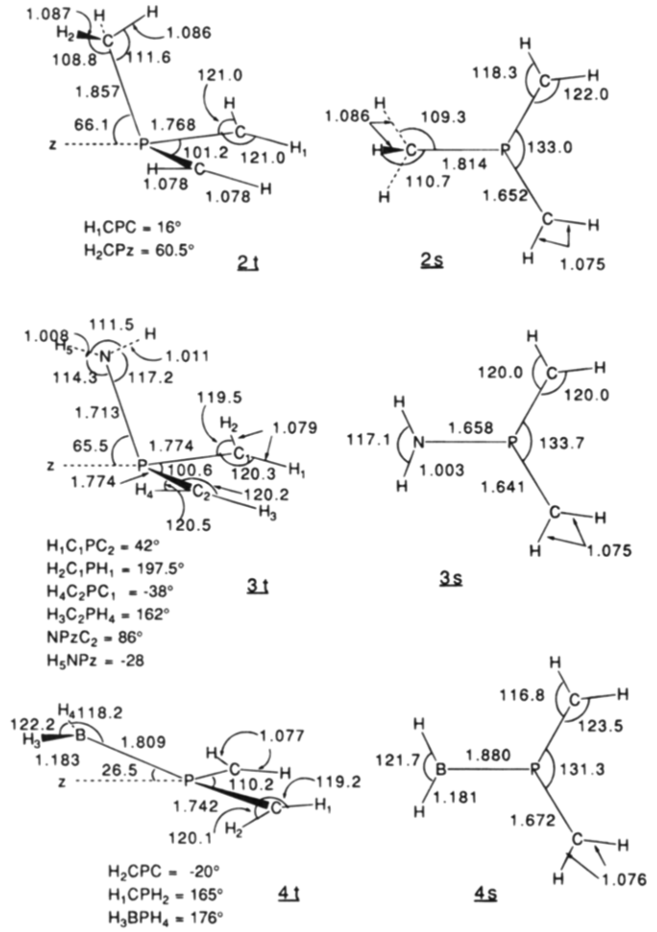

Figure 4. Optimized geometries (/MP26-31G**) of substituted bis(methylene)phosphoranes 2−4, in their GS (**2t**−**4t**) and in their lowest triplet state (**2t**−**4t**).

triplet separation is strongly dependent on the electron correlation. At the SCF level, the triplet state is found at lower energy than the singlet state. The same result is found at a limited MCSCF (ca. 15 configurations) level, except for **4**. At the higher MP2 level, the singlet is the most stable for all species. The singlet−triplet separation is smaller at the MP4 level than at the MP2 level, but at both, the same ordering is found for this gap: **6** > **2** > **1** > **3** > **4**.

As compared with the parent **1**, the singlet−triplet separation is weakly decreased by NH_2 substitution, weakly increased by CH_3 substitution, but strongly decreased by the presence of BH_2. To first examine the effect of substituents on the singlet compounds, the HOMOs of the singlet species, exemplified by the a_2 MO of 4s (Figure 5), are allyl-like, with a noticeable contribution (ca. 0.1−0.15 MO coefficient) of the d OA of phosphorus of suitable symmetry. For symmetry reasons, their overlap is zero with the p-type nonbonding MO of the substituent which thus influences mainly by σ effect. The σ-electron withdrawing substituent, NH_2, tends to stabilize these HOMOs and the σ-donor substituents (CH_3 and BH_2) tend to destabilize them. The trend is the same on the triplet symmetrical SOMO, but the effect is enhanced by the strong coefficient on phosphorus, on the one hand; on the other hand, only one electron is involved, which minimizes the overall effect. The π effect on the triplet SOMO is destabilizing for the π-donating CH_3 substituent, but is relatively weak in the case of NH_2, the optimal conformation of which minimizes this interaction. It is noteworthy that, as previously reported, the other **3t** conformer, in which this interaction is not minimum, is destabilized by 9.3 kcal mol^{-1}, and that, in this case, the singlet−triplet separation (22.6 kcal mol^{-1}) is increased by NH_2, with respect to the **1s**−**1t** couple (16.9 kcal mol^{-1}). The π effect is strongly stabilizing for the π-accepting BH_2. A quasi-planar geometry of the phosphorus results in **4t**, with a shortening of the P−B bond with respect to **4s**, a charge transfer from phosporus to boron (the SCF net charge of phosporus and boron are respectively 0.42/ −0.15 in **4t**, and 0.60/0.13 in **4s**), and a strong delocalization of the symmetrical SOMO 14a′ on the boron atom (see Figure 5). On the other hand, the stabilization of the $2b_1$ MO of **4s** by participation of the empty p AO of boron is, in fact, very weak, due to the large energy gap between these MOs.

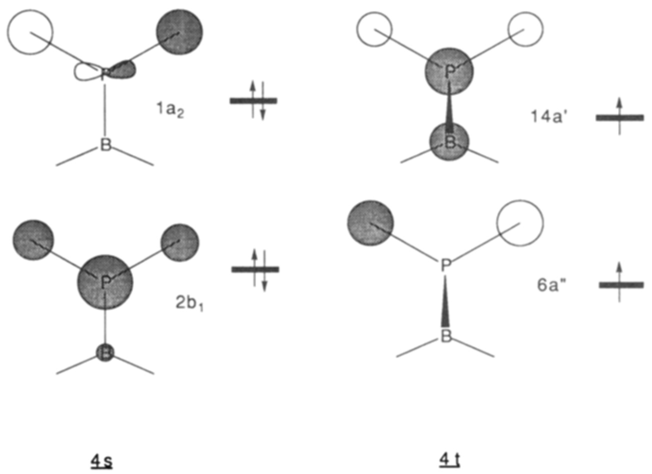

Figure 5. Schematical drawings of frontier MOs of **4s** and **4t**.

Phosphirane−Bis(methylene)phosphorane Interconversion. Description of the Reaction Coordinate. The crucial part of the RC of the C−C cleavage of phosphirane **5**, yielding bis(methylene)phosphorane **1s**, has been studied at the 6-31G**/GVB level. The CPC angle was taken as the leading parameter, and Figure 6 shows the evolution of the system for three values of this angle ranging from 90° to 110°. For a frozen value of the CPC angle of 90°, the optimized geometry **7** shows a face-to-face conformation of CH_2, i.e. the rotation of these groups has not begun at this stage of the RC. The phosphorus atom is strongly pyramidal, with a pyramidalization angle HPz (as defined in Figure 1) of 76.7°. The transition state (TS) **8** is reached for a CPC angle of 100.9° (Figure 7), at 7.8 kcal mol^{-1} above the open planar form **1s**. It is still strongly pyramidal (HPz = 75.4°) and exhibits a disrotatory conformation, in contrast to the conrotatory prediction of the Woodward−Hoffmann rules. One calculated vibration frequency is imaginary (229i cm^{-1}) . The optimized geometry for a CPC angle of 110° (**9**) shows that the flattening of the phosphorus pyramid is now beginning (HPz = 64.1°). The conformation of the CH_2 groups is still disrotatory, but different from the TS (**8**) conformation. Indeed, the nonequivalence of both faces of the CPC plane involves the possibility of two qualitatively different disrotatory conformations. The first one, optimal for the triplet structures already described **1t-4t** and for structure **9**, will be labeled disrot1 in the following discussions. The second one, optimal for the TS **8**, will be labeled disrot2. Several points deserve comment.

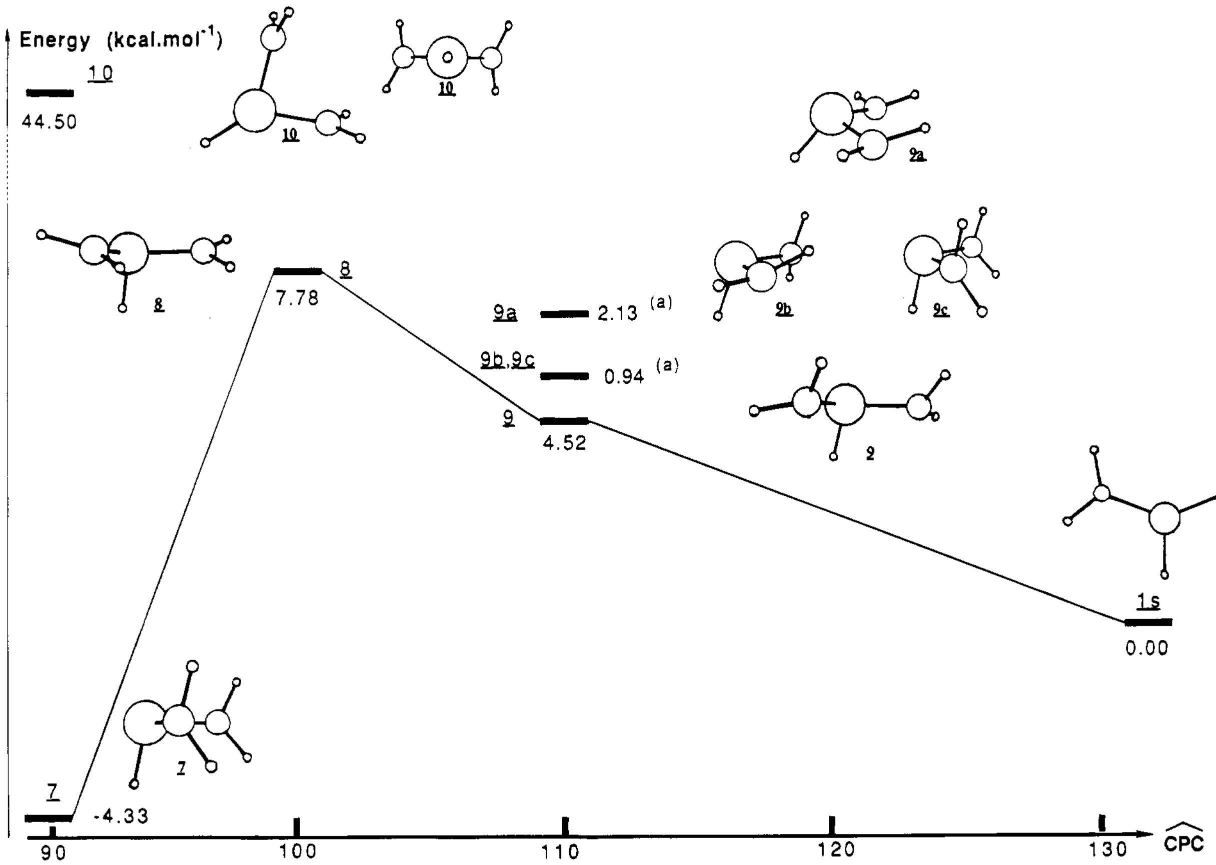

Figure 6. Optimized (6-31G**/GVB) crucial part of the GS RC of phosphirane (5) opening into bis(methylene)phosphorane (**1s**). Structure **8** is the TS, structures **9a**, **9b** and **9c** are conformers of **9**, structure **10** is the TS for a planar phosphorus center (see text). See also Figure 7 and Table 2. (a) Energies that are referred to the optimized conformer **9** are labeled a.

Disrotatory vs Conrotatory Phosphirane–Bis(methylene)phosphorane Interconversion. Comparison with Aziridine Opening. The disrotatory structure of the TS **8** is in apparent contradiction with Woodward–Hoffmann rules.[6] Any attempt to optimize a conrotatory saddle point has failed—when starting from a conrotatory conformation, the system evolves toward **8** during the optimization process. A structure constrained in a conrotatory conformation, with the same PCP angle and the same absolute values of CH_2 torsional angles as in **8**, has been found only 1.4 kcal mol^{-1} below **8**. This means that both conrotatory and disrotatory processes are very close in energy; there is almost a free rotation of the CH_2 groups in this region and thus there is no separate conrotatory reaction coordinate. These findings suggest that the reaction is not pericyclic, which is confirmed by the GVB analysis of **8**, which exhibits a dominent diradical character (ca. 80%). It arises from the strong pyramidalization of this structure in that the phosphorus lone pair has a strong 3s character and thus a weak overlap with the 2p AOs of the CH2 groups. This prevents the formation of a homoaromatic system. With these conditions, the disrotatory conformation of **8** results from very weak MO interactions, which will be discussed below.

Two pieces of evidence support the preceding assertions.

First, if the HPCC group is kept planar, the phosphorus lone pair becomes purely 3p and can overlap with the 2p AOs of the neighboring groups to participate in a ring delocalization. With this constraint, a TS (structure **10**) is found at 36.51 kcal mol^{-1} above the TS **8** and 44.5 kcal mol^{-1} above the final species **1s**. Structure **10** is

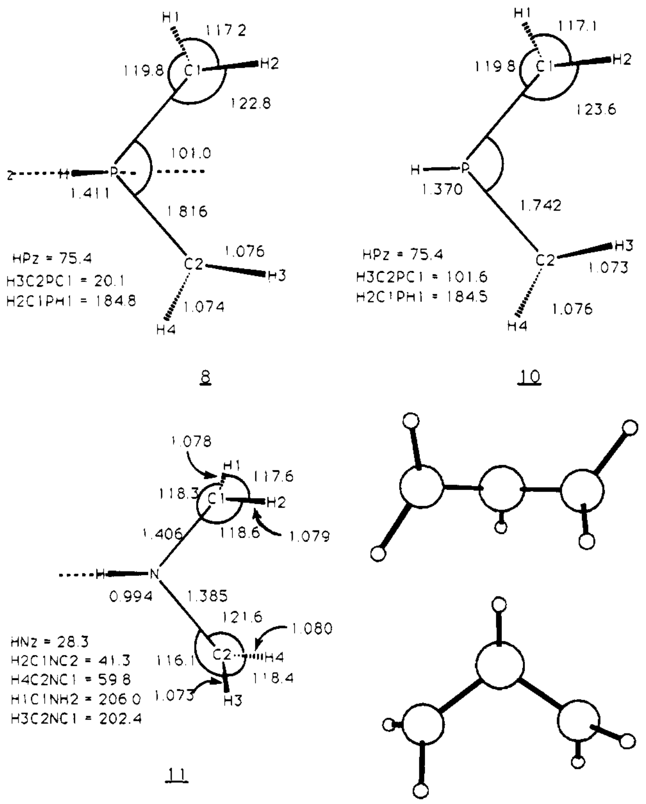

Figure 7. Optimized geometries (GVB/6-31G**) of phosphirane (**8**) and aziridine (**11**) opening transition states. Two different views of 11 are given in the lower right part.

Table 2. Main Geometrical Parameters of Structures 7, 9, 9a–c (see Text and Figure 6)[a]

species	7	9	9a	9b	9c
R, Å					
PH	1.404	1.398	1.397	1.401	1.402
PC1	1.791	1.774	1.773	1.793	1.812
C1H1	1.077	1.077	1.077	1.076	1.077
C1H2	1.078	1.077	1.078	1.077	1.078
C2H3	1.078	1.077	1.078	1.078	1.077
C2H4	1.077	1.077	1.077	1.077	1.078
Angles, deg					
C1PC2	90	110	110	110	110
HPz	76.7	66.3	64.1	70.2	76
dihedral angles, deg					
H3C2PC1	94.2	166.8	180	-90	-90
H2C1PC2	112.9	82.7	180	180	90

[a] The valence angles of CH_2 groups have been omitted.

displayed in Figure 7 and two different views, in the upper left part of Figure 6, show that its geometry is clearly conrotatory, in agreement with Woodward–Hoffmann rules, although the rotation angles are weak at this stage of the RC. This structure has a strong closed-shell character (ca. 80%). It exhibits two imaginary frequencies (451i and 1095i cm^{-1}), since its represents a TS for both ring opening and phosphorus inversion processes.

Second, the TS **11** of aziridine opening has been optimized at the same level of calculation as **8**. The geometry of **11**, together with two different views of this TS are shown in Figure 7 (lower part). Its energy lies 21.1 kcal mol^{-1} above the open form **6s**; its conformation is clearly conrotatory, and since the structure has no symmetry element, the rotation angle is not the same for both methylene groups. The nitrogen group is considerably flattened (HNz = 28.3°), which allows the participation of the nitrogen lone pair of strong 2p character to a delocalized π system, and the species has a strong closed-shell character (ca. 70%)

These results are a confirmation of the preceding discussion and suggest that the high inversion barrier of phosphorus could be responsible of the nonpericyclic character of the phosphirane opening. Let us recall that this barrier is 5.8 kcal mol^{-1} [17] for ammonia and 37.2 kcal mol^{-1} for phosphine.[18] It can be evaluated at ca. 20 kcal mol^{-1} from experimental[19] and theoretical results[20] for aziridine, and has been estimated at 33,[21] 39.9,[13b] and 80.4 kcal mol^{-1} for phosphirane.[13k,22] Nevertheless, more recently, an attempt to calculate this barrier by constraining phosphirane to a C_{2v} geometry led to the dissociation of the molecule into phosphinidene and ethylene.[7]

With these conditions, during the ring opening of phosphirane, the TS is reached before the flattening of the phosphorus group, and the main characteristics of this TS, stated above, appear as a consequence of its strong pyramidalization. In contrast, for aziridine opening, the easier flattening of the nitrogen group occurs earlier in the reaction coordinate, with the opposite consequences.

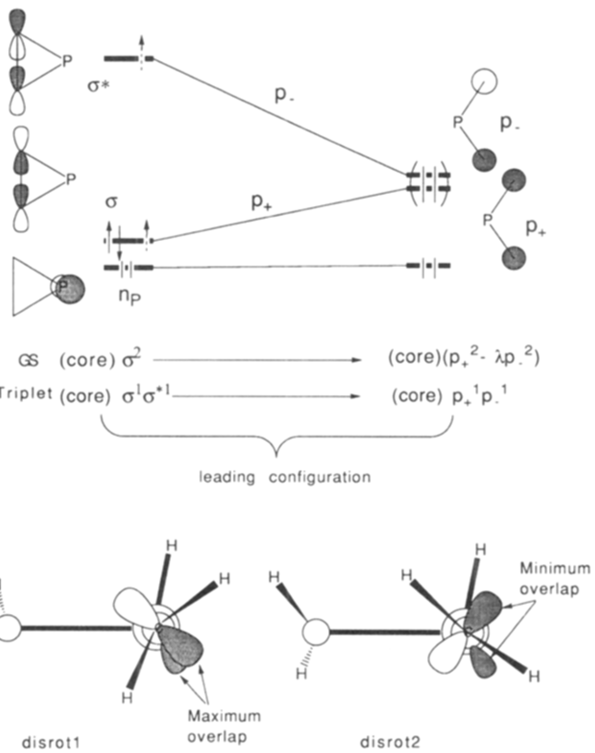

Figure 8. Conformation of the open forms $HP(CH_2)_2$. The upper part shows the schematic evolution of the frontier MOs during the opening process. For the cyclic starting compound, arrows with full solid lines refer to the GS, arrows with dotted lines refer to the triplet state. The lower part exhibits the interactions of phosphorus lone pair with a carbon 2p AO of the p_+ MO, in the disrot1 and disrot2 conformations, respectively.

Orbital Control of the CH_2 Conformation in Triplet and Singlet Pyramidal Open Forms 1t–4t, 7, 8, and 9.

The conformation of the CH_2 groups in all the singlet or triplet pyramidal open forms is controlled by the interaction of the 2p AOs of the carbon atoms with the lone pair of the phosphorus atom. Although these interactions, as pointed out, are very weak, their analysis allows for a qualitative interpretation of the conformations adopted in the various open forms.

Let us first examine the singlet structures **7–9** encountered during the phosphirane opening. In Figure 8 is displayed the qualitative evolution of the interacting MOs. In the open forms, the frontier MOs consist of the two combinations of 2p AOs of carbon atoms : p_+ (in phase), and p_- (out of phase). This couple is correlated with the σ and σ^* MOs of the C–C bond (note that, in all of these MOs, the 2s character is negligible) and can interact with the lone pair of phosphorus, n_P. In fact, if the C_s symmetry is preserved, n_P only interacts with p_+; when the symmetry is broken the n_P–p_- overlap is no longer zero, but remains negligible, at least for a qualitative discussion. Let us first examine the singlet GS involved in the ring opening of phosphirane **5**. Three limiting situations are found:

(i) At the beginning of the RC, the configuration is mainly monoconfigurational $|(\text{core})\, p_+^2|$; p_+ resembles the σ MO and has a strong bonding character; the most stable conformation corresponds to a face-to-face arrangement of both CH_2 extremities, in order to increase the 2p–2p overlap (structure **7**).

(ii) When the CPC angle increases, the 2p–2p overlap rapidly decreases and is no longer the dominant inter-

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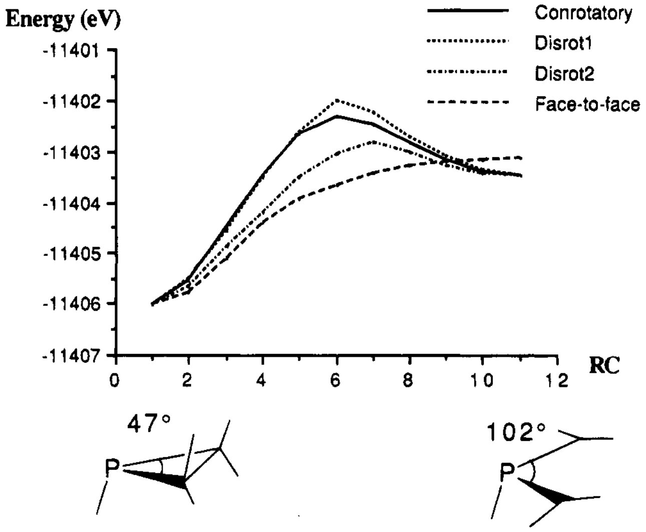

Figure 9. Plot of model opening processes of phosphirane **5** in its GS, using the QPES method.

action, although the $|(\mathrm{core})(p_+)^2|$ configuration remains prominent. The leading interaction is now $n_P - p_+$, which is a four-electron destabilizing interaction. The optimal conformation tends to minimize the overlap of these orbitals, and adopts the disrot2 conformation (structure **8**) as shown in Figure 8 (lower part).

(iii) As the diradical character increases, the wave function becomes more and more biconfigurational $|(\mathrm{core})(p_+^2 - \lambda p_-^2)|$, with $0 < \lambda < 1$, and tends toward $|(\mathrm{core})(p_+^2 - p_-^2)|$ for a pure homosymmetric diradical.[15] The mean occupancy of p_+ decreases, and the $n_P - p_+$ interaction tends toward three-electron stabilization. The optimal conformation is thus disrot1 (structure **9**), for which the interacting lobes are eclipsed in order to increase their overlap (see Figure 8).

If we now come back to the triplet open forms **1t**–**4t**, one can expect that the situation iii is encountered regardless of the angle CPC may adopt, since the configuration is $|(\mathrm{core})p_+^1 p_-^1|$, and the $n_P - p_+$ interaction always involves three electrons. Structures **1t**–**4t** are thus of disrot1 type. Moreover, it can be expected that the photochemical opening of **5** occurs via a disrot1 transition state.

This discussion is confirmed by model calculations using the QPES method, which mimics the first part of the reaction coordinate during which the flattening of the phosphorus group is almost negligible. Potential energy surfaces (PESs) for conrotatory, disrot1, disrot2, and face-to-face processes are reported in Figure 9 (GS) and Figure 10 (lowest excited triplet state). In these potential energy scans, the various processes have been simulated by a linear variation of the angular parameters and PC bond lengths, from their optimized values in **5** (47°) up to their optimized values in **1t** (102°). The PH and CH bond lengths, and the pyramidalization angle of phosphorus have been frozen at their initial value in **5**, and a coplanar conformation of CH_2-P-CH_2 atoms has been taken for the final open species.

For the GS, the calculated PESs show that the face-to-face process is favored at the beginning of the reaction. Then, the so-called disrot2 process becomes favored over the other processes. As a matter of fact, the closed-shell configuration is the leading one all along this part of the RC. For the lowest excited triplet state, Figure 10 shows that, as expected by the previous discussion, the disrot1 process is now favored over the disrot2 one. In both singlet and triplet cases, the conrotatory PES takes place between the disrot1 and disrot2 ones, since in this conformation, one $\langle 2p|n_P\rangle$ overlap is maximum and the other one is minimum. In these calculations, the difference between both disrotatory processes is overestimated due, in part, to the freezing of secondary geometry parameters.

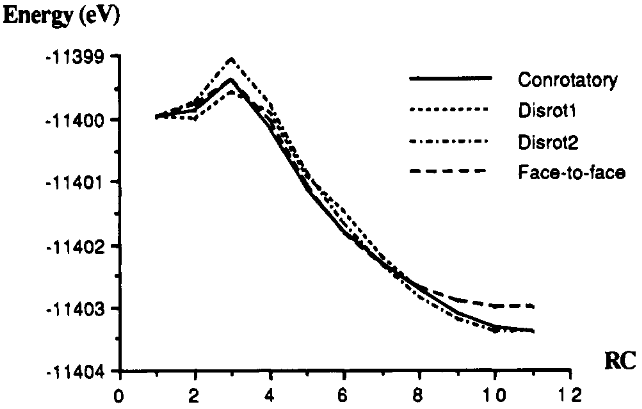

Figure 10. Plot of model opening processes of phosphirane **5** in its lowest triplet state, using the QPES method.

Comparison with Experimental Results. These results are in apparent contradiction with experimental observations[5] of a conrotatory ring reclosure of a substituted bis(methylene)phosphorane. In fact, this disagreement could arise for several reasons:

(i) In the reported experimental results, all bis(methylene)phosphoranes are substituted on the P atom, in most cases by bulky groups such as dialkylamino and $(TMS)_2N$ (**1**). These groups favor a flattening of the pyramidal phosphorus center, increasing the 3p character of its lone pair and thus the participation of its nonbonding MO to the TS, and finally a conrotatory process. Calculations at the MP2/6-31G** SCF level[23] show that the pyramidalization angle RPz in P-substituted phosphiranes, as defined in Figure 1, is 80.2° (R = CH_3) and 76.8° (R = NH_2) respectively, vs 84.7° for R = H. For example, the latter substituted phosphirane has, at the beginning of the RC (CPC ca. 47°), a pyramidal angle that the unsubstituted species only reaches for CPC = 90°.

(ii) Carbon atoms also bear bulky substituents—at least two TMS groups, often together with other TMS groups, or substituents such as phenyl and chlorine. With this condition, the stereochemistry of the ring closure could remain under steric control. In the 100–110° section of the reaction coordinate (Figure 6), the methylene rotational barriers are almost vanishing at our calculation level (GVB/6-31G**). As benchmarks, the energies of three limiting conformers were calculated, for a CPC angle of 110° (Figure 6) in which two PCH planes are taken to be both coplanar (**9a**), perpendicular/coplanar (**9b**), or both perpendicular (**9c**) to the CPC plan respectively, the remaining parameters being optimized. All these conformations range in a ca. 2 kcal mol^{-1} interval with respect to the optimal conformation **9**. This value, of the same order of magnitude as the ethane rotational barrier, allows a "free rotation" of methylenes. This means that when bulky groups are present, a conrotatory conformation, which minimizes steric hindrances, could be preferred to the disrotatory conformation of the

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unsubstituted entity. Moreover, it has been shown that various substituted bis(methylene)phosphoranes are twisted in a conrotatory fashion, with twisting angles in a 35°–50° range.[3] On the other hand, the calculated geometry of *P*-chlorobis(methylene)phosphorane also exhibits a ca. 15° twisting angle of the methylene groups.[7]

Conclusion

According to the calculational results, the main differences between the phosphorus systems studied and their nitrogen analogs appear to arise from the higher inversion barrier of phosphorus vs nitrogen compounds.

(i) Although the closed-shell planar bis(methylene)phosphoranes **1s**–**4s** exhibit a strong double–bond character along P–C, partly due to the d AOs of phosphorus, their lowest pyramidal triplet diradical states lie at lower energy than in the corresponding nitrogen compounds. The singlet–triplet separation is only 9.4 kcal mol^{-1} for the **4s**–**4t** couple.

(ii) Regarding the C–C ring-opening reaction, the phosphirane constrasts with aziridine. The latter compound is known to undergo a pericyclic reaction with a conrotatory stereochemistry,[24] as shown by the optimized TS **11**, and in agreement with theoretical studies.[25] For phosphirane opening, our calculations show that the TS **8** is strongly pyramidal, thus with a strong 3s character to the phosphorus lone pair, and with a dominent diradical character. Its conformation is disrotatory, with, however, very weak rotational barriers of the CH_2 groups; the reaction is not pericyclic and its stereochemistry is controlled by weak MO interactions. With these conditions, when bulky substituents are present on C atoms, one can expect that the stereochemistry of this reaction is no longer under orbital control, but under streric control, which favors a conrotatory conformation. On the other hand, if a bulky substituent is present on the phosphorus atom, the flattening of its pyramidal environment is favored, which increases the 3p character of the phosphorus lone pair, and the reaction could become pericyclic. Indeed, if the HPCC group is kept planar, a conrotatory TS, **10**, is found.

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