Inorg. Chem. **1986**, *25*, 2185–2190

Contribution from the Department of Chemistry,
University College, Belfield, Dublin 4, Ireland

R_2PCR: λ^3-Phosphinocarbene vs. λ^5-Phosphaacetylene. Theoretical Study of the CH_3P Isomers

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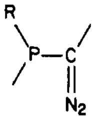
Received September 12, 1985

An ab initio study of part of the singlet and triplet $[CH_3P]$ energy surfaces is reported. Local minima corresponding to methylphosphinidene (CH_3P), phosphaethene (CH_2PH), and phosphinocarbene ($CHPH_2$) were obtained at HF/3-21G* level. Transition states linking these species via 1,2-hydrogen shifts were also located. Vibrational frequencies of the species considered are reported. At the MP4SDQ/6-31++G*//HF/3-21G* level plus zero-point energy contributions, singlet phosphaethene is found to be the global minimum, lying 43 kcal/mol below singlet methylphosphinidene, which could isomerize to the former via an energy barrier of 13.5 kcal/mol. Singlet phosphinocarbene lies 60 kcal/mol above phosphaethene and is separated from it by a barrier of 18 kcal/mol. These low barriers render observation of singlet $CHPH_2$ and CH_3P unlikely. On the triplet surface, the energy barriers are larger (34 kcal/mol for the $CHPH_2 \rightarrow CH_2PH$ conversion and 25 kcal/mol for the $CH_2PH \rightarrow CH_3P$ pathway); thus, observation of the triplet species might be possible. The triplet–singlet energy separations in $CHPH_2$, CH_2PH, and CH_3P amount to 3, 39, and −33 kcal/mol, respectively. Calculated results appear to support the proposition that $R_2P–CR$ species are key intermediates in the photolysis of phosphinodiazomethanes. These species possess a singlet ground state and can best be considered as λ^3-phosphinocarbenes rather than λ^5-phosphaacetylenes.

Introduction

Recently, Baceiredo, Bertrand, and Sicard[1] successfully prepared the first thermally stable diazo derivative possessing a λ^3-phosphino substituent. When the phosphino–diazomethane **1** was irradiated at room temperature in the presence of different trapping agents AX, the adducts **2** were obtained. Neither typical carbene reactions nor a Wolff-type rearrangement yielding phosphaalkenes **3** was observed.[1] The behavior of phosphinodiazomethanes **1** under photochemical conditions thus quite closely resembles that of phosphinoazides ($>PN_3$).[2] As in the latter case, the reported data[1] appear to endorse the existence of the phosphacarbene **4** as a discrete intermediate during the photolysis of **1**. In a recent ab initio study of the H_2PN energy surface,[3a] we showed that the phosphinonitrene ($H_2P{=}N$), once formed from the decomposition of phosphinoazide H_2PN_3, is stable under inert matrix conditions and can only rearrange to its thermodynamically more stable isomer via a sizable energy barrier to 1,2-hydrogen shift. Furthermore, the calculations clearly demonstrated that the PN bond in H_2PN is best regarded as a dative double bond ($>P{\rightarrow}N$) rather than a triple bond (λ^5-phosphinonitrile, $>P{\equiv}N$; see also ref 3b,c).



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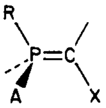

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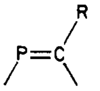

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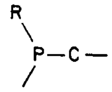

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With regard to the structure and stability of phosphinocarbene **4**, we now wish to describe the results of ab initio calculations on the energy surface of the model CH_3P system. This exhibits a number of stationary points, including local minima corresponding to phosphinocarbene, H_2PCH, phosphaethene, $H_2C{=}PH$, and methylphosphinidene, CH_3P, and saddle points connecting them. The H_3PC system[4] was not investigated in this study. The transition structures separating the three stable molecular forms involve successive unimolecular 1,2-hydrogen shifts between the carbon and phosphorus atoms. The interconversion pathway is examined in both the lowest lying singlet and triplet electronic states.

Calculations

In order to facilitate comparison, we adopt the same strategy as in previous papers.[3] The equilibrium and transition structures were located by using analytically computed energy gradients at the single-determinantal SCF level. The unrestricted Hartree–Fock (UHF) method was used for the triplet states. It is well established that the basis sets of split valence and double ζ reproduce the best geometric parameters for classical multiple-bond-containing P atoms (such as $C{\equiv}P$ and $C{=}P$).[16] Inclusion of polarization functions provides the bond lengths by about 0.03–0.04 Å too short. Nevertheless, the latter are necessary in predicting geometries of nonclassical species. To maintain coherency, we employ, as a compromise, the 3-21G* basis set,[5] which includes d-functions on phosphorus only. Energy differences were computed with values calculated by Møller–Plesset perturbation theory at fourth order (MP4SDQ, including all single, double, and quadruple, electron excitations),[6] using SCF wave functions computed at the 3-21G* optimized geometries with the 6-31++G* basis set[7] for generating electronic configurations (the latter basis is of the 6-31G type, augmented with a set of polarization d-functions and diffuse s- and p-functions on phosphorus and carbon and a set of diffuse s-functions on hydrogen). Harmonic vibrational frequencies were determined with the 3-21G* basis, and some molecular properties were computed at the HF/6-31++G* level. All computational procedures are implemented in the MONSTERGAUSS[8] and GAUSSIAN-82[9] programs.

Results and Discussion

(1) The Singlet States. The 3-21G*-optimized geometries of three stationary points **5**–**7** of the singlet phosphaethene–methylphosphinidene rearrangement are displayed in Figure 1. There have been a number of previous ab initio calculations at various levels of accuracy on phosphaethene **5**.[10–16] Thomson[10] reported

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(1) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781.

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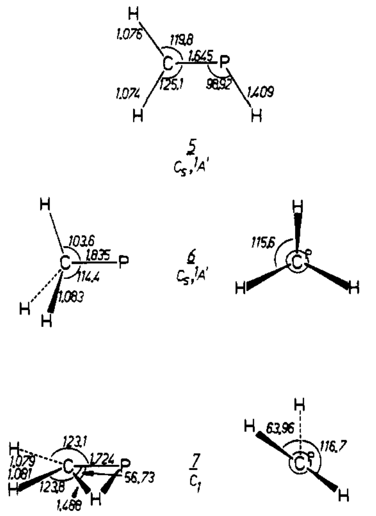
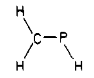
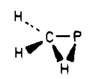
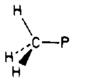


Figure 1. 3-21G*-optimized geometries of three stationary points in the singlet $H_2C{=}PH/H_3CP$ rearrangement. Bond lengths are in angstroms and bond angles in degrees.

Table I. Total (au) and Relative (kcal/mol) Energies[a] for the Singlet $H_2C{=}PH \rightarrow CH_3P$ Rearrangement

	 5 $^1A'$	 7 ^1A	 6 $^1A'$
	Total Energies		
HF/3-21G*	-378.44631	-378.34427	-378.38958
HF/6-31++G*	-380.28977	-380.19417	-380.23586
MP4SDQ/6-31++G*	-380.55382	-380.46064	-380.48674
ZPE	22.8	20.8	23.7
	Relative Energies		
HF/3-21G*	0.0	64.0	35.6
HF/6-31++G*	0.0	60.0	33.8
MP4SDQ/6-31++G*	0.0	58.5	42.1
estd[b]	0.0	56.5	43.0

[a] Using 3-21G* optimized geometries given in Figure 1. Zero-point vibrational energies (ZPE) are given in kcal/mol. [b] Including the MP4SDQ/6-31++G* relative energies and ZPE contributions.

a study of the stereomutation of **5** and showed that the barrier to rotation is smaller (by 9 kcal/mol at HF/4-31G) than that to inversion. The electronic configuration, charge distribution, and substituent effects on the $^1A'$ ground state have been examined in detail by several workers.[11-14] The proton affinity[15] as well as reactivity toward metal complexes[12] has also been investigated. A comparison between the geometry of **5** computed by different methods and that obtained from microwave structural data[16-18] reveals, as mentioned above, that a split-valence basis set reproduces the experimental geometry best, due to a mutual cancellation of correlation and polarization effects.

In fact, when the correlation energy is neglected, the CP bond length of 1.645 Å in **5** computed at the HF/3-21G* level is only about 0.03 Å shorter than the experimental value of 1.671-1.673 Å.[17-18] As far as we know, no previous calculations on H_2PCH and H_3CP have been reported.

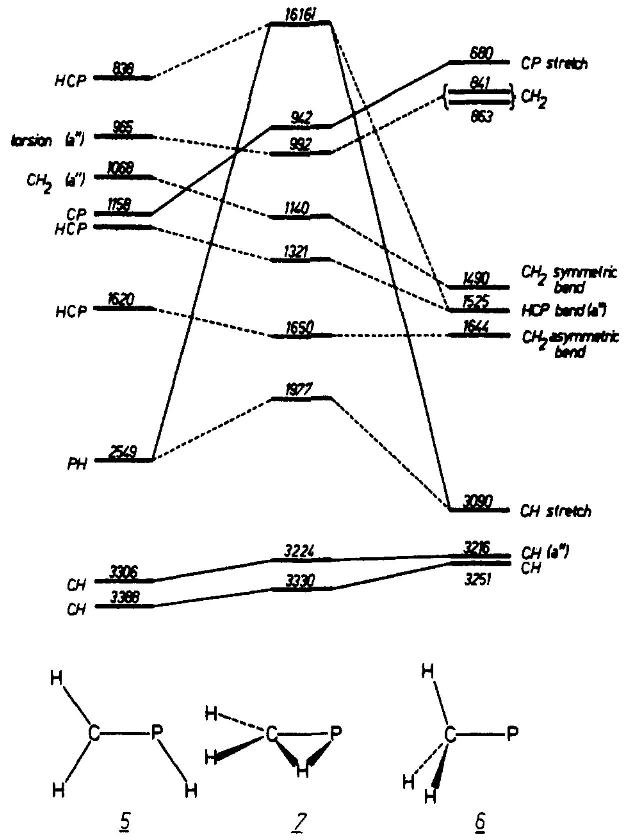


Figure 2. Vibrational frequency correlation diagram for species **5**–**7**. Values were calculated at the HF/3-21G* level and are in cm^{-1} (the scale is arbitrary).

Table II. Harmonic Vibrational Frequencies (cm^{-1}) of the Phosphaethene ($H_2C{=}PH$) **5** Calculated with Different Basis Sets[a]

		3-21G	4-31G	3-21G*	4-31G*	assignt
A'	γ_1	3421	3435	3388	3358	CH str
	γ_2	3328	3342	3306	3278	CH str
	γ_3	2321	2205	2549	2429	PH str
	γ_4	1603	1607	1620	1623	HCC bend
	γ_5	1132	1145	1158	1156	HCC bend
	γ_6	1042	1038	1117	1114	CP str
	γ_7	835	840	838	844	HCP bend
A''	γ_8	1062	1060	1068	1059	CH_2 wag
	γ_9	942	950	965	980	torsion

[a] Using the corresponding optimized geometries.

As expected, the singlet methylphosphinidene **6** is subject to a Jahn-Teller distortion and consequently possesses C_s rather than C_{3v} symmetry. The latter geometry in fact represents a saddle point in the HF/3-21G* energy surface. The angular distortion in CH_3P **6** is significantly larger (11°) than that calculated for the singlet silylphosphinidene H_3SiP (5°)[4] or methylnitrene CH_3N (1°).[19] The CP bond length in **6** is about 0.2 Å longer than the C=P double bond in **5**. However, the ratio of the CP bond lengths in **5** and **6** is similar to that of the CN bonds in $CH_2{=}NH$ and CH_3N.

Transition state **7**, separating **5** from **6**, possesses no elements of symmetry. To convert to **6**, the H(P) atom in **5** follows an out-of-plane migration pathway that is accompanied by a distortion of the CH_2 moiety in the opposite direction. Such a process is similar to the pathway converting ethylene to methylcarbene.[20,21]

The preference of the 1,2-hydrogen rearrangement for the nonsymmetrical geometry **7** rather than the symmetrical structure

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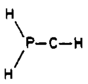
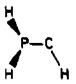
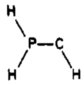
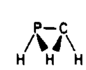
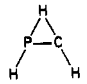
Table III. Total (au) and Relative (kcal/mol) Energies of Five Stationary Points, **9–13**, Relevant to the H_2PCH Species

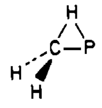
method[a]	 9(C_{2v})	 10(C_1)	 11(C_s)	 12(C_1)	 13(C_s)
			Total Energies		
HF/3-21G*	−378.33849	−378.34523	−378.34339	−378.30712	−378.24559
HF/6-31++G*	−380.17846	−380.19538	−380.19238	−380.16167	−380.09259
MP4SDQ/6-31++G*	−380.43755	−380.44655	−380.45271	−380.42189	−380.38219
ZPE[b]	20.2	19.6	19.5	18.2	17.4
		Relative Energies with Respect to $H_2C{=}PH$ (**5**)			
HF/3-21G*	67.7	63.4	64.6	87.3	126.0
HF/6-31++G*	69.8	59.2	61.1	80.4	123.7
MP4SDQ/6-31++G*	73.0	67.3	63.4	82.8	107.7
estd[c]	70.4	64.1	60.1	78.2	102.3

[a] Using the 3-21G* geometries given in Figure 3. [b] Zero-point vibrational energies calculated at the HF/3-21G* level. [c] Including the MP4SDQ/6-31++G* relative energies and ZPE contributions.

Table IV. Harmonic Vibrational Frequencies (cm^{-1}) of Five Stationary Points, **9–13**, on the Singlet Surface (3-21G*)

9 (C_{2v})	**10** (C_1)	**11** (C_s)	**12** (C_1)	**13** (C_s)
3610 (a_1, CH)	3220	3335 (a′)	3232	3327 (a′, CH)
2658 (a_1, PH)	2707	2783 (a′)	2402	2321 (a′, PH)
2640 (b_2, PH)	2612	2650 (a′)	1938	2118 (a′, PH)
1364 (a_1, HPH)	1274	1266 (a′)	1214	1156 (a′, CP)
1306 (a_1, CP)	1052	1143 (a′, CP)	1143	982 (a″, out)
950 (b_1, out)	893 (CP)	1002 (a″)	993 (CP)	914 (a′, HPC)
873 (b_2, HPH)	881 (tors)	816 (a′)	956	863 (a′, HCP)
300 (b_1, PH_2)	738 (HCP)	605 (a′)	820	984*j* (a″, out)
320*i* (b_2, HCP)	354 (inv)	215*i* (a″, inv)	1222i (H-mig)	2274*i* (a′, H-mig)

8 (which has two imaginary vibrational frequencies) has been discussed in our previous paper.[3] The CP bond length in **7** is intermediate between those in **5** and **6**.



8(C_s)

The best estimates of the total energies of **5–7**, listed in Table I, show that the singlet methylphosphinidene **6** lies 43 kcal/mol above the global minimum phosphaethene **5** and may undergo rearrangement to the latter with an energy barrier of 13.5 kcal/mol. This is appreciable when compared with the closed-shell singlet methylnitrene (CH_3N, $^1A'$), which isomerizes with zero activation energy to methyleneamine (methanimine) ($H_2C{=}NH$, $^1A'$).[22,23]

The vibrational frequencies of **5–7** are depicted in Figure 2. For comparison, values calculated for **6** from a number of different basis sets are reported in Table II.

The PH and CP stretching frequencies computed with the 3-21G* or 4-31G* bases are, as expected, about 7–8% larger than those derived from the 3-21G or 4-31G wavefunctions. In an infrared study of the $F_2C{=}PH$ molecule,[24] frequencies of 2327 and 1350 cm^{-1} were measured and attributed to the PH and CP stretching modes, respectively. Thus, the observed PH frequency lies within the range of calculated values in such a way that the latter can be regarded as its lower (without d-functions) and upper (with d-functions) limits. In contrast, it is somewhat surprising that all calculated CP frequencies are found to be smaller (by about 18%) than the experimentally assigned value. This large difference can hardly be accounted for by the effects of the fluorine atoms on the CP bond. It could be due to the lack of polarization d-functions in the carbon basis set. Such a basis reduces the C=P distance and consequently increases its stretching frequency. However, the relevant calculated bond length (1.62 Å) is too short with respect to the experimental value of 1.672 Å.[17-18] In addition, in our previous work,[3] we showed that the calculated 3-21G* and

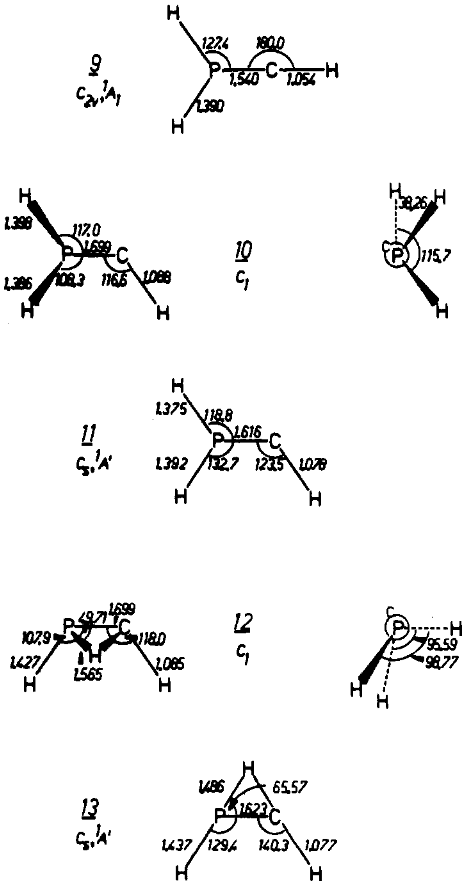


Figure 3. 3-21G*-optimized geometries of stationary points relevant to the H_2PCH species. Bond lengths are in angstroms and bond angles in degrees.

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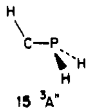
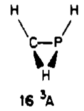
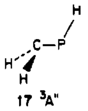
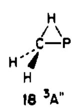
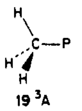
Table V. Charge Distributions in Stationary Points on the Singlet Energy Surface (HF/6-31++G*)

		$H_2P—CH$ **11**	$H_2P—CH$ **9**	$HP{=}CH_2$ **5**	CH_3P **6**
net charges	C	−0.45	−0.45	−0.56	−0.75
	P	0.23	0.21	0.18	0.09
	H(C)	0.18	0.26	0.21	0.22
	H(P)	−0.01	−0.01	0.05	
	H(C or P)	0.05	−0.01	0.22	0.22 (×2)
overlap pops.	CP	1.24	1.52	0.68	0.10

Table VI. Total (au) and Relative (kcal/mol) Energies[a] of Five Stationary Points on the Triplet Energy Surface

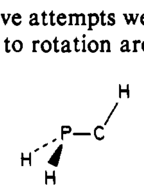
	 **15** $^3A''$	 **16** ^3A	 **17** $^3A''$	 **18** $^3A''$	 **19** ^3A
		Total Energies			
HF/3-21G*	−378.38797	−378.31128	−378.41626	−378.35743	−378.46248
HF/6-31++G*	−380.22987	−380.15691	−380.26108	−380.20458	−380.30693
MP4SDQ/6-31++G*	−380.44762	−380.38938	−380.48815	−380.44605	−380.54036
ZPE[b]	19.3	16.9	20.4	18.9	24.3
		Relative Energies			
HF/3-21G*	46.8	94.9	29.0	65.9	0.0
HF/6-31++G*	48.4	94.1	28.8	64.2	0.0
MP4SDQ/6-31++G*	58.2	94.7	32.8	59.2	0.0
estd[c]	53.2	87.3	28.9	53.8	0.0

[a] Using the 3-21G* geometries given in Figure 4. [b] Zero-point vibrational energies calculated at the HF/3-21G* level. [c] Including MP4SDQ/6-31++G* relative energies and ZPE contributions.

4-31G* frequencies of the PN bond in HP=NH (1250–1260 cm^{-1}) are comparable to those (1240–1250 cm^{-1}) measured for a number of amino-*tert*-butylphosphanes ($R_2NP{=}NC(CH_3)_3$). Further investigations appear to be necessary to clarify this discrepancy. The CP stretching frequency in methylphosphinidene **6** (680 cm^{-1} at 3-21G*) is about half of the double-bond value in **5** (Figure 2).

The molecular structure of H_2PCH is of particular interest. Figure 3 shows the optimized geometries of some stationary points related to this species. The calculated energetic data and harmonic vibrational frequencies are collected in Tables III and IV, respectively.

The data in Table IV indicate that, at the HF/3-21G* level, the pyramidal phosphinocarbene **10** is the only local minimum among the five stationary points considered. Planar **11** corresponds to the transition structure for inversion at the phosphorus atom, and nonplanar **12**, to the hydrogen migration converting **10** to phosphaethene **5**. Planar structure **13** possesses two imaginary frequencies, the first corresponding to the hydrogen migration and the second to the out-of-plane motion. Linear and planar structure **9** (C_{2v}), which can be regarded as a λ^5-phosphaacetylene possessing a P≡C triple bond, is also calculated to be a saddle point. Its imaginary frequency (320*i*) describes the HCP bending mode, indicating that it is the transition structure for inversion at the carbenic center. Extensive attempts were made to locate saddle point **14**, corresponding to rotation around the CP bond in **10**, but such a structure has not been found, all optimizations starting with C_s symmetry finally converging to inversion structure **9**.



14 (C_s)

As seen from Table III, planar conformation **11** remains a saddle point with the larger 6-31++G* basis set. However, it turns out to have a lower energy than **11** after incorporation of the correlation energies. As expected, the correlation correction due to the delocalization from the phosphorus lone pair into the vacant p-orbital of the carbenic center is significantly larger than that in the localized structure **10** and thus reverses the ordering. For the remaining conformations, the order of stability is not altered by the correlation effect. The final estimation places **10** above **11** on the energy scale by about 4 kcal/mol. As a consequence, at the MP4 level, **10** does not correspond to a stationary point on the singlet hypersurface at all. It can therefore be concluded that the local minimum H_2PCH features a planar carbene structure. This simplest λ^3-phosphinocarbene (**11**) undergoes stereomutation by inversion via the λ^5-phosphaacetylene transition structure (**9**) with an energy barrier of 10.3 kcal/mol and rearranges to phosphaethene **5** through the nonplanar 1,2-hydrogen-shift transition structure **12** with a barrier of 18.1 kcal/mol (cf. Table III). In addition, carbene **11** is found to be the least stable among the three local minima examined; 60.1 and 17.1 kcal/mol above $H_2C{=}PH$ (**5**) and H_3CP (**6**), respectively. In comparison with the nitrogen analogues, singlet phosphinocarbene **11** is markedly less stable. Indeed, aminocarbene, H_2NCH, which also possesses a planar structure, lies about 39 kcal/mol above methyleneamine ($H_2C{=}NH$) and the barrier to conversion to the latter is 47 kcal/mol (at the MP4SDTQ/6-31G** level).[23]

The net charges and overlap populations derived from a Mulliken analysis of some stationary points at the HF/6-31++G* level are listed in Table V. In all cases, the carbon atom bears a negative charge while the phosphorus atom is positively charged. The charge distribution differs only marginally between the linear and bent conformations of $H_2P–CH$, and it is thus scarcely possible to predict substituent effects on the energy difference between two conformations on the basis of the classical inductive or conjugation effects.

The CP overlap population in phosphinocarbene **9** or **11** is noticeably larger than that of the C=P double bond in phosphaethene **5**. This is a reflection of the π-delocalization and is in line with the rather short CP distances of 1.54 Å in **9** and 1.62 Å in **11** in comparison with 1.67 Å in **5** (at the HF/3-21G* level—Figures 1 and 3). Hence, both geometric and electronic characteristics point to a more-than-double-bond character for the CP bond in phosphinocarbene.

(2) The Triplet States. The 3-21G*-optimized geometries of the five stationary points **15**–**19** on the lowest triplet CH_3P energy surface are given in Figure 4. Relevant energetic data are listed in Table VI, and vibrational frequencies are presented as a correlation diagram in Figure 5.

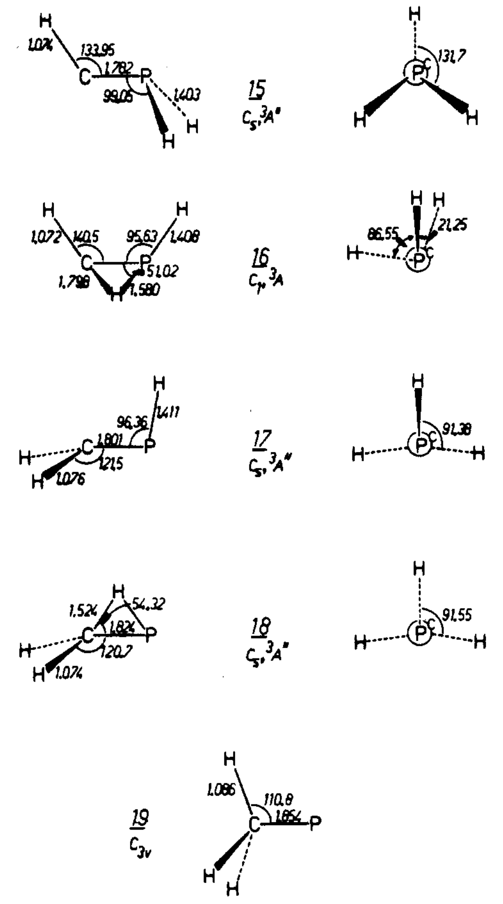


Figure 4. 3-21G*-optimized geometries of five stationary points on the triplet energy surface. Bond lengths are in angstroms and bond angles in degrees.

Examination of Figure 4 shows that the shape of the triplet CH_3P species possesses several qualitative similarities to that of triplet CH_3N.[19,22,23] The local minima of both phosphinocarbene **15** and phosphaethene **17** adopt twisted, pyramidalized, and trans-bent conformations. Like the triplet methylnitrene CH_3N and silylphosphinidene SiH_3P,[4] methylphosphinidene **19** has C_{3v} symmetry ($^3A_2$). In **15**, the pyramidalization of the phosphorus atom is strong and close to that in H_2PN ($^3A''$), while the CH_2 group marginally distorts in the opposite direction from the ideal twisted conformation (less than 2°). The degree of pyramidalization of the carbon atom in **15** is therefore much smaller than that found in triplet H_2CNH.[23]

The geometry of transition state **18** is rather close to that of **17**. The migration of the hydrogen atom from carbon to phosphorus seems to strongly "depyramidalize" the carbon atom. This difference between the CH_3N and CH_3P species could arise from the fact that the CP separation is much larger than the CN distance, and thus interaction between the phosphorus lone pair and vacant p-orbitals on carbon is negligible. Transition structure **16** possesses no elements of symmetry (C_1) and quite closely resembles the saddle point for conversion of triplet H_2PN to HP=NH.[3] In all cases, the CP bond lengths are calculated to be much larger than those of the corresponding singlet species.

It is interesting to note that the CP distance in **15** is shorter (0.04 Å) than that in **17**, while the PN bond in triplet H_2PN is larger (0.07 Å) than that of triplet HP=NH.[3] This may indicate that there is a certain amount of multiple-bond character in the CP bond in phosphacarbene in its excited triplet state.

Figure 5 emphasizes that the elongation of the CP bond (0.01 Å) is accompanied by a decrease of 10 cm^{-1} in the stretching frequency. Overall, the CP stretching frequency in the triplet compound is predicted to lie in the 700–800-cm^{-1} region. The absolute values of the imaginary frequencies are consistent with the fact that transition state **16** is of higher energy (33.5 kcal/mol) than **18**. In the portions of the triplet energy surface explored, the most stable structure is methylphosphinidene **19**. Analogous to the singlet case, the stabilities decrease in the order **19** > **17** (29 kcal/mol) > **15** (53 kcal/mol).

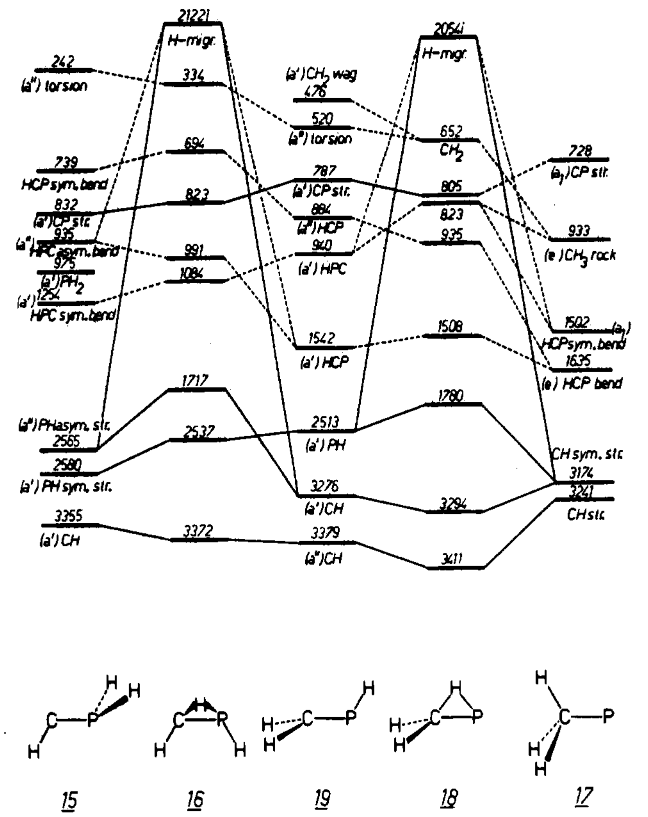


Figure 5. Vibrational frequency correlation diagram for the five triplet species **15**–**19**. Values were calculated at the HF/3-21G* level and are in cm^{-1} (the scale is arbitrary).

When the reaction is viewed as starting from phosphinocarbene, the successive conversion of **15** to **17** and **17** to **19** requires 34.1 and 24.9 kcal/mol, respectively. As the reaction proceeds in the endothermic direction, the nondissociative rearrangement **19** → **17** → **15** is much more difficult to achieve, with energy barriers of 53.8 and 58.4 kcal/mol, respectively.

Comparing this reaction pathway with that occurring in the triplet CH_3N species, i.e.

$$HCNH_2\ (23\ \text{kcal/mol}) \rightarrow HC(H)NH^{\ddagger}\ (64) \rightarrow H_2CNH\ (18) \rightarrow H_2C(H)N^{\ddagger}\ (49) \rightarrow CH_3N\ (0)$$

(values at MP4SDTQ/6-31G** + ZPE taken from ref 24), we note that when the nitrogen atom in CH_3N is formally replaced by phosphorus, isomers with low-valency carbon become appreciably destablized and are more easily converted to subsequent more stable species. These observations reflect the reluctance of the phosphorus atom to form CP multiple bonds in excited triplet states.

Replacement of the CH moiety by a nitrogen atom in the $HC{-}PH_2$ **15** → $H_2C{-}PH$ **17** rearrangement makes the process a little bit more difficult. The heat of reaction for the transformation of the isoelectronic species $^3NPH_2 \rightarrow {}^3HN{-}PH$ has been computed to be −10.5 kcal/mol and the energy barrier 30.1 kcal/mol at the same level of calculation.[3]

Summary

Figure 6 displays the energy profile for the singlet and triplet electronic states of the $[CH_3P]$ species considered in this work. Singlet phosphaethene **5** is, as expected, the globally most stable structure and lies 10 kcal/mol below the most stable triplet methylphosphinidene **19**. The singlet–triplet energy separations between the local minima are of interest. The triplet–singlet gap in phosphaethene ($H_2C{=}PH$) is predicted to be 39 kcal/mol and lies in the same region as that of *trans*-iminophosphane (HN=PH, 36 kcal/mol calculated at the same level of theory).[3] By contrast,

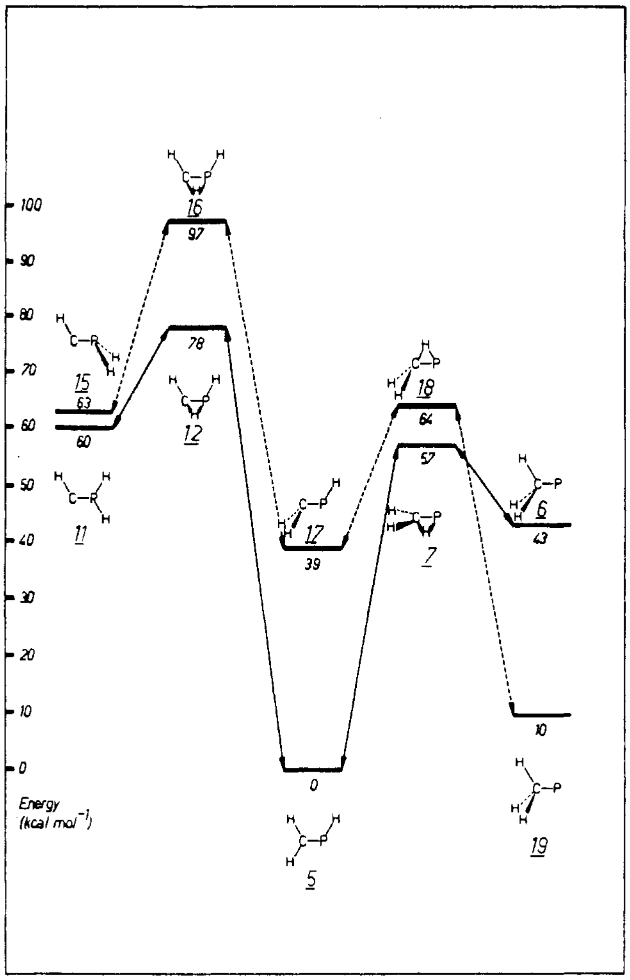


Figure 6. Relative energies, in kcal/mol, of the pathways for isomerization of the singlet and triplet [CH_3P] species.

only 3 kcal/mol separates triplet phosphinocarbene **15** from its singlet ground state **11**. This is slightly smaller than the corresponding value of 7 kcal/mol for the phosphinonitrene, H_2PN.[3] Technically, it is well-known that such quantities cannot be accurately estimated by SCF calculations alone, which reverse the order of stability (see Tables I and VI). Finally, the closed-shell singlet excited state **6** of methylphosphinidene (H_3CP) is 33 kcal/mol less stable than its triplet counterpart **19**. This is smaller than the gap found in methylnitrene (CH_3N, 44 kcal/mol)[23] and differs only slightly from the predicted value of 37 kcal/mol for the prototype phosphinidene PH (at the MP4SDQ/6-31G** level).[16] It is well-known that methyl substitution exerts little effect on the energy difference between singlet and triplet states of carbene[21] and silylene.[25]

As stated above, both the nonclassical structures H_2P–CH and H_3CP seem to be unstable on the singlet energy surface and undergo unimolecular rearrangement to doubly bonded isomer **5**. In contrast, the local minima in the triplet energy surface are separated by much more sizable energy barriers, rendering these species as more likely candidates for separate detection during photochemical reactions of phosphorus compounds under matrix conditions at low temperature. Like methylnitrene,[22] the triplet methylphosphinidene can be expected to be a stable species in the absence of molecular collisions. In particular, because of the very small triplet–singlet energy separation in phosphinocarbene (H_2PCH), this species, even if produced in its singlet ground state, could easily change its multiplicity and would consequently not isomerize to phosphaethene. In cases where the hydrogen atoms are substituted by poorer migrating groups such as bulky alkyl substituents,[1] the intermediacy of phosphinocarbene is even more likely.

In conclusion, the most significant chemical results of our calculations are a support for the proposition that the species R_2P–CR are key intermediates in the photolysis of phosphinodiazomethanes and a prediction of their molecular structures. These nonclassical molecules possess a singlet ground state (although the triplet–singlet energy separation is rather small) and can best be regarded as λ^3-phosphinocarbenes rather than λ^5-phosphaacetylenes, although the CP bond possesses a more-than-double-bond character.

Acknowledgment. We are indebted to the Irish Government (Department of Education) for financial support. We also thank the UCD Computer Centre for a grant of facilities.

Registry No. Methylenephosphine, 61183-53-7; methylphosphinidene, 23582-08-3; phosphinocarbene, 101541-74-6.

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