Effect of Fluorine and Chlorine Substituents on Stabilities of Diphosphaallene, Diphosphirene, and Phosphanylphosphaalkyne Isomers ($XX'CP_2$ Species with X, X' = H, F, and Cl)

Noel J. Fitzpatrick*[a], **Dermot F. Brougham**[a], **Peter J. Groarke**[a], and **Minh Tho Nguyen***[b]

Department of Chemistry, University College[a],
Belfield, Dublin 4, Ireland

Department of Chemistry, University of Leuven[b],
Celestijnenlaan 200 F, B-3001-Leuven, Belgium

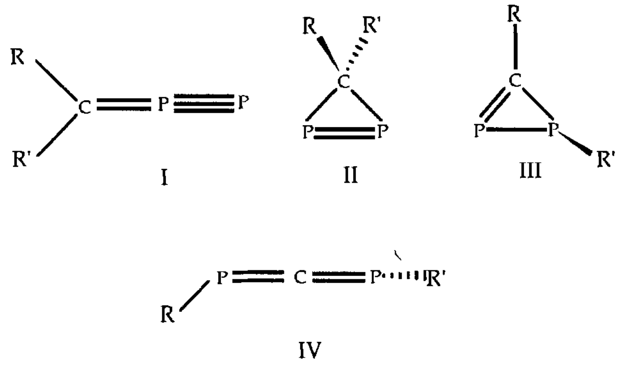
Received November 12, 1993

Key Words: Diphosphaallenes / 1*H*-Diphosphirenes / 3*H*-Diphosphirenes / Phosphanylphosphaalkynes / Calculations, ab initio MO

Ab initio MO calculations at the QCISD(T)/6-31G**//MP2/6-31G** + ZPE level on the $XX'CP_2$ isomers (X = H, F and Cl) show that the energies of the isomeric species are often reordered following halogen substitution. The phosphorus-halogen moiety behaves as the main stabilizing factor on the rest of the molecular structure. This is particularly true when X = F is involved. In the dihalogenated series phosphanylphosphaalkyne (**4**) becomes the most stable species followed by diphosphaallene (**3**) and 1*H*-diphosphirene (**6**). The effect on the geometry following halogenation is larger if substitution takes place at carbon than at phosphorus. The behaviour of the P species is found to be quite different from, if not opposite to, that of their nitrogen analogues. Finally, the infrared spectra of the most stable isomers are also predicted.

It is now established that the molecular structures and stabilities of phosphorus compounds at low coordination differ significantly from those of their nitrogen analogues. For example, while diazoalkane compounds ($RR'C{=}N{=}N$) are widely employed as starting materials in organic synthesis, the phosphorus (designated hereafter as P) counterparts **I** containing a linear framework have not yet been observed.

Scheme 1



Similarly, while a diazirine compound exists mainly in the 3-*H* form[1], the P-analogue (**II**) has only been postulated as a transient intermediate leading to its cyclodimer[2]. In contrast, a 1*H*-diphosphirene (**III**) isomer has recently been reported to be a quite stable chemical species[3]. An X-ray structure determination[3] has indicated that the three-coordinated P atom in **III** is strongly pyramidal, thus avoiding an unfavourable "anti-aromatic" system. Among the remaining possible isomers of **I**, **II**, and **III**, only the diphosphaallenes **IV**, P-analogues of carbodiimides, have been observed. The synthesis and characterization of **IV** have been reported, since 1984, by various groups[4]. Thus, of the compounds having a ($RR'CP_2$) general formula, only 1*H*-diphosphirenes **III** and diphosphaallenes **IV** are presently known[3,4]. The other isomers continue to elude synthesis. This fact raises the question as to whether the non-observation of some isomers is simply due to a thermodynamic problem.

In a recent paper[5], it has been demonstrated that the relative thermodynamic stabilities between three-membered phosphirene rings and the corresponding non-cyclic isomers can be modified fundamentally by fluorine and chlorine substituents. For instance, *P*-fluoro-1*H*-phosphirene turns out to be the most stable form among (C_2PH_2F) isomers, mainyl due to the inherent strength of the phosphorus-halogen bond. In view of this remarkable effect, we have extended our theoretical study by examining the structures and stabilities of several ($RR'CP_2$) isomeric systems where R and R' stands for H, F, and Cl. This systematic investigation allows a quantification of the effect of fluorine and chlorine atoms.

Computational Details

Ab initio molecular orbital calculations were carried out with a local version of the Gaussian 92 program[6]. The stationary points were initially located at the Hartree-Fock

(HF) level using both 3-21G* and 6-31G** basis sets[6]. These points were characterized by harmonic vibrational analyses at the HF/6-31G** level. Geometrical parameters were then refined using second-order Møller-Plesset perturbation theory calculations (MP2/6-31G**). All the electron correlation calculations were performed within the frozen core approximation. Improved relative energies were subsequently obtained from calculations using the MP2/6-31G** geometries with incorporation of electron correlation probed by full-fourth-order perturbation theory (MP4SDTQ) and quadratic configuration interaction [QCISD(T)] with the 6-31G** basis set. The zero-point corrections were estimated from the HF/6-31G** harmonic vibrational wavenumbers. Vibrational analyses of several structures of interest have also been performed using MP2/6-31G** calculations with analytical force constants in order to characterize them further. For the sake of simplicity, the levels HF/6-31G** and MP2/6-31G** will be designated hereafter by HF and MP2, respectively. Similarly, the terms local minimum and transition structure will be noted as LM and TS, respectively.

Results and Discussion

We have considered six isomeric systems including the unsubstituted H_2CP_2, the monosubstituted $HFCP_2$ and $HClCP_2$, and the disubstituted F_2CP_2, Cl_2CP_2, and $FClCP_2$. Each of the isomeric systems comprises the diphosphaalkenyne **1**, 3*H*-diphosphirene **2**, diphosphaallene **3**, phosphanylphosphaalkyne **4**, the nitrilimine analogue **5**, 1*H*-diphosphirene **6** and the cyclic carbene **7**. The structures examined are displaced in Figure 1.

In general, each structure examined is designated by a number ranging from **1** to **7** and one or two letters, namely **H** for H_2CP_2, **F** for $HFCP_2$, **Cl** for $HClCP_2$, **FF** for F_2CP_2, **ClCl** for Cl_2CP_2, and **FCl** for $FClCP_2$. In the mixed series, **5** and **6** are split into **5a** and **5b**, **6a** and **6b** due to the existence of two distinct sites of substitution. The optimized geometries for the minima of all six series are shown in Figures 2a, 2b, and 2c, in each case the MP2 geometries are displayed.

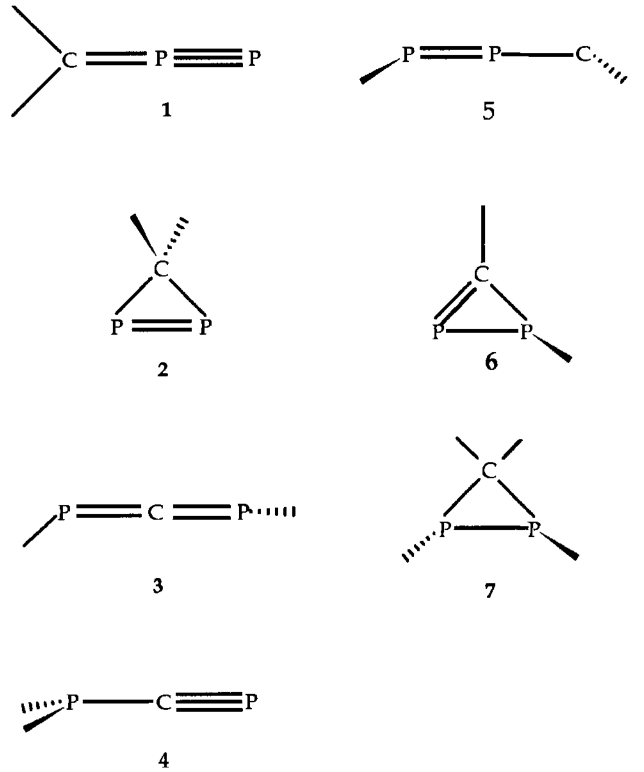


Figure 1. Isomers of $RR'CP_2$. Lines represent arbitrary substituents (R)

1. Identity of Stationary Points

The identity of each structure considered is determined by vibrational analysis at both the HF and MP2 levels. Whenever there is an inconsistency, we consider the characterization given by the MP2 calculation to be more accurate, despite the fact that it does not contain single excitations. This can lead to erroneous results, and the quality of the stationary points should be judged with caution. For all six series, the structures **2**, **3**, **4**, and **6** are calculated without ambiguity as energy minima. In contrast, there are some inconsistencies regarding the structures **1**, **5**, and **7**. The situation is summarized in Table 1.

(i) **1H** is characterized as a LM at the HF level but as a TS at the MP2 level. On the contrary, **1F** is a TS at the HF level but a LM at the MP2 level. For the remaining series, **1** is a LM at both levels. Thus, the characterization of **1** as equilibrium structures in the halogenated species are internally consistent.

(ii) Except for **5H**, which is shown to be a LM, the halogenated structures are not LM at all.

(iii) Similarly, **7** are mostly TSs or even do not exist as stationary points. The dichloro species **7FCl** is the only case of a cyclic carbene which was characterized as a LM. However this must be viewed with some scepticism.

In summary, the structures which proved to be TSs are:

1, **7**	for H_2CP_2	**5**	for F_2CP_2
5a, **5b**	for $HFCP_2$	**5**, **7**	for Cl_2CP_2
5a, **5b**	for $HClCP_2$	**5b**	for $FClCP_2$

Table 1. Identity of the structures considered[a] (LM = local minimum; TS = transition structure)

Series	**1**		**5a** (X on C)		**5b** (X on P)		**7**	
	HF	MP2	HF	MP2	HF	MP2	HF	MP2
H_2CP_2	LM	TS	LM	LM	-	-	LM	TS
$HFCP_2$	TS	LM	LM	TS	TS	TS	[c]	[c]
$HClCP_2$	LM	LM	TS	TS	TS	TS	LM	[d]
F_2CP_2	LM	LM	TS[b]	-	-	-	TS	[c]
Cl_2CP_2	LM	LM	TS	TS	-	-	LM	TS
$FClCP_2$	LM	LM	TS[b]	-	TS	TS	LM	LM

[a] Structures **2**, **3**, **4**, and **6** are local minima in all six series. – [b] Having two imaginary wavenumbers. – [c] Collapses to **3**. – [d] Collapses to **6b**.

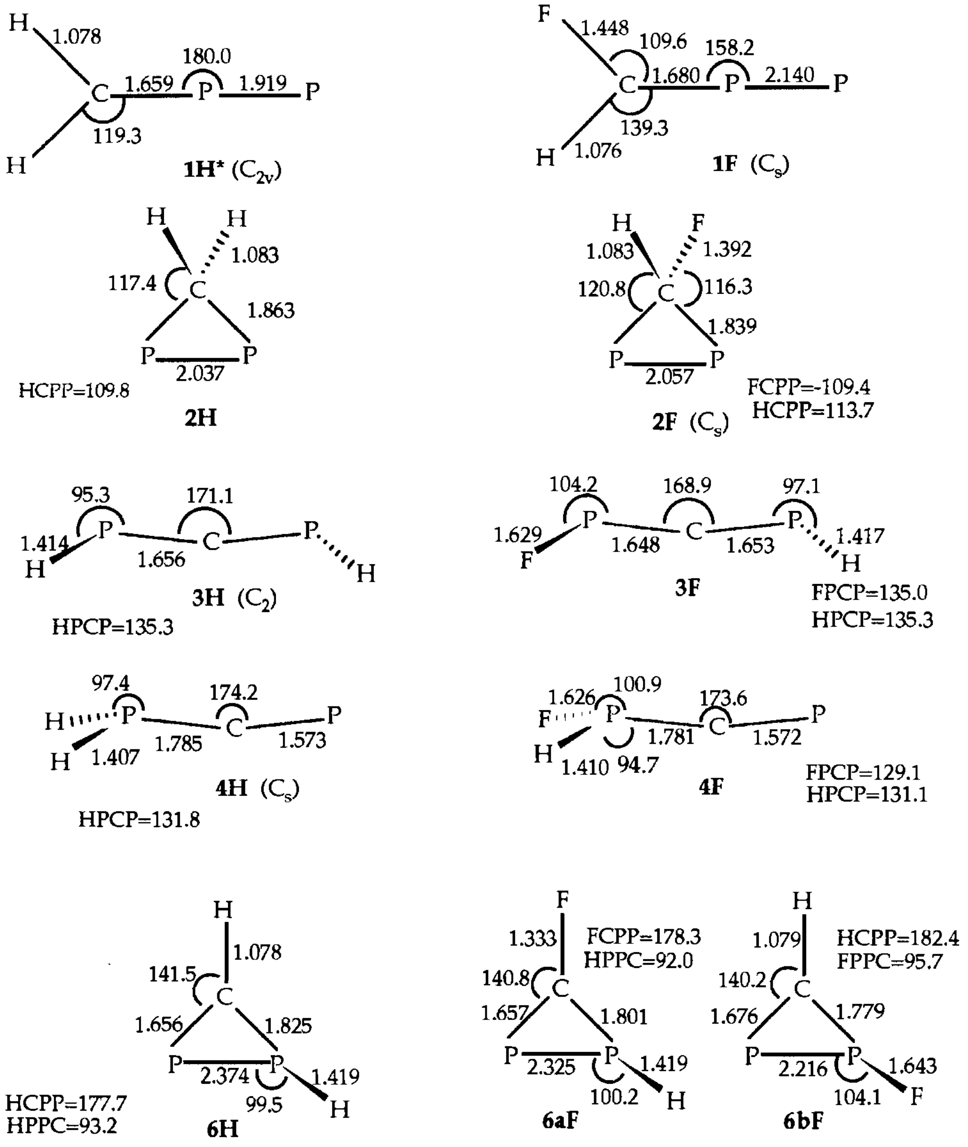


Figure 2a. Optimized geometries of the isomers of H_2CP_2 and $HFCP_2$. Bond lengths are in Å and bond lengths in degrees. The structure marked with an asterisk is a non-equilibrium structure

Structures **5** and **7** will be largely omitted from the following discussion.

2. Geometries

In isomer **1**, both C–P and P–P distances are slightly longer than those of the corresponding double bonds. While Cl does not have any effect on the C–P–P linearity, F induces a strong bending either in **1F** or in **1FCl**. The linearity in **1FF** is probably due to the molecular symmetry. The C–P bond in **1FF** is particularly long (1.785 Å).

In 3*H*-diphosphirene **2**, the P=P bond appears to be somewhat elongated upon halogenation, while the C–P bond is shortened. Note that a cyclodimer of **2** has been synthesized and characterized by X-ray spectrometry[2]. The C–P distance of 1.87 Å in this dimer is of the same order of magnitude as the value in **1H** (1.865 Å).

The geometry of diphosphaallene **3H** has been analyzed earlier[7]. The calculated C–P distance in **1H** can be compared with the X-ray value of 1.63 Å in diaryl derivatives[4b]. The non-linearity of the P–C–P framework is also reproduced by calculation. It had been originally suggested that this was due to packing effects in the crystal or to steric effects between bulky substituents in the real molecule. However, it appears that it is rather due to an electronic character within the PCP backbone itself. This is similar to the behaviour of carbodiimides or isocyanate analogues[8]. It is worth noting that substitution by halogens tends to accentuate the bending.

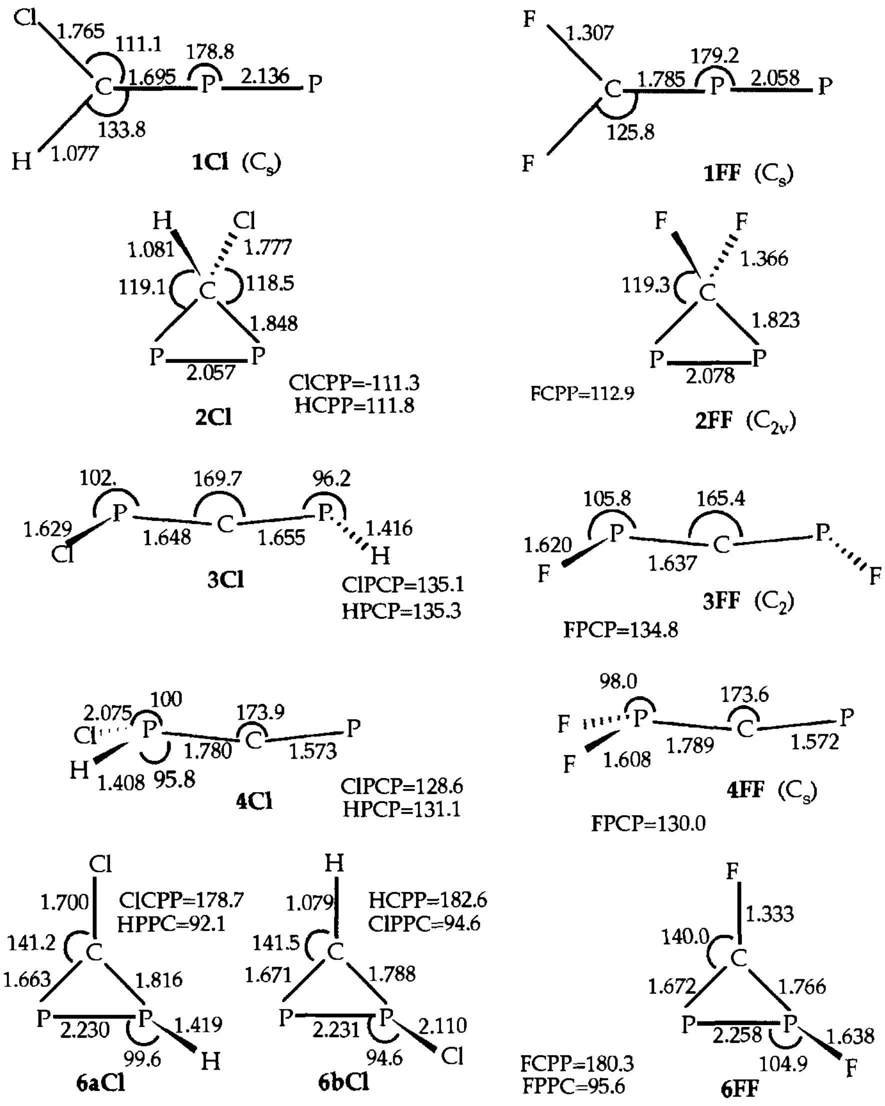
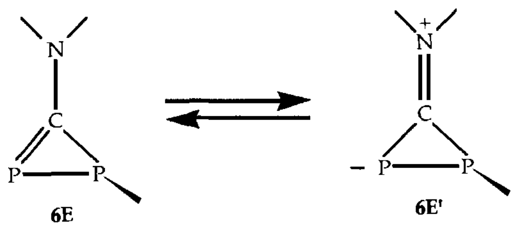


Figure 2b. Optimized geometries of the isomers of $HClCP_2$ and F_2CP_2. Bond lengths are in Å and bond lengths in degrees

The experimental geometry of 1*H*-diphosphirene **6** is available for the species **6E**. The MP2 calculated bond distances for **6H** differ from the crystal values by an average of 0.08 Å. The reason for this large variance is probably an important contribution of the resonance structure **6E'**, whose effect is a stretching of the P–C distance and an enlarging the CPP bond angle.

Scheme 2



It is important to note that the optimized geometries do not change significantly on going from the HF/3-21G* to the HF/6-31G** level. For the H_2CP_2 series, HF calculations using the larger 6-311++G** basis set induce only marginal changes in geometrical parameters. On the contrary, inclusion of correlation energy is more important than improving the basis set. MP2/6-31G** geometries are the closest to the experimental ones (when available for comparison). In general, the optimized bond lengths of the central carbon atom to halogen atoms can be compared with the values for carbon–halogen and phosphorus–halogen in other systems. For the CX_4 systems, the experimental C–F bond length is 1.32 Å and the C–Cl bond length 1.77 Å[9]. The average C–F bond length predicted at the MP2 level in this study is 1.34 Å and the C–Cl bond length is 1.74 Å. Similarly, the experimental P–F distance is 1.57 and the P–Cl distance 2.04 Å in PX_3 species[10]. In this study, the average P–F distance is 1.62 and the P–Cl dis-

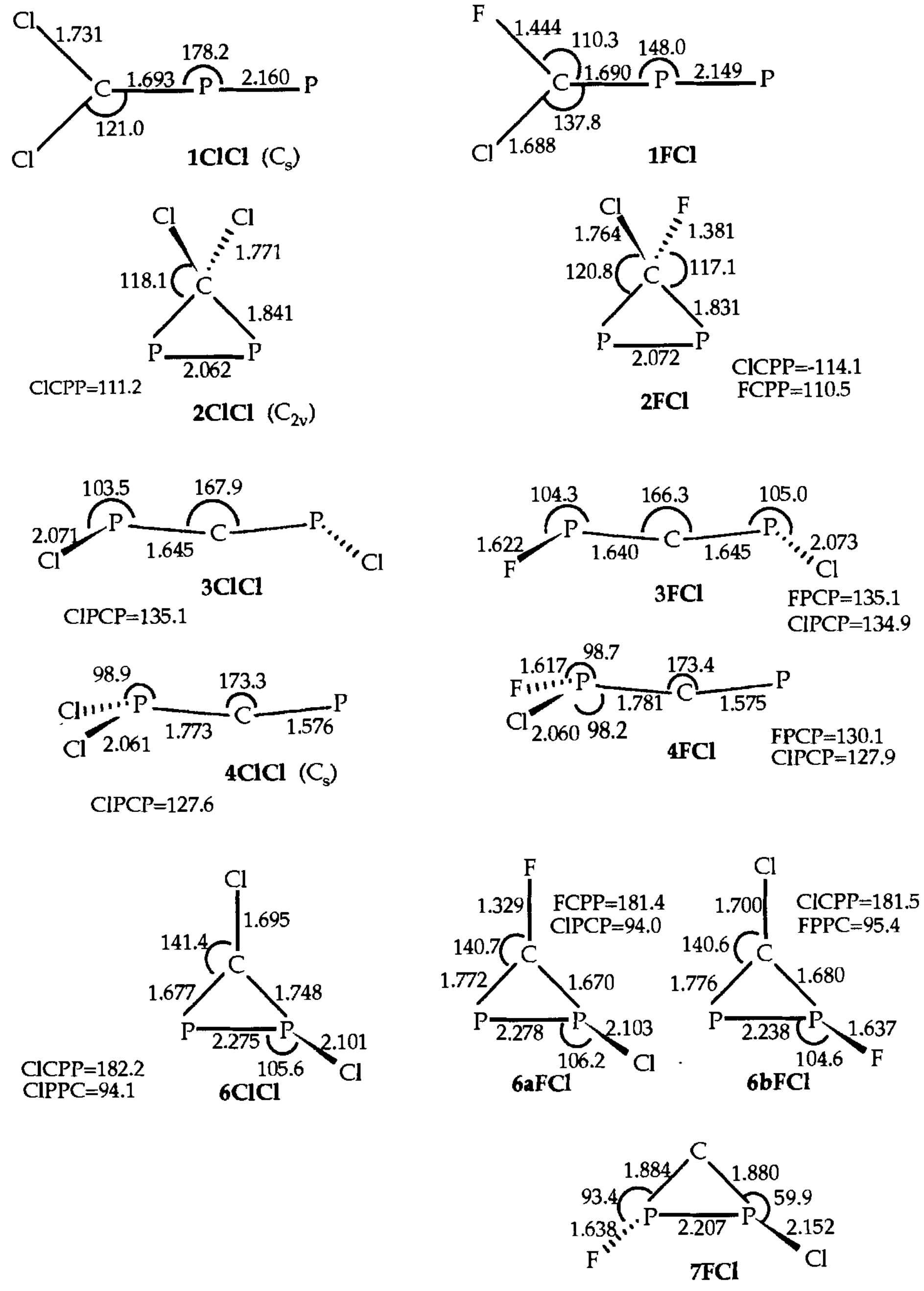


Figure 2c. Optimized geometries of the isomers of Cl_2CP_2 and $FClCP_2$. Bond lengths are in Å and bond lengths in degrees

tance 2.07 Å. Thus, the bonds to halogens appear to be realistically modelled by the calculations. The most obvious geometric effect of halogen substitution is a decrease in the C−P bond distances in **2**, **3**, and **4** and an increase in **1**. The effect is larger when substitution is at carbon.

3. Relative Stabilities of Isomers

The calculated total and relative energies of the six series considered are recorded in Table 2. For the reasons mentioned previously the energies of both structures **5** and **7** are not included. In general, the energy ordering remains unchanged at all levels of theory. The relative energies obtained by both MP4SDTQ and QCISD(T) are very close to each other, except for **3F** where the difference is 5 kcal/mol. This indicates that these species can be adequately described by single reference wavefunctions. Unless otherwise stated, the values quoted hereafter refer to our best values obtained at the QCISD(T)/6-31G**//MP2/6-31G** + ZPE level. Figure 3 displays an energy correlation diagram for the six series of isomers.

(a) *H_2CP_2 Series:* For the unsubstituted species, the energy ordering is as follows (values in kcal/mol)

2H (0.0) < **4H** (10.2) < **6H** (14.5) < **3H** (23.4)
< **1H** (41.2)

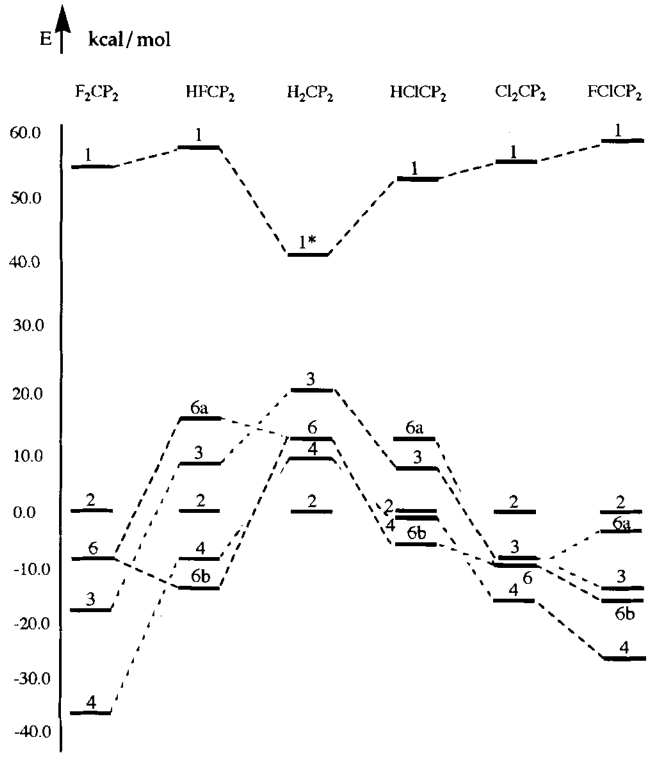


Figure 3. Energy correlation diagram for the six series of this study, energies are calculated at the QCISD(T)/6-321G**//MP2/6-31G** + ZPE level

The 3*H*-diphosphirene **2H** is unambiguously the global minimum of the series.

(b) *$HFCP_2$ and $HClCP_2$ Series:* The energy ordering for both monosubstituted species is similar (values in kcal/mol):

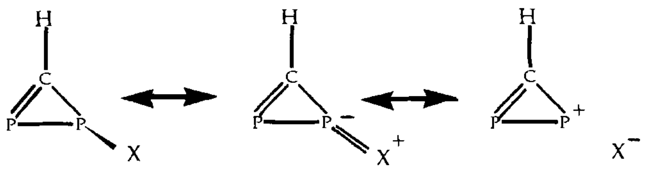
$HFCP_2$: **6bF** (0.0) < **4F** (6.9) < **2F** (16.5) < **3F** (24.3)
< **6aF** (33.5) < **1F** (72.5)

$HClCP_2$: **6bCl** (0.0) < **4Cl** (6.0) ≈ **2Cl** (6.4) < **3Cl** (15.7)
< **6aCl** (20.6) < **1Cl** (59.1)

Except for **1** the energies of the $HClCP_2$ isomers are very close to each other. The energies of **4Cl** and **2Cl** are almost identical, so that their relative ordering could be reversed at higher levels of theory. The *P*-halogenated 1*H*-diphosphirene **6b** becomes thus the global minimum in both monosubstituted series. The (halogenophosphanyl)phosphaalkyne **4** is also stabilized, becoming the second most stable isomer lying below **2**, particularly in the fluorine series. The large energy difference between **6a** and **6b** arises no doubt from the difference between the bond energies of the P–X and C–X bonds[5]. For instance, the P–F bond energy is 132 kcal/mol while the C–F bond only amounts to 116 kcal/mol[11]. As a consequence, halogenation at phosphorus is often favoured over halogenation at carbon. This is also the reason for the destabilization of **2** relative to **4** and **6b**.

Relative to **2**, the diphosphaallene **3** is also stabilized but the stabilization upon halogenation is apparently not large enough to overcome the inherent instability of a cumulene structure. The higher stability of **6b** over **4**, in which a P–X bond is also present, can be understood in terms of an additional stabilization of **6b** arising from the resonance structures in Scheme 3.

Scheme 3



(c) *F_2CP_2, Cl_2CP_2 and $FClCP_2$:* In the disubstituted series, the energy ordering is again modified with **4** becoming the most stable isomer (values in kcal/mol):

F_2CP_2: **4FF** (0.0) < **3FF** (19.7) < **6FF** (29.1) < **2FF** (37.3)
< **1FF** (89.7)

Cl_2CP_2: **4ClCl** (0.0) < **6ClCl** (8.2) < **3ClCl** (8.8)
< **2ClCl** (17.7) < **1ClCl** (71.8)

$FClCP_2$: **4FCl** (0.0) < **6bFCl** (10.9) < **3FCl** (13.4)
< **6aFCl** (24.4) < **2FCl** (28.4) < **1FCl**
(85.9)

The global minimum character of **4** in all three disubstituted series can be understood by an amplifying effect of two P–X bonds.

3FF is now more stable than **6FF** because the former has two P–F bonds whereas the latter only has one. In both Cl_2CP_2 and $FClCP_2$ series, **3** and **6** lie much closer in energy, probably due to the fact that the C–Cl and P–Cl bond energies are similar, namely 78 kcal/mol for C–Cl in CCl_4 and also 78 kcal/mol for P–Cl in PCl_3. In agreement with this finding, the most stable of the two possibilities for isomer **6** in the $FClCP_2$ series is the one with a P–F bond, **6bFCl**, and **3FCl** is intermediate in stability between both forms of isomer **6**. With regards to the cyclic isomer **2**, the global minimum of the unsubstituted species, a major change on replacing H by X is its large destabilization.

A clear trend emerges. The isomer with the more P–X bonds is the more stable, and if there is competition between F and Cl, the isomer with more P–F bonds is dominating. In contrast, the reverse is true for the unsubstituted series; the species with the most C–H bonds being the most stable. This consideration explains the order of stability between both diphosphirene forms in which the halogenated 1*H* form **6** is much more stable than the 3*H* form **3**.

Another clear trend is that phosphanylphosphaalkyne **4** is consistently more stable than diphosphaallene **3**. A remarkable feature of both isomers is that the geometry of the PCP backbone changes very little as the substituents vary (see Figures 2). The nature of the substituents also does not modify the bonding of the PCP backbone greatly. For instance, for any given series, the electronic charges on the substituents in **3** and **4** are quite similar. This indicates that the substituents, be they H, F, Cl or any combination of the above, are in a similar chemical environment created by the PCP backbone. As a consequence, the energy difference between both isomers **3** and **4** remains almost constant upon halogenation, the maximum variation being about 5

Table 2. Total energies (a.u.) and relative energies (kcal/mol in parentheses) for the six series of species considered using the 6-31G** basis set

	HF[a]	MP2[b]	MP4SDTQ[b]	QCISD(T)[b]	ZPE[c]
H_2CP_2					
1H	-720.35691 (43.2)	-720.71941 (62.2)	-720.76956 (42.8)	-720.76946 (43.2)	15.4 (41.2)[d]
2H	-720.42577 (0.0)	-720.81847 (0.0)	-720.83769 (0.0)	-720.83832 (0.0)	17.4 (0.0)
3H	-720.38640 (24.7)	-720.76814 (31.6)	-720.79421 (26.8)	-720.79480 (27.3)	13.5 (23.4)
4H	-720.41498 (6.8)	-720.79804 (12.8)	-720.81892 (11.8)	-720.81687 (13.4)	14.2 (10.2)
6H	-720.40489 (13.1)	-720.79050 (17.6)	-720.81118 (16.6)	-720.81187 (16.6)	15.3 (14.5)
$HFCP_2$					
1F	-819.19171 (66.6)	-819.69392 (79.9)	-819.75196 (74.1)	-819.75117 (73.2)	11.2 (72.5)
2F	-819.26710 (19.3)	-819.79518 (16.3)	-819.84520 (15.6)	-819.84326 (15.4)	13.0 (16.5)
3F	-819.26509 (20.6)	-819.78164 (24.8)	-819.85916 (20.7)	-819.82659 (25.8)	10.4 (24.3)
4F	-819.29050 (4.6)	-819.80878 (7.8)	-819.85916 (6.8)	-819.85545 (7.7)	11.1 (6.9)
6aF	-819.240221 (36.2)	-819.76313 (36.4)	-819.81559 (34.2)	-819.81319 (34.3)	11.1 (33.5)
6bF	-819.29784 (0.0)	-819.82120 (0.0)	-819.87004 (0.0)	-819.86778 (0.0)	11.9 (0.0)
$HClCP_2$					
1Cl	-1179.25043 (56.5)	-1179.71934 (62.9)	-1179.78271 (59.7)	-1179.78363 (59.1)	11.2 (59.1)[d]
2Cl	-1179.32214 (11.5)	-1179.81130 (5.2)	-1179.86949 (5.3)	-1179.86897 (5.5)	12.1 (6.4)
3Cl	-1179.31116 (18.4)	-1179.78505 (21.6)	-1179.84976 (17.6)	-1179.85037 (17.2)	9.7 (15.7)
4Cl	-1179.33449 (3.7)	-1179.80921 (6.5)	-1179.86915 (5.5)	-1179.86698 (6.8)	10.4 (6.0)
6aCl	-1179.29984 (25.5)	-1179.78480 (21.8)	-1179.84493 (20.7)	-1179.84372 (21.4)	10.4 (20.6)
6bCl	-1179.34045 (0.0)	-1179.81952 (0.0)	-1179.87786 (0.0)	-1179.87776 (0.0)	11.2 (0.0)
F_2CP_2					
1FF	-918.05706 (79.7)	-918.71702 (117.9)	-918.77375 (92.4)	-918.77198 (89.6)	7.5 (89.7)
2FF	-918.11628 (42.7)	-918.84166 (39.7)	-918.86115 (37.5)	-918.85698 (36.3)	8.1 (37.3)
3FF	-918.15020 (21.4)	-918.86620 (24.3)	-918.88702 (21.3)	-918.88300 (20.0)	7.1 (19.7)
4FF	-918.18436 (0.0)	-918.90490 (0.0)	-918.92096 (0.0)	-918.91483 (0.0)	7.4 (0.0)
6FF	-918.13253 (32.5)	-918.82210 (52.0)	-918.87436 (29.2)	-918.86895 (28.8)	7.7 (29.1)
Cl_2CP_2					
1ClCl	-1638.13669 (73.6)	-1638.73121 (77.2)	-1638.80698 (73.9)	-1638.80696 (71.9)	5.8 (71.8)[d]
2ClCl	-1638.20866 (17.4)	-1638.82653 (39.7)	-1638.89606 (18.0)	-1638.89378 (17.4)	6.2 (17.7)
3ClCl	-1638.23665 (10.9)	-1638.83280 (13.5)	-1638.90742 (10.8)	-1638.90742 (8.9)	5.8 (8.8)
4ClCl	-1638.25399 (0.0)	-1638.85431 (0.0)	-1638.92468 (0.0)	-1638.92154 (0.0)	5.9 (0.0)
6ClCl	-1638.23381 (12.7)	-1638.84130 (8.2)	-1638.91093 (8.6)	-1638.90887 (8.0)	6.1 (8.2)
$FClCP_2$					
1FCl	-1278.08256 (84.7)	-1278.71371 (92.1)	-1278.78285 (86.8)	-1278.78055 (85.3)	7.3 (85.9)
2FCl	-1278.15929 (36.6)	-1278.81472 (28.8)	-1278.87486 (29.1)	-1278.87188 (28.0)	7.1 (28.4)
3FCl	-1278.19317 (15.3)	-1278.83175 (18.1)	-1278.89678 (15.3)	-1278.89678 (13.6)	6.5 (13.4)
4FCl	-1278.21758 (0.0)	-1278.86054 (0.0)	-1278.92122 (0.0)	-1278.91650 (0.0)	6.7 (0.0)
6aFCl	-1278.17402 (27.3)	-1278.81943 (25.8)	-1278.88129 (25.1)	-1278.87801 (24.2)	6.9 (24.4)
6bFCl	-1278.19231 (15.9)	-1278.84331 (10.8)	-1278.90345 (11.2)	-1278.89934 (10.8)	6.8 (10.9)

[a] Based on the HF/6-31G** geometries. – [b] Based on the MP2/6-31G** geometries shown in Figures 2a, 2b, and 2c. – [c] Values at the HF/6-31G** level, scaled by 0.9. – [d] Relative energies at the QCISD(T)/6-31G** level with ZPE correction.

kcal/mol. It can also be concluded that the greater stability of **4**, relative to **3**, is due to the electronic nature of the PCP backbone. A single C–P bond plus a triple C–P bond is favoured over two double cumulenic C=P bonds.

It should be noted that experimentally the existence of a substituted phosphoanylphosphalkyne **4** has not been reported yet, whereas diphosphaallenes **3** bearing bulky substituents are known to be stable compounds which do not isomerize to **4**. It is in fact not easy to stabilize **4** sterically, due to the obvious large repulsion between both substituents.

In the light of the above findings, it is perhaps of interest to consider the "perfluoro effect". This term describes a fact that when two F atoms are in a geminal position, they tend to accentuate the stabilization. Such stabilization is well documented in carbon and silicon compounds[12]. We have considered the following bond separation reactions:

For X_2CP_2 (X = F or Cl):

$$X_2CP_2 + H_2CP_2 \rightarrow 2\,HXCP_2 \qquad (1)$$

For $FClCP_2$:

$$FClCP_2 + H_2CP_2 \rightarrow HFCP_2 + HClCP_2 \qquad (2)$$

The bond separation energies for isomers **2**, **3**, and **4** listed in Table 3 are calculated at the QCISD(T)/6-31G**// MP2/6-31G** + ZPE level. A positive value indicates that the geminal X atoms stabilize the relevant species to a greater extent than the sum of two independent X atoms. The results indicates rather a small perfluoro effect.

As a matter of fact, the stabilization in **3**, which has no possibility for a geminal P-X interaction, varies to an extent comparable to those in **4** where geminal effects could exist. The C−Cl bonds present even a small destabilization, in **2**, probably due of the intrinsic weakness of the C−Cl bond (78 kcal/mol, about 12 kcal/mol weaker than the C−H bond).

With regards to the isomer **1**, it is further destabilized upon halogenation, even though its equilibrium structure character remains. The energy difference between **1** and **2** can be understood by considering them as formed from the interaction of carbene (X_2C) and P_2 moieties. The HOMO of P_2, which is a π(P=P) orbital, interacts preferentially with the LUMO of the singlet carbene giving rise to the cyclic species **2**. Halogen substitutions of the carbene leads to a stabilization of its LUMO and, as a consequence, the resulting cyclic form **2**.

Table 3. Bond separation energies (ΔE, kcal/mol), calculated from the isodesmic reactions. Energies calculated at the QCISD(T)/6-31G**// MP2/6-31G** level, with ZPE correction. Note: ΔE positive, stabilizing geminal effect; ΔE negative, destabilizing geminal effect

Series	Isomer 2	Isomer 3	Isomer 4
F_2CP_2	+11.6	+15.6	+13.7
Cl_2CP_2	-3.0	+1.1	+3.6
$FClCP_2$	-0.7	+9.3	+7.5

4. Comparison with the XX′CN₂ Systems

A theoretical study of some nitrogen analogous $XX'CN_2$ has recently been reported[13]. Isomers analogous to **1**, **2**, **4**, **5**, and **6** for F_2CN_2, and to **1** and **2** for H_2CN_2 and $HFCN_2$ have been investigated. Accordingly, the order of stability of the nitrogen series turns out to be quite different from that which we found for the phosphorus series in this study. In the notation of the present study, with N substituted for P, it has been found:

H_2CN_2: (1) < (2)
$HFCN_2$: (2) < (1)
F_2CN_2: (2) < (1) < (4) < (6) < (5)

These findings are in agreement with experimental observations, namely diazomethane is more stable than diazirine while difluorodiazirine is known but difluorodiazomethane has evaded synthesis[13]. The non-observation of $F_2C{=}N{=}N$ has been rationalized by its rather small dissociation energy giving $CF_2 + N_2$ (54 kcal/mol). The most startling difference between the F_2CN_2 and F_2CP_2 series is the high thermodynamic stability of the isomers **1** and **2** in the N series. This arises from the greater strengths of nitrogen-nitrogen multiple bonds, which stabilize the relevant molecule relative to those species without such multiple bond.

Not only are **1** and **2** relatively stabilized in the H_2CN_2 series, there is also a reversal in the energy ordering as compared to the P analogues, diazomethane being more stable than diazirine. This behaviour can again be rationalized by the bonding interaction between the CH_2 and N_2 groups. A similar argument can also be applied to rationalize the energy ordering mentioned above following fluorination. Note that the isomers **1** of X_2CN_2 are characterized as transition structures (at the MP2/6-31G**) level rather than equilibrium structures, a behaviour exactly opposite to that of the P species.

For other isomers common to both F_2CN_2 and F_2CP_2 series, the order of stability **4** < **6** < **5** is the same in both cases.

It is of interest to note that it has been shown[14] on the basis of quantum mechanical calculations that phosphorus-containing rings have relatively little strain.

5. Vibrational Analysis

In order to gain some useful spectroscopic information, we have carried out a vibrational analysis for the most stable species of each series under consideration. The infrared spectra are given in Tables 4a−4f. The predicted wavenumbers are obtained from harmonic values at the MP2/ 6-31G** and scaled by 0.95 to account for a systematic overestimation at this level of theory. The IR intensities are normalized to the most intense absorption.

(i) The spectrum of **2H** (Table 4a) contains eight absorbances of appreciable intensity. The ring torsion shows vanishingly small intensity at 905 cm^{-1}.

(ii) Tables 4b and 4c give the predicted spectra for both fluoro- and chloro-1*H*-diphosphirenes **6F** and **6Cl**. In both cases, all absorbances exhibit appreciable intensities. The strongest absorbances are at 768 and 447 cm^{-1} corresponding to the P−F and P−Cl stretches, respectively. Assuming a harmonic oscillator, these wavenumbers are indicative of a force constant for the P−F about 1.5 times greater than that for the P−Cl bond.

(iii) Tables 4d, 4e, and 4f give the predicted IR spectra of isomer **4**, phosphanylphosphaalkynes, in the disubstituted series. In Table 4d the most intense bands are centred at 825 and 832 cm^{-1} corresponding to both symmetric and asymmetric P−F stretching modes, respectively. Again, the P−Cl bond vibrates at lower wavenumbers, namely 490 and 500 cm^{-1} (Table 4e). In the mixed species ($FClCP_2$) **4FCl** (Table 4f) the strongest absorbances also relate to theP−F

Table 4a. Theoretical infrared spectrum of **2H**

Wavenumber (cm^{-1})	Relative intensity	Assignment
497	0.17	CP_2 asymm. str.
559	0.36	CP_2 symm. bend
799	0.41	CP_2 symm. str.
905	0.00	ring torsion
917	0.63	CH_2 asymm. rock
980	1.00	CH_2 rock
1461	0.53	CH_2 symm. bend
3046	0.72	CH_2 symm. str.
3111	0.30	CH_2 asymm. str.

Table 4b. Theoretical infrared spectrum of **6bF**

Wavenumber (cm^{-1})	Relative intensity	Assignment
210	0.01	PF bend
308	0.03	C(H)(P)(P) str.
444	0.04	PCP scissors
694	0.12	CH out of plane str.
723	0.09	PCP in plane rock
768	1.00	PF str.
963	0.11	HCP(F) bend, ring expansion
1005	0.03	HCP(F)bend, ring contraction
3153	0.01	CH out of plane bend

Table 4c. Theoretical infrared spectrum of **6bCl**

Wavenumber (cm^{-1})	Relative intensity	Assignment
164	0.02	PCl bend
249	0.04	C(H)(P)(P) str.
424	0.06	PCP scissors
447	1.00	PCl str.
694	0.62	CH out of plane str.
706	0.12	PCP in plane rock
953	0.12	HCP(Cl)bend, ring expansion
1013	0.04	HCP(Cl)bend, ring contractn.
3158	0.03	CH out of plane bend

Table 4d. Theoretical infrared spectrum of **4FF**

Wavenumber (cm^{-1})	Relative intensity	Assignment
110	0.00	PCP bend
139	0.02	PCP in plane bend
296	0.03	$CP(F_2)$ bend
373	0.08	PCP torsion
394	0.12	PCP symm. bend
549	0.93	$(F_2)P$-C str.
825	1.00	PF_2 symm. str.
832	0.95	PF_2 asymm str.
1345	0.59	PC-P str.

Table 4e. Theoretical infrared spectrum of **4ClCl**

Wavenumber (cm^{-1})	Relative intensity	Assignment
88	0.00	PCP bend
118	0.01	PCP in plane bend
184	0.01	$CP(Cl_2)$ bend
329	0.03	$(Cl_2)P$-C str.
337	0.02	PCP torsion
490	0.53	PCl_2 symm. str.
500	1.00	PCl_2 asymm. str.
518	0.44	PCP in plane wag
1338	0.34	PC-P str.

Table 4f. Theoretical infrared spectrum of **4FCl**

Wavenumber (cm^{-1})	Relative intensity	Assignment
96	0.00	PCP bend
135	0.01	PCP in plane bend
239	0.01	CP(ClF) bend
337	0.03	PCP torsion
374	0.08	PCP symm. bend
512	1.00	PCl str.
533	0.59	(ClF)P-C str.
813	0.91	PF str.
1346	0.47	PC-P str.

(813 cm^{-1}) and P–Cl (512 cm^{-1}) bonds. In all cases, the P–C–P bending mode shows no significant absorption. The single P–C bond stretches centred in the region of 530–550 cm^{-1} are also of moderately strong intensity.

Conclusion

In the present theoretical study on the relative stabilities of the $XX'CP_2$ isomers, we have shown that the energies of the isomeric species are often reordered following halogen substitution. The phosphorus-halogen moiety behaves as the main stabilizing factor on the rest of the molecular structure. This is particularly true when the fluorine atom is involved. This argument can also explain the peculiar stability of the cyclic halogeno-1*H*-diphosphirene. This suggests the possibility of synthesizing some X_2CP_2 compounds never known before including (difluorophosphanyl)- and (dichlorophosphanyl)phosphaalkynes, and fluoro- and chloro-1*H*-diphosphirenes.

It is also found that the effect on the geometry following halogenation is larger if the substitution takes place at carbon than at phosphorus, partly due to a greater contraction of the covalent radius of carbon on halogenation.

The behaviour of P species is found to be quite different from, if not opposite to, that of their nitrogen analogues.

Finally, it may be noted that many of the arguments in this paper can be extrapolated by a thermochemical analysis[12a]. However, the detailed calculations provide greater chemical insight.

M.T.N. thanks the *Belgian National Fund for Scientific Research* (NFWO) and the *Belgian Government* (DPWB) for continuing financial support.

---

[1] S. A. Paulsen, *Angew. Chem.* **1960**, *72*, 781.

[2] E. Niecke, R. Streubel, M. Nieger, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 90; *Angew. Chem.* **1991**, *103*, 103.

[3] E. Niecke, R. Streubel, M. Nieger, D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1673; *Angew. Chem.* **1989**, *101*, 1708.

[4] [4a] M. Yoshifuji, K. Toyota, N. Inamato, *J. Chem. Soc., Chem. Commun.* **1984**, 689. – [4b] H. H. Karsch, F. H. Köhler, H.-U. Reisacher, *Tetrahedron Lett.* **1984**, *25*, 3687. – [4c] R. Appel, P. Folling, B. Josten, M. Siray, V. Winkhaus, F. Knoch, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 619; *Angew. Chem.* **1984**, *96*, 620.

[5] M. T. Nguyen, H. Vansweevelt, L. C. Vanquickenborne, *Chem. Ber.* **1992**, *125*, 923.

[6] *Gaussian92*, Revision A, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1992**.

[7] M. T. Nguyen, A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2* **1985**, 2005.

[8] M. T. Nguyen, N. V. Riggs, L. Radom, M. Winnewisser, B. P. Winnewisser, M. Birk, *Chem. Phys.* **1988**, *122*, 305.

[9] C. R. Patrick, *Adv. Fluorine Chem.* **1961**, *2*, 1.

[10] F. R. Hartley, *The Chemistry of Organophosphorus Compounds*, **1990**, *1*, 15.

[11] J. E. Huheey, *Inorganic Chemistry*, Harper Row, New York, **1972**, p. 694.

[12] [12a] J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London and New York, **1970**. – [12b] A. E. Reed, P. von Ragué Schleyer, *J. Am. Chem. Soc.* **1987**, *109*, 7362.

[13] A. I. Boldyrev, P. von Ragué Schleyer, D. Higgins, C. Thomson, S. S. Kramarenko, *J. Comp. Chem.* **1992**, *13*, 1066.

[14] W. W. Schoeller, *J. Mol. Struct.* **1993**, *284*, 61, and references therein.

[370/93]