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Structure and Bonding in Diphosphanylcarbenes. An *ab Initio* Investigation

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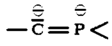
Abstract: Self consistent field calculations, supplemented by Møller–Plesset second-order estimates of correlation effects, are presented for the compounds R_2PCPR_2, R = NH_2 and R = $N(iPr)_2$, as well as for species resulting from protonation or addition of H_2 and HF. The relative stability of possible isomers is computed and discussed. Diphosphanylcarbenes always prefer an asymmetric PC multiple-bond structure such as $>P—C^{\ominus}{=}P^{\oplus}<$, incorporating alkylidynephosphorane and vinyl ylide characteristics.

I. Introduction

Various attempts have been made to isolate stable carbenes which still show carbene reactivity.[1] For molecules which can be described by a multiple-bond structure as well as by a carbene structure, the question arises whether they can be looked upon as stabilized carbenes. It was the main motivation of the present study to answer this question for several molecules containing phosphorus–carbon bonds. Alkylidynephosphoranes or λ^5-phosphaalkynes (**A1**) belong to this group of compounds, since they

$—C{\equiv}P<$

(A1)



$—\overset{\ominus}{\overline{C}}{=}\overset{\oplus}{P}<$

(A2)

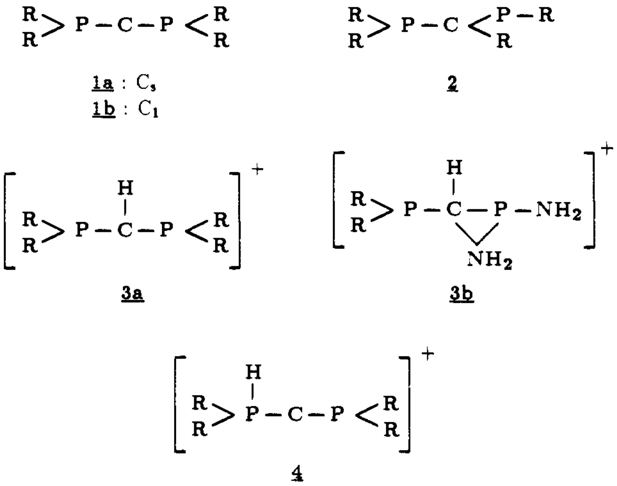
$—\overline{C}—\overline{P}<$

(A3)

can also be regarded as phosphorus vinyl ylides (**A2**) or λ^3-phosphanylcarbenes (**A3**). The recent isolation of stable alkylidynephosphoranes by Bertrand et al.[2] has prompted discussions about their electronic structure.[3] Bertrand et al. have isolated *P*-bis(diisopropylamino)-*C*-(trimethylsilyl)-λ^5-phosphaalkyne, $R'_3Si—C{\equiv}PR_2$, as the first stable compound formally featuring a tricoordinated, pentavalent triple-bonded phosphorus atom. It combines carbene and phosphorus–carbon multiple-bond reactivity, as shown by cyclopropanation, migration, and insertion reactions and [1 + 2] and [2 + 2] cycloaddition, respectively.[2] NMR data are in favor of a PC multiple bond. According to theoretical investigations by Dixon et al.,[4] the hydrogen analogue (i.e. R = R′ = H) favors a multiple-bond structure as given by **A2** with small admixtures of **A1**.

In this context the question arises if diphosphanylcarbene **1** (see Chart I) featuring two formally identical phosphanyl groups prefers a symmetric carbene structure or an asymmetric phosphorus–carbon multiple-bond structure similar to that of Bertrand's silylphosphacarbene.[2] The same question of symmetry arises for the C-protonated species **3**. The P-protonated species **4** is of special interest, since phosphonio and silyl groups are isoelectronic and isovalent.

Chart I



1a : C_s
1b : C_1

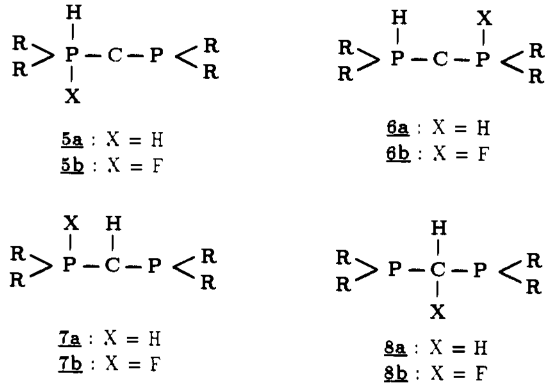
2

3a

3b

4

Chart II



5a : X = H
5b : X = F

6a : X = H
6b : X = F

7a : X = H
7b : X = F

8a : X = H
8b : X = F

In the present work we report and discuss the results of a theoretical study undertaken to answer the just mentioned problems. In the first part we deal with compounds **1**–**4** (Chart I); the second part is devoted to dihydrogen and HF derivatives **5**–**8** (Chart II) of the parent compound **1**. We treat especially two structures of **1** in symmetry C_s (**1a**) and C_1 (**1b**) as well as two conformations of **3**, open (**3a**) and closed (**3b**). The computations have been performed for R = NH_2 throughout. Since **4** has been isolated for R = $N(iPr)_2$ (*i*Pr = isopropyl C_3H_7)

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Table I. Computed Structural Constants, in pm and degrees, at the SCF Level (If Not Stated Differently), Shared Electron Numbers (SEN), and Atomic Net Charges of Compounds **1–4**

1a	structure	PC 171.9, PN 170.2/172.3, PCP 131.4
	SEN	PC 1.55, PN 1.20
	charge	$C^{-0.5}$, $P^{+0.6}$
1b	structure	P(1)C 176.5, P(2)C 153.3, P(1)N 171.4/174.1, P(2)N 167.5/167.8, P(1)CP(2) 160.5
	SEN	P(1)C 1.40, P(2)C 2.30, PN 1.1–1.2
	charge	$C^{-0.8}$, $P(1)^{+0.6}$, $P(2)^{+1.0}$
2	structure	P(1)C 185.6, P(2)C 171.5, P(1)N 169.7/171.5, P(2)N(2) 176.4, CN(1) 133.7, P(1)CP(2) 119.6, P(1)CN(1)115.3, P(2)CN(1) 124.8
	SEN	P(1)C 1.25, P(2)C 1.77, P(1)N 1.21, P(2)N(2) 1.18, CN(1) 1.64
	charge	$C^{-0.1}$, $P(1)^{+0.6}$, $P(2)^{+0.0}$, $N(1)^{-0.2}$, $N(2)^{-0.5}$
3a	structure	P(1)C 185.8, P(2)C 160.6, P(1)N 167.7/173.3, P(2)N 161.2/161.9, P(1)CP(2) 127.0, P(1)CH(1) 117.2, P(2)CH(1) 115.4
	SEN	P(1)C 1.23, P(2)C 1.96, P(1)N 1.17/1.28, P(2)N 1.41/1.43
	charge	$C^{-0.5}$, $P(1)^{+0.6}$, $P(2)^{+1.1}$
3b	structure	P(1)C 188.0, P(2)C 180.7, P(1)N 168.6/169.5, P(2)N(1) 193.3, P(2)N(2) 164.3, CN(1)148.0, P(1)CP(2) 118.0, P(2)N(1)C62.3, N(1)CP(2) 71.2, CP(2)N(1) 46.5
	SEN	P(1)C 1.19, P(2)C 1.35, CN(1) 1.19, P(1)N 1.24/1.25, P(2)N(1) 0.75, P(2)N(2) 1.46
	charge	$C^{-0.2}$, $P(1)^{+0.6}$, $P(2)^{+0.7}$, $N(1)^{-0.2}$, $N(2)^{-0.4}$, $N(i)^{-0.5}$
4	structure	P(1)C 167.4, P(2)C 153.1, P(1)N 164.9/164.9, P(2)N 162.6/162.9, P(1)CP(2) 162.0
	SEN	P(1)C 1.49, P(2)C 2.19, PN 1.2–1.3
	charge	$C^{-1.0}$, $P(1)^{+1.2}$, $P(2)^{+1.3}$
4	with R = NH_2 on the MP2 level	
	structure	P(1)C 169.2, P(2)C 157.9, P(1)N 165.9/166.0, P(2)N 163.9/164.8, P(1)CP(2) 135.7
	SEN	P(1)C 1.46, P(2)C 2.10, PN 1.2–1.3
	charge	$C^{-0.9}$, $P(1)^{+1.1}$, $P(2)^{+1.1}$
4	with R = N(*i*Pr)$_2$ on the SCF level	
	structure	P(1)C 169.8, P(2)C 155.7, P(1)N 166.2/166.6, P(2)N 165.0/165.8, P(1)CP(2) 151.2
	SEN	P(1)C 1.46, P(2)C 2.18, PN 1.2–1.3
	charge	$C^{-0.9}$, $P(1)^{+1.1}$, $P(2)^{+1.1}$

with triflate $CF_3SO_3^-$ as counterion, we also considered R = N(*i*Pr)$_2$ in this case.

Only singlet carbenes are taken into consideration, since spectroscopic data of **4** (with R = N(*i*Pr)$_2$) point at a singlet ground state. Furthermore, calculations of related compounds[4–6] and tentative investigations by ourselves predict singlet carbenes to be more stable than triplet carbenes.

II. Methods

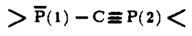
SCF and MP2 calculations were performed with the program system TURBOMOLE[7] on IBM 6000/32H workstations. Basis sets of split valence plus polarization type (SVP) were employed[8] for P, C, F, and N. For H we used a basis of DZ (double ζ) type (or SV (split valence), which is identical in this case), i.e. polarization functions were considered to be unnecessary. A molecule-optimized basis was employed for *i*Pr groups, where only the α carbon atom has an SV basis (for all basis set data see ref 8) and all other atoms are described by minimal basis sets of three Gaussians for the 1s atomic orbital (AO) of H and four Gaussians for the 1s, two Gaussians for the 2s, and three Gaussians for the 2p AOs of C. This procedure has proven very economic and reliable.[8] All molecules were treated as closed shell systems. Equilibrium geometries were determined by a geometry relaxation procedure based on analytical gradients.[9] These geometries were obtained on the SCF level for all compounds and additionally for **4** by a Møller–Plesset second-order (MP2) estimate of correlation effects.[10] Second-order analytical gradients were computed to confirm that a minimum was found. This was not feasible for the *i*Pr analogue of **4** (i.e. $-NH_2 \rightarrow -N(iPr)_2$).

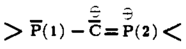
Atomic charges and shared electron numbers (SEN) were obtained by population analyses based on occupation numbers.[11] The discussion of electronic structures (such as **A1**, **A2**, and **A3**) will be based mainly on computed structure parameters (i.e., PC bond lengths of 186, 165, and 152 pm will be associated with single, double, or triple bonds) and the results of population analyses: SEN of 1.31, 2.16, and 3.10 corresponding to covalent single, double, and triple PC bonds.[12] Because of bond polarities the SEN have to be considered with caution. Bond distances are certainly a more reliable indication of bond strength.

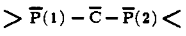
III. Results and Discussion

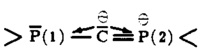
(a) Diphosphacarbene and Its Protonated Derivatives (1–4). The most instructive results of the present investigations concerning the compounds **1–4** are given in Table I (structural properties) and Table II (energies), always for R = NH_2, if not stated differently. The optimized geometries are depicted in Figure 1. All energy differences quoted below refer to SCF data (MP2 in parentheses, as computed at the SCF structure).

The C_s structure **1a** shows two very strong PC single bonds (171.9 pm, SEN 1.5) and a PCP bond angle of 131.4 degrees, which is in line with the idea of a singlet carbene (B3). However, this structure represents a saddle point of the energy hypersurface. Removing the symmetry restrictions leads to the C_1 minimum **1b**, which is more stable than **1a** by 24 kJ/mol (62 kJ/mol) and possesses an extremely short and strong P(2)C bond (153.3 pm, SEN 2.3) as well as a significantly longer and weaker P(1)C bond (176.5 pm, SEN 1.4) in combination with a large PCP bond angle of 160.5°. In agreement with atomic charges $P(1)^{+0.6}$, $C(1)^{-0.8}$, and $P(2)^{+1.0}$, the short bond can be described as a strong covalent double bond with additional Coulomb attractions (resulting in an effective triple bond) as represented by structure **B2** with admixtures of **B1**. No indication is detected that **B3** plays a role in **1b**. The best description of bonding is probably given by **B4**, since an inspection of the MOs reveals a slight delocalization of the carbon lone pair into low-lying orbitals of the two phosphorus atoms.


(B1)


(B2)


(B3)


(B4)

The symmetry lowering $C_s \rightarrow C_1$ can be considered as a typical second-order Jahn–Teller effect:[13] a CI (configuration interaction) including the SCF function and all single excitations (in C_s) yields an excitation energy $1\ {}^1A' \rightarrow 2\ {}^1A'$ of only 1.6 eV (with the *a′* HOMO–LUMO replacement as leading term with a CI coefficient of 0.89).

We now turn to **2**, which, for R = N(*i*Pr)$_2$, is obtained by deprotonation[14] of **4** or by photolysis[15] of >P–C(N_2)–P<. **2** is, for R = NH_2, more stable than **1b** by 215 kJ/mol (223 kJ/mol). The P(2)C bond properties (171.5 pm, SEN 1.8) as well as the CN(1) bond constants (133.7 pm, SEN 1.6) indicate that the N(1) lone pair is to some extent delocalized into the P(2)C bond. This reasoning is in line with computed charges $P(2)^{0.0}$ and $N(1)^{-0.2}$, which may be compared to those in the P(1)(NH_2)$_2$ moiety: $P(1)^{+0.6}$ and $N^{-0.5}$. The electronic structure of **2** is thus

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(6) Hoffmann, M. R.; Kuhler, K. *J. Chem. Phys.* **1991**, *94*, 8029.

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(9) Geometry optimization terminated after the total gradient norm was smaller than 10^{-3} for Cartesian coordinates (in atomic units) and for internal coordinates (atomic units and radians).

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(12) The following data are obtained with the same basis sets as used here: SEN = 1.31 (single bond in H_3CPH_2), SEN = 2.16 (double bond in H_2CPH), and SEN = 3.10 (triple bond in HCP).

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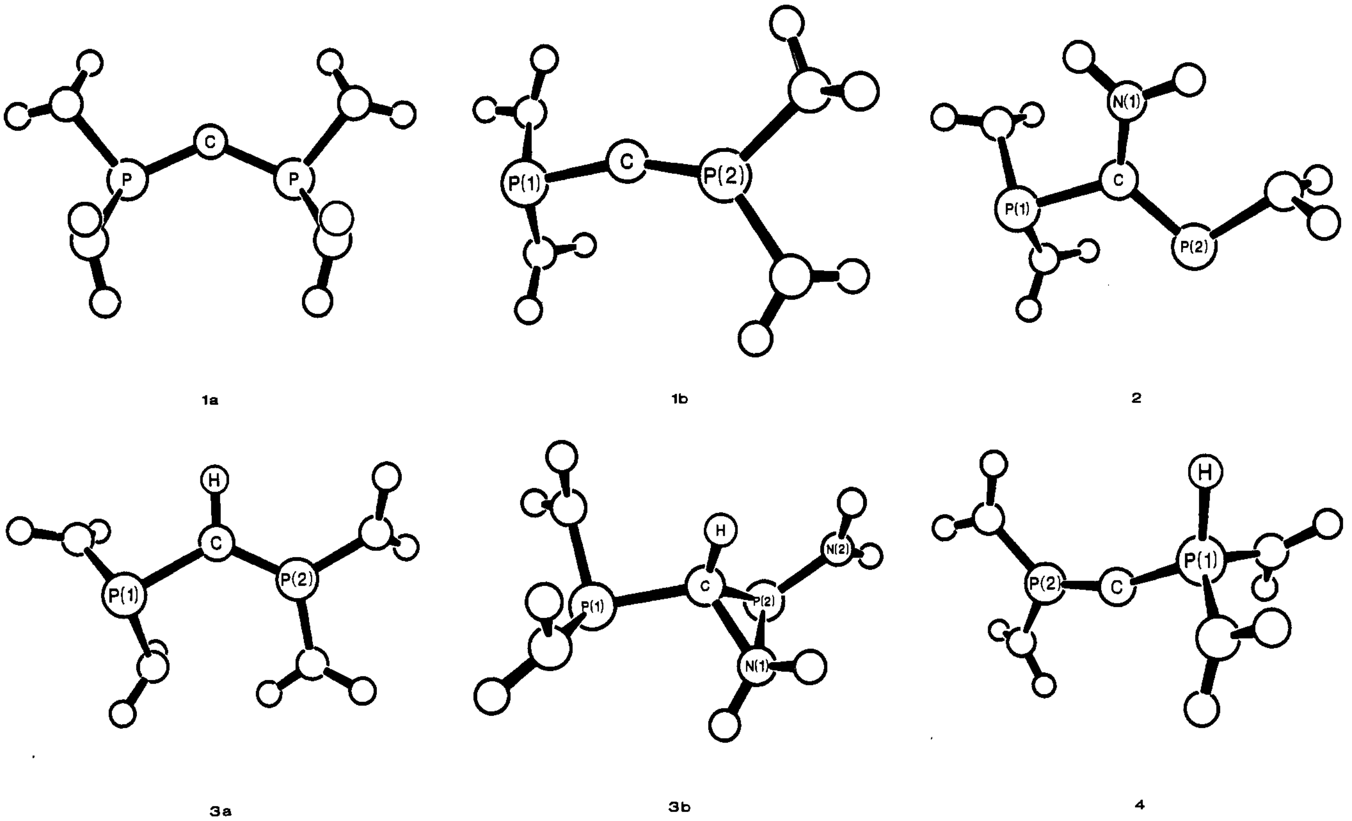
Table II. Computed SCF and SCF + MP2 Energies for Compounds **1–8** with R = NH_2

compound	SCF energy[a] absolute	SCF energy[a] relative[b]	SCF + MP2 energy[a] absolute	SCF + MP2 energy[a] relative[b]
1a	–941.237 573 8	+0.091 165 5	–942.240 931 8	+0.108 955 6
1b	–941.246 815 7	+0.081 923 6	–942.264 576 6	+0.085 310 8
2	–941.328 739 3	0.0	–942.349 887 4	0.0
3a	–941.689 694 0	+0.014 785 7	–942.703 108 2	+0.014 890 4
3b	–941.704 479 7	0.0	–942.717 998 6	0.0
4	–941.669 222 7	+0.035 257 0	–942.676 353 9	+0.041 644 7
5a	–942.356 268 0	+0.166 776 7	–943.392 794 7	+0.148 108 6
6a	–942.424 065 2	+0.098 979 5	–943.446 154 8	+0.094 748 5
7a	–942.469 180 3	+0.053 864 4	–943.488 953 4	+0.051 949 9
8a	–942.523 044 7	0.0	–943.540 903 3	0.0
5b	–1041.204 312 2	+0.094 754 3	–1042.415 959 4	+0.083 721 8
6b	–1041.257 185 7	+0.041 880 8	–1042.455 461 7	+0.044 219 5
7b	–1041.299 066 5	0.0	–1042.499 681 2	0.0
8b	–1041.282 525 5	+0.016 541 0	–1042.476 773 2	+0.022 908 0

[a] All energies (au) refer to structure obtained on the SCF level. [b] Relative energy refers to minimum in each block with the energy 0.0.



1a

1b

2

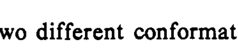
3a

3b

4

Figure 1. Optimized geometries of molecules **1–4** as obtained on the SCF level.

dominantly **C1** with some admixture of **C2**, which is in agreement with the structure constants of X-ray investigations[16] of related compounds.



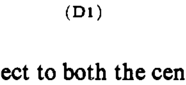
$$>\overline{P}(1)-C\begin{smallmatrix}\nearrow\!\!\!\!= \overline{P}(2)-N(2)H_2\\ \searrow \overline{N}(1)H_2\end{smallmatrix}$$

(C1)

$$>\overline{P}(1)-C\begin{smallmatrix}\nearrow \overset{\ominus}{\underline{\overline{P}}}(2)-N(2)H_2\\ \searrow\!\!\!\!= \underset{\ominus}{N}(1)H_2\end{smallmatrix}$$

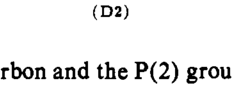
(C2)

Two different conformations of the C-protonated species **3** (open (**3a**) and closed (**3b**)) could be located as minima which both have no symmetry. The open structure **3a** (**D1**) is planar



$$\begin{smallmatrix}>\overline{P}(1)\\ H\end{smallmatrix}\!>C=\overset{\ominus}{P}(2)<$$

(D1)



$$\begin{smallmatrix}>\overline{P}(1)\\ H\end{smallmatrix}\!>C<\begin{smallmatrix}\overline{P}(2)-N(2)H_2\\ |\ominus\\ N(1)H_2\end{smallmatrix}$$

(D2)

with respect to both the central carbon and the P(2) group. The P(2)C bond properties agree with a short and polar double bond (160.6 pm, SEN 2.0) while the pyramidal P(1) group possesses a typical PC single bond (185.8 pm, SEN 1.2). The positive charge is delocalized over P(2) and its amino groups, in line with its planarity and short P(2)N bonds (161–162 pm). It should be noted that the P(1)C bond in **3a** is comparable to the one in $(Me_3Si)_2C{=}P^+R_2$, for which X-ray and ab initio results yield a bond length of 162 pm.[17]

The closed structure **3b** (**D2**) is more stable than **3a** by 39 kJ/mol on both the SCF and MP2 levels. It has a CP(2)N(1) ring with two single bonds (CN 148.0 pm, SEN 1.2, and PC 180.7 pm, SEN 1.4) and a very weak PN bond (193.2 pm, SEN 0.8). The smallest ring bond angle (46.5°) is located at P(2). In contrast to the case of the open structure, there is no PC multiple bond, and both phosphorus atoms are trivalent.

The P(1)-protonated derivative **4** of the parent compound **1** has a shorter P(1)C bond (167.4 pm) than **1b**, in line with increased

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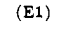
(16) For a review, see: Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; p 181.

(17) (a) Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853. (b) Ehrig, M.; Horn, H.; Kölmel, C.; Ahlrichs, R. *J. Am. Chem. Soc.* **1991**, *113*, 3701.

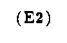
atomic charges $P(1)^{+1.2}$ and $C^{-1.0}$ and SEN 1.5. Most other structural properties are similar to those of the parent compound **1b**, e.g. the PCP bond angle (162.0°), P(2)C bond length (153.1 pm), or the planarity of the P(2) group. All data for **4** mentioned above were obtained on the SCF level. Structure optimization on the MP2 level yields only slightly longer PC bonds (2–4 pm) but a significantly smaller PCP bond angle of 135.7°. The PCP bending mode is very floppy, and neither SCF nor MP2 can be expected to yield accurate results. A comparison of SCF calculations by Nguyen et al.[5] with higher level calculations by Hoffmann and Kuhler[6] on the related compound H_2PCH also shows a lengthening of the PC distance and a decrease of the carbene bond angle as a result of effects of electron correlation.

Calculations for the *i*Pr analogue of **4** on the SCF level (i.e. $-NH_2 \rightarrow -N(iPr)_2$) do not lead to significant structural changes: there is a slight increase in bond lengths, probably resulting from steric requirements. **4** can be described by the electronic structure **E2** with small admixtures of **E1** and **E3** or by the summarizing formula **E4**. An X-ray structure analysis (with $CF_3SO_3^-$ as counterion),[18] obtained after completion of our theoretical treatment, turned out to be very difficult, since the only crystal available was 'disordered'. There were two different conformations of $N(iPr)_2$ groups (on the P(1) side) with a statistical 62:38 distribution. As a consequence, no reliable structural data could be deduced. With the aid of a riding model[19] it was possible, however, to bracket structural data as follows: 160.7 pm ≤ P(1)C ≤ 170.9 pm. This is in line with our result (167.4 pm). X-ray data and the present results agree for the P(2)C bond (X-ray 154.8 ± 0.4 pm, computed 155.7 pm with R = $N(iPr)_2$), P(2)N bonds, and the angles of the P(2) group.



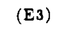
$>\overset{\oplus}{P}(1)-C\equiv P(2)<$

(E1)



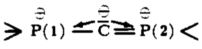
$>\overset{\oplus}{P}(1)-\overset{\ominus}{\bar{C}}=\overset{\oplus}{P}(2)<$

(E2)



$>P(1)=C=\overset{\oplus}{P}(2)<$

(E3)



$>\overset{\oplus}{P}(1)\leftharpoondown\overset{\ominus}{\bar{C}}\rightleftharpoons\overset{\oplus}{P}(2)<$

(E4)

Although both conformations of the C-protonated species **3** are much more stable than the P-protonated species **4** (**3a** by nearly 93 kJ/mol (109 kJ/mol), **3b** still by 54 kJ/mol (70 kJ/mol)), no H shift of the isolated *i*Pr analogue of **4** has been observed.[14]

(b) H,H and H,F Derivatives of Diphosphacarbene (5–8). The most instructive results of the present investigations concerning the compounds **5–8** are given in Table II (energies) and Table III (structural constants) (always for R = NH_2). The optimized geometries are depicted in Figure 2. All energy differences quoted below refer to SCF data (MP2 in parentheses, as computed at the SCF structure).

The stability of the dihydrogen derivatives **5–8** increases in the order **5a** < **6a** < **7a** < **8a** whereas the order of the hydrogen fluoride derivatives is **5b** < **6b** < **8b** < **7b**. These results are in agreement with observed shifts[14] of *i*Pr analogues **6a** → **7a** → **8a** and **6b** → **7b** $\nrightarrow$ **8b**. There are no significant differences in geometrical properties between H,H and H,F analogues.

The most unstable H,H isomer **5a** (438 kJ/mol (389 kJ/mol) above the most stable isomer **8a**) features a planar phosphanyl and a trigonal bipyramidal phosphoranyl group. The properties of both PC bonds are comparable to those of the parent species **1**. Computed bond lengths differ by less than 3 pm whereas the PCP angle has decreased (by more than 30°) to 127.4°. In analogy to the H,H compounds, **5b** represents the most unstable H,F isomer, which is 249 kJ/mol (220 kJ/mol) less stable than **7b**.

Table III. Computed Structural Constants, in pm and degrees, at the SCF level (If Not Stated Differently), Shared Electron Numbers (SEN), and Atomic Net Charges of Compounds **5–8**

5a	structure	P(1)C 177.9, P(2)C 156.1, P(1)N 169.2/172.1, P(2)N 167.1/167.4, P(1)CP(2) 127.4, HP(1)H 175.9
	SEN	P(1)C 1.40, P(2)C 2.17, PN 1.2–1.3
	charge	$C^{-0.7}$, $P(1)^{+0.7}$, $P(2)^{+1.0}$
5b	structure	P(1)C 176.0, P(2)C 155.7, P(1)F 169.3, P(1)N167.6/170.1, P(2)N 166.7/167.3, P(1)CP(2) 128.6, HP(1)F 176.2
	SEN	P(1)C 1.33, P(2)C 2.18, P(1)F 0.20, PN 1.1–1.2
	charge	$C^{-0.8}$, $P(1)^{+1.4}$, $P(2)^{+1.0}$, $F^{-0.8}$
6a	structure	P(1)C 162.3, P(2)C 162.9, P(1)N 168.5/170.0, P(2)N 167.9/169.8, P(1)CP(2) 131.6, HP(1)P(2)H 290.0
	SEN	P(1)C 1.63, P(2)C 1.63, PN 1.1
	charge	$C^{-1.2}$, $P(1)^{+1.2}$, $P(2)^{+1.2}$
6b	structure	P(1)C 162.6, P(2)C 160.3, P(2)F 160.7, P(1)N 168.3/168.9, P(2)N 166.3/168.1, P(1)CP(2) 136.6, HP(1)P(2)F 268.8
	SEN	P(1)C 1.62, P(2)C 1.82, P(2)F 0.49, PN 1.1–1.2
	charge	$C^{-1.2}$, $P(1)^{+1.2}$, $P(2)^{+1.5}$, $F^{-0.6}$
7a	structure	P(1)C 167.4, P(2)C 179.5, P(1)N 167.3/167.6, P(2)N 172.2/176.0, P(1)CP(2) 126.5, HCP(1)H 264.3
	SEN	P(1)C 1.53, P(2)C 1.36, PN 1.1–1.2
	charge	$C^{-0.9}$, $P(1)^{+1.2}$, $P(2)^{+0.6}$
7b	structure	P(1)C 164.6, P(2)C 181.1, P(1)F 160.2, P(1)N 165.5/166.2, P(2)N 171.4/174.9, P(1)CP(2) 129.5, HCP(1)F 268.8
	SEN	P(1)C 1.78, P(2)C 1.32, PN 1.2–1.3
	charge	$C^{-0.8}$, $P(1)^{+1.5}$, $P(2)^{+0.6}$, $F^{-0.6}$
8a	structure	P(1)C 186.0, P(2)C 185.2, P(1)N 171.4/171.6, P(2)N170.9/171.3, P(1)CP(2) 115.8
	SEN	P(1)C 1.30, P(2)C 1.31, PN 1.2
	charge	$C^{-0.3}$, $P(1)^{+0.6}$, $P(2)^{+0.5}$
8b	structure	P(1)C 187.5, P(2)C 185.7, CF 139.0, P(1)N169.7/174.1, P(2)N 170.5/170.7, P(1)CP(2) 116.3
	SEN	P(1)C 1.19, P(2)C 1.26, P(2)F 0.95, PN 1.2
	charge	$C^{+0.0}$, $P(1)^{+0.6}$, $P(2)^{+0.5}$, $F^{-0.3}$

Species **6a** possesses two similar PC bonds (162.3/162.9 pm). High atomic charges $P(1)^{+1.2}$, $C^{-1.2}$ and $P(2)^{+1.2}$, short bond lengths, and a relatively small SEN (1.63) indicate strongly polarized PC double bonds and high electron density at the central carbon. The structural properties, especially the PCP angle of 131.6°, together with the lone pair at carbon are in line with the idea of a typical carbodiphosphorane[20] which can be described by a double ylide structure. Substitution of the P(2) hydrogen by fluorine (**6b**) shortens the P(2)C bond and enlarges both its covalent and ionic strength (160.3 pm, SEN 1.8, atomic charges $C^{-1.2}$ and $P(2)^{+1.5}$).

The H shift from P(2) to C leads to **7**, which is more stable than **6** by 118 kJ/mol (112 kJ/mol) for the H,H isomers (**7a** versus **6a**) and 110 kJ/mol (116 kJ/mol) for the H,F isomer (**7b** versus **6b**). Both compounds **7** have a singly bonded P(2) phosphanyl and a doubly bonded P(1) phosphoranyl group. The P(1)C multiple-bond properties (**7a**: 167.4 pm, SEN 1.5. **7b**: 164.6 pm, SEN 1.8) in conjunction with high atomic charges (**7a**: $P(1)^{+1.2}$ and $C^{-0.9}$. **7b**: $P(1)^{+1.5}$ and $C^{-0.8}$) are in agreement with a semipolar double bond as described by ylene and ylide structures.

Compound **8a** is the most stable H,H isomer, being 141 kJ/mol (137 kJ/mol) below **7a**. This is in contrast to the H,F isomer **8b**, which is less stable than **7b** by 43 kJ/mol (60 kJ/mol). All PC bonds of **8a** and **8b** are single bonds (185–188 pm, SEN 1.2–1.3).

IV. Conclusions

The calculations demonstrate that diphosphanylcarbene **1** prefers the asymmetric PC multiple-bond structure **1b** instead of

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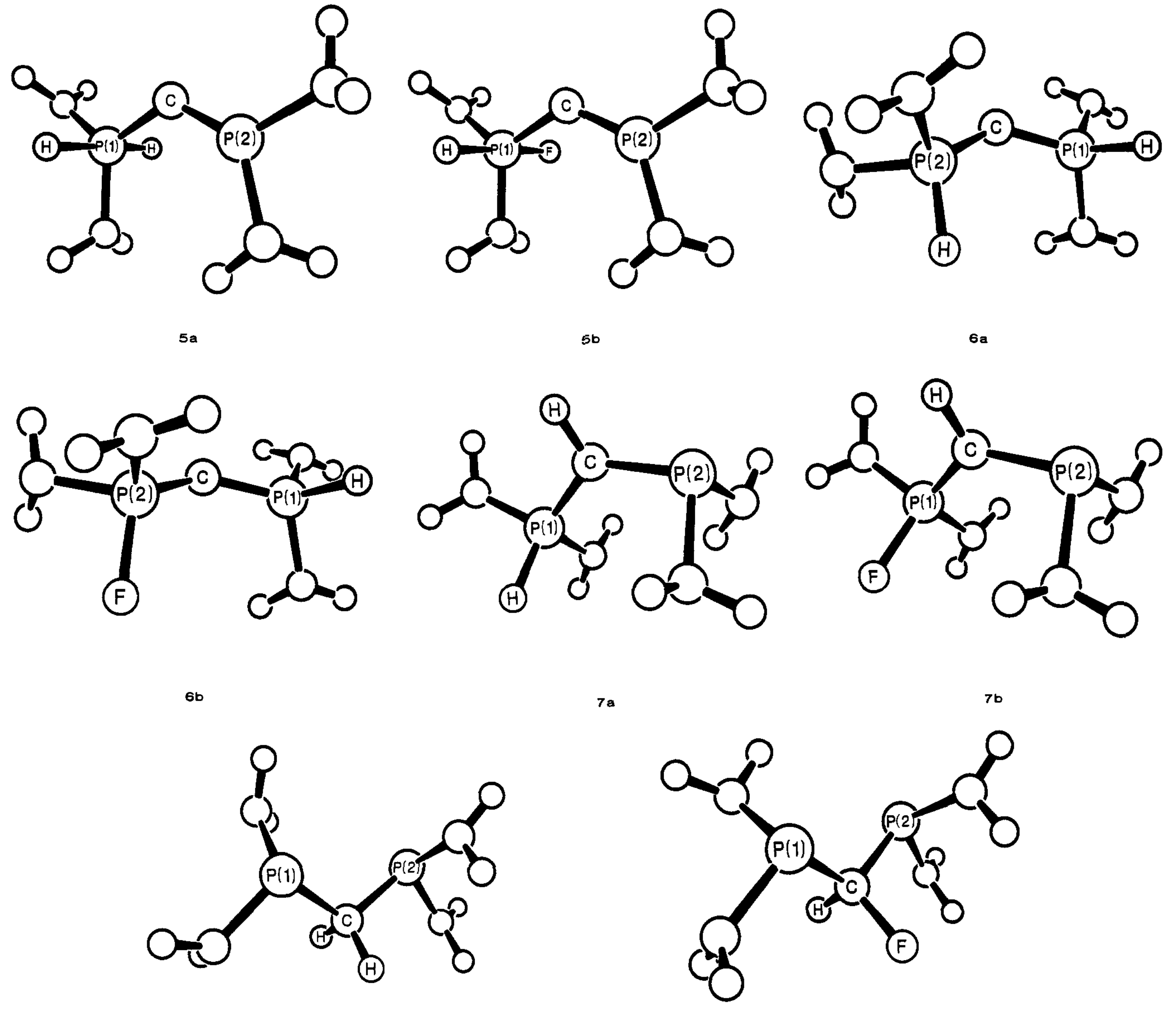

5a 5b 6a 6b 7a 7b 8a 8b

Figure 2. Optimized geometries of molecules **5–8** as obtained on the SCF level.

the symmetric carbene structure **1a**, which can be rationalized as a second-order Jahn–Teller effect. The relatively small energy difference (24 kJ/mol) between the carbene and PC multiple-bond structures (**1a** versus **1b**) in combination with large differences in geometry and electronic structure should lead to a multiple-bond equilibrium structure together with carbene reactivity. This ambiguity is well-known for alkylidynephosphoranes like Bertrand's $R'_3Si—C{\equiv}PR_2$, which also combines carbene and phosphorus–carbon multiple-bond reactivity, as shown by cyclopropanation, migration, and insertion reactions and [1 + 2] and [2 + 2] cycloaddition, respectively.[2] NMR data are in favor of a PC multiple bond.[2] Thus diphosphanylcarbenes can be considered as special alkylidynephosphoranes $R'—C{\equiv}PR_2$ with $R' = R''_2P$.

There are at least two equilibrium structures of the C-protonated diphosphanylcarbene which are more stable than theP-protonated species, whereby large N substituents might enforce the open conformation. Since the P-protonated species is stable with respect to possible H migration, there should be a remarkable barrier.

The energetic ordering of H,H and H,F derivatives shows a preference for conformers with trivalent phosphorus and tetrahedrally coordinated carbon, with the exception of **7b** as discussed below. The compounds featuring low-coordinated carbon and two pentavalent phosphorus atoms (**5** and **6**) lie above the compounds with high-coordinated carbon and one and two, respectively, trivalent phosphorus atoms (**7** and **8**). The combination of two $\lambda^5\sigma^4$ phosphorus atoms and two PC double bonds (**6**) seems to be more stable than a $\lambda^5\sigma^5$ phosphorus atom combined with a $\lambda^5\sigma^3$ phosphorus atom possessing a PC single and triple bond (**5**). Pentavalent phosphorus can be stabilized by electronegative fluorine substituents so that **7b** with a $\lambda^5\sigma^3$ phosphorus atom is more stable than **8b** possessing only $\lambda^3\sigma^3$ phosphorus atoms. The expected order is found for the dihydrogen derivatives **7a** and **8a** (**8a** more stable than **7a**).

Short PC distances in combination with high atomic charges enhanced by electronegative amino groups point at remarkable Coulomb stabilization of these phosphorus–carbon multiple bonds.