On the Electronic Structure of Phosphabutatriene and Related Phosphacumulenes. A Theoretical Study

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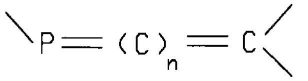
The title compound phosphabutatriene possesses two energetically closely spaced frontier orbitals, as in methylenephosphane and in phosphaallene. They are built up from the π system or the σ orbital of phosphorus by interaction with neighboring π bonds. The extension of these frontier orbitals over all (heavy) atoms makes self-dimerization to different cyclobutane derivatives feasible. Substituent effects on the ordering of σ and π are analyzed. Vibrational analyses indicate P = C vibrations of low intensity which decrease with increasing length of the heterocumulene chain. The analysis is extended to the two next higher homologs, which are hitherto experimentally unknown.

The syntheses and structural elucidations of low-coordinated phosphorus compounds have been the aim of several groups during the last decade. Review articles on this subject have appeared in the meanwhile[1]. Here we report quantum chemical investigations on phosphabutatriene (**1a**) (n = 2) and its higher homologs **1b** (n = 3) and **1c** (n = 4) and relate it to phosphaallene (**2**) and to methylenephosphane (**3**). Phosphabutatriene has been synthesized and its reactivity investigated by Märkl et al.[2], while phosphaallenes and methylenephosphanes have been extensively studied by Appel and co-workers[3]. The higher phosphacumulenes **1b** and **1c** are hitherto experimentally unknown.



1a - 1c	n = 2-4
2	1
3	0

Results and Discussion

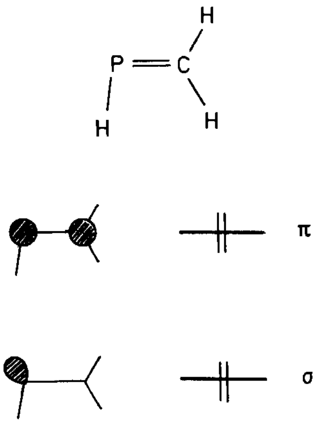
a) *Geometries:* We first performed geometry optimization on the structures **1** to **4**. The resulting bonding parameters are summarized in Figure 1.

All of the species adopt C_s symmetry. For a derivative of **1a** an X-ray structure has recently been reported[2a]. The experimental observations are in excellent accord with our theoretical results. For **2** a previous quantum chemical study has been reported[9], the results being in complete accord with our findings.

In **1a** to **1c** the carbon atoms are in alignment, as one would expect in the case of cumulenes. Consequently the central carbon atoms adopt sp hybridization. On this basis, the central CC bonds are compressed, resulting in shorter bonds than in ethene (**4**). This is due to an increased s contribution in the σ bonds. The bonds at C(1) deviate slightly from linearity so as to promote an *all-trans* conformation. This is caused by repulsive interaction of the lone pair at phosphorus with the neighboring π system, which is made up of the atoms C(1) and C(2) (vide infra). In addition, the PC double bonds in **1a** to **1c** are slightly shorter than in **3**, but longer than in **2**.

For **1a** we have also examined a geometry with a linear arrangement of the P and C atoms. It is slightly higher in energy (0.8 kJ) and relaxes without energy barrier to the equilibrium geometry of **1a**.

b) *Energies, Frontier Orbitals:* As we have shown previously[10], **3** possesses two energetically closely spaced frontier orbitals, comprised of the π system or the σ orbital at the phosphorus atom, respectively. This prediction is confirmed by photoelectron spectroscopy[11].



In the heterocumulenes **1** and **2** this frontier orbital system is extended by conjugation with the neighboring π system. For **1a**, Scheme 1 results.

The π orbital splits into orbitals π_1 and π_2 of a butadiene system. The σ orbital at phosphorus interacts with the neighboring π system, in the same plane as the lone pair orbital, forming a bonding (σ_1) and an antibonding (σ_2) combination. Similar considerations hold for the higher homologues **1b** and **1c**. The frontier orbital energies of **1** to **4** at the ab initio level are collected in Table 1.

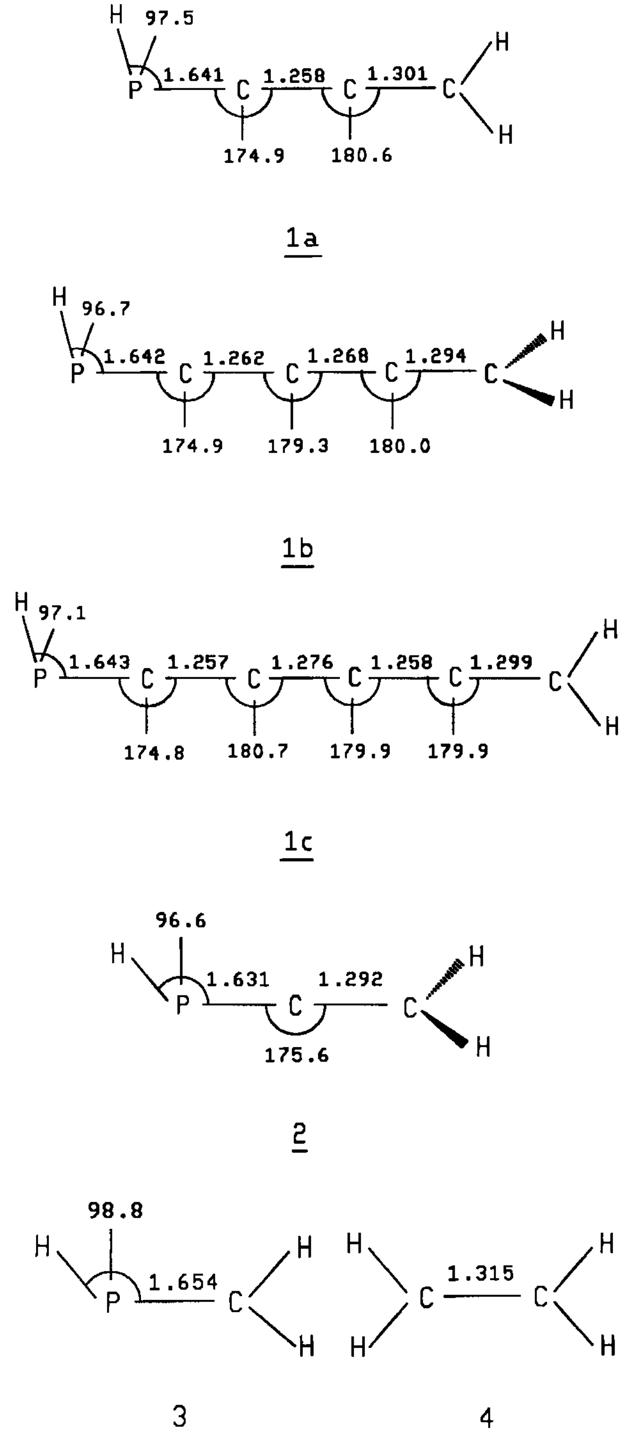


Figure 1. Geometrical parameters of **1** to **4**, bond lengths in Ångstrøm units, bond angles in degrees

Since the π effects are in fact larger in magnitude than the σ effects, the energy splitting between π and σ is slightly increased with reference to **2**.

Scheme 1

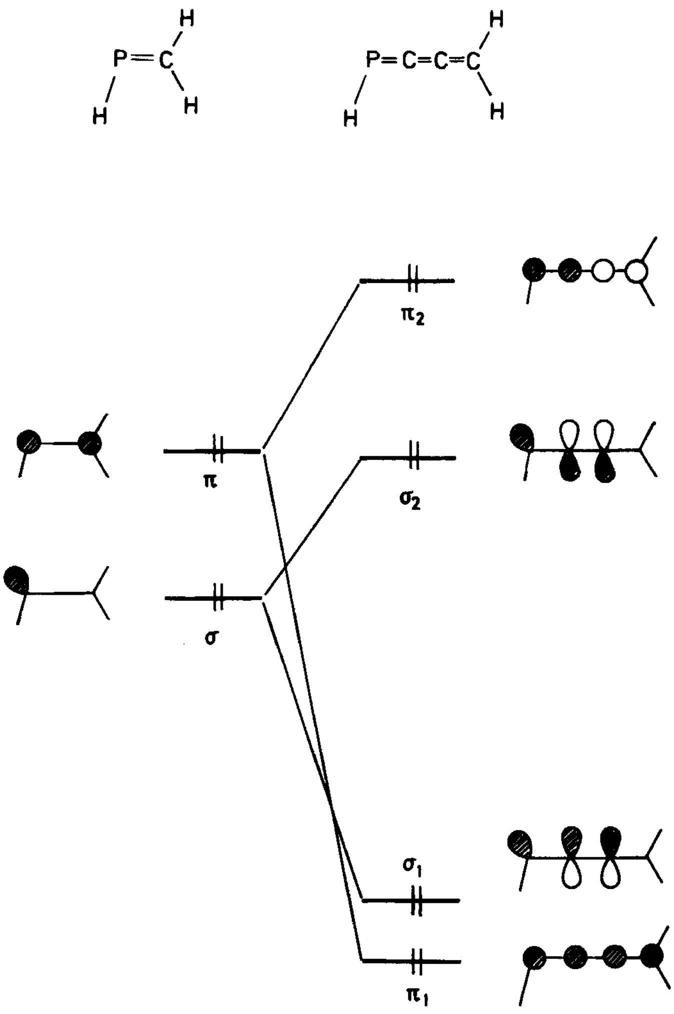


Table 1. Frontier orbital energies (negative, in eV) for **1** to **4**, obtained at the ab initio SCF level

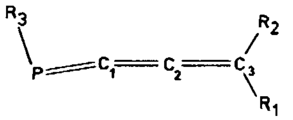
Structure	HOMO	HOMO-1	ΔE
1a	8.8 (π)	9.9 (σ)	1.1
1b	8.7 (π)	9.2 (σ)	0.5
1c	8.3 (π)	9.2 (σ)	0.9
2	9.6 (π)	10.0 (σ)	0.4
3	9.8 (π)	10.7 (σ)	0.9
4	10.3 (π)	13.8[a]	3.5

[a] Orbital comprised of the C−C σ bond.

From an experimental viewpoint, only the phosphacumulene **1a** is known. It is substituted by sterically demanding groups in order to protect the system kinetically. To examine these effects on the frontier orbitals of **1** we performed (computationally less expensive) MNDO calculations on various substituted structures **1**. The results on the frontier orbital energies are summarized in Table 2.

In most cases the effects on the frontier orbital energies are small. A phenyl group at carbon tends to raise the π orbital while its effect on the σ orbital is negligibly small. On the other hand silyl groups at carbon or phosphorus exert a considerable effect on the σ orbital, lifting its energy level. The σ and π become fairly close in energy. In other words the inductive effect of the silyl groups turns out to be stronger than the mesomeric effect[12].

Table 2. Frontier orbitals (negative, in eV) of various substituted **1**, obtained from MNDO calculations



R_1	R_2	R_3	π	σ	Δ*E*
H	H	H	9.3	10.1	0.8
phenyl	H	H	8.3	9.8	1.5
p-F-phenyl	H	H	8.5	9.9	1.4
p-H_2N-phenyl	H	H	8.1	9.9	1.8
H	H	CH_3	9.1	9.8	0.7
CH_3	CH_3	H	8.9	9.9	1.0
CH_3	CH_3	CH_3	8.8	9.7	0.9
H	H	SiH_3	9.3	9.3	0
SiH_3	SiH_3	H	9.4	9.3	−0.1
SiH_3	SiH_3	SiH_3	9.6	9.2	−0.4

Table 3. Frequencies ν_{CP} (unscaled) for P=C vibration (in cm^{-1}) and dipole moments μ (in Debye) of **1** to **4**

Structure	ν_{CP}	μ
1a	694 (2.5)[a]	1.484
1b	598 (0.6)	1.833
1c	531 (2.7)	1.948
2	827 (3.0)	1.350
3	1084 (1.3)	0.981
4	–	0.0

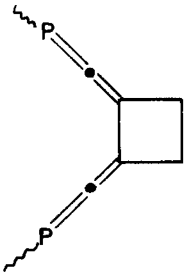
[a] In parentheses relative intensities with respect to the most intense IR band (PH vibration taken as 100).

c) *Vibrational Frequencies, Dipole Moments:* To complete the picture of the bonding properties on **1** in comparison to **2** to **4** we performed calculations of the vibrational frequencies of these species. Only the results obtained for the P=C vibration will be listed here (Table 3).

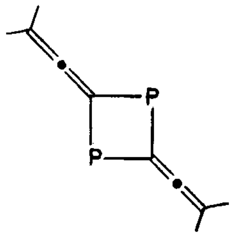
Of the phosphorus compounds **1** to **3** the most intense vibration, with relative intensity of 100, refers to PH which appears at almost the same frequency (**1**: 2483 cm^{-1}; **2**: 2484; **3**: 2489). In comparison, the P=C vibration (Table 3) has much lower intensity[13]. The frequency decreases with increasing length of the heterocumulene chain. In other words, it is lowest in **1c** and highest in **3**. All vibrations in **1** to **3** are Raman- as well as IR-active.

On lengthening of the cumulene system from **3** to **1c**, one observes a slight increase in the resulting dipole moment (Table 3). It is nonetheless fairly small in all of the investigated structures.

d) *Dimerization:* Experimentally, two types of dimers have been found in the self-addition of phosphabutatrienes[2b,c].



a



b

In **a**, dimerization has occurred via an intermediary biradical system[14], while **b** has been formed via [2 + 2] reaction of two phosphabutatrienes. The present analysis does not allow a simple rationale for the outcome of **a** or **b**. The frontier orbitals are delocalized over all atoms, although in **1** the magnitude of the coefficients at the PC bond are larger than at the terminal CC bond (in the HOMO as well as in the LUMO). Consequently one would expect the predominant regioselective formation[15] of **b** rather than **a**. On the other hand, in the experiments **1** is always protected by sterically bulky substituents which kinetically stabilize the structure. However, bulky groups at the terminal carbon atom C(3) will tend to promote the less sterically crowded product **b**. This view seems to be supported by the reported experimental investigations on the self dimerization behavior[2b,c] of the various substituted **1**.

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Calculations

The *quantum chemical calculations* were based on the results of MNDO[4] and ab initio calculations at the double-ζ level. For the latter the following basis sets were constructed from Huzinaga bases[5], augmented by polarization functions for all atoms:

C (9 s, 5 p) in the contraction [5, 4 × 1/3, 2 × 1] + 1 d (0.8),
P (11 s, 7 p) in the contraction [5, 2, 4 × 1/4, 3 × 1] + 1 d (0.5),
H (5 s) in the contration [3, 2 × 1] + 1 p (0.65).

All calculations were determined at the (single determinant) SCF level, utilizing the Karlsruhe version of the COLUMBUS set of programs[6]. The energy optimizations of structures were directed with the Murtagh-Sargent algorithm[7]. All energy minima were obtained with an accuracy of 10^{-7} au. In this way we obtained the bond lengths (bond angles) with an accuracy of 0.1 pm (0.05 degrees). All of the considered structures were subjected to vibrational analyses within the harmonic approximation with the TURBOMOLE program systems[8]. For the calculation of second energy derivatives, gradients of the energy optimized structures were evaluated. Full details of the vibrational analyses are available on request.

CAS Registry Numbers

1a: 128632-36-0 / **1b**: 128632-37-1 / **1c**: 128632-38-2 / **2**: 102146-31-6 / **3**: 61183-53-7 / $HP{=}C{=}C{=}CHC_6H_5$: 128632-39-3 / $HP{=}C{=}C{=}CHC_6H_4F$-*p*: 128632-40-6 / $HP{=}C{=}C{=}CHC_6H_4$-NH_2-*p*: 128632-41-7 / $MeP{=}C{=}C{=}CH_2$: 128632-42-8 / $HP{=}C{=}C{=}C(CH_3)_2$: 128632-43-9 / $MeP{=}C{=}C{=}C(CH_3)_2$: 128632-44-0 / $H_3SiP{=}C{=}C{=}CH_2$: 128659-36-9 / $HP{=}C{=}C{=}C(SiH_3)_2$: 128632-45-1 / $H_3SiP{=}C{=}C{=}C(SiH_3)_2$: 128632-46-2

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[12] For the differentiation between inductive and mesomeric effects of substituents see G. W. Klumpp, *Reaktivität in der organischen Chemie, I,* Thieme Verlag, Stuttgart 1977.

[13] In detail the vibrational frequencies (in cm^{-1}) of the normal modes are (relative intensities in parentheses): (a) methylenephosphane: $^1A''$ symmetry, 940 (12.8); 1019 (43.0); $^1A'$ symmetry, 806 (7.0); 1084 (1.3); 1124 (2.5); 1584 (1.9); 2489 (100.0); 3277 (3.1); 3366 (1.2). – (b) phosphaallene: $^1A'$ symmetry, 355 (16.3); 814 (0.7); 1066 (1.0); 3338 (1.1); $^1A'$ symmetry, 348 (29.2); 827 (3.0); 992 (10.3); 1041 (39.4); 1519 (5.3); 1939 (69.5); 2484 (100.0); 3260 (2.3). – (c) phosphabutatriene: $^1A''$ symmetry, 206 (6.4); 582 (0.3); 733 (0.0); 1024 (39.7); $^1A'$ symmetry, 201 (18.3); 435 (2.2); 694 (2.5); 1005 (11.3); 1117 (0.1); 1431 (13.4); 1626 (12.8); 2239 (1.7); 2483 (100.0); 3278 (0.0); 3363 (1.2). – (d) phosphapentatetraene: $^1A''$ symmetry, 137 (1.2); 369 (0.0); 563 (0.9); 670 (0.5); 1098 (0.0); 3350 (0.1); $^1A'$ symmetry, 138 (3.5); 347 (1.9); 615 (2.5); 987 (7.7); 1018 (14.1); 1217 (12.0); 1560 (0.2); 1943 (2.2); 2323 (100.0); 2484 (30.0); 3269 (0.3). – (e) phosphahexapentaene: $^1A''$ symmetry, 98 (7.8); 100 (2.7); 262 (0.0); 536 (7.8); 590 (3.4); 614 (0.4); 629 (0.3); 1023 (40.4); $^1A'$ symmetry, 265 (4.8); 403 (10.0); 994 (25.9); 1059 (30.3); 1109 (0.2); 1521 (0.9); 1690 (2.0); 2164 (100.0); 2335 (0.1); 2484 (96.7); 3274 (0.0); 3359 (0.2).

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