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Electron attachment by phosphirene and various fluoro-, cyano- and trifluoromethyl-substituted phosphirenes: A theoretical exploratory study

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Summary — Vertical electron affinities (EA) of phosphirene and a series of various fluoro-, cyano- and trifluoromethyl-substituted phosphirenes have been computed. The medium size 6-311G** basis set has been used at the MP2 level, which allows the calculation of negative EA with a satisfactory accuracy. Most of these compounds have a negative EA ranging from −2.3 to −0.7 eV. Nevertheless, 2,3-dicyanophosphirene has a positive EA (0.32 eV) and is thus expected to yield a stable anion. The same result is found for the corresponding 1,2-dicyanocyclopropene. The nature of the SOMO of the anion as a function of substituents, and the correlation between EA and the LUMO energy of the neutral species are discussed.

phosphirene / vertical electron affinity / ab initio calculation

Résumé — Affinité électronique du phosphirène et de divers phosphirènes fluoro-, cyano- et trifluorométhyl-substitués: une étude théorique exploratoire. Nous avons calculé les affinités électroniques (AE) verticales du phosphirène et d'une série de phosphirènes substitués par des groupements fluoro-, cyano- et trifluorométhyle. Nous avons utilisé la base de taille moyenne 6-311G** au niveau MP2, ce qui permet de calculer des AE négatives avec une précision suffisante. La plupart de ces composés ont une AE négative, variant de −2,3 à −0,7 eV. Toutefois, le 2,3-dicyanophosphirène a une AE positive (0,32 eV) et doit donc conduire à un anion stable. Nous avons obtenu le même résultat pour le 1,2-dicyanocyclopropène. Nous discutons aussi la nature de la SO de l'anion en fonction du substituant, et la corrélation entre l'AE et l'énergie de la BV des espèces neutres.

phosphirène / affinité électronique verticale / calcul ab initio

Introduction

Upon electron impact in the gas phase, (Electron Transmission Spectroscopy, ETS conditions), molecules bearing a second-row heteroatom such as P, S or Cl, generally yield resonant states of low vertical negative electron affinity (EA), in the range 2-4 eV. The so-called resonant states generally have a short lifetime (10^{-13}-10^{-15}s) and are unstable with respect to the system composed of the neutral ground state (GS) + one electron, {GS + e}, so that electron detachment occurs quite spontaneously [1-16]. When electron capture is not too endothermic, the system might possess enough time to evolve through an exothermic path, leading to relaxation, rearrangement or dissociation, all being generally accompanied by delayed electron detachment. When dealing with phosphorus compounds, it has been shown that a particularly favourable situation is found in three-membered ring compounds. The reason is that, in order to minimize the ring strain, they possess bonds that are generally longer than standard values, thus yielding valence σ^* MOs of lower energy [17]. On the other hand, the presence of a double bond in the ring also might provide low-lying acceptor π^* MOs. In these derivatives, the various low-energy σ^* and π^* MOs can be selectively stabilized or destabilized upon suitable substitution. In the aim of finding low-energy electron acceptors, or even possibly, stable anionic systems, the phosphirene molecule **1** (see table I for model structure) and some typical substituted derivatives: 2,3-difluorophosphirene **2**, 1,2,3-trifluorophosphirene **3**, 1-fluorophosphirene **4**, 2,3-bis(trifluoromethyl)phosphirene **5**, 1-cyanophosphirene **6**, 2-cyanophosphirene **7** and 2,3-dicyanophosphirene **8**, provide interesting model compounds. For the sake of comparison, 1,2-dinitrocyclopropene **9** has been added to this series. Our goal in this exploratory study was to design molecules having as low a negative electron affinity (EA) as possible, to study the substituent effects on the acceptor MOs and then to rationalize the evolution of the anion, towards electron detachment or structure relaxation. The preceding substituents have been selected for their inductive and conjugating properties: F is a good σ electron-withdrawing atom and a

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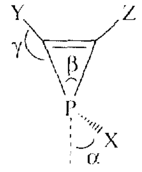
Table I. Optimized geometry parameters for neutral compounds **1**–**9**.



Compound	*P–X (Å)*	*P–C (Å)*	*C=C (Å)*	*C–Y/C–Z (Å)*	*C≡N (C–F in **5**) (Å)*	*α (°)*	*β (°)*	*γ (°)*
1 (X=Y=Z=H)	1.425	1.847	1.306	1.079		80.0	41.4	145.3
2 (X=H, Y=Z=F)	1.427	1.841	1.300	1.317		79.0	41.4	143.4
3 (X=Y=Z=F)	1.633	1.796	1.317	1.315		73.4	43.0	145.6
4 (X=F, Y=Z=H)	1.643	1.793	1.325	1.081		74.8	43.4	148.4
5 (X=H, Y=Z=CF_3)	1.421	1.847	1.306	1.485	1.336 to 1.339 (C–F)	81.4	41.4	145.9
6 (X=CN, Y=Z=H)	1.817	1.836	1.308	1.080	1.180	78.8	41.7	144.5
7 (X=H, Y=H; Z=CN)	1.422	1.843/1.856	1.313	1.080/1.403	1.180	80.8	41.6	146.7/145.9
8 (X=H, Y=Z=CN)	1.421	1.855	1.321	1.401	1.181	81.7	41.7	146.7
9 (cyclopropene, Y=Z=CN)	1.088 (C–H)	1.515 (C–C)	1.318	1.400	1.180	58.1	51.6	146.3

mild π-donor; CN is both σ and π acceptor and CF_3 is a powerful σ-electron-withdrawing group, with no associated π effects.

Computational details

All calculations have been performed with the Gaussian 94 series of programs [18a]. The choice of a basis set aimed at reproducing the properties of anionic species *unstable* with respect to electron detachment, ie when the anion is *less* stable than the system {GS + e}, is delicate. The 6-311G** basis set [19] provides good valence and polarization functions, and is suitable for adequately describing the *valence* properties of the vertical anions. Nevertheless, a word of caution remains necessary regarding the use of such a basis set. It has been emphasized that basis sets containing more diffuse so-called Rydberg functions, such as 6-311++G** for instance, are more suitable for describing the actual energetics of anions which are *stable* with respect to the neutral parent, ie having positive EAs. The situation is different when dealing with compounds having high negative EAs, such as most of the vertical anions studied thereafter. In these species, the unpaired electron is likely to escape, as soon as sufficient space is available. It is observed that through the addition of very diffuse functions, the calculated anion energy drops to that of the neutral compound, reflecting the fact that, in reality, the electron is not bound to the system [11]. In order to reproduce as closely as possible the actual behaviour of the temporary anion states, the less diffuse 6-311G** basis set was therefore used throughout for the full geometry optimization of all neutral described structures, at the MP2 level of electronic correlation. In UHF runs, we have checked that spin contamination remained small and is not likely to affect significantly the corresponding calculated geometries and the energies of stationary points. The latter requirement can be easily fulfilled by comparing the calculated MP2 energy (EUMP2) to the projected energy (PMP2) [18b] which eliminates the eventual spin contamination. In the course of preceding studies [**9**–**12**] we have observed that MP4 calculations, with the same basis set, yield, as expected, better absolute energies, but the EAs thus obtained are practically equal to those obtained through the MP2 procedure. Consequently, in the rest of the discussion, the calculated values refer to MP2/6-311G** calculations when not specified. MP2/6-311++G** calculations have also been performed for the anions that are stable or likely to be stable (compounds **5** and **7**–**9**). Our calculated values are not ZPE-corrected. The order of magnitude of the correction is less than 0.1 eV, and in most cases it does not change qualitative results, except when dealing with compound **7**, which will be briefly discussed later.

Results and discussion

The optimized structures and energies of compounds **1**–**9** are given in tables I and II, respectively. In a first step we will briefly discuss the geometry trends observed in the neutral optimized compounds (table I). Focusing our attention on the calculated bond lengths, two points are worth examining.

(i) F-substitution on the double bond practically brings no change neither to the C=C bond length nor to the adjacent PC bond lengths, as shown by comparison of structures **1** and **2**. The same absence of significant skeletal response is found when two CF_3 groups are present, as in **5**. On the other hand, F-substitution on P yields a small contraction of the adjacent PC bonds. It might thus be inferred that inductive effects will dominate in the series **1**–**5**.

(ii) CN substitution does not bring very important structural changes. When this group is linked to P, only very small variations are found, as shown by the comparison of **1** and **6**. When this substituent is present on the C=C linkage, a weak stretching of the adjacent PC bond(s) is observed. It can thus be anticipated that the conjugation effect will dominate in the **6**–**8** series. Both types of effects will be examined in the next paragraph, the discussion being limited to the two lowest unoccupied empty MOs, W* and π^* whose actual nature will be defined in the next paragraph.

Table II. Calculated energies of neutral compounds in their ground state (in au, column 2), vertical electronic affinities (in eV, columns 2, 3), and EAs for the relaxed anions of compounds **6**–**9** (column 5).

Compound	*Energy (au)*	*Vertical EA (eV)*	*Vertical EA (eV)*[a]	*Relaxed EA (eV)*
1	−418.54506	−2.3404		−1.3047
2	−616.66324	−1.6860		
3	−715.78410	−2.0243		
4	−517.66316	−3.4735		
5	−1091.42303	−1.3727	−0.9309	
6	−510.58604	−1.4977		−0.5559
7	−510.57958	−0.7425	−0.3725	−0.1292
8	−602.61067	+0.3224	+0.6017	+0.7353
9	−300.34191	+0.1299	+0.4208	+0.2938

[a] MP2/6-311++G** level.

Nature of the low-lying acceptor MOs

Let us first examine the parent prototype, phosphirene **1**. The dominant character of the three lowest energy vacant MOs, which is typical of the series **1**–**8**, is schematically displayed in figure 1. The first one, labelled W* (fig 1), might be considered as an antibonding in-plane Walsh MO, mostly located on the phosphorus atom. The next one is the classical π^*_{CC} MO, labelled π^* in the rest of the discussion for the sake of simplicity. Then, one finds a fairly delocalized σ^* MO bearing strong antibonding PH and/or PC character. The doublet states whose leading electronic configuration corresponds to the presence of the odd electron in one of these MOs have the $^2A_2$ (W*) or $^2B_2$ (π^*) symmetry in compound **9** (C_{2v} point group), or the $^2A''$ (W* or π^*) symmetry in compounds **1**–**6** and **8** (C_s point group). These species respectively become of $^2A_1$ (C_{2v}) or $^2A'$ symmetry when σ^* is involved (see fig 1). In table III the calculated energy and symmetry of the three lowest energy vacant MOs of compounds **1**–**9** are collected. In **9** which contains a strongly conjugated C=C double bond, the first low-lying empty MO is of π^*-type, then, at much higher energy, one finds the valence MOs of W* and σ^*-type, very close in energy. This situation is no longer encountered when a second-row atom is present in the ring system. The various energetic trends are shown in figure 2. They are briefly discussed thereafter.

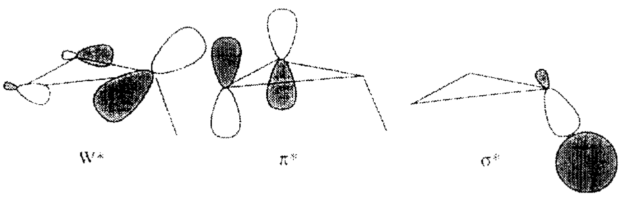


Fig 1. Schematic drawing of the low-lying valence MOs of compounds **1**–**8** (in **9**, the σ^* MO is symmetrical with respect to the CCC plane).

Table III. Energies of the low-lying virtual MOs of neutral compounds **1**–**9** (in au).

Compound (point group)	*E (in-plane W*)*	*E (π^*)*	*E (out of plane σ^*)*
1 (C_s)	0.1138 ($^2A''$)	0.1425 ($^2A''$)	0.1492 ($^2A'$)
2 (C_s)[a]	0.0891 ($^2A''$)	0.1763 ($^2A''$)	0.1243 ($^2A'$)
3 (C_s)	0.0980 ($^2A''$)	0.1593 ($^2A''$)	0.1279 ($^2A'$)
4 (C_s)	0.1176 ($^2A''$)	0.1304 ($^2A''$)	0.1486 ($^2A'$)
5 (C_s)	0.0794 ($^2A''$)	0.0830 ($^2A''$)	0.1145 ($^2A'$)
6 (C_s)	0.0829 ($^2A''$)	0.1054 ($^2A''$)	0.1162 ($^2A'$)
7 (C_1)	0.0802 (A)	0.0661 (A)	0.1173 (A)
8 (C_s)	0.0495 ($^2A''$)	0.0093 ($^2A''$)	0.0886 ($^2A'$)
9 (C_{2v})	0.1238 ($^2B_2$)	0.0122 ($^2A_2$)	0.1260 ($^2A_1$)

[a] The third lowest empty MO is not the π^* but a second σ^* at 0.1593 au.

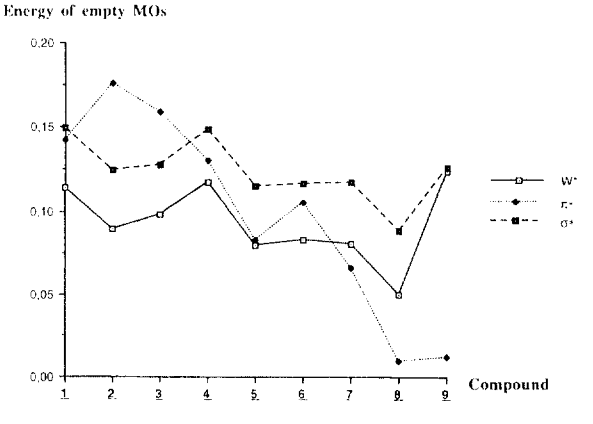


Fig 2. Variation of the calculated energies of the three lowest lying virtual MOs of neutral compounds **1**–**9**.

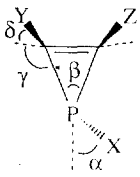
W MOs*

Let us first consider the role of F-substituents, taking **1** as a reference. The presence of two strong σ-withdrawing substituents in **2** decreases the contributions of the C atoms in this type of MO, and thus lowers the overall antibonding character. On the contrary, the presence of a F atom on P in **4** induces a strong destabilization of this level, by introducing an important new antibonding contribution, arising through the occupied MOs of P and F of same local symmetry. In **3**, the competition between stabilization due to F-substituents on C atoms, and destabilization due to the presence of a F-substituent on P compete and thus lead to a compromise situation. The comparison of **2** and **5** illustrates the fact that σ-inductive effects are essential since in both cases the W* MOs have comparable low energies. When dealing with the **6**–**8** series, the situation is more complex, since both the σ and π effects of the CN group are effective, as shown by the similitude between **6** and **7**. It is only in **8** that a neat stabilizing effect is observed.

π^* MOs

The situation is simpler than in the preceding case, and depends on two distinct trends: the presence of a F substituent on the π system destabilizes the lowest-energy π^* MO, as shown by comparison of **1** and **2**, while the presence of a CN group has a contrary effect, as shown by comparison of **1** and **7**. The π-destabilizing effect of F-substitution is even so strong in **2** that in fact the third lowest empty MO is not the π^* but a second σ^* at 0.16 au. Is is also clearly illustrated by the low energy of π^* in **4**. Along the whole series of substituents it is

Table IV. Optimized geometry parameters for anion compounds **7a**–**9a** obtained from compounds **7**–**9**.



Compound	*P–H (Å)*	*P–C (Å)*	*C=C (Å)*	*C–Y/C–Z (Å)*	*C≡N (Å)*	*α (°)*	*β (°)*	*γ (°)*	*δ (°)*
7a (X=H, Y=H; Z=CN)	1.428	1.858/1.849	1.406	1.096/1.408	1.178	78.9	44.6	143.5/144.1	47.7/39.7
8a (X=H, Y=Z=CN)	1.424	1.853	1.409	1.416	1.165	80.6	44.7	144.9	40.7
9a (cyclopropenium, Y=Z=CN)	1.095 (C–H)	1.502 (C–C)	1.379	1.376	1.167	56.9	54.6	145.4	0.0

noteworthy that in **7** and **8**, one observes a change in the nature of the LUMO which is now of π^* type and no longer W*.

Vertical EAs of compounds 1–9

The calculated EAs of compounds **1**–**9** are given in table II. A good correlation (correlation coefficient 0.907) is observed between the EAs and the LUMO energies of the neutral species as displayed in figure 3. Let us first look at the series of compounds **1**–**6**, for which the lowest-energy electron capture is likely to occur via the W* MO, through an endothermic process. The best candidate for low-energy electron attachment is **5** whose EA is −1.37 eV. However, this energy range remains too high for potentially obtaining through geometry relaxation a species which would be stable with respect to the {GS + e} system. This point is comforted by the MP2/6-311++G** EA of −0.93 eV obtained for this anion (table II), which shows, as stated in the methodological section, that the odd electron is not bound to the molecule and would escape provided that sufficient very diffuse space is available. Let us focus our attention on the **7**, **8** couple. We see that only **8** has a positive vertical EA (0.32 eV), and this energy raises to 0.60 eV, using the MP2/6-311++G** technique. It is noteworthy that a parallel behaviour is found with **9**, although a substantial ring strain is present in the latter molecule.

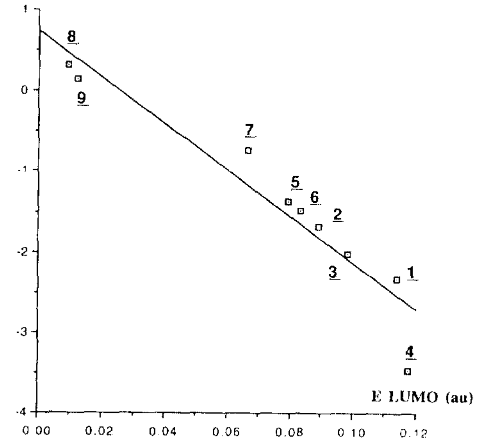


Fig 3. Vertical EAs of compounds **1**–**9** as a function of the GS LUMO energy, in au.

Structural relaxation of anions 7a–9a

The optimized geometry of anions **7a**–**9a** is given in table IV. In the classical sense, **7a** is not a *true* stable molecule since its calculated EA is −0.13 eV, but it might be considered that it is very likely to yield a long-lived anion species, especially when taking into account the difference of zero-point correction between the neutral and anionic species of about 0.05 eV. Two striking features arise from the comparison of **8** and **8a**. (i) An important relaxation of the C=C double bond is found, from 1.321 to 1.409 Å, while the PC bonds remain practically unchanged. (ii) A syn out-of-plane distortion of the CN groups is observed, (40.7°, table IV), in the half-space which does not contain the PH bond. It is noteworthy that the other configuration is quite of the same energy (only 0.0078 eV higher). The pyramidalization is thus effective, but its orientation is not well defined. No such effect is observed in **9a**, which remains symmetrical with respect to the plane of the cycle.

Conclusion

This series of phosphirene derivatives exhibits various behaviours regarding electron capture. Most of them have a negative EA, with occupancy of the Walsh-type MO by the extra electron. Nevertheless, by suitable substitution (cyano groups on the carbons), the π^* MO becomes the lowest empty orbital, and the corresponding compounds may lead to stable anions. A good correlation is observed between the EAs and the LUMO energies of neutral species, which allows predicting of the EAs by simple examination of the LUMO energy. We hope that these results could be a useful guideline for further experimental studies.

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