An EPR and ab initio Study of a Phosphaalkene Radical Anion, and Comparison with other Phosphorus-Containing Radical Ions

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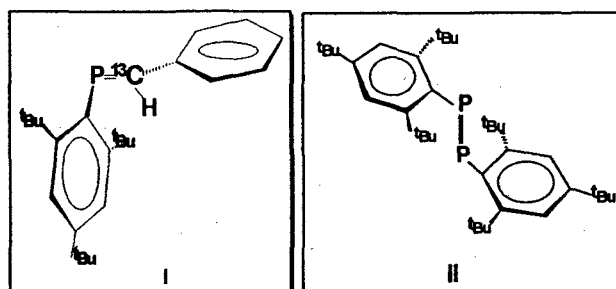**Université de Provence, CNRS-URA 1412, 13397 Marseille Cedex 13 (France)**

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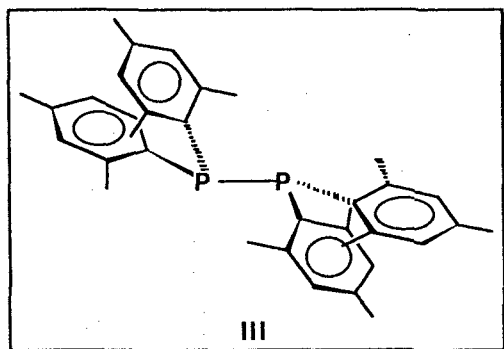
1 Introduction

Electron Paramagnetic Resonance (EPR) is an efficient method to obtain information about the spin densities in organic radicals containing a heteroatom and, when used in conjonction with *ab initio* calculations, this spectroscopy can yield a precise description of the structure of these species. In the present study, our purpose is to compare the spin delocalization on the following three paramagnetic moieties $(\text{-P}=^{13}\text{C}<)^{-}$, $(\text{-P}=\text{P}-)^{-}$ and $(>\text{P}-\text{P}<)^{+}$ and to verify to what extent the *ab initio* predictions agree with the experimental hyperfine tensors. For each of these species the unpaired electron is expected to be mainly localized on both a phosphorus and an adjacent atom and the experimental parameters will consist in the ^{31}P and ^{13}C coupling tensors obtained from frozen solutions.

Organic molecules containing a trivalent dicoordinated phosphorus atom are very reactive; they can nevertheless be isolated at room temperature when the organic group which is linked to the phosphorus atom by a single bond is very cumbersome. 2,4,6-tri(*tert*.butyl)phenyl-phenylmethylenphosphaalkene **I** and bis(2,4,6-tri-*tert*-butylphenyl)diphosphene **II** are good examples of such compounds.

The syntheses of these compounds, described during the ten past years [1,2], leads to stable crystalline materials. We have taken advantage of this stability to add an electron on a P=C or

a P=P bond and to record the EPR spectrum of the corresponding frozen solution. Diphosphines are well known stable molecules and we have measured the ^{31}P anisotropic hyperfine interaction after freezing a solution of tetra,2,4,6,trimethylphenyldiphosphine [3] **III** previously oxidized in an electrolytic cell.

III

2 Experimental

The various compounds have been obtained by adapting already published syntheses: ArP=C(H)Ar' [1], ArP=PAr [2] and Ar"$_2$P-PAr"$_2$ [3] (where Ar: trit-t-butyl phenyl, Ar: phenyl, Ar": 2,4,6, trimethylphenyl). The electrolyses were performed in the EPR cavity of an X-band Bruker spectrometer by using solutions of the organophosphorus compound in presence of tetra-n-butyl amonium hexafluor phosphate. The ^{31}P, ^{13}C and ^{1}H isotropic and anisotropic coupling constants were obtained after simulation of the experimental spectrum with a program using second order perturbation.

The *ab initio* calculations were carried out on a Silicon Graphics (Iris 4D) and a Vax 6700

computer by using G-82 and G-90 Gaussian programs [4]. The 6-31G* basis set was generally used and annihilation of the spin contamination was performed for the UHF calculations. The coupling constants were obtained by calculating the expectation values of the Fermi contact interaction and of the hyperfine dipolar interaction. ROHF calculations were also carried out, in particular when the UHF method led to final $<S^2>$ values which were not equal to 0.75.

3 Results and Discussion

EPR spectra.

(ArP=C(H)Ar')⁻: The liquid solution spectrum is characterized by a large splitting of 152 MHz and a rather broad linewidth exhibiting a poorly resolved additional structure [5]. Full deuteration of the C(H)C$_6$H$_5$ fragment only affects the linewidth which is then equal to 8 MHz . The spectrum obtained with ArP=C(H)C$_6$D$_5$ clearly shows a coupling of 11 MHz with the ethylenic proton while the spectrum obtained with ArP=^{13}C(H)C$_6$H$_5$ indicates a ^{13}C coupling equal to16 MHz. From these couplings and from the observed linewidth one can conclude that an appreciable spin delocalization occurs onto the phenyl ring and the simulated spectra are consistent with the following three additional proton couplings: 11MHz, 7MHz and 7MHz. The frozen solution spectrum obtained with (ArP=C(H)Ar')⁻ is characterized by an axial hyperfine coupling with ^{31}P: T$_{//}$=455MHz and T$_\perp$ =1 MHz; the full deuteration of the C(H)C$_6$H$_5$ fragment only decreases the

linewidth whereas the use of the $^{13}C(H)C_6H_5$ fragment leads to an additional hyperfine interaction: ^{13}C-$T_{//}$=47 MHz, ^{13}C-$T_{\perp}$=1 MHz.

(ArP=PAr)⁻ : As already mentioned [6,7,8], the liquid solution spectrum exhibits a ^{31}P isotropic coupling constant equal to 158 MHz. The frozen solution spectrum has still not been reported; it is characterized (Fig.1) by an axial coupling tensor :^{31}P: $T_{//}$=458 MHz and $T_{\perp}$ =10 MHz. No additional ^1H coupling is observed with this compound.
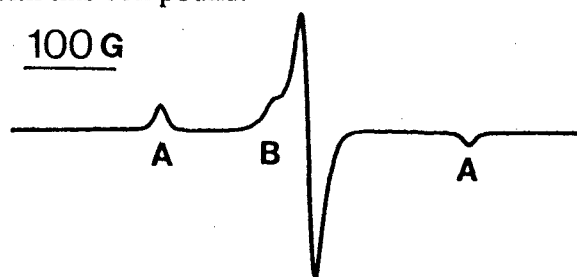

Fig 1. EPR spectrum obtained with a frozen solution of (ArP=PAr)⁻

(Ar''₂P-PAr''₂)⁺:Only the liquid solution spectrum has been previously reported [9], the splittings observed with the frozen solution spectrum (Fig. 2) show that the two phosphorus nuclei are equivalent and that their hyperfine tensors exhibit an axial symmetry: $T_{//}$= 796 MHz and $T_{\perp}$ =356 MHz.
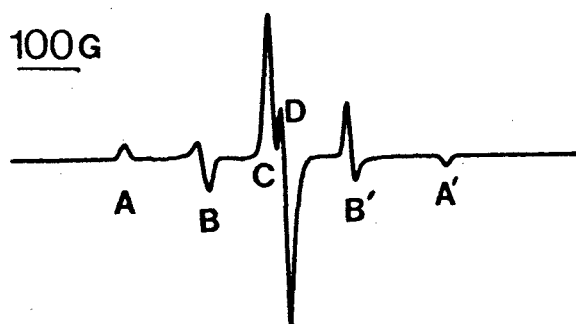

Fig. 2. EPR spectrum obtained with a frozen solution of (Ar''₂P-PAr''₂)⁺.

Assuming a positive sign for all the hyperfine eigenvalues leads to the isotropic and anisotropic coupling constants shown in Table 1 together with the spin densities calculated by using the atomic parameters obtained from [10].

Table 1. Experimental coupling constants (MHz) and spin densities

radical		A_{iso}	$T_{//}$	$T_{\perp}$	ρ_s	ρ_p
ArP=CHR⁻	^{31}P	152	303	-152	0.01	0.41
	^{13}C	16	31	-15	0.00	0.18
ArP=PAr⁻	^{31}P	158	300	-148	0.01	0.41
	^{31}P	158	300	-148	0.01	0.41
Ar'₂PPAr'₂	^{31}P	502	293	-146	0.04	0.39
	^{31}P	502	293	146	0.04	0.39

ab initio calculations.

Phosphaalkene radical anion: In the C_S symmetry, the UHF optimized structure for $(HP=CH_2)⁻$ is characterized by HPC=97.5°, P-C =1.791 Å, P-H= 1.428 Å; using the ROHF method does not significantly affect these parameters. The structure of $(HP=C(H)Ar')⁻$ was optimized (ROHF calculations) by fixing the geometry of the phenyl group and by assuming a planar structure: HPC=96.6°, H-P= 1.420 Å and P-C = 1.761 Å.

Diphosphene anion and diphosphine cation. The optimized structures of these two species are known [11,12,13] and agree with our UHF results : for $(HP=PH)⁻$: HPH=95.8°, P-P= 2.133Å (C_S symmetry) and for $(H_2P-PH_2)⁺$: HPH= 102.2°, PPH=104.09° and P-P= 2.164 Å

(C_{2h} symmetry). For these two ions $\langle S^2 \rangle = 0.750$

The various hyperfine coupling constants resulting from UHF calculations are given in Table 2 . For both the phosphaalkene and the diphosphene anions, the "parallel" ^{31}P coupling eigenvectors are oriented perpendicular to the molecular plane (π structure), whereas for the diphosphine cation these eigenvectors make an angle of 45° with the P-P bond direction in accordance with the orientation of the n⁻ orbital.

Table 2. Calculated ^{31}P hyperfine coupling constants (MHz).

radical	A_{iso}	$\tau_{//}$	$\tau_{\perp 1}$	$\tau_{\perp 2}$
$(HP=CH_2)^-$	25	130	-60	-70
$(HP=PH)^-$	70	279	-136	-142
$(H_2PPH_2)^+$	445	328	-153	-174

For the radical ions containing no phenyl ring, the various spin densities calculated by using the UHF method are very similar to those obtained from ROHF calculations. These spin densities are shown in Table 3.
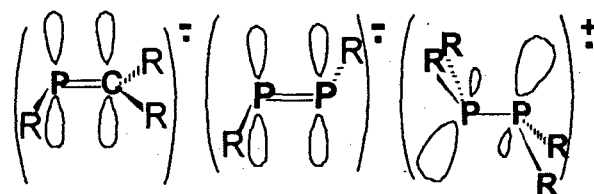
Table 3. Calculated spin densities.

radical	phosphorus		adjacent carbon or phosphorus		phenyl
	ρ_s	ρ_p	ρ_s	ρ_p	
$(HP=CH_2)^-$ a	0.00	0.22	0.00	0.77	
$(HP=CHAr')^-$ a	0.00	0.44	0.00	0.33	0.22
$(HP=PH)^-$ a	0.00	0.49	0.00	0.49	
$(H_2P-PH_2)^+$ b	0.06	0.42	0.06	0.42	

a) ROHF calculations, b) UHF calculations.

These data show that the substitution, in the phosphaalkene anion, of an ethylenic hydrogen atom by a phenyl ring drastically decreases the spin density on the carbon atom and increases the spin density on the phosphorus atom. The spin delocalisation onto the phenyl ring is in good accordance with the variation of the linewidth observed after deuteration of the benzene ring.

The calculated hyperfine tensors for $(HP=PH)^-$ and $(H_2P-PH_2)^+$ reasonably agree with the values measured for $(ArP=PAr)^-$ and $(Ar''_2PPAr''_2)^+$. For $(HP=CH_2)^-$, the isotropic and anisotropic coupling constants are quite different from those measured for $(ArP=CHAr')^-$, but, as indicated by the spin densities calculated for $(HP=CHAr')^-$, this difference is due to the spin delocalisation induced by the phenyl ring.

In summary, the frozen solution EPR spectra confirm the π^* structure for phosphaalkene and diphosphene radical anions (negligible contribution of the s orbitals of the phosphorus or carbon atom to the SOMO) and the non-bonding character of the SOMO for the diphosphine cation.

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