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Structure of C₃⁺P and C₄⁺ Phosphoranyl and C₄⁺ Phosphorane Anion Radicals. A Quai Chemical Study

R. A. J. Janssen,* G. J. Visser, and H. M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands 5600 MB. Received September 28, 1983

Abstract: Ab initio molecular orbital calculations on various C₃⁺ phosphoranyl radicals and the C₄⁺ PF₅⁻ phosphorane anion radical are presented. By the unrestricted Hartree–Fock method with a 4-31G basis set the geometries for C₃⁺ X₅PX₅⁻ (X⁺ = apical ligand, X⁻ = equatorial ligand) radicals were optimized for X = H, F, and Cl. All C₃⁺ radicals reveal a trigonal-bipyramidal structure with the unpaired electron in apical position. The optimized PF₅⁻ radical is octahedral with the unpaired electron acting as a ligand. The calculated isotropic hyperfine coupling constants are in good agreement with the experimental values. Variation of the apical-equatorial bond angle for HPH₃ and PF₅⁻ leads to u*-arrangements. A detailed study of the C₃⁺ PH₃ + H⁺ potential energy surface is described. It appears that a u*-arrangement is not stable but leads to dissociation. The stability of X⁺PH₃ with respect to dissociation into PH₃ and X⁺ is described, and transition state calculations are started. HPH₃ lies 45.2 kJ mol⁻¹ below its transition state, FPH₃ (9.8 kJ mol⁻¹), whereas CIPH₃ is unstable.

I. Introduction

A number of single-crystal ESR studies have shown that phosphoranyl radicals (PX₃) can adopt different configurations depending on the ligands attached to phosphorus and steric constraints of ring structures.1–4 Most frequently a C₃ᵥ geometry is encountered. The electronic structure of these C₃ᵥ phosphoranyl radicals is well established and may be described as a trigonal bipyramidal (TBP) with the unpaired electron acting as a fifth ligand in an equatorial position.²⁻⁵ In contrast to the structure of C₄ᵥ phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C₄ᵥ geometry and phosphorane anion radicals with a C₄ᵥ geometry. The unpaired electron in the Ph₃P═C radical, which possesses a C₄ᵥ geometry, is believed to reside in a σ* P–Cl orbital,¹ accounting for the high spin density found on chlorine and the fact that the ³¹P tensor

\[\begin{align*}
\chi_{P} & = \frac{1}{2} \left( \sigma_{P} + \sigma_{C} \right) 
\end{align*}\]

that the unpaired electron resides in the apical position of a TBP (TBP-a).¹⁺ The near isotropic ¹⁴N hyperfine coupling of 22 G

\[\begin{align*}
\chi_{N} & = 22 \text{ G} 
\end{align*}\]

is parallel to the ³¹Cl tensor. By contrast the extensive studies on the C₃ᵥ radical -P(OCH₂CH₂)₃N⁺BF₄⁻ show unambiguously

\[\begin{align*}
\chi_{P} & = \chi_{N} 
\end{align*}\]
The stability of D. J.; Schlegel, H. B.; Topiol, set was used. The structures were fully optimized with respect
directed along the P-Cl linage.12 The chlorine hyperfine coupling
detailed study is made of the
difficulties and electronic structures of various
these confusing differences and to examine the preferred geom-
indicates a small spin density on the apical nitrogen atom. Similar
apical position, the 31P, 35Cl, and 37Cl tensors are coincident and
PH3, no stable geometry could

to all bond lengths and bond angles within the symmetry con-
Isotopic hyperfine coupling constants (a[Nuc]) were
calculated from the Fermi contact integrals (p(Nuc)):
\[
\rho(\mathbf{R}_{\text{Nuc}}) = \sum_{\mu \nu} p_{\mu \nu} \phi_{\mu} \phi_{\nu} \rho(\mathbf{R}_{\text{Nuc}})
\]
(1)
\[
a_{\text{Nuc}} = (4\pi/3)\rho(\mathbf{R}_{\text{Nuc}})\rho(\mathbf{R}_{\text{Nuc}})
\]
(2)
in which P_{\mu \nu} is the first-order spin density matrix and \phi_{\mu} and
\phi_{\nu} are the atomic basis functions. Orbital spin densities were
obtained by performing a Mulliken population analysis on the
single determinant wave function. Correlation energies were
calculated by Möller–Plesset perturbation theory to second and
third order (UMP2 and UMP3) and by configuration interaction
with all double substitutions (CID). Transition states were
calculated with the GAUSSIAN80 saddle-point-search algorithm.
At stationary points the second derivative matrix possesses a single
negative value.

III. Geometry and Electronic Structure

(1) Optimized Geometries for C_4X Radicals. The geometries of the radicals X^4P^4 have been optimized for all combinations
of X^4 and X^4 with X = H, F, or Cl within a C_4 symmetry
constraint.15 The optimized parameters for these radicals are collected in Table I together with the calculated UHF energies and the expectation values of S^2. The geometric parameters for HPH_3 and FPF_3 differ slightly from those previously reported by Howell et al., because in our study we included the apical-equatorial bond
angle (\phi) in the optimization. For CIPH_3 no stable geometry could be calculated (vide infra). Characteristic for all these C_4 radicals is the apical-equatorial bond angle \phi that is near to 90°.

The singly occupied molecular orbital (SOMO) determines the distribution of the unpaired electron in the radical. The calculated

(15) Without this symmetry constraint optimization would probably reveal C_3 or C_2 geometries (see, e.g., ref 2, 5, 7, and 10).

### Table I. Optimized Geometries, UHF Energies, and <S^2> Values of the C_3 X^4PX^4 Radicals

<table>
<thead>
<tr>
<th>X^4PX^4</th>
<th>P-X^4</th>
<th>P-X^4</th>
<th>\phi</th>
<th>E(UHF)</th>
<th>&lt;S^2&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH_3</td>
<td>1.43</td>
<td>1.59</td>
<td>89.5</td>
<td>-342.47245</td>
<td>0.8328</td>
</tr>
<tr>
<td>FPH_3</td>
<td>1.79</td>
<td>1.43</td>
<td>85.7</td>
<td>-441.245124</td>
<td>0.7579</td>
</tr>
<tr>
<td>CIPH_3</td>
<td>1.39</td>
<td>1.70</td>
<td>92.7</td>
<td>-638.78236</td>
<td>0.7787</td>
</tr>
<tr>
<td>FPF_3</td>
<td>1.61</td>
<td>1.67</td>
<td>91.6</td>
<td>-737.549048</td>
<td>0.7798</td>
</tr>
<tr>
<td>CIPF_3</td>
<td>2.21</td>
<td>1.69</td>
<td>92.0</td>
<td>-1097.199849</td>
<td>0.7981</td>
</tr>
<tr>
<td>HPCI_3</td>
<td>1.42</td>
<td>2.35</td>
<td>93.9</td>
<td>-1717.851382</td>
<td>0.9580</td>
</tr>
<tr>
<td>FPCI_3</td>
<td>1.64</td>
<td>2.36</td>
<td>95.7</td>
<td>-1816.592299</td>
<td>1.0054</td>
</tr>
<tr>
<td>CIPCl_3</td>
<td>2.22</td>
<td>2.39</td>
<td>98.7</td>
<td>-2176.272556</td>
<td>1.0907</td>
</tr>
</tbody>
</table>

### Table II. Fermi Contact Integrals \( \rho(\mathbf{R}_{\text{Nuc}}) \) and Isotopic Hyperfine Coupling Constants \( a_{\text{Nuc}} \) of the C_3 X^4PX^4 Radicals

<table>
<thead>
<tr>
<th>( \rho(\mathbf{R}_{\text{p}}) )</th>
<th>( a_{\text{iso}} )</th>
<th>( \rho(\mathbf{R}_{\text{x}}) )</th>
<th>( a_{\text{iso}} )</th>
<th>( \rho(\mathbf{R}_{\text{X}}) )</th>
<th>( a_{\text{iso}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH_3</td>
<td>1.252</td>
<td>809</td>
<td>0.007</td>
<td>12</td>
<td>0.125</td>
</tr>
<tr>
<td>FPH_3</td>
<td>0.280</td>
<td>181</td>
<td>0.195</td>
<td>292</td>
<td>0.048</td>
</tr>
<tr>
<td>CIPF_3</td>
<td>1.920</td>
<td>1241</td>
<td>-0.019</td>
<td>-29</td>
<td>0.152</td>
</tr>
<tr>
<td>HPCI_3</td>
<td>2.006</td>
<td>1296</td>
<td>0.007</td>
<td>1</td>
<td>0.154</td>
</tr>
<tr>
<td>FPCI_3</td>
<td>1.218</td>
<td>787</td>
<td>-0.055</td>
<td>-82</td>
<td>0.042</td>
</tr>
<tr>
<td>CIPCl_3</td>
<td>1.357</td>
<td>903</td>
<td>-0.027</td>
<td>-41</td>
<td>0.042</td>
</tr>
</tbody>
</table>

*Bond lengths in angstroms, bond angles in degrees, and UHF energies in atomic units.

---

Table III. Valence Orbital Spin Densities of the C$_3$e X$^+$(PX$_3$) Radicals$^*$

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>X$^a$</th>
<th>X$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3s</td>
<td>3p</td>
<td>ns</td>
</tr>
<tr>
<td>HPH$_3$</td>
<td>0.08</td>
<td>0.20</td>
<td>-0.01</td>
</tr>
<tr>
<td>FPH$_3$</td>
<td>0.04</td>
<td>0.57</td>
<td>-0.01</td>
</tr>
<tr>
<td>HPF$_3$</td>
<td>0.31</td>
<td>0.37</td>
<td>0.00</td>
</tr>
<tr>
<td>FPF$_3$</td>
<td>0.31</td>
<td>0.33</td>
<td>0.00</td>
</tr>
<tr>
<td>HPC$_1$</td>
<td>0.10</td>
<td>0.14</td>
<td>0.00</td>
</tr>
<tr>
<td>FPC$_1$</td>
<td>0.06</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>CIPCl$_3$</td>
<td>0.09</td>
<td>0.03</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$^*$The listed values are summations over the inner and outer orbitals of the split valence 4-31G basis set. $^a np_x$ is the equatorial contribution, calculated as $np_x$ + $np_y$.

Figure 1. Schematic representation of the SOMOs of C$_3$e phosphoranyl radicals. (A) HPH$_3$, (B) FPF$_3$, (C) FPH$_3$, (D) HPF$_3$.

SOMOs indicate that all studied radicals have a TBP-a structure and not a $^{a*}$-arrangement. This is depicted in Figure 1, where a schematic representation of the SOMO is given for some of the studied radicals. To characterize the electronic structure of these C$_3$e phosphoranyl radicals, we calculated the Fermi contact integrals ($\rho (R_{\text{med}})$) and the isotropic hyperfine coupling constants ($\alpha_{\text{Nuc}}^{(\text{iso})}$) together with the valence orbital spin densities. These values are given in Tables II and III. The listed values for the three X$^+$(PC$_1$)$_3$ radicals must be regarded with some scepticism because the ($S^2$) values of their wave functions include a considerable amount of contaminating higher multiplicities (Table I). It appears that roughly speaking all TBP-a radicals have a similar spin density distribution, in which the major part is located on phosphorus and the equatorial ligands. The apical ligand possesses a near zero spin density, which is a direct result of the fact that its atomic orbitals do not contribute significantly to the SOMO. This calculated general structure is in perfect agreement with the experimental values of the C$_3$e $\Gamma(\text{OCH$_2$CH$_2$})$_3$N$^+$BF$_4^-$ radical and therefore confirms its assignment as TBP-a (vide supra).

In comparison with the other calculated C$_3$e radicals the electronic structure of FPH$_3$ shows some remarkable differences. Relative to HPH$_3$ there is a serious decrease of the contribution to the SOMO of the phosphorus 3s orbital and the 1s orbital of the equatorial hydrogen atoms. Simultaneously the contribution of the phosphorus 3p$_x$ and of the apical ligand is increased. It has been frequently suggested by various authors$^{16-19}$ that a radical like FPH$_3$, with one strongly electronegative ligand, preferentially occupies a tetrahedral geometry with the unpaired electron in an antibonding $a^*$ orbital. However, our calculations show that for FPH$_3$ the optimized value of $\phi$ (85.9$^\circ$) does not confirm a tetrahedral geometry and that the electronic structure of FPH$_3$ is clearly TBP-a (Figure 1). In order to get an indication of the distance between phosphorus and the point of the maximum probability of finding the unpaired electron along the C$_3$ axis, we have calculated for HPH$_3$ the radial spin density distribution $r^2 \rho (r)$, where $r$ is the radius centered on phosphorus and $\rho (r)$ is defined by eq 1 (section II). Figure 2 reveals that this distance is 0.93 Å. As can be seen from Table I the optimized apical bond length for those radicals where X$^+=X^*$ (HPH$_3$, FPF$_3$, and CIPCl$_3$) is considerably shorter than the corresponding equatorial bond. In view of their TBP-a structures this is a remarkable result. It is a well-known fact that for pentacoordinated phosphorus compounds with a TBP geometry the axial bonds are longer than the equatorial bonds when identical ligands are involved$^{20}$ The same bond-length rule applies for TBP-e (C$_2$e) phosphoranyl radicals as was shown by Howell et al.$^7$ The question arises of why the TBP-a radicals form an exception and possess a short apical bond. To answer this question one must be aware of the fact that both phosphoranyl radicals and pentacoordinated phosphorus compounds are hypervalent species with more than eight electrons around phosphorus. To accommodate the extra electron(s) the HOMO$^1$ will possess some antibonding character. For phosphoranyl radicals this HOMO is identical with the SOMO. The HOMOs for the PH$_3$ molecule and the C$_2$ and C$_3$ PH$_3$ radicals are depicted in Figure 3. The schematic representations indicate that, for the three examples, in the ligands that contribute most to the HOMO the bond length is increased, while the ligands with a smaller contribution possess a normal bond length (ca. 1.43 Å).

Figure 2. Radial spin density probability along the C$_3$ axis for the HPH$_3$ radical.

$^{20}$ Holmes, R. J. ACS Monogr. 1980, No. 175.
$^{21}$ Abbreviations used are HOMO for highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital.
Figure 3. Geometries (ref 7, Table I) and calculated antibonding molecular orbitals of PH₅, C₅H₅, and C₅H₄, PH₄.

Figure 4. Optimized geometry of PF₅ (E(UHF) = -836.982 786 au; \( S^2 = 0.7626 \)) and a schematical representation of the SOMO.

It is obvious that the increased bond length is a direct result of the antibonding character. The participation of d orbitals in pentavalent phosphorus compounds is still a subject of controversy. A number of ab initio studies on pentacoordinated phosphorus compounds and phosphoranyl radicals revealed that the principal concepts of the bonding are adequately described without the introduction of d functions. However, for numerically highly accurate results in the determination of bond lengths and bond energies they are found to be essential merely because their inclusion will increase the completeness of the basis set that is used. From Figure 3 it is clear that the symmetry of the HOMO of PH₅ fits exactly to the phosphorus 3d₂ orbital, when this is provided with a negative coefficient. Therefore the 3d₂ orbital will contribute to some extent to the HOMO and thus to the bonding in PH₅.

(2) Optimized Structure for C₅PF₅. Optimization of PF₅ within a C₅ symmetry constraint revealed an exact C₅ geometry. This optimized structure of PF₅ is analogous to the C₅ optimized structure of FPF₃. The bond angle between the apical bond and the four equatorial bonds is 90.6°, and again the apical bond is substantially shorter than the equatorial bond (Figure 4). This is in accordance with the fact that the equatorial ligands contribute more to the antibonding SOMO than the apical ligand. The calculated isotropic hyperfine coupling constants are in good agreement with the experimental values (Table IV).

The SOMO of the PF₅ phosphorane anion radical indicates that this radical can be described as octahedral \( O_6 \) with the unpaired electron acting as a sixth ligand. The electronic structure of PF₅ is essentially the same as for the TBP- radicals, in which phosphorus and the equatorial fluorines possess a large spin density and the apical ligand a very small spin density.

(3) Geometry Variations and Electronic Structures. Until now all calculations revealed radicals in which the unpaired electron occupies an orbital directed toward the missing ligand of a TBP or \( O_6 \) structure. This resulted in a small spin density on the apical ligand. In a \( \sigma^* \) structure the unpaired electron occupies an an-
tribonding orbital and is located between phosphorus and the apical ligand. This structure has been assigned to the Ph3PCL radicals in order to explain the high spin density on the apical chlorine. For a further insight in these differences, we have calculated the effect of geometry variations on the spin density distribution. For the HPH3 radical the angle \( \phi \) between the apical and the three equatorial bonds was varied from 80° to 130°. During the variation of \( \phi \) all bond lengths were fixed at the optimized values. The calculated isotropic hyperfine coupling constants arising from the Fermi contact integrals at the phosphorus and hydrogen nuclei are given as a function of \( \phi \) in Figure 5. Figure 6 represents the corresponding UHF energy during this variation of \( \phi \) relative to the energy of the optimized radical (\(-342.472475\) au). The phosphorus isotropic hyperfine coupling constant reaches a maximum value at \( \phi = 117° \). At this point the phosphorus 3p\(_a\) orbital inverts and gives no contribution to the spin density distribution. This is the transition point where the structure changes formally from TBP-a to \( \sigma^*\)-C\(_{3e}\). Figure 6 indicates that the \( \sigma^*\)-C\(_{3e}\) arrangement lies some 150 kJ mol\(^{-1}\) above the optimized C\(_{3v}\) structure. Attempts to optimize the \( \sigma^* \) structure were not successful, but led to the dissociation into PH3 and H\(-\) (vide infra).

The most important difference between the TBP-a and the \( \sigma^*\)-C\(_{3e}\) radical is the distribution of the unpaired electron over the hydrogen atoms. The \( \sigma^*\)-C\(_{3e}\) arrangement is characterized by a high spin density in the \( C_1 \) axis of the radical. This results in large isotropic couplings on phosphorus and the apical hydrogen atom. Going from TBP-a toward \( \sigma^*\)-C\(_{3e}\), a continuous transfer of spin density from the equatorial nuclei to the apical nucleus has been calculated. This transfer starts at approximately \( \phi = 108° \), before the actual inversion takes place. Therefore a nonzero spin density on an apical ligand in a \( C_{3v} \) phosphoranyl radical gives no definite proof of a \( \sigma^*\)-arrangement. Nevertheless the calculated spin density distribution for the HPH3 \( \sigma^* \) structure is comparable with the experimental values of the related \( C_{3v} \) CIP(\( O\_2\_C\_6\_H\_4\)\(_2\)Cl)\(_2\) radical where a large spin density on the apical ligand is observed. Both the \( O_6 \) and \( \sigma^* \) structure exhibit a large phosphorus isotropic hyperfine coupling. This relative high spin density in the \( C_1 \) axis of the PF5\(_2\) radical anion possessing a \( \sigma^*\)-arrangement is comparable with the experimental values of the related \( C_{3v} \) CIP(\( O\_2\_C\_6\_H\_4\)\(_2\))\(_2\) radical where a high spin density in the \( P-\)Cl axis has been found. From this point of view it may be suggested that the CIP(\( O\_2\_C\_6\_H\_4\)\(_2\))\(_2\) radical anion possesses a \( \sigma^*\)-C\(_{3v}\) structure. This possibility was already recently suggested by Symons. Figure 10 gives a schematical representation of the SOMO of \( \sigma^*\)-C\(_{3v}\) structure of C\(_{3v}\) HPH3 and PF5\(_2\).

**Figure 7.** Calculated isotropic hyperfine coupling constants (\( \rho_{Nmol}^{esc} \)) of PF5\(_2\) as a function of the apical-equatorial bond angle \( \phi \); values for \( \rho_{Nmol}^{esc} \) are in gauss.

**Figure 8.** Calculated valence p orbital populations as a function of the apical-equatorial bond angle \( \phi \) relative to the optimized radical, values in kJ mol\(^{-1}\).

**Figure 9.** Energy of PF5\(_2\) as a function of the apical-equatorial bond angle \( \phi \) relative to the optimized radical, values in kJ mol\(^{-1}\).

**Figure 10.** Schematic representation of the SOMOs of \( \sigma^*\)-arrangements of HPH3 and PF5\(_2\).

### IV. Stability of X\(_2\)PH3 radicals

As we showed in section III(1) the optimized \( C_{3v} \) HPH3 radical possesses a TBP-a structure. The question arises of whether this optimized structure represents the only stable structure for the

---

A considerable amount of spin density is found on the four equivalent hydrogen nuclei (0.099 electrons Bohr^{-2}; \(a_p=158\) G). The LUMO-TS (\(r_e=1.82; \phi=73.9^\circ\)) lies 41.1 kJ mol^{-1} below the HOMO-TS. The electronic structure of this LUMO-TS is characterized by a low phosphorus Fermi contact integral (0.368 electrons Bohr^{-2}; \(a_{p}\) \(=238\) G) and a high value on the approaching hydrogen nucleus (0.216 electrons Bohr^{-2}; \(a_{p}\) \(=345\) G). SOMOs of both transition states are depicted in Figure 14.

The potential surface shows further that the energy barrier for LUMO approach is smaller than for HOMO approach. We have calculated fully optimized structures for the HOMO- and LUMO-loose complexes. Their PH3 fragments are identical with each other and with the optimized PH3 molecule. The P–H distances differ: 4.18 Å for the LUMO and 3.86 Å for the HOMO. The energy of these loose complexes lies slightly below that of the isolated PH3 + H. This difference has no physical significance and is probably due to a small calculated interaction between the outer 4-31G orbitals of PH3 and H. Using the saddle-point optimization method, we have optimized the LUMO-TS with respect to all geometric parameters within \(C_{3v}\) symmetry (Figure 15). This LUMO-TS lies 178.3 kJ mol^{-1} above the isolated PH3 + H and 43.2 kJ mol^{-1} above the optimized \(C_{3v}\) HPH3 radical. This demonstrates that the dissociation of HPH3 is not a wholly downhill process as previously suggested by Howell et al. Despite many trial geometries we were not able to calculate a saddle point that could be attributed to a HOMO-TS. All efforts led to nonoptimized structures with very short apical bonds and large values of \(\phi\) or to the previously optimized LUMO-TS. For the \(C_{3v}\) HPH3 radical, the LUMO-TS, and both loose complexes we have calculated correlation energies by Möller–Plesset perturbation theory (UMP2 and UMP3) and configuration interaction. These values are listed in Table VI. The post SCF calculations do not change the conclusions based on the UHF calculations. The energy difference between LUMO-TS and isolated PH3 + H is lowered from 178.3 to 147.9 kJ mol^{-1} after configuration interaction, while the stability of the \(C_{3v}\) radical relative to the LUMO-TS rises from 43.2 to 51.1 kJ mol^{-1} (Table VI). The most important result that can be derived from the potential surfaces is that for all geometries where the electronic structure is \(\pi-C_{3v}\), the radical dissociates directly without any energy barrier (Figure 13). Therefore the ligand exchange processes of nonrigid TBP-e phosphoryl radicals via

| Table V. Energies\(^{a}\) of the Minima and Transition States on the Cross Sections of the Potential Surface |
|---|---|---|
| \(r_e=1.6\) Å | \(r_e=1.5\) Å | \(r_e=1.4\) Å |
| \(C_{3v}\) radical | \(0.051 494 (135.2)\) | \(0.055 675 (146.2)\) |
| LUMO-TS | \(0.079 576 (208.9)\) | \(0.069 342 (182.1)\) |
| HOMO-TS | \(0.095 208 (250.0)\) | \(0.090 016 (225.0)\) |
| LUMO-TC \(C_{3v}\) | \(0.022 120 (58.1)\) | \(0.004 045 (10.6)\) | \(0.001 106 (2.9)\) |
| HOMO-TC \(C_{3v}\) | \(0.022 094 (58.0)\) | \(0.004 016 (10.5)\) | \(0.001 062 (2.8)\) |

\(^{a}\) Energies are relative to PH3 + H. Values between brackets refer to differences in kJ mol^{-1}. TS = transition state. \(^{1}\) LC = loose complex.
a $\sigma^*$ intermediate seems questionable.

(2) Stability of FPH$_3$ and CIPH$_3$. The energy of FPH$_3$ lies 120.9 kJ mol$^{-1}$ above the energy of isolated PH$_3$ and F$^-$. The geometry of this radical differs from the related radicals (Table I). The equatorial bond length of 1.43 Å is considerably shorter than that of the same bond in HPH$_3$ (1.59 Å) but identical with the bond length in the PH$_3$ molecule. The angle $\phi$ (85.9°) is smaller and the P–F bond length of 1.79 Å is longer than for FPF$_3$ and FPCl$_3$. This structure actually resembles the LUMO-TS for HPH$_3$. As in the case of HPH$_3$, we have found two loose complexes for FPH$_3$ both for HOMO and LUMO approach. Their PH$_3$ fragments are identical with the PH$_3$ molecule, the P–F distances are 3.21 and 3.73 Å, respectively. By means of the

Figure 13. Potential energy surfaces of the PH$_3$ + H$-$ system. Geometric parameters are $r_e$, $r_g$, and $\phi$ (see text). Cross sections are drawn for three values of $r_g$: (A) $r_g = 1.4$ Å, (B) $r_g = 1.5$ Å, (C) $r_g = 1.6$ Å. The dotted lines indicate the edge between TBP-$\alpha$ and $\sigma^*$ structures.

---

Table VI. Correlation Energies$^a$ of HPH$_3$ for the Optimized Structures and the Transition State

<table>
<thead>
<tr>
<th></th>
<th>$E(\text{UHF})$</th>
<th>$E(\text{UMP2})$</th>
<th>$E(\text{UMP3})$</th>
<th>$E(\text{CID})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3p$ radical</td>
<td>$-342.472 475 (135.1)$</td>
<td>$-342.555 382 (114.8)$</td>
<td>$-342.572 836 (105.9)$</td>
<td>$-342.582 713 (96.8)$</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>$-342.456 009 (178.3)$</td>
<td>$-342.537 795 (160.9)$</td>
<td>$-342.554 448 (154.2)$</td>
<td>$-342.563 243 (147.9)$</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>$-342.523 978 (-0.2)$</td>
<td>$-342.599 037 (0.0)$</td>
<td>$-342.613 133 (0.0)$</td>
<td>$-342.619 516 (0.0)$</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>$-342.524 016 (-0.2)$</td>
<td>$-342.599 090 (-0.1)$</td>
<td>$-342.613 186 (-0.1)$</td>
<td>$-342.619 570 (-0.2)$</td>
</tr>
<tr>
<td>PH$_3$ + H$^-$</td>
<td>$-342.523 923$</td>
<td>$-342.599 056$</td>
<td>$-342.613 152$</td>
<td>$-342.619 497$</td>
</tr>
</tbody>
</table>

$^a$Values between brackets refer to differences relative to PH$_3$ + H$^-$ in kJ mol$^{-1}$.

Table VII. Energies$^a$ and $(S^2)$ Values of the Optimized Structures and the Transition State of FPH$_3$ and ClPH$_3$

<table>
<thead>
<tr>
<th></th>
<th>FPH$_3$</th>
<th>ClPH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(S^2)$</td>
<td>$(S^2)$</td>
</tr>
<tr>
<td>TBP-a</td>
<td>0.7579</td>
<td>0.7502</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>0.7519</td>
<td>0.7510</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>0.7508</td>
<td>0.7509</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>0.7509</td>
<td>0.7509</td>
</tr>
<tr>
<td>PH$_3$ + X$^+$</td>
<td>0 + 0.7500</td>
<td>0 + 0.7500</td>
</tr>
</tbody>
</table>

$^a$Values between brackets refer to differences relative to PH$_3$ + X$^+$ in kJ mol$^{-1}$.

Figure 14. SOMOs for the transition states for LUMO and HOMO approach on the $r_e = 1.6$ Å surface.

Figure 15. LUMO-TS of the PH$_3$ + H$^-$ = HPH$_3$ system. Calculated isotropic hyperfine coupling constants are $a_{\text{ph}} = 199$, $a_{\text{ph}}^{\text{iso}} = 260$, and $a_{\text{ph}}^{\text{iso}} = 124$ G.

saddle-point optimization method the F-PH$_3$ transition state for LUMO approach was calculated. Its structure (Figure 16) and energy (Table VII) are close to those of the optimized FPH$_3$ radical.

The energy of this transition state is 130.7 kJ mol$^{-1}$ higher than the isolated PH$_3$ and F$. The energy difference between FPH$_3$ radical and transition state is only 9.8 kJ mol$^{-1}$ indicating that the radical is rather unstable. In section III(1) of this paper we mentioned that for ClIP$_3$ no stable geometry could be calculated. On attempted optimization all trial geometries revealed a HOMO-loose complex (PH$_3$ + Cl$^-$; distance 3.21 Å) or a LUMO-loose complex (PH$_3$ + Cl$^-$; distance 4.18 Å). The energies of these loose complexes are essentially the same as for the isolated PH$_3$ and Cl$^-$ (Table VII).

V. Conclusions

The calculations showed that all studied C$_3p$ X$^+$PX$_3$$^+$ phosphoranyl radicals possess a TBP-a structure. The calculated electronic structure of these radicals is in good agreement with the experiments on the P(OCH$_2$CH$_2$)$_3$N$^+$BF$_4^-$ radical. Geometry variations for HPH$_3$ reveal a $\sigma^*$-arrangement, which, however, is unstable and dissociates directly into PH$_3$ and H$^-$. The calculated electronic structure of this $\sigma^*$-arrangement is comparable with the experimental values for the Ph$_3$PCI radical reported by Berclaz et al.$^7$ and therefore gives support to their $\sigma^*$-assignment. The structure of C$_6p$ PF$_3^-$ is octahedral with the unpaired electron in apical position. This structure is fully analogous to the TBP-a structures. The calculated isotropic hyperfine coupling constants of PF$_3^-$ are in excellent agreement with the experimental values obtained by Morton et al.$^7$ Variation of the apical-equatorial bond angle for PF$_3^-$ leads to a $\pi^*$-arrangement. Comparison of the electronic structures of this $\sigma^*$ PF$_3^-$ radical anion and the experimental values obtained for the CIP(O$_2$C$_6$H$_4$)$_2^-$ radical anion indicates that the latter possibly possess a $\sigma^*$-C$_6p$ arrangement. Despite many geometry variations and a number of different radicals it was not possible to optimize the geometry of a $\sigma^*$-C$_6p$ or $\sigma^*$-C$_3p$ radical. This suggests that $\sigma^*$ structures are not stable. Nevertheless the calculated electronic structures for the $\sigma^*$-arrangements of HPH$_3$ and PF$_3^-$ are in correspondence with the experimental values obtained for the Ph$_3$PCI and CIP(O$_2$C$_6$H$_4$)$_2^-$ radicals, respectively. It is possible that the apparent formation and existence of a $\sigma^*$ structure for Ph$_3$PCI and CIP(O$_2$C$_6$H$_4$)$_2^-$ is the result of the geometry of their precursors and of matrix effects which may prevent geometrical isomerizations and control cage reactions. However, the possibility that Ph$_3$PCI and CIP(O$_2$C$_6$H$_4$)$_2^-$ represent stable $\sigma^*$ radicals cannot be excluded. The stability of these radicals should then be the result of a subtle intrinsic stabilizing energy effect which could not be abstracted from the calculations on the HPH$_3$ and PF$_3^-$ model systems. Therefore it may be of interest to mention the recent work of Clark$^9$ on the structure of H$_3$PX$^*$$^*$ radical cations (X = Ph$_3$, H$_2$S, HCl), which revealed a $\sigma^*$ structure for H$_3$PPH$_3$$^*$$^*$. The H$_3$PSH$_2$$^*$$^*$ and H$_2$PClH$_3$$^*$$^*$ radical cations possess structures that deviate more or less from the ideal $\sigma^*$ structure toward TBP-a. Clark pointed out that the existence of a $\sigma^*$ structure is extremely dependent on the energy levels of the HOMO and SOMO of X and Ph$_3$$^*$$^*$.

Electronic Structure of 1,5-Dithia-2,4,6,8-tetrazocine.
Model Calculations and Spectroscopic Investigations

Rolf Gleiter,*t Richard Bartetzko,t and Dieter Cremert

Abstract: Model calculations (ab initio and MNDO) on 1,5-dithia-2,4,6,8-tetrazocine (2) show that the electron-rich 10-π system prefers a planar monocyclic structure. π-Donor substituents can, however, induce a pseudo-Jahn-Teller distortion leading to a bicyclic 8-π system with a transannular S-S bond. The results obtained are best understood by assuming b_α(π) and a_α(π) as the two highest occupied and b_β(π) and b_β(π) as the lowest unoccupied MOs of 2.

The structure of S_4N_4 (1a) can be deduced by starting with a planar ring (1b) in which each sulfur center contributes two electrons and each nitrogen one to the π system, leading to 12 π electrons.1,2 The degeneracy of the half-filled highest occupied eg orbital of 1b (D_3h) is removed by forming two transannular S-S bonds in 1a (D_2h). If one adopts this point of view the related system of 1,5-dithia-2,4,6,8-tetrazocine (2) in which two opposite sulfur centers of 1 are formally replaced by carbon centers should have 10 π electrons if planar since each carbon contributes one π electron to the π system.

2a

2b

2c

Recently derivatives of 2 have been synthesized,3 and it has been shown by means of X-ray analysis that the 3,7-di-tert-butyl derivative of 2 (3) has a planar eight-membered ring with an average S-N distance of 1.564 Å and an average C-N distance of 1.323 Å. The two phenyl groups are only slightly (9.7°) distorted out of the plane. It is interesting to note that the 3,7-bis(dimethylamino) derivative of 2 (4) shows a remarkable difference in its molecular shape. In contrast to the planar ring in 3, the ring of 4 is folded along an axis through the two sulfur atoms with an interplanar angle of 101° thus giving rise to a transannular S-S distance of

\[ 1.564 \text{ Å} \]

respectively. Only in the case that these energy levels are degenerated (or nearly) a σ* structure can be expected.

Acknowledgment. This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. HPH, 25530-87-4; FF, 1485-36-8; FPH, 56360-19-1; HPF, 56360-18-0; PF, 8925-40-1; PH, 7803-51-2; H, 12385-13-6; CIPh, 89746-27-0; CIPh, 89746-28-1; HPCl, 89746-29-2; FPCl, 89746-30-5; CIPCl, 20762-59-8.

Table I. Calculated Total Energies (hartree) and Energy Differences (kcal/mol) of 2a, 2b, and 2c

<table>
<thead>
<tr>
<th>basis</th>
<th>geometry</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>exptl</td>
<td>-1076.99720</td>
<td>-1077.06465</td>
<td>-42.3</td>
</tr>
<tr>
<td>STO-3G</td>
<td>STO-3G</td>
<td>-1077.0273</td>
<td>-1077.06884</td>
<td>-1077.17102</td>
</tr>
<tr>
<td>STO-3G+</td>
<td>exptl</td>
<td>-1088.0443</td>
<td>-1088.01958</td>
<td>0</td>
</tr>
<tr>
<td>STO-3G+</td>
<td>STO-3G</td>
<td>-1088.09202</td>
<td>-1088.04741</td>
<td>-1088.02269</td>
</tr>
<tr>
<td>MNDO</td>
<td>MNDO</td>
<td>-58.24313</td>
<td>-58.21361</td>
<td>-58.16849</td>
</tr>
</tbody>
</table>

The experimental geometries 2a and 2b have been derived from reported data of 3 and 4.

1,548 Å, a value close to the transannular S-S distance found in S_4N_4 (2.58 Å). The average S-N distance (1.605 Å) as well as the average C-N distance in 4 (1.348 Å) is longer than the corresponding values found for 3.

Both structural differences manifest themselves in the electronic absorption spectra. Compound 3 shows a long-wavelength band at 409 nm followed by a series of bands around 300 nm while 4 shows a maximum at 229 nm.

In order to understand the electronic structure of the eight-membered 1,5-dithia-2,4,6,8-tetrazocine ring, we have carried out model calculations on 2. Furthermore, we have synthesized the 3,7-di-tert-butyl derivative of 2 (5). For 3, 4, and 5 we investigated the He I photoelectron (PE) spectra, and for 3 and 5 we recorded the electronic absorption spectra using the stretched film technique.


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