Structure of C3v phosphoranyl and C4v phosphorane anion radicals. A quantum chemical study

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hand, the catalyzed oxidation currents were reproducible at the PB-modified electrodes. Eventually, we conclude that the oxidized form of PB is one of the best catalysts toward \( \text{H}_2\text{O}_2 \) oxidation in acidic solutions. It is reasonable to believe that the catalyzed oxidation of \( \text{H}_2\text{O}_2 \) proceeds in crystals of the oxidized form of PB just as expected for the reduction of \( \text{H}_2\text{O}_2 \) because the catalyzed oxidation also showed first-order dependence on the concentrations of \( \text{H}_2\text{O}_2 \) and \( \Gamma_{PB} \).

It is noteworthy that the stability of the catalyst represented here was excellent under certain conditions. The stability of the wave of PB itself was extremely high as described in our previous papers.4 For this reason, the PB-modified electrode can be applied in an electrochromic display device.8 Toward \( \text{O}_2 \) reduction, a lifetime experiment showed that only a few percent decrease in the catalyzed current was observed after 30 h holding the electrode potential at -0.2 V vs. SCE. Such a high durability should be important for its application such as fuel cells and air batteries.

However, we found a gradual loss in activity when a large amount of PB (20 mC/cm²) was employed in order to obtain higher current densities. When observed under a microscope, the film of PB was sometimes partially removed. This behavior may be explained by poor adhesion of the PB film on the GC surface.

Finally, we briefly mention Prussian blue analogues. It has already been shown that iron–ruthenium cyanide (ruthenium purple; RP), \( \text{Fe}_2^{3+}[\text{Ru}^{II}(\text{CN})_6]_3 \), and iron–osmium cyanide, \( \text{Fe}_2^{3+}[\text{Os}^{III}(\text{CN})_6]_3 \), can be prepared by an electrochemical method.15 It was found that both were active for the reduction of \( \text{O}_2 \). Applications as catalysts can be readily expected from the above results.

**Acknowledgment.** We acknowledge Professors R. M. De La Rue (Glasgow) and T. Osa (Tohoku) for comments on this manuscript.

### Registry No. Fe, 7439-89-6; \( \text{O}_2 \), 7782-44-7; \( \text{H}_2\text{O}_2 \), 7722-84-1; \( \text{H}_2\text{O} \), 7732-18-5; C, 7440-44-0; PB, 12240-15-2; Prussian white, 81681-39-2.

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**Structure of \( C_{3v} \) Phosphoranyl and \( C_{6v} \) Phosphorane Anion Radicals: A QuasiChemical Study**

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

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**Abstract:** Ab initio molecular orbital calculations on various \( C_n \) phosphoranyl radicals and the \( C_{6v} \) \( \text{PF}_5^- \) phosphorane anion radical are presented. By the unrestricted Hartree–Fock method with a 4-31G basis set the geometries for \( C_3 \) \( \text{PX}_3 \) (\( X^a \) = apical ligand, \( X^e \) = equatorial ligand) radicals were optimized for \( X = \text{H, F, and Cl} \). All \( C_3 \) radicals reveal a trigonal-bipyridim-like structure with the unpaired electron in apical position. The optimized \( \text{PF}_5^- \) 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 \( \text{HPF}_3 \) and \( \text{PF}_3^- \) leads to \( ñ^\star \)-arrangements. A detailed study of the \( C_3 \), \( \text{PH}_3^- \) + \( \text{H}^- \) potential energy surface is described. It appears that a \( ñ^\star \)-arrangement is not stable but leads to dissociation. The stability of \( \text{X}^a_3\text{PH}_3 \) with respect to dissociation into \( \text{PH}_3 \) and \( \text{X}^a \) is described, and transition states are calculated. \( \text{HPF}_3 \) lies 43.2 \( \text{kJ mol}^{-1} \) below its transition state, \( \text{FPF}_3 \) (9.8 \( \text{kJ mol}^{-1} \)), whereas \( \text{ClPF}_3 \) is unstable.

**I. Introduction**

A number of single-crystal ESR studies have shown that phosphoranyl radicals (\( \text{PX}_3 \)) can adopt different configurations depending on the ligands attached to phosphorus and steric constraints of ring structures.1–4 Most frequently a \( C_{3v} \) geometry is encountered. The electronic structure of these \( C_3 \) phosphoranyl radicals is well established and may be described as a trigonal bipyramid (TBP) with the unpaired electron acting as a fifth ligand in an equatorial position.2–5 In contrast to the structure of \( C_3 \), phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a \( C_{6v} \) geometry and phosphorane anion radicals with a \( C_{6v} \) geometry. The unpaired electron in the \( \text{Ph}_3\text{PCI}^- \) radical, which possesses a \( C_{6v} \) geometry, is believed to reside in a \( ñ^\star \) P–Cl orbital,6 accounting for the high spin density found on chlorine and the fact that the \( 31^\text{P} \) tensor is parallel to the \( 35\text{Cl} \) tensor. By contrast the extensive studies on the \( C_{3v} \) radical \( \cdot \text{P(OCH}_2\text{CH}_3)_3\)\( \text{N}^+\text{BF}_4^- \) show unambiguously that the unpaired electron resides in the apical position of a TBP (TBP-a).1,8 The near isotropic \( 14\text{N} \) hyperfine coupling of 22 G

The stability of the set was used. The structures were fully optimized with respect to all bond lengths and bond angles within the symmetry constraints. Isotropic hyperfine coupling constants \( a_{\text{iso}} \) were calculated from the Fermi contact integrals \( \rho(\vec{R}_{\text{Nuc}}) \):

\[
\rho(\vec{R}_{\text{Nuc}}) = \sum_{\mu \nu} P_{\mu \nu} \phi_{\mu}(\vec{R}_{\text{Nuc}}) \phi_{\nu}(\vec{R}_{\text{Nuc}}) \tag{1}
\]

\[
a_{\text{iso}} = \left( 4/3 \right) g \beta \gamma_{\text{Nuc}}(S_z)^{-1} \rho(\vec{R}_{\text{Nuc}}) \tag{2}
\]

in which \( P_{\mu \nu} \phi_{\mu} \phi_{\nu} \) 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 (CISD). 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 \( C_3 \) Radicals

The geometries of the radicals \( X^+PX^3 \) have been optimized for all combinations of \( X^+ \) and \( X^3 \) with \( X = H, F, \) or Cl within a \( C_3 \) symmetry constraint. 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 \( FPPF_3 \) 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 \( CIPF_3 \) no stable geometry could be calculated (vide infra). Characteristic for all these \( C_3 \) 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

#### Table I. Optimized Geometries, UHF Energies, and \( \langle S^2 \rangle \) Values of the \( C_3 \) \( X^+PX^3 \) Radicals

<table>
<thead>
<tr>
<th>( X^+PX^3 )</th>
<th>( P-X^+ )</th>
<th>( P-X^3 )</th>
<th>( \phi )</th>
<th>( E(\text{UHF}) )</th>
<th>( \langle S^2 \rangle )</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>-441.24512</td>
<td>0.7579</td>
</tr>
<tr>
<td>( CIPF_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>-737.54904</td>
<td>0.7798</td>
</tr>
<tr>
<td>( CIIP_3 )</td>
<td>2.21</td>
<td>1.67</td>
<td>92.0</td>
<td>-1097.19984</td>
<td>0.7981</td>
</tr>
<tr>
<td>( HPF_3 )</td>
<td>1.42</td>
<td>2.35</td>
<td>93.9</td>
<td>-1717.85132</td>
<td>0.9580</td>
</tr>
<tr>
<td>( CIPC_3 )</td>
<td>1.64</td>
<td>2.36</td>
<td>95.7</td>
<td>-1816.59922</td>
<td>1.0054</td>
</tr>
<tr>
<td>( CIPC_3 )</td>
<td>2.22</td>
<td>2.39</td>
<td>98.7</td>
<td>-2176.27256</td>
<td>1.0907</td>
</tr>
</tbody>
</table>

\( ^* \) Bond lengths in angstroms, bond angles in degrees, and UHF energies in atomic units.

#### Table II. Fermi Contact Integrals \( \rho(\vec{R}_{\text{Nuc}}) \) and Isotropic Hyperfine Coupling Constants \( a_{\text{iso}} \) of the \( C_3 \) \( X^+PX^3 \) Radicals

<table>
<thead>
<tr>
<th>( X^+ )</th>
<th>( \rho(\vec{R}_{\text{P}}) )</th>
<th>( a_{\text{iso}} )</th>
<th>( \rho(\vec{R}_{\text{X}}) )</th>
<th>( a_{\text{iso}} )</th>
<th>( \rho(\vec{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>
<td>199</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>
<td>77</td>
</tr>
<tr>
<td>( HPF_3 )</td>
<td>2.032</td>
<td>1313</td>
<td>-0.013</td>
<td>-22</td>
<td>0.158</td>
<td>237</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>
<td>228</td>
</tr>
<tr>
<td>( HPCl_3 )</td>
<td>2.006</td>
<td>1296</td>
<td>0.007</td>
<td>1</td>
<td>0.154</td>
<td>232</td>
</tr>
<tr>
<td>( FPCl_3 )</td>
<td>1.400</td>
<td>905</td>
<td>-0.005</td>
<td>-8</td>
<td>0.048</td>
<td>8</td>
</tr>
<tr>
<td>( CIIP_3 )</td>
<td>1.218</td>
<td>787</td>
<td>-0.055</td>
<td>-82</td>
<td>0.042</td>
<td>7</td>
</tr>
<tr>
<td>( CIPC_3 )</td>
<td>1.357</td>
<td>903</td>
<td>-0.027</td>
<td>-41</td>
<td>0.042</td>
<td>7</td>
</tr>
</tbody>
</table>

\( ^a \rho(\vec{R}_{\text{Nuc}}) \) in electrons Bohr\(^{-3} \). \( ^b a_{\text{iso}} \) in gauss.

indicates a small spin density on the apical nitrogen atom. Similar differences in the structure of \( C_3 \) phosphorane anion radicals (PX\(_3\)) have been reported. The isotropic hyperfine pattern of the PFX\(_2\) radical shows a large coupling and one with a small coupling arising from the unique apical fluorine. The same structure has been proposed for \( PCl_3 \) and the isoelectronic \( SF_3 \). For the \( CIP(\text{OCH}_2\text{H})_2\) radical, which adopts a local \( C_3 \) symmetry with chlorine in the apical position, the \( ^3\text{P} \), \(^3\text{Cl} \), and \(^3\text{Cl} \) tensors are coincident and directed along the P–Cl linkage. The chlorine hyperfine coupling shows in sharp contrast to PFS– a large spin density on the apical position; this clearly indicates a local \( C_3 \) symmetry in these confusing differences and to examine the preferred geometries and electronic structures of various \( C_3 \) an \( C_3 \) radicals. A detailed study is made of the \( C_3 \) radicals \( HPH_3, FPH_3 \), and \( CIPH_3 \). The calculated geometries (see, e.g., ref 2, 5, 7, and 10).

---

**Table III. Valence Orbital Spin Densities of the $C_3$,$X^pPX^c$ Radicals**

<table>
<thead>
<tr>
<th></th>
<th>$X^p$</th>
<th>$X^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$ns$</td>
<td>$np_z$</td>
</tr>
<tr>
<td>$\text{HFP}_3$</td>
<td>0.04</td>
<td>-0.01</td>
</tr>
<tr>
<td>$\text{FFP}_3$</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>$\text{HPF}_3$</td>
<td>0.31</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{FPC}_1$</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>$\text{CPC}_1$</td>
<td>0.09</td>
<td>0.04</td>
</tr>
</tbody>
</table>

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

**Figure 1.** Schematic representation of the SOMOs of $C_3$ phosphoranyl radicals. (A) HFP$_3$, (B) FFP$_3$, (C) FPH$_3$, (D) HFP$_3$.

**SOmos indicate that all studied radicals have a TBP-a structure and not a $e^*$-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 $C_3$ phosphoranyl radicals, we calculated the Fermi contact integrals ($\rho(\mathbf{R}_{\text{mol}})$) and the isotropic hyperfine coupling constants ($\alpha_{\text{Nuc}}^{(1)}$) together with the valence orbital spin densities. These values are given in Tables II and III. The listed values for the three $X^pCPC_1$ radicals must be regarded with some scepticism because the $S2$ 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 $C_3$,$\cdot\text{P(OCH}_3\text{CH}_3)_3\text{NBF}_4$ radical and therefore confirms its assignment as TBP-a (vide supra).

In comparison with the other calculated $C_3$ 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 is orbital of the equatorial hydrogen atoms. Simultaneously the contribution of the phosphorus 3p, 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 $e^*$ 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 $\text{Å}$. As can be seen from Table I the optimized apical bond length for those radicals where $X^p = X^c$ (HPH$_3$, FFP$_3$, 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 ($C_2$) 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[21] 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 $C_3$ PHS 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 $\text{Å}$).

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[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 PH$_5$, C$_{3v}$ PH$_4$, and C$_{4v}$ PH$_4$.

Figure 4. Optimized geometry of PF$_5^-$ (E(UHF) = -836.982 786 au; $\langle S^2 \rangle = 0.7626$) 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 PHS fits exactly to the phosphorus 3d$_{z^2}$ orbital, when this is provided with a negative coefficient. Therefore the 3d$_{z^2}$ orbital will contribute to some extent to the HOMO and thus to the bonding in PH$_5$.

(2) Optimized Structure for C$_{4v}$ PF$_5^-$ Optimization of PF$_5^-$ within a C$_{4v}$ symmetry constraint revealed an exact C$_{4v}$ geometry. This optimized structure of PF$_5^-$ is analogous to the C$_{4v}$ optimized structure of FPF$_3$. 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 PF$_5^-$ phosphorane anion radical indicates that this radical can be described as octahedral (O$_h$) with the unpaired electron acting as a sixth ligand. The electronic structure of PF$_5^-$ is essentially the same as for the TBP-$\pi$ 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$_h$ structure. This resulted in a small spin density on the apical ligand. In a $\sigma^*$ structure the unpaired electron occupies an an-
tribbing orbital and is located between phosphorus and the apical ligand. This structure has been assigned to the Ph3PCl radical 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 \( \phi = 117^\circ \). At this point the phosphorus 3p \( \alpha \) 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 \( \sigma^* - C_{3v} \). Figure 6 indicates that the \( \sigma^* - C_{3v} \) 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 \( \sigma^* - C_{3v} \) radical is the distribution of the unpaired electron over the hydrogen atoms. The \( \sigma^* - C_{3v} \) 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 \( \sigma^* - C_{3v} \), a continuous transfer of spin density from the equatorial nuclei to the apical nucleus has been calculated. This transfer starts at approximately \( \phi = 108^\circ \), 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 \( C_3 \) phosphoranyl radical anion possessing a \( \sigma^* - C_{3v} \) structure. This possibility was already recently suggested by Symons. Figure 10 gives a schematical representation of the SOMOs of \( \sigma^* \)-arrangements of HPH3 and PF5-

structure the equatorial ligands possess a large spin density whereas the \( \sigma^* - C_{4v} \) radical is characterized by a high spin density on the apical ligand. Both the \( \sigma^* \) and \( \sigma^* \)-structure exhibit a large phosphorus isotropic hyperfine coupling. This relative high spin density in the \( C_1 \) axis of the PF5- radical anion possessing a \( \sigma^* \)-structure is comparable with the experimental values of the related \( C_{4v} \) CI(\( O_2C_6H_{12} \))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 CI(\( O_2C_6H_{12} \))2- radical anion possesses a \( \sigma^* - C_{4v} \) structure. This possibility was already recently suggested by Symons. Figure 10 gives a schematical representation of the SOMOs of the \( \sigma^* \) structures of HPH3 and PF5-

IV. Stability of \( XPH_3 \) 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

Figure 7. Calculated isotropic hyperfine coupling constants (\( \phi_{\text{Nuc}} \)) of PF5- as a function of the apical-equatorial bond angle \( \phi \); values for \( \phi_{\text{Nuc}} \) are in gauss.

Figure 8. Calculated valence p orbital populations as a function of the apical-equatorial bond angle \( \phi \). Values are obtained from a Mulliken population analysis.

Figure 9. Energy of PF5- 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-.
a considerable amount of spin density is found on the four

phosphorus Fermi contact integral is, due to the absence of
constant while the apical bond length

approach

three minima were calculated, one for a stable TBP-a radical

(4.29; 3.90; 1.5, and 1.6

= 0.051 494 (135.2) 0.055 675 (146.2) 0.079 576 (208.9) 0.069 342 (182.1) 0.095 208 (250.0) 0.022 120 (58.1) 0.004 045 (10.6) 0.001 106 (2.9) 0.022 094 (58.0) 0.004 016 (10.5) 0.001 062 (2.8)

 Energies a of the Minima and Transition States on the Cross Sections of the Potential Surface

\( r_e = 1.6 \text{ Å} \quad r_e = 1.5 \text{ Å} \quad r_e = 1.4 \text{ Å} \)

radical

LUMO-

TS a

HOMO-

TS a

LUMO-

LC a

HOMO-

LC a

\footnote{a Energies are relative to PH3 + H- (-342.523 923 au). Values between brackets refer to differences in kJ mol\(^{-1}\). b TS = transition state. LC = loose complex.}

Figure 11. C\(_3\)v optimized geometry for PH\(_3\) (\(E(UHF) = -342.025 690 \text{ au}\)).

Figure 12. Two possible routes for H- attack toward PH\(_3\). Route A, LUMO approach; route B, HOMO approach.

C\(_3\)v HPH\(_3\) radical. In principle it could be possible that there are more stable geometries for a C\(_3\)v HPH\(_3\) radical. Furthermore it is important to know the stability of the C\(_3\)v HPH\(_3\) radical, for example, with respect to the dissociation into PH\(_3\) and H-.

(1) Potential Surface PH\(_3\)+H-. The PH\(_3\) molecule is pyramidal and possesses a C\(_3\)v geometry. In its 4-31G optimized structure the P–H bond length is 1.43 Å, and the angle between each P–H bond and the C\(_3\) axis is 58.3° (Figure 11).

The calculated energy difference between the optimized C\(_3\)v HPH\(_3\) radical and the sum of isolated PH\(_3\) and H- is 0.051 449 au (135 kJ mol\(^{-1}\)) in favor of the dissociation. The HOMO of PH\(_3\) contains the two nonbonding electrons. Attack of a hydrogen atom along the P–H axis leads to a C\(_3\)v HPH\(_3\) radical. There are two possible routes for this attack (Figure 12): an approach of H- toward the LUMO of the PH\(_3\) molecule or an approach toward the HOMO. Likewise the dissociation of a C\(_3\)v HPH\(_3\) radical can proceed along these two routes. To determine the route with the lowest energy barrier three cross sections through the multidimensional potential energy surface were calculated. For each cross section the equatorial bond lengths \( r_e \) were kept constant while the apical bond length \( r_a \) and the apical–equatorial bond angle \( \phi \) were varied from 1.4 to 4.3 Å and from 55° to 125°, respectively. Cross sections were calculated for \( r_e = 1.4, 1.5, \) and 1.6 Å (Figure 13). The potential surfaces differ in the number of minima and transition states. For the \( r_e = 1.6 \text{ Å} \) surface three minima were calculated, one for a stable TBP-a radical \( r_e = 1.43; \phi = 89.5° \) and two "loose complexes", for both HOMO approach \( r_e = 3.90; \phi = 123.4° \) and LUMO approach \( r_e = 4.29; \phi = 56.6° \). On this surface there are two transition states (TS). The HOMO-TS possesses a perfect tetrahedral geometry \( r_e = 1.60; \phi = 109.4° \) and a symmetrical SOMO (i.e., only the s orbitals of phosphorus and hydrogen are involved). The phosphorus Fermi contact integral is, due to the absence of 3p\(_z\) contribution, very high (2.265 electrons Bohr\(^{-1}\)).

The TBP-a radical relative to the LUMO-TS rises from 43.2 kJ mol\(^{-1}\) above the isolated PH\(_3\) + H- and 43.2 kJ mol\(^{-1}\) above the optimized C\(_3\)v HPH\(_3\) radical. This demonstrates that the dissociation of HPH\(_3\) is not a wholly downhill process as previously suggested by Howell et al.\(^{7}\) 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 TBP-a. For the C\(_3\)v HPH\(_3\) radical, the LUMO-TS, and both loose complexes we have calculated correlation energies by Moller–Plesset perturbation theory (UIMP2 and UIMP3) 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 PH\(_3\)+H- is lowered from 178.3 to 147.9 kJ mol\(^{-1}\) after configuration interaction, while the stability of the C\(_3\)v 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 \( \sigma^*-C_3 \), the radical dissociates directly without any energy barrier (Figure 13). Therefore the ligand exchange processes of nonrigid TBP-e phosphoranyl radicals via...
Phosphoranyl and Phosphane Anion Radicals

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

1.5
2.0
2.5
3.0 3.5 4.0

a \( \sigma^* \) intermediate\(^{15} \) seem questionable.

(2) Stability of FPH\(_3\) and CIPH\(_3\). The energy of FPH\(_3\) lies 120.9 \( \text{kJ mol}^{-1} \) 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 \( \text{Å} \) is considerably shorter than that of the same bond in HPH\(_3\) (1.59 \( \text{Å} \)) but identical with the bond length in the PH\(_3\) molecule. The angle \( \phi \) (85.9\(^\circ\)) is smaller and the P–F bond length of 1.79 \( \text{Å} \) is longer than for FPF\(_3\) and FPC\(_3\)\(_\text{H}\). 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 \( \text{Å} \), respectively. By means of the

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saddle-point optimization method the FLPH, transition state for HPH, is unstable and dissociates directly into PH, and variations for HPH, reveal a $a^*$-arrangement, which, however, of these loose complexes are essentially the same as for the isolated radical. In section III(4) the electronic structure of these radicals is in good agreement with the experiments on the $P(OCH_2CH_2)_N^+$ radical. Geometry variations for HPH reveal a $a^*$-arrangement, which, however, is unstable and dissociates directly into PH and H-. The calculation electronic structure of this $a^*$-arrangement is comparable with the experimental values for the PH$_3$PCI radical reported by Berczal et al. and therefore gives support to the $a^*$-assignment. The structure of C$_{as}$PF$_5^-$ 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$_5^-$ are in excellent agreement with the experimental values reported by Morton et al. Variation of the apical–equatorial bond angle for PF$_5^-$ leads to a $u^*$-arrangement. Comparison of the electronic structures of this $u^*$-PF$_5^-$ 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 $u^*$-arrangement. Despite many geometry variations and a number of different radicals it was not possible to optimize the geometry of a $\sigma^+$-C$_{as}$ or $\sigma^-$-C$_{as}$ radical. This suggests that $\sigma^*$ structures are not stable. Nevertheless the calculated electronic structures for the $\sigma^*$-arrangements of HPH$_3$ and PF$_5^-$ 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 of a new $u^*$-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$_5^-$ model systems. Therefore it may be of interest to mention the recent work of Clark et al. on the structure of Ph$_3$PX$^+$- radical cations (X = Ph$_3$, H$_3$S, HCl), which revealed a $\sigma^*$ structure for Ph$_3$PPH$_3^+$. The H$_3$PS$_2^+$ and H$_3$PCH$_3^+$ radical cations possess structures that deviate more or less from the ideal $\sigma^*$ structure toward TBP-e. 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$_3^+$. 

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

<table>
<thead>
<tr>
<th></th>
<th>E(UHF)</th>
<th>E(UMP2)</th>
<th>E(UMP3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3s$ radical</td>
<td>-342.472475 (135.1)</td>
<td>-342.555382 (114.8)</td>
<td>-342.572836 (105.9)</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>-342.456009 (178.3)</td>
<td>-342.537795 (160.9)</td>
<td>-342.554448 (154.2)</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>-342.523978 (-0.2)</td>
<td>-342.599037 (0.0)</td>
<td>-342.613133 (0.0)</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>-342.524016 (-0.2)</td>
<td>-342.599090 (-0.1)</td>
<td>-342.613186 (-0.1)</td>
</tr>
<tr>
<td>PH$_3$ + H-</td>
<td>-342.523923</td>
<td>-342.599056</td>
<td>-342.613152</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 $\langle S^2 \rangle$ Values of the Optimized Structures and the Transition State of FPH$_3$ and ClPH$_3$

<table>
<thead>
<tr>
<th></th>
<th>E(UHF)</th>
<th>$\langle S^2 \rangle$</th>
<th>E(UHF)</th>
<th>$\langle S^2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPH$_3$</td>
<td></td>
<td></td>
<td>ClPH$_3$</td>
<td></td>
</tr>
<tr>
<td>TBP-a</td>
<td>-341.245134 (120.9)</td>
<td>0.7579</td>
<td>-800.997249 (-0.2)</td>
<td>0.7502</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>-341.241399 (130.7)</td>
<td>0.7819</td>
<td>-801.000448 (-8.6)</td>
<td>0.7510</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>-341.291240 (-0.2)</td>
<td>0.7508</td>
<td>-800.997165</td>
<td>0 + 0.7500</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>-341.292633 (-3.8)</td>
<td>0.7509</td>
<td>-800.997165</td>
<td>0 + 0.7500</td>
</tr>
<tr>
<td>PH$_3$ + X*</td>
<td>-341.291171</td>
<td>0 + 0.7500</td>
<td>-800.997165</td>
<td>0 + 0.7500</td>
</tr>
</tbody>
</table>

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

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**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 $a_{H}^{N} = 199$, $a_{H}^{P} = 260$, and $a_{H}^{N} = 124$ G.

**Figure 16.** LUMO-TS of the PH$_3$ + F- = FPH$_3$ system. Calculated isotropic hyperfine coupling constants of this structure are $a_{H}^{N} = 144$, $a_{H}^{P} = 341$, and $a_{H}^{N} = 48$ G.
Electronic Structure of 1,5-Dithia-2,4,6,8-tetrazocine. Model Calculations and Spectroscopic Investigations

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Contribution from the Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany, and the Lehrstuhl für Theoretische Chemie der Universität Köln, D-5000 Köln, West Germany. Received September 30, 1983

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 of these model calculations are substantiated by investigation of the newly synthesized 3,7-di-tert-butyl derivative of 2 (5), the 3,7-diphenyl derivative (3), and the 3,7-bis(dimethylamino) derivative (4) by means of He I PE spectroscopy and linear dichroic absorption spectroscopy in the visible and near-UV region. The results obtained are best understood by assuming b_{\pi}(\pi) and a_{\pi}(\pi) as the two highest occupied and b_{\pi}(\pi) and b_{\pi}(\pi) as the lowest unoccupied MOs of 2.

The structure of S_{2}N_{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 \(e_{g}\) orbital of 1b (\(D_{2h}\)) 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.

Recently derivatives of 2 have been synthesized,\(^{3}\) and it has been shown by means of X-ray analysis that the 3,7-diphenyl derivative of 2 (3) has a planar eight-membered ring with an average S-N distance of 1.56 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 Å.

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.

\[\text{Table I. Calculated Total Energies (hartree) and Energy Differences (kcal/mol) of 2a, 2b, and 2c}\]

<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></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>4-31G</td>
<td>exptl</td>
<td>-1088.0443</td>
<td>-1088.01958</td>
<td>-90.1</td>
</tr>
<tr>
<td>4-31G</td>
<td>STO-3G</td>
<td>-1088.09220</td>
<td>-1088.04741</td>
<td>-1088.02269</td>
</tr>
<tr>
<td>STO-3G+d</td>
<td>exptl</td>
<td>-1077.53955</td>
<td>-1077.53770</td>
<td></td>
</tr>
<tr>
<td>MNDO</td>
<td>MNDO</td>
<td>-58.24313</td>
<td>-58.21361</td>
<td>-58.16849</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.5</td>
<td>25.3</td>
<td></td>
</tr>
</tbody>
</table>

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

2.428 Å, a value close to the transannular S-S distance found in S_{2}N_{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.

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