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 H₂O₂ oxidation in acidic solutions. It is reasonable to believe that the catalyzed oxidation of H₂O₂ proceeds in crystals of the oxidized form of PB just as expected for the reduction of H₂O₂ because the catalyzed oxidation also showed first-order dependence on the concentrations of H₂O₂ and Γₚ₈.

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. For this reason, the PB-modified electrode can be applied in an electrochromic display device. Toward O₂ 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), Fe₂⁺[Ru[II](CN)₆]₃, and iron–osmium cyanide, Fe₂⁺[Os[II](CN)₆]₃, can be prepared by an electrochemical method. It was found that both were active for the reduction of O₂. 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; O₂, 7782-44-7; H₂O₂, 7722-84-1; H₂O, 7732-18-5; C, 7440-44-0; PB, 12240-15-2; Prussian white, 81681-39-2.
Table I. Optimized Geometries, UHF Energies, and \((S^2)\) Values of the C\(_{3v}\) X\(^2\)PX\(^2\)\(_{3v}\) Radicals

<table>
<thead>
<tr>
<th>X(^2)PX(^2)(_{3v})</th>
<th>P-P</th>
<th>P-X</th>
<th>(\phi)</th>
<th>(E) (UHF)</th>
<th>((S^2))</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>ClPH(_3)</td>
<td>1.39</td>
<td>1.70</td>
<td>92.7</td>
<td>-638.782376</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>CIF(_3)</td>
<td>2.21</td>
<td>1.67</td>
<td>92.0</td>
<td>-1097.199849</td>
<td>0.7981</td>
</tr>
<tr>
<td>HPCl(_3)</td>
<td>1.42</td>
<td>2.35</td>
<td>93.9</td>
<td>-1717.851382</td>
<td>0.9580</td>
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<tr>
<td>FPCl(_3)</td>
<td>1.64</td>
<td>2.36</td>
<td>95.7</td>
<td>-1816.599229</td>
<td>1.0054</td>
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<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>

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

Table II. Fermi Contact Integrals \(\rho(\bar{R}_{\text{Nucl}})\) and Isotopic Hyperfine Coupling Constants \(a_{\text{Nucl}}^{iso}\) of the C\(_{3v}\) X\(^2\)PX\(^2\)\(_{3v}\) Radicals

<table>
<thead>
<tr>
<th>(\rho(\bar{R}_{P}))</th>
<th>(a_P^{iso})</th>
<th>(\rho(\bar{R}_{X}))</th>
<th>(a_X^{iso})</th>
<th>(\rho(\bar{R}_{X}))</th>
<th>(a_X^{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>HPF(_3)</td>
<td>2.032</td>
<td>1313</td>
<td>-0.013</td>
<td>-22</td>
<td>0.158</td>
</tr>
<tr>
<td>FPF(_3)</td>
<td>1.920</td>
<td>1241</td>
<td>-0.019</td>
<td>-29</td>
<td>0.152</td>
</tr>
<tr>
<td>CIF(_3)</td>
<td>2.066</td>
<td>1296</td>
<td>0.007</td>
<td>1</td>
<td>0.154</td>
</tr>
<tr>
<td>HPCI(_3)</td>
<td>1.400</td>
<td>905</td>
<td>-0.005</td>
<td>-8</td>
<td>0.048</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>CIPCI(_3)</td>
<td>1.357</td>
<td>903</td>
<td>-0.027</td>
<td>-41</td>
<td>0.042</td>
</tr>
</tbody>
</table>

\(a(\bar{R}_{\text{Nucl}})\) in electrons Bohr\(^3\). \(a_{\text{Nucl}}^{iso}\) in gauss.

does not indicate a small spin density on the apical nitrogen atom. Similar differences in the structure of C\(_{3v}\) phosphorane anion radicals \((PX_3^-)\) have been reported. The isotropic hyperfine pattern of the FPF\(_3\) radical anion shows four equivalent equatorial fluorines with a large coupling and one with a small coupling arising from the unique apical fluorine. The same structure has been proposed for PCI\(_3\)-lo and the isoelectronic SFS\(_3\). For the CIP(O-C\(_6\)H\(_4\))\(_2\) radical, which adopts a local C\(_{3v}\) symmetry with chlorine in the apical position, the \(^{31}\)P, \(^{35}\)Cl, and \(^{37}\)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 nitrogen atom. Similar differences in the structure of C\(_{3v}\) phosphorane anion radicals \((PX_3^-)\) have been reported. The structures were fully optimized with respect to all bond lengths and bond angles within the symmetry constraints. Isotopic hyperfine coupling constants \(a_{\text{Nucl}}^{iso}\) were calculated from the Fermi contact integrals \(\rho(\bar{R}_{\text{Nucl}})\):

\[
\rho(\bar{R}_{\text{Nucl}}) = \sum_{\mu\nu} P_{\mu\nu} \sigma^\dagger \phi^\dagger_{\mu}(\bar{R}_{\text{Nucl}}) \phi_{\nu}(\bar{R}_{\text{Nucl}}) \tag{1}
\]

\[
a_{\text{Nucl}}^{iso} = (4\pi/3)\rho(\bar{R}_{\text{Nucl}})(S^2)^{-1}\rho(\bar{R}_{\text{Nucl}}) \tag{2}
\]

in which \(P_{\mu\nu} \sigma^\dagger \phi^\dagger_{\mu}(\bar{R}_{\text{Nucl}}) \phi_{\nu}(\bar{R}_{\text{Nucl}})\) is the first-order spin density matrix and \(\phi_{\nu}(\bar{R}_{\text{Nucl}})\) 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 eigenvalue.

III. Geometry and Electronic Structure

(1) Optimized Geometries for C\(_{3v}\) Radicals. The geometries of the radicals X\(^2\)PX\(^2\)\(_{3v}\) have been optimized for all combinations of X*, X\(^*\) with X = H, F, or Cl within a C\(_{3v}\) 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 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 CIPCl\(_3\) no stable geometry could be calculated (vide infra). Characteristic for all these C\(_{3v}\) 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\(_{3h}\) or C\(_i\) geometries (see, e.g., ref 2, 5, 7, and 10).
The SOMOs of the phosphorus 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 (vide supra) that its atomic orbitals do not contribute significantly to the electronic structure of FPH, because the radical 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 radical and therefore confirms its assignment as TBP-a (vide supra).

In comparison with the other calculated C3e radicals the SOMO of the phosphorus 3s orbital and the 1s orbital of the equatorial hydrogen atoms. The apical ligand like FPH3, with one strongly electronegative ligand, preferentially occupies a tetrahedral geometry with the unpaired electron in an antibonding σ* orbital. However, our calculations show that for FPH3 the optimized value of ϕ (85.9°) does not confirm a tetrahedral geometry and that the electronic structure of FPH3 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 C3 axis, we have calculated for HPH1 the radial spin density distribution r2φ(r), where r is the radius centered on phosphorus and φ(r) is defined by eq 1 (section II). Figure 2 reveals that this distance is 0.93 Å. As can be seen from Table 1 the optimized apical bond length for those radicals where X* = X* (HPH3, FPH3, and CIPCl3) 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 (C3e) 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 will possess some antibonding character. For phosphoranyl radicals this HOMO is identical with the SOMO. The HOMOs for the PH3 molecule and the C2e PH3 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).

### Table III. Valence Orbital Spin Densities of the C3e X*PX*3 Radicals

<table>
<thead>
<tr>
<th></th>
<th>3s</th>
<th>3p</th>
<th>ns</th>
<th>np1</th>
<th>np2</th>
<th>ns</th>
<th>np3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH3</td>
<td>0.08</td>
<td>0.20</td>
<td>-0.01</td>
<td>0.11</td>
<td>0.42</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>FPH3</td>
<td>0.04</td>
<td>0.57</td>
<td>-0.01</td>
<td>0.04</td>
<td>0.00</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>HPCl3</td>
<td>0.31</td>
<td>0.33</td>
<td>0.00</td>
<td>-0.02</td>
<td>0.00</td>
<td>0.46</td>
<td>0.50</td>
</tr>
<tr>
<td>HPCl3</td>
<td>0.10</td>
<td>0.14</td>
<td>0.01</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.04</td>
<td>0.55</td>
</tr>
</tbody>
</table>

*The listed values are summations over the inner and outer orbitals of the split valence 4-31G basis set. np1 is the equatorial contribution, calculated as npx + npy.*

![Figure 1](source)

**Figure 1.** Schematic representation of the SOMOs of C3e phosphoranyl radicals. (A) HPH3, (B) FPH3, (C) FPH3, (D) HPCl3.

**Figure 2.** Radial spin density probability along the C3 axis for the HPH1 radical.

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(20) Holmes, R. R. ACS Monogr. 1980, No. 175.
(21) Abbreviations used are HOMO for highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital.
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 orbital, when this is provided with a negative coefficient. Therefore the 3d orbital will contribute to some extent to the HOMO and thus to the bonding in PH₅.

(2) Optimized Structure for \( \text{PF}_5^- \). Optimization of \( \text{PF}_5^- \) within a \( \text{C}_5 \) symmetry constraint revealed an exact \( \text{C}_5 \) geometry. This optimized structure of \( \text{PF}_5^- \) is analogous to the \( \text{C}_5 \) optimized structure of \( \text{FPF}_3 \). 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 \( \text{PF}_5^- \) phosphorane anion radical indicates that this radical can be described as octahedral (\( \text{O}_h \)) with the unpaired electron acting as a sixth ligand. The electronic structure of \( \text{PF}_5^- \) is essentially the same as for the TBP-a 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 \( \text{O}_h \) structure. This resulted in a small spin density on the apical ligand. In a \( \sigma^* \) structure the unpaired electron occupies an anti-

---

Table IV. Experimental and Calculated Isotropic Hyperfine Coupling Constants of \( \text{PF}_5^- \)

<table>
<thead>
<tr>
<th>exp( \text{calcd} )</th>
<th>( a_P )</th>
<th>( a_F )</th>
<th>( a_P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>expt( a )</td>
<td>1356</td>
<td>1323</td>
<td>-17</td>
</tr>
</tbody>
</table>

\( a \) See ref 9. \( \text{Values in gauss.} \)

---

Figure 3. Geometries (ref 7, Table I) and calculated antibonding molecular orbitals of \( \text{PH}_5 \), \( \text{C}_5 \) \( \text{PH}_5 \), and \( \text{C}_5 \) \( \text{PH}_4 \).

Figure 4. Optimized geometry of \( \text{PF}_5^- \) \( (E(\text{UHF}) = -836.982786 \text{ au}) \) and a schematical representation of the SOMO.

Figure 5. Calculated isotropic hyperfine coupling constants \( (\sigma_{\text{Nucl}}) \) of \( \text{HPh}_5 \) as a function of the apical-equatorial bond angle \( \phi \); values for \( \sigma_{\text{Nucl}} \) are in gauss.

Figure 6. Energy of \( \text{HPh}_5 \) as a function of the apical-equatorial bond angle \( \phi \) relative to the optimized radical, values in kJ mol\(^{-1}\).

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(22) Coulson, C. A. Nature (London) \( 1969, 221, 1106. \)
(26) Rauk, A.; Allen, L. C.; Minos, K. J. Am. Chem. Soc. \( 1972, 94, 3035. \)
(29) Keil, F.; Kutzelnigg, W. J. Am. Chem. Soc. \( 1975, 97, 3623. \)
the HPH, 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$_z$ 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 PH$_3$ 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 HPH$_3$ $\sigma^*$ structure is comparable with the experimental values of the related $C_{3v}$ CIP(O$_2$C$_6$H$_4$)$_2$ 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$_4$)$_2$ radical possesses a $\sigma^*-C_{3v}$ structure. This possibility was already recently suggested by Symons.31 Figure 10 gives a schematic representation of the SOMO for the $\sigma^*$ structures of HPH$_3$ and PF$_5$. IV. Stability of XaPH$_3$ radicals As we showed in section III(1) the optimized $C_{3v}$ HPH$_3$ radical possesses a TBP-a structure. The question arises of whether this optimized structure represents the only stable structure for the...
C₃ᵥ HPH₃ radical. In principle it could be possible that there are more stable geometries for a C₃ᵥ HPH₃ radical. Furthermore it is important to know the stability of the Cₓ HPH₃ radical, for example, with respect to the dissociation into PH₃ and H·.

(I) Potential Surface PH₃ + H·. The PH₃ molecule is pyramidal and possesses a C₃ᵥ 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 C₃ axis is 58.3° (Figure 11).

The calculated energy difference between the optimized C₃ᵥ HPH₃ radical and the sum of isolated PH₃ and H· is 0.051 449 au (135 kJ mol⁻¹) in favor of the dissociation. The HOMO of PH₃ contains the two nonbonding electrons. Attack of a hydrogen atom along the PH₃ C₃ axis leads to a Cₓ HPH₃ radical. There are two possible routes for this attack (Figure 12): an approach of H· toward the LUMO of the PH₃ molecule or an approach toward the HOMO. Likewise the dissociation of a C₃ᵥ HPH₃ 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 (rₑ) were kept constant while the apical bond length (rₐ) and the apical–equatorial bond angle (φ) were varied from 1.4 to 4.3 Å and from 55° to 125°, respectively. Cross sections were calculated for rₑ = 1.4, 1.5, and 1.6 Å (Figure 13). The potential surfaces differ in the number of minima and transition states. For the rₑ = 1.6 Å surface three minima were calculated, one for a stable TBP-a radical (rₐ = 1.43; φ = 89.5°) and two "loose complexes", for both HOMO approach (rₑ = 3.90; φ = 123.4°) and LUMO approach (rₑ = 4.29; φ = 56.6°). On this surface there are two transition states (TS). The HOMO-TS possesses a perfect tetrahedral geometry (rₑ = 1.60; φ = 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, contribution, very high (2.265 electrons Bohr⁻¹; ΔEH = 1698 G), and a considerable amount of spin density is found on the four equivalent hydrogen nuclei (0.099 electrons Bohr⁻¹; ΔEH = 158 G). The LUMO-TS (rₑ = 1.82; φ = 73.9°) 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⁻¹; ΔEH = 238 G) and a high value on the approaching hydrogen nucleus (0.216 electrons Bohr⁻¹; ΔEH = 345 G). SOMOs of both transition states are depicted in Figure 14.

For the rₑ = 1.5 Å surface again three minima were calculated. The TBP-a radical (rₑ = 1.44 Å; φ = 89.6°), the HOMO-loose complex (rₑ = 3.89 Å; φ = 122.5°), and the LUMO-loose complex (rₑ = 4.23 Å; φ = 57.5°). On this surface only one transition state, namely for the LUMO approach, is found (rₑ = 1.76 Å; φ = 78.6°). Its structure is comparable with the LUMO-TS on the rₑ = 1.6 Å surface. Finally the rₑ = 1.4 Å surface possesses only two specific points; a HOMO-loose complex (rₑ = 3.86 Å; φ = 121.2°) and a LUMO-loose complex (rₑ = 4.17 Å; φ = 58.8°). Table V summarizes the energies of the various minima and transition state relative to the energy of isolated PH₃ and H· (-342.523 923 au). From these potential surfaces it is clear that the TBP-a structure represents the only stable HPH₃ radical. None of the surface indicates a minimum that could belong to a stable σ*-C₃ᵥ arrangement. The potential surface shows furthermore 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 C₃ᵥ 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 C₃ᵥ 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 φ or to the previously optimized LUMO-TS. For the C₃ᵥ 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 C₃ᵥ radical relative to the LUMO-TS arises 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 σ*-C₃ᵥ, the radical dissociates directly without any energy barrier (Figure 13). Therefore the ligand exchange processes of nonrigid TBP-e phosphoranyl radicals via

![Figure 11. C₃ᵥ optimized geometry for PH₃ (E(UHF) = -342.025 690 au).](image)

![Figure 12. Two possible routes for H· attack toward PH₃. Route A, LUMO approach; route B, HOMO approach.](image)

<table>
<thead>
<tr>
<th>Table V. Energies of the Minima and Transition States on the Cross Sections of the Potential Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>rₑ</td>
</tr>
<tr>
<td>Cₑ</td>
</tr>
<tr>
<td>LUMO-</td>
</tr>
<tr>
<td>TS⁺</td>
</tr>
<tr>
<td>HOMO-</td>
</tr>
<tr>
<td>TS⁻</td>
</tr>
</tbody>
</table>

* Energies are relative to PH₃ + H· (-342.523 923 au). Values between brackets refer to differences in kJ mol⁻¹. # TS = transition state. ¹ LC = loose complex.
Figure 13. Potential energy surfaces of the PH$_3$ + H-system. Geometric parameters are $r_a$, $r_e$, and $\phi$ (see text). Cross sections are drawn for three values of $r_e$: (A) $r_e = 1.4$ Å, (B) $r_e = 1.5$ Å, (C) $r_e = 1.6$ Å. The dotted lines indicate the edge between TBP-a and $\sigma^*$ structures.

a $\sigma^*$ intermediate seems questionable.

(2) Stability of FPH$_3$ and ClPH$_3$. 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

---

saddle-point optimization method the FLPH, transition state for
is unstable and dissociates directly into PH, and variations for HPH, reveal an a*-arrangement, which, however,
of these loose complexes are essentially the same as for the isolated

electronic structure of these radicals is in good agreement with
phoranyl radicals possess a TBP-a structure. The calculated
PH3 and C1. (Table VII).

V. Conclusions
On attempted optimization all trial geometries revealed a
approach on the
Figure 14.
LUMO-TS (C3v)

Figure 15. LUMO-TS of the PH3 + H-. The energy of this transition state is
130.7 kJ mol⁻¹ higher than
was calculated. Its structure (Figure 16) and energy (Table VII) are close to those of the optimized FPH3
radical.

The energy of this transition state is 130.7 kJ mol⁻¹ higher than
the isolated PH3 and F-. The energy difference between FPH3
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 CIP1, no stable geometry could be calculated. On attempted optimization all trial geometries revealed a
HOMO-loose complex (PH3 + Cl; distance 3.21 Å) or a
LUMO-loose complex (PH3 + Cl; distance 4.18 Å). The energies of these loose complexes are essentially the same as for the isolated
PH3 and Cl-. (Table VII).

V. Conclusions
The calculations showed that all studied C3p, XaPXa₃, phos-
phoranyl radicals possess a TBP-a structure. The calculated
electronic structure of these radicals is in good agreement with
the experiments on the -P(OCHCH₂CH₂)₃N⁺BF₄⁻ radical. Geometry
variations for HPH3 reveal a σ*-arrangement, which, however,
is unstable and dissociates directly into PH3 and H-. The cal-
culated electronic structure of this σ*-arrangement is comparable
with the experimental values for the Ph₃PCI radical reported by
Bergclaz et al. and therefore gives support to their σ*-assignment.
The structure of C₆H₆PF₃⁺ 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 PF₃⁻ are in excellent agreement with the experimental values
reported by Morton et al. Variation of the apical-equatorial bond
angle for PF₃⁻ leads to a σ*-arrangement. Comparison of the
electronic structures of this σ*- PF₃⁻ radical anion and the ex-
perimental values obtained for the CIP(O₂C₆H₄)₂⁻ radical anion
indicates that the latter possibly possess a σ*-C₆H₄⁻ arrangement.

Despite many geometry variations and a number of different
radicals it was not possible to optimize the geometry of a σ*-C₆H₄⁻ radical. This suggests that σ*-structures are not stable.

Nevertheless the calculated electronic structures for the σ*-arrangements of HPH3 and PF₃⁻ are in correspondence with the
experimental values obtained for the Ph₃PCI and CIP(O₂C₆H₄)₂⁻
radicals, respectively. It is possible that the apparent formation
and existence of a σ* structure for Ph₃PCI and CIP(O₂C₆H₄)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 Ph₃PCI and CIP-
(O₂C₆H₄)₂⁻ represent stable σ* 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 HPH3 and PF₃⁻ model systems.

Therefore it may be of interest to mention the recent work of
Clark⁴⁰ on the structure of H₃PX⁺⁺ radical cations (X = Ph₃, H₂S,
HCl), which revealed a σ structure for H₃PPH₃⁺⁺. The H₃PSH₂⁺⁺
and H₂PClH⁺ radical cations possess structures that deviate more
or less from the ideal σ*-structure toward TBP-e. Clark pointed
out that the existence of a σ*-structure is extremely dependent
on the energy levels of the HOMO and SOMO of X and Ph₃⁺⁺.


Table VI. Correlation Energies* of HPH3 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>
<th>E(CID)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃p radical</td>
<td>-342.472475 (135.1)</td>
<td>-342.555382 (114.8)</td>
<td>-342.572836 (105.9)</td>
<td>-342.582713 (96.8)</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>
<td>-342.563243 (147.9)</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>
<td>-342.619516 (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>
<td>-342.619570 (-0.2)</td>
</tr>
<tr>
<td>PH₃ + H-</td>
<td>-342.523923</td>
<td>-342.599056</td>
<td>-342.613152</td>
<td>-342.619497</td>
</tr>
</tbody>
</table>

Values between brackets refer to differences relative to PH₃ + H⁻ in kJ mol⁻¹.

Table VII. Energies* and (S²) Values of the Optimized Structures and the Transition State of FPH3 and ClPH3

<table>
<thead>
<tr>
<th></th>
<th>E(UHF)</th>
<th>(S²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPH3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBP-a</td>
<td>-441.245124 (120.9)</td>
<td>0.7579</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>-441.241399 (130.7)</td>
<td>0.7819</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>-441.291240 (-0.2)</td>
<td>0.7508</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>-441.292633 (-3.8)</td>
<td>0.7509</td>
</tr>
<tr>
<td>PH₃ + X⁺</td>
<td>-441.291171</td>
<td>0 (± 0.7500)</td>
</tr>
</tbody>
</table>

Values between brackets refer to differences relative to PH₃ + X⁺ in kJ mol⁻¹.
Electronic Structure of 1,5-Dithia-2,4,6,8-tetrazocine. Model Calculations and Spectroscopic Investigations

Rolf Gleiter,* Richard Bartetzko,† and Dieter Cremer‡

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 10π system prefers a planar monocyclic structure. π-Donor substituents can, however, induce a pseudo-Jahn-Teller distortion leading to a bicyclic 8-A 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 b1(π) and a2(π) as the two highest occupied and b2g(σ) and b3g(σ) as the lowest unoccupied MOs of 2.

The structure of S2N4 (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 (D2h) is removed by forming two transannular S-S bonds in 1a (D2). 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 1.564 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 2.428 Å, a value close to the transannular S-S distance found in S2N4 (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.

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>expt</td>
<td>-1076.99720</td>
<td>-1077.06465</td>
<td></td>
</tr>
<tr>
<td>STO-3G</td>
<td></td>
<td>-42.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-3G</td>
<td>expt</td>
<td>-1077.02733</td>
<td>-1077.17102</td>
<td></td>
</tr>
<tr>
<td>STO-3G</td>
<td></td>
<td>0</td>
<td>-26.0</td>
<td>-90.1</td>
</tr>
<tr>
<td>4-31G</td>
<td>expt</td>
<td>-1088.08443</td>
<td>-1088.01958</td>
<td></td>
</tr>
<tr>
<td>4-31G</td>
<td></td>
<td>0</td>
<td>40.7</td>
<td></td>
</tr>
<tr>
<td>4-31G</td>
<td>expt</td>
<td>-1088.09202</td>
<td>-1088.04741</td>
<td>-1088.02269</td>
</tr>
<tr>
<td>4-31G</td>
<td></td>
<td>0</td>
<td>28</td>
<td>43.5</td>
</tr>
<tr>
<td>MNDO</td>
<td>MNDO</td>
<td>-58.24313</td>
<td>-58.21361</td>
<td>-58.18649</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>18.5</td>
<td>25.3</td>
</tr>
</tbody>
</table>

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

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; FPF, 14855-36-8; FPH, 56360-19-1; HPF, 56360-18-0; PF, 89255-40-1; PH, 7803-51-2; H, 12385-13-6; CIPh, 89746-27-0; CIPF, 89746-28-1; HPCL, 89746-29-2; FPCI, 89746-30-5; CIPCl, 20762-59-8.

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2 Universitüt Heidelberg.
3 Universität Köln.


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