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

Citation for published version (APA):

DOI:
10.1021/ja00324a008

Document status and date:
Published: 01/01/1984

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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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 H$_2$O$_2$ oxidation in acidic solutions. It is reasonable to believe that the catalyzed oxidation of H$_2$O$_2$ proceeds in crystals of the oxidized form of PB just as expected for the reduction of H$_2$O$_2$, because the catalyzed oxidation also showed first-order dependence on the concentrations of H$_2$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. For this reason, the PB-modified electrode can be applied in an electrochromic display device. Toward O$_2$ reduction, a lifetime experiment showed that only a few percent decrease in the catalyzed current was observed after 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/cm$^2$) 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), Fe$_2^{4+}$[Ru$^{II}$Cl$_3$], and iron–osmium cyanide, Fe$_2^{4+}$[Os$^{II}$Cl$_3$], can be prepared by an electrochemical method. It was found that both were active for the reduction of 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; O$_2$, 7782-44-7; H$_2$O$_2$, 7722-84-1; H$_2$O, 7732-18-5; C, 7440-44-0; PB, 12240-15-2; Prussian white, 81681-39-2.

Structure of C$_{3v}$ Phosphoranyl and C$_{4v}$ Phosphorane Anion Radicals. A Quasi-Chemical Study

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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 C$_{3v}$ phosphoranyl radicals and the C$_{4v}$ PF$_5^{-}$ phosphorane anion radical are presented. By the unrestricted Hartree–Fock method with a 4-31G basis set the geometries for C$_{3v}$ XPX$_5^{-}$ (X$^a$ = apical ligand, X$^e$ = equatorial ligand) radicals were optimized for X = H, F, and Cl. All C$_{3v}$ radicals reveal a trigonal-bipyrimidal structure with the unpaired electron in apical position. The optimized 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 HPH$_3$ and PF$_5^{-}$ leads to u* -arrangements. A detailed study of the C$_{3v}$, PH$_3$ + H$^+$ potential energy surface is described. It appears that a u* -arrangement is not stable but leads to dissociation. The stability of X$^a$PH$_3$ with respect to dissociation into PH$_3$ and X$^a$ is described, and transition state structures are calculated. HPH$_3$ lies 43.2 kJ mol$^{-1}$ below its transition state, FPH$_3$ (9.8 kJ mol$^{-1}$), whereas ClPH$_3$ is unstable.

I. Introduction

A number of single-crystal ESR studies have shown that phosphoranyl radicals (PX$_3$) can adopt different configurations depending on the ligands attached to phosphorus and steric constraints of ring structures. Most frequently a C$_{3v}$ geometry is encountered. The electronic structure of these C$_{3v}$ 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. In contrast to the structure of C$_{3v}$, phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C$_{4v}$ geometry and phosphorane anion radicals with a C$_{4v}$ geometry. The unpaired electron in the Ph$_3$PCI radical, which possesses a C$_{4v}$ geometry, is believed to reside in a $\sigma^*$ P–Cl orbital, accounting for the high spin density found on chlorine and the fact that the $^{31}$P tensor is parallel to the $^{35}$Cl tensor. By contrast the extensive studies on the C$_{3v}$ radical –P(OCH$_2$CH$_2$)$_3$N$^+$BF$_4^-$ show unambiguously that the unpaired electron resides in the apical position of a TBP (TBP-a). The near isotropic $^{14}$N hyperfine coupling of 22 G

indicates a small spin density on the apical nitrogen atom. Similar
differences in the structure of the C₅₉ phosphanor anion radicals
(PX₃) have been reported. The isotropic hyperfine pattern of the
PX₃ radical shows a large spin density on the apical position, which
adopts a local C₅₉ symmetry with chlorine in the apical position, the
³¹P, ³⁵Cl, and ³⁷Cl 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

III. Geometry and Electronic Structure
(1) Optimized Geometries for C₅₉ Radicals. The geometries of the
radicals X⁴PX₅³ have been optimized for all combinations of X⁴ and X⁵ with X = H, F, or Cl within a C₅₉ symmetry
constraint. The optimized parameters for these radicals are
collected in Table I together with the calculated UHF energies and
the expectation values of S². The geometric parameters for HPH₃
and FP₃, differ slightly from those previously reported by Howell
et al., because in our study we included the apical–equatorial bond
angle (φ) in the optimization. For CIP₃H₃, no stable geometry could
be calculated (vide infra). Characteristic for all these radicals is the
apical–equatorial bond angle (φ) 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 (S²) Values of the C₅₉ X⁴PX₅³ Radicals

<table>
<thead>
<tr>
<th>X⁴PX₅³</th>
<th>P–X⁴</th>
<th>P–X⁵</th>
<th>φ</th>
<th>E(UHF)</th>
<th>(S²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH₃</td>
<td>1.43</td>
<td>1.59</td>
<td>89.5</td>
<td>-342.472754</td>
<td>0.8328</td>
</tr>
<tr>
<td>FPH₃</td>
<td>1.79</td>
<td>1.43</td>
<td>85.7</td>
<td>-441.245124</td>
<td>0.7579</td>
</tr>
<tr>
<td>CIP₃H₃</td>
<td>1.39</td>
<td>1.70</td>
<td>92.7</td>
<td>-638.782736</td>
<td>0.7787</td>
</tr>
<tr>
<td>HPF₃</td>
<td>1.61</td>
<td>1.67</td>
<td>91.6</td>
<td>-737.549048</td>
<td>0.7798</td>
</tr>
<tr>
<td>CIP₅</td>
<td>2.21</td>
<td>1.69</td>
<td>92.0</td>
<td>-1097.198949</td>
<td>0.7981</td>
</tr>
<tr>
<td>HPCI₃</td>
<td>1.42</td>
<td>2.35</td>
<td>93.9</td>
<td>-1717.851382</td>
<td>0.9580</td>
</tr>
<tr>
<td>FPCI₃</td>
<td>1.64</td>
<td>2.36</td>
<td>95.7</td>
<td>-1816.599229</td>
<td>1.0054</td>
</tr>
<tr>
<td>CIPCI₃</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 ρ(Φ₅₉) and Isotropic Hyperfine Coupling Constants aₙuo of the C₅₉ X⁴PX₅³ Radicals

<table>
<thead>
<tr>
<th>X⁴PX₅³</th>
<th>P–X⁴</th>
<th>P–X⁵</th>
<th>φ</th>
<th>ρ(Φ₅₉)</th>
<th>aₙuo</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH₃</td>
<td>1.252</td>
<td>8090</td>
<td>0.007</td>
<td>12</td>
<td>0.125</td>
</tr>
<tr>
<td>FPH₃</td>
<td>0.280</td>
<td>181</td>
<td>0.195</td>
<td>292</td>
<td>0.048</td>
</tr>
<tr>
<td>CIP₃H₃</td>
<td>2.032</td>
<td>1313</td>
<td>0.013</td>
<td>-22</td>
<td>0.158</td>
</tr>
<tr>
<td>HPF₃</td>
<td>1.920</td>
<td>1241</td>
<td>-0.019</td>
<td>-29</td>
<td>0.152</td>
</tr>
<tr>
<td>CIP₅</td>
<td>2.006</td>
<td>1296</td>
<td>0.007</td>
<td>1</td>
<td>0.154</td>
</tr>
<tr>
<td>HPCI₃</td>
<td>1.400</td>
<td>905</td>
<td>-0.005</td>
<td>-8</td>
<td>0.048</td>
</tr>
<tr>
<td>FPCI₃</td>
<td>1.218</td>
<td>787</td>
<td>-0.055</td>
<td>-82</td>
<td>0.042</td>
</tr>
<tr>
<td>CIPCI₃</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 \( C_3 \) \( X^2PX^2 \), Radicals* 

<table>
<thead>
<tr>
<th></th>
<th>( 3s )</th>
<th>( 3p_z )</th>
<th>( ns )</th>
<th>( np_x )</th>
<th>( np_y )</th>
<th>( ns )</th>
<th>( np_x )</th>
<th>( np_y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HFP}_3 )</td>
<td>0.08</td>
<td>0.20</td>
<td>-0.01</td>
<td>0.11</td>
<td>0.42</td>
<td>0.00</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>( \text{FPH}_3 )</td>
<td>0.04</td>
<td>0.57</td>
<td>-0.01</td>
<td>0.13</td>
<td>0.16</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>( \text{HPP}_3 )</td>
<td>0.31</td>
<td>0.37</td>
<td>0.04</td>
<td>-0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>( \text{FPP}_3 )</td>
<td>0.31</td>
<td>0.33</td>
<td>0.00</td>
<td>-0.10</td>
<td>-0.01</td>
<td>0.00</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>( \text{HPCl}_3 )</td>
<td>0.33</td>
<td>0.52</td>
<td>0.01</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.00</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>( \text{FPCl}_3 )</td>
<td>0.10</td>
<td>0.14</td>
<td>0.01</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.00</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>( \text{IPCl}_3 )</td>
<td>0.06</td>
<td>0.12</td>
<td>0.00</td>
<td>0.04</td>
<td>-0.01</td>
<td>0.00</td>
<td>0.55</td>
<td></td>
</tr>
</tbody>
</table>

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

Figure 1. Schematic representation of the SOMOs of \( C_3 \) phosphoranyl radicals. (A) HPH, (B) FPH, (C) FPH, (D) HPF.

SOMOs indicate that all studied radicals have a TBP-\( a \) structure and not a \( \sigma^* \)-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 (\( \rho(R_{\text{osc}}) \)) and the isotropic hyperfine coupling constants (\( \sigma_{\text{Nuc}}(\text{ns}) \)) together with the valence orbital spin densities. These values are given in Tables II and III. The listed values for the three \( X^2PX^2 \) 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 \( C_3 \) \( \text{P(OCH}_2\text{CH}_2\text{)}_2\text{N}^+\text{BF}_4^- \) radical and therefore confirms its assignment as TBP-\( a \) (vide supra).

In comparison with the other calculated \( C_3 \) radicals the electronic structure of \( \text{FPH}_3 \) shows some remarkable differences. Relative to \( \text{HPH}_3 \) 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 and of the apical ligand is increased. It has been frequently suggested by various authors that a radical like \( \text{FPH}_3 \), with one strongly electronegative ligand, preferentially occupies a tetrahedral geometry with the unpaired electron in an antibonding \( \sigma^* \) orbital. However, our calculations show that for \( \text{FPH}_3 \) the optimized value of \( \phi \) (85.9°) does not confirm a tetrahedral geometry and that the electronic structure of \( \text{FPH}_3 \) 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 \( \text{HPH}_3 \) 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 \( X^* = X^* \) (\( \text{HPH}_3 \), \( \text{FPH}_3 \), and \( \text{CIPCl}_3 \)) 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. The same bond-length rule applies for TBP-\( e \) \( C_3 \) phosphoranyl radicals as was shown by Howell et al. 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 \( \text{PH}_3 \) molecule and the \( C_3 \) and \( C_3 \) \( \text{PH}_3 \) 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).

(21) Abbreviations used are HOMO for highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital.
Figure 3. Geometries (ref 7, Table 1) and calculated antibonding molecular orbitals of PH₅, C₂₅H₂₄, and C₂₅H₄.

Figure 4. Optimized geometry of PF₅⁻ (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 compound 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 3dz² orbital, when this is provided with a negative coefficient. Therefore the 3dz² orbital will contribute to some extent to the HOMO and thus to the bonding in PH₅.


Table IV. Experimental* and Calculated Isotropic Hyperfine Coupling Constants of PF₅⁻. Values in gauss.

<table>
<thead>
<tr>
<th>expt</th>
<th>calcd</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{P}^{iso} )</td>
<td>1356</td>
</tr>
<tr>
<td>( a_{N}^{iso} )</td>
<td>3</td>
</tr>
<tr>
<td>( a_{F}^{iso} )</td>
<td>197</td>
</tr>
</tbody>
</table>

*See ref 9. Values in gauss.

Figure 5. Calculated isotropic hyperfine coupling constants \( a_{Nucl}^{iso} \) of HPH₁ as a function of the apical-equatorial bond angle \( \phi \); values for \( a_{Nucl}^{iso} \) are in gauss.

Figure 6. Energy of HPH₁ as a function of the apical-equatorial bond angle \( \phi \) relative to the optimized radical, values in kJ mol⁻¹.
...tibonding orbital and is located between phosphorus and the apical ligand. This structure has been assigned to the Ph₃PCI 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 φ between the apical and the three equatorial bonds was varied from 80° to 130°. During the variation of φ 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 φ in Figure 5. Figure 6 represents the corresponding UHF energy during this variation of φ relative to the energy of the optimized radical (~-342.472 475 au). The phosphorus isotropic hyperfine coupling constant reaches a maximum value at φ = 117°. At this point the phosphorus 3p 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 σ*-C₃v. Figure 6 indicates that the σ*-C₃v arrangement lies some 150 kJ mol⁻¹ above the optimized C₃v structure. Attempts to optimize the σ* 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 σ*-C₃v radical is the distribution of the unpaired electron over the hydrogen atoms. The σ*-C₃v arrangement is characterized by a high spin density in the C₁ axis of the radical. This results in large isotropic couplings on phosphorus and the apical hydrogen atom. Going from TBP-a toward σ*-C₃v a continuous transfer of spin density from the apical ligand to the apical nucleus has been calculated. This transfer starts at approximately φ = 108°, before the actual inversion takes place. Therefore a nonzero spin density on an apical ligand in a C₃v phosphoranyl radical gives no definite proof of a σ*-arrangement. Nevertheless the calculated spin density distribution for the HPH₃ σ* structure is comparable with the experimental values of the Ph₃PCI radical and supports the σ* assignment for Ph₃PCI. For PF₅⁻ we have performed a similar structure variation of the bond angle φ. Variation of φ revealed a transition from O₈ to σ*-C₃v at φ = 108°. The calculated parameters (φ_{HF}, spin density in the valence p orbitals and UHF energy) are depicted in Figures 7-9. The energy difference between the optimized PF₅⁻ radical and its σ*-C₃v arrangement is approximately 215 kJ mol⁻¹. Analogous to the C₃v radicals, there is a difference in the electronic structure of the optimized PF₅⁻ radical and its σ*-arrangement. For the optimized octahedral structure the equatorial ligands possess a large spin density whereas the σ*-C₃v radical is characterized by a high spin density on the apical ligand. Both the O₈ and σ* structure exhibit a large phosphorus isotropic hyperfine coupling. This relative high spin density in the C₁ axis of the PF₅⁻ radical is comparable with the experimental values of the related C₃v CIP(O₂C₆H₄)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(O₂C₆H₄)₂⁻ radical possesses a σ*-C₃v structure. This possibility was already recently suggested by Symons. Figure 10 gives a schematical representation of the SOMO for the σ* structures of HPH₃ and PF₅⁻.

IV. Stability of XPH₃ radicals

As we showed in section III(1) the optimized C₃v 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 phosphorus Fermi contact integral is, due to the absence of a constant while the apical bond length $r_{ap} = 4.29\ A$. With the lowest energy barrier three cross sections through the structure the equatorial bond lengths $r_{eq} = 1.43\ A$, and the apical-quatorial $r_{aq} = 1.82\ A$ (Figure 13). This demonstrates that the dissociation of $\text{HPH}_3$ 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 stable $\pi^*-\sigma$-arrangement. 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 $\text{PH}_3$ fragments are identical with each other and with the optimized $\text{PH}_3$ molecule. The $P-H^+$ distances differ: $4.18\ A$ for the LUMO and $3.86\ A$ for the HOMO. The energy of these loose complexes lies slightly below that of the isolated $\text{PH}_3 + \text{H}^+$. This difference has no physical significance and is probably due to a small calculated interaction between the outer 4-31G orbitals of $\text{PH}_3$ and $\text{H}^+$. 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 $\text{PH}_3 + \text{H}^+$ and 43.2 kJ mol$^{-1}$ above the optimized $\text{C}_3v$ $\text{PH}_3$ radical. This demonstrates that the dissociation of $\text{HPH}_3$ is not a wholly downhill process as previously suggested by Howell et al.\textsuperscript{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 LUMO-TS. For the $C_{3v}$ $\text{PH}_3$ radical, the LUMO-TS, and both loose complexes we have calculated correlation energies by Muller-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 $\text{PH}_3 + \text{H}$ 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 $\sigma^* - C_{3v}$, the radical dissociates directly without any energy barrier (Figure 13). Therefore the ligand exchange processes of nonrigid TBP-e phosphoranyl radicals via

### Table V. Energies$^a$ of the Minima and Transition States on the Cross Sections of the Potential Surface

<table>
<thead>
<tr>
<th>$r_e$ (Å)</th>
<th>$C_{3v}$</th>
<th>LUMO-TS$^b$</th>
<th>HOMO-TS$^b$</th>
<th>LUMO$^c$</th>
<th>HOMO$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>0.051494 (135.2)</td>
<td>0.079576 (208.9)</td>
<td>0.095208 (250.0)</td>
<td>0.022120 (58.1)</td>
<td>0.022094 (58.0)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.055675 (146.2)</td>
<td>0.069342 (182.1)</td>
<td>0.004045 (10.6)</td>
<td>0.004016 (10.5)</td>
<td>0.00416 (10.5)</td>
</tr>
<tr>
<td>1.4</td>
<td>0.055675 (146.2)</td>
<td>0.069342 (182.1)</td>
<td>0.004045 (10.6)</td>
<td>0.004016 (10.5)</td>
<td>0.00416 (10.5)</td>
</tr>
</tbody>
</table>

$^a$Energies are relative to $\text{PH}_3 + \text{H}^+$ ($-342.532923\ au$). Values between brackets refer to differences in kJ mol$^{-1}$. $^b$TS = transition state. $^c$LC = loose complex.

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![Figure 11. $C_{3v}$ optimized geometry for PH$_3$ ($E$(UHF) = $-342.025690\ au$).](image1)

![Figure 12. Two possible routes for H-attack toward PH$_3$. Route A, LUMO approach; route B, HOMO approach.](image2)
a $\sigma^*$ intermediate seem 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 $r_a$, $r_e$, and $\phi$ (see text). Cross sections are drawn for three values of $r_c$: (A) $r_c = 1.4$ Å, (B) $r_c = 1.5$ Å, (C) $r_c = 1.6$ Å. The dotted lines indicate the edge between TBP-$\sigma$ and $\sigma^*$ structures.
saddle-point optimization method the FLPH, transition state for 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 is rather unstable. In section III(3436)
electronic structure of these radicals is in good agreement with phoranyl radicals possess a TBP-a structure. The calculated geometry of this transition state is only 

| Correlation Energies* of HPH₃ for the Optimized Structures and the Transition State |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                 | E(UHF)          | E(UMP2)         | E(UMP3)         | E(CID)          |
| C₃₃ radical                     | -342.472 475 (135.1) | -342.555 382 (114.8) | -342.572 836 (105.9) | -342.582 713 (96.8) |
| LUMO-TS                         | -342.456 009 (178.3) | -342.537 795 (160.9) | -342.554 448 (154.2) | -342.562 243 (147.9) |
| LUMO-LC                         | -342.523 978 (-0.2)  | -342.599 037 (0.0)  | -342.613 133 (0.0)  | -342.619 516 (0.0)  |
| HOMO-LC                         | -342.524 016 (-0.2)  | -342.599 090 (-0.1)  | -342.613 186 (-0.1)  | -342.619 570 (-0.2)  |
| PH₃ + H⁻                      | -342.523 923 (0.0)  | -342.599 056 (-0.1)  | -342.613 152 (0.0)  | -342.619 497 (0.0)  |

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

The calculations showed that all studied C₃₃, X⁺PX⁺₅ phosphoranyl radicals possess a TBP-a structure. The calculated electronic structure of these radicals is in good agreement with the experiments on the P(OCH₂CH₂)₃⁺ radical. Geometry variations for HPH₃ reveal a σ*-arrangement, which, however, is unstable and dissociates directly into PH₃ and H⁻. The calculated electronic structure of this σ*-arrangement is comparable with the experimental values for the PH₃PCI radical reported by Berczaj et al. The structure of C₃₃⁺PF₅⁺ 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 the apical-equatorial bond angle for PF₅⁻ leads to a σ*-arrangement. Comparison of the electronic structures of this σ*-PF₅⁻ radical anion and the experimental values obtained for the CIP(O₂C₆H₄)₂⁻ radical anion indicates that the latter possibly possess a σ*-C₆E₆ arrangement. Despite many geometry variations and a number of different radicals it was not possible to optimize the geometry of a σ*-C₃₀ or σ*-C₆₀ radical. This suggests that σ*-structures are not stable. Nevertheless the calculated electronic structures for the σ*-arrangements of HPH₃ and PF₅⁻ 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 PF₅⁻ model systems. Therefore it may be of interest to mention the recent work of Clark[33] on the structure of H₃PX⁺ radical cations (X = Ph₃, H₂S, HCl), which revealed a σ*-structure for H₃PPH₃⁺. The H₃PSH⁺ and H₃PClH⁺ radical cations possess structures that deviate more or less from the ideal σ*-structure toward TBP-a. 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⁺.


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 PH₃ + H⁻ = HPH₃ system. Calculated isotropic hyperfine coupling constants are a_H = 199, a_H^iso = 260, and a_H = 124 G.

Figure 16. LUMO-TS of the PH₃ + F⁻ = FPH₃ system. Calculated isotropic hyperfine coupling constants of this structure are a_H = 144, a_H^iso = 341, and a_H = 48 G.
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 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_{a1}(π) and a_{a1}(π) as the two highest occupied and b_{a1}(π) and b_{a1}(π) 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. The degeneracy of the half-filled highest occupied ε_{π} orbital of 1b (D_{2h}) is removed by forming two transannular S-S bonds in 1a (D_{2d}). 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, 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 1.564 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.

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

<table>
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<tr>
<th>basis</th>
<th>geometry</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
</tr>
</thead>
<tbody>
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<td>STO-3G</td>
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<tr>
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<td>-1088.09105</td>
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<tr>
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<td>-1088.02269</td>
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<tr>
<td>STO-3G+d</td>
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<td>-1077.53750</td>
<td>43.5</td>
</tr>
<tr>
<td>MNDO MNDO</td>
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<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 University of Heidelberg.
2 University of Cologne.
3 University of Heidelberg.