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
\( \Gamma_{\text{PB}} \).

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.\(^5\) 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 \(-0.2 \text{ V vs. SCE} \). 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), \( \text{Fe}^{3+} [\text{Ru}^3\text{I}(\text{CN})_6]\), and iron–osmium cyanide,
\( \text{Fe}^{3+} [\text{Os}^3\text{I}(\text{CN})_6]\), can be prepared by an electrochemical
method.\(^6\) 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.

Structure of \( \text{C}_3\text{~F} \) Phosphoranyl and \( \text{C}_4\text{~P} \) Phosphorane Anion
Radicals. A Qua Chemical Study

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

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

Abstract: Ab initio molecular orbital calculations on various \( \text{C}_3\text{~F} \) phosphoranyl radicals and the \( \text{C}_4\text{~P} \) PF\(_5\)-phosphorane anion radical are presented. By the unrestricted Hartree–Fock method with a 4-31G basis set the geometries for \( \text{C}_3\text{X}_2\text{PX}_3 \) (\( \text{X} = \text{apical ligand}, \text{X}^* = \text{equatorial ligand}\) radicals were optimized for \( \text{X} = \text{H}, \text{F}, \text{and Cl}\). All \( \text{C}_3\text{~F} \) radicals reveal a trigonal-bipyramidal 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 \( \sigma^*\)-arrangements. A detailed study of the \( \text{C}_3\text{~F} \), \( \text{PH}_3\)+, \( \text{PF}_5\)- potential energy surface is described. It appears that a \( \sigma^*\)-arrangement is not stable but leads to dissociation. The stability of \( \text{X}^*\text{PH}_3\) with respect to dissociation into \( \text{PH}_3\) and \( \text{X}^*\) is described, and transition states are calculated. HPH\(_3\) lies 43.2 kJ mol\(^{-1}\) below its transition state, FPH\(_3\) (9.8 kJ mol\(^{-1}\)), whereas CIPH\(_3\) 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.\(^1\) Most frequently a \( \text{C}_3\text{~F} \) geometry
is encountered. The electronic structure of these \( \text{C}_3\text{~F} \) 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.\(^2\)\(^5\)\(^-\)\(^7\) In contrast to the structure of \( \text{C}_4\text{~P} \),
phosphoranyl radicals, conflicting ideas exist on the electronic
structure of phosphoranyl radicals with a \( \text{C}_3\text{~F} \) geometry and phosphorane anion radicals with a \( \text{C}_4\text{~P} \) geometry. The unpaired
electron in the \( \text{PH}_3\)PCI radical, which possesses a \( \text{C}_3\text{~F} \) geometry,
is believed to reside in a \( \sigma^* \) P-Cl orbital,\(^8\) accounting for the high
spin density found on chlorine and the fact that the \( ^3\text{P} \) tensor
is parallel to the \( ^3\text{Cl} \) tensor. By contrast the extensive studies
on the \( \text{C}_3\text{~F} \) radical -\( \text{P}(\text{OCH}_2\text{CH}_2)_3\)N\(^+\)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

\(^2\) Hasegawa, A.; Ohnishi, K.; Sogabe, K.; Miura, M. Mol. Phys. 1975,
30, 1367.
\(^3\) Bercrzt, T.; Geoffroy, M.; Lucken, E. A. C. Chem. Phys. Lett. 1975,
36, 677.
\(^5\) Colussi, A. J.; Morton, J. R.; Preston, K. F. J. Phys. Chem. 1975,
79, 1855.
\(^6\) Hamerlinck, J. H. H.; Hermnks, P. H. H.; Schipper, P.; Buck, H. M.
1980, 102, 5679.
indicates a small spin density on the apical nitrogen atom. Similar differences in the structure of C₅₆ phosphorane anion radicals (PX₅⁺) have been reported. The isotropic hyperfine pattern of the PFX₃⁻ radical shows four equivalent equatorial fluorines with a large coupling and one with a small coupling arising from the unique apical fluoride. The same structure has been proposed for PCls⁻ and the isoelectronic SFS⁻.₁₁ For the C₅₆ radicals HPH₃, FPH₃, and CIPH₃, the unique apical fluoride, 31P, 35Cl, and 37Cl tensors are coincident and indicate the apical-equatorial bond angle (φ) is the first-order spin density matrix and φₚ and φₜ 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 GAUSSIAN03 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 C₅₆ Radicals. The geometries of the radicals X₀PX₅⁺ have been optimized for all combinations of X⁰ and X⁺ with X = H, F, or Cl within a C₅₆ 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 FPH₃ 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 CIPH₃ no stable geometry could be calculated (vide infra). Characteristic for all these C₅₆ 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 C₅₆ X₀PX₅⁺ Radicals

<table>
<thead>
<tr>
<th>X₀PX₅⁺</th>
<th>P-X⁰</th>
<th>P-X⁺</th>
<th>φ</th>
<th>E(UHF)</th>
<th>&lt;S²&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH₃</td>
<td>1.43</td>
<td>1.59</td>
<td>89.5</td>
<td>-342.472475</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>CIPH₃</td>
<td>1.39</td>
<td>1.70</td>
<td>92.7</td>
<td>-638.782736</td>
<td>0.7787</td>
</tr>
<tr>
<td>FF₃</td>
<td>1.61</td>
<td>1.67</td>
<td>91.6</td>
<td>-737.549048</td>
<td>0.7798</td>
</tr>
<tr>
<td>CIPF₃</td>
<td>2.21</td>
<td>2.16</td>
<td>92.0</td>
<td>-1097.199849</td>
<td>0.7981</td>
</tr>
<tr>
<td>HPCI₃</td>
<td>1.42</td>
<td>1.35</td>
<td>93.9</td>
<td>-1717.851382</td>
<td>0.9380</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>1.0097</td>
</tr>
</tbody>
</table>

*S Bond lengths in angstroms, bond angles in degrees, and UHF energies in atomic units.
Table III. Valence Orbital Spin Densities of the C$_3$e X$^\alpha$PX$^\alpha$ Radicals$^a$

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>X$^a$</th>
<th>X$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3s</td>
<td>3p$_z$</td>
<td>ns</td>
</tr>
<tr>
<td>HPH$_3$</td>
<td>0.08</td>
<td>0.20</td>
<td>-0.01</td>
</tr>
<tr>
<td>FPH$_3$</td>
<td>0.04</td>
<td>0.57</td>
<td>-0.01</td>
</tr>
<tr>
<td>HPF$_3$</td>
<td>0.31</td>
<td>0.37</td>
<td>0.04</td>
</tr>
<tr>
<td>FPF$_3$</td>
<td>0.31</td>
<td>0.33</td>
<td>0.00</td>
</tr>
<tr>
<td>HPCl$_3$</td>
<td>0.10</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>FPCl$_3$</td>
<td>0.06</td>
<td>0.12</td>
<td>0.01</td>
</tr>
<tr>
<td>CIPC1$_3$</td>
<td>0.09</td>
<td>0.03</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$^a$The listed values are summations over the inner and outer orbitals of the split valence 4-31G basis set.
$^b$np$_z$ is the equatorial contribution, calculated as np$_x$ + np$_y$.


---

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

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

In comparison with the other calculated C$_3$e radicals the electronic structure of FPH$_3$ shows some remarkable differences. Relative to HPH$_3$ there is a serious decrease of the contribution to the SOMO of the phosphorus $3s$ orbital and the $1s$ orbital of the equatorial hydrogen atoms. Simultaneously the contribution of the phosphorus $3p_z$ 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 $\alpha^*$ orbital. However, our calculations show that for FPH$_3$ the optimized value of $\Phi$ (85.9°) does not confirm a tetrahedral geometry and that the electronic structure of FPH$_3$ is clearly TBP-a (Figure 1). In order to get an indication of the distance between phosphorus and the point of the maximum probability of finding the unpaired electron along the C$_3$ axis, we have calculated for HPH$_3$ the radial spin density distribution $r^2\rho(r)$, where $r$ is the radius centered on phosphorus and $\rho(r)$ is defined by eq 1 (section II). Figure 2 reveals that this distance is 0.93 Å. As can be seen from Table I the optimized apical bond length for those radicals where X$^\alpha$ = X$^\alpha$ (HPH$_3$, FPF$_3$, and CIPC$_3$) 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$_2$e) phosphoranyl radicals as was shown by Howell et al.$^7$ The question arises of why the TBP-a radicals form an exception and possess a short apical bond. To answer this question one must be aware of the fact that both phosphoranyl radicals and pentacoordinated phosphorus compounds are hydervalent species with more than eight electrons around phosphorus. To accommodate the extra electron(s) the HOMO$^1$ will possess some antibonding character. For phosphoranyl radicals this HOMO is identical with the SOMO. The HOMOs for the PH$_3$ molecule and the C$_2$e and C$_3$e 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).

$^{(20)}$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.
Figure 3. Geometries (ref 7, Table I) and calculated antibonding molecular orbitals of PH₅, Cₓ, PH₄, and Cₓ, PH₄.

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

It is obvious that the increased bond length is a direct result of the antibonding character. The participation of d orbitals in pentavalent phosphorus compounds is still a subject of controversy. A number of ab initio studies on pentacoordinated phosphorus compounds and phosphoranyl radicals revealed that the principal concepts of the bonding are adequately described without the introduction of d functions. However, for numerically highly accurate results in the determination of bond lengths and bond energies they are found to be essential merely because their inclusion will increase the completeness of the basis set that is used. From Figure 3 it is clear that the symmetry of the HOMO of PH₅ fits exactly to the phosphorus 3d,2 orbital, when this is -3dz².

Table IV. Experimental and Calculated Isotropic Hyperfine Coupling Constants of PF₅⁻

<table>
<thead>
<tr>
<th></th>
<th>exp¹</th>
<th>calc²</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_P)</td>
<td>1356</td>
<td>1323</td>
</tr>
<tr>
<td>( a_H)</td>
<td>3</td>
<td>-17</td>
</tr>
<tr>
<td>( a_F)</td>
<td>197</td>
<td>174</td>
</tr>
</tbody>
</table>

¹See ref 9. ²Values in gauss.

Figure 5. Calculated isotropic hyperfine coupling constants (\( a_Nuc\)) of HPH₁ as a function of the apical-equatorial bond angle \( \phi \); values for \( a_Nuc\) 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.

tribond orbital and is located between phosphorus and the apical ligand. This structure has been assigned to the Ph$_3$PCl 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 HPH$_3$ radical the angle $\phi$ between the apical and the three equatorial bonds was varied from 80° to 130°. During the variation of $\phi$ all bond lengths were fixed at the optimized values. The calculated isotropic hyperfine coupling constants arising from the Fermi contact integrals at the phosphorus and hydrogen nuclei are given as a function of $\phi$ in Figure 5. Figure 6 represents the corresponding UHF energy during this variation of $\phi$ relative to the energy of the optimized radical (-342.472475 au). The phosphorus isotropic hyperfine coupling constant reaches a maximum value at $\phi = 117°$. At this point the phosphorus 3p$_z$ 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 $\phi = 108°$, 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 has been found. From this point of view it may be suggested that the C$_{3v}$ 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 7. Calculated isotropic hyperfine coupling constants ($\Delta_{ISO}^N$) of PF$_5^-$ as a function of the apical-equatorial bond angle $\phi$. Values are obtained from a Mulliken population analysis.

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 PF$_5^-$ 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 HPH$_3$ and PF$_5^-$.

Structure the equatorial ligands possess a large spin density whereas the $\sigma^*-C_{3v}$ 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 PF$_5^-$ radical anion possessing a $\sigma^*$-arrangement is comparable with the experimental values of the related C$_{3v}$ CIP(O$_2$C$_6$H$_4$)$_2$ 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 schematical representation of the SOMO for the $\sigma^*$ structures of HPH$_3$ and PF$_5^-$. For the optimized octahedral structure the equatorial ligands possess a large spin density whereas the $\sigma^*-C_{3v}$ 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 PF$_5^-$ radical anion possessing a $\sigma^*$-arrangement is comparable with the experimental values of the related C$_{3v}$ CIP(O$_2$C$_6$H$_4$)$_2$ 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

IV. Stability of $X^+PH_3$ 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
A considerable amount of spin density is found on the four phosphorus Fermi contact integral, due to the absence of approach bond angle $4.29^\circ$; with the lowest energy barrier three cross sections through the number of minima and transition states. For the each cross section the equatorial bond lengths $1.43$ Å (135 kJ mol$^{-1}$) in favor of the dissociation. The HOMO of each P-H bond and the radical and the sum of isolated PH$_3$ and H$^-$ is 0.051 449

C$_3v$, HPH$_3$ radical. In principle it could be possible that there are more stable geometries for a C$_3v$, HPH$_3$ radical. Furthermore it is important to know the stability of the C$_3v$, 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$_3v$ 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 $58.3^\circ$ (Figure 11).

The calculated energy difference between the optimized C$_3v$, 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 C$_3$ P$_3$ axis leads to a C$_3v$, 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$_3v$, 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 $55^\circ$ to $125^\circ$, 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 $r_e = 1.6$ Å surface three minima were calculated, one for a stable TBP-a radical ($r_a = 1.43$; $\phi = 89.5^\circ$) and two "loose complexes", for both HOMO approach ($r_e = 3.90$; $\phi = 123.4^\circ$) and LUMO approach ($r_e = 4.29$; $\phi = 56.6^\circ$). On this surface there are two transition states (TS). The HOMO-TS possesses a perfect tetrahedral geometry ($r_e = 1.60$; $\phi = 109.4^\circ$) 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$^{-3}$; $\alpha_{2p} = 1698$ G), and a considerable amount of spin density is found on the four equivalent hydrogen nuclei (0.099 electrons Bohr$^{-3}$; $\alpha_{2p} = 158$ G). The LUMO-TS ($r_e = 1.82$; $\phi = 73.9^\circ$) lies $41.1$ kJ mol$^{-1}$ below the HOMO-TS. The electronic structure of this LUMO-TS is characterized by a low phosphorus Fermi contact integral (0.368 electrons Bohr$^{-3}$; $\alpha_{2p} = 238$ G) and a high value on the approaching hydrogen nucleus (0.216 electrons Bohr$^{-3}$; $\alpha_{2p} = 345$ G). SOMOs of both transition states are depicted in Figure 14.

For the $r_e = 1.5$ Å surface again three minima were calculated. The TBP-a radical ($r_e = 1.44$ Å; $\phi = 89.0^\circ$), the HOMO-loose complex ($r_e = 3.89$ Å; $\phi = 122.5^\circ$), and the LUMO-loose complex ($r_e = 4.23$ Å; $\phi = 57.5^\circ$). On this surface only one transition state, namely for the LUMO approach, is found ($r_e = 1.76$ Å; $\phi = 78.6^\circ$). Its structure is comparable with the LUMO-TS on the $r_e = 1.6$ Å surface. Finally the $r_e = 1.4$ Å surface possesses only two specific points; a HOMO-loose complex ($r_e = 3.86$ Å; $\phi = 121.2^\circ$) and a LUMO-loose complex ($r_e = 4.17$ Å; $\phi = 58.8^\circ$). Table V summarizes the energies of the various minima and transition state relative to the energy of isolated PH$_3$ and H$^-$ (-342.523 923 au). From these potential surfaces it is clear that the TBP-a structure represents the only stable HPH$_3$ radical. None of the surface indicates a minimum that could belong to a stable $\sigma^*-$C$_3v$ 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 PH$_3$ fragments are identical with each other and with the optimized PH$_3$ 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 PH$_3$ + H$^-$. This difference has no physical significance and is probably due to a small calculated interaction between the outer 4-31G orbitals of PH$_3$ and H$^-$. Using the saddle-point optimization method, we have optimized the LUMO-TS with respect to all geometric parameters within C$_3v$ symmetry (Figure 15). This LUMO-TS lies $178.3$ kJ mol$^{-1}$ above the isolated PH$_3$ + H$^-$ and $43.2$ kJ mol$^{-1}$ above the optimized C$_3v$, 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 LUMO-TS. For the C$_3v$, HPH$_3$ 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 PH$_3$ + H$^-$ is lowered from 178.3 to 147.9 kJ mol$^{-1}$ after configuration interaction, while the stability of the C$_3v$ radical relative to the LUMO-TS rises from 43.2 to 51.1 kJ mol$^{-1}$ (Table VI). The most important result that can be derived from the potential surfaces is that for all geometries where the electronic structure is $\pi^*-$C$_3v$, the radical dissociates directly without any energy barrier (Figure 13). Therefore the ligand exchange processes of nonrigid TBP-e phosphoranyl radicals via

![Figure 11. C$_3v$ optimized geometry for PH$_3$ (E(UHF) = -342.025 690 au).](image)

![Figure 12. Two possible routes for H$^-$ attack toward PH$_3$. Route A, LUMO approach; route B, HOMO approach.](image)

<table>
<thead>
<tr>
<th>$r_e$ (Å)</th>
<th>$C_{tx}$</th>
<th>LUMO-</th>
<th>HOMO-</th>
<th>HOMO-LC$^c$</th>
<th>LUMO-LC$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>0.051 494 (135.2)</td>
<td>0.055 675 (146.2)</td>
<td>0.079 576 (208.9)</td>
<td>0.069 342 (182.1)</td>
<td>0.092 120 (58.1)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.095 208 (250.0)</td>
<td>0.069 342 (182.1)</td>
<td>0.095 208 (250.0)</td>
<td>0.069 342 (182.1)</td>
<td>0.022 094 (58.0)</td>
</tr>
<tr>
<td>1.4</td>
<td>0.022 094 (58.0)</td>
<td>0.004 016 (10.5)</td>
<td>0.004 016 (10.5)</td>
<td>0.004 016 (10.5)</td>
<td>0.001 062 (2.8)</td>
</tr>
</tbody>
</table>

$^a$Energies are relative to PH$_3$ + H$^-$ (-342.523 923 au). Values between brackets refer to differences in kJ mol$^{-1}$. $^b$TS = transition state. $^c$LC = loose complex.


Janssen, Visser, and Buck
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 $r_a$: (A) $r_a = 1.4$ Å, (B) $r_a = 1.5$ Å, (C) $r_a = 1.6$ Å. The dotted lines indicate the edge between TBP-a and $\sigma^*$ structures.

a $\sigma^*$ intermediate seem 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 FPCI$_3$. 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 a a*-arrangement, which, however,
the radical is rather unstable. In section III(

electronic structure of these radicals is in good agreement with
phoranyl radicals possess a TBP-a structure. The calculated
the experiments on the .P(OCH2CH2),N+BF4- radical. Geometry
LUMO-loose complex (PH,

The energy difference between FPH,

values of the Optimized Structures and the Transition State of FPH, and ClPH,

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

\[
\begin{array}{ccc}
\text{FPH}\(_3\) & \text{ClPH}\(_3\) & \\
\text{E(UHF)} & \langle S^2 \rangle & \text{E(UHF)} & \langle S^2 \rangle \\
\text{TBP-a} & -342.245 124 (120.9) & 0.7579 & -800.997 249 (-0.2) & 0.7502 \\
\text{LUMO-TS} & -342.241 399 (130.7) & 0.7819 & -801.000 448 (-8.6) & 0.7510 \\
\text{LUMO-LC} & -342.291 240 (-0.2) & 0.7508 & -800.997 165 0 + 0.7500 \\
\text{HOMO-LC} & -342.292 633 (-3.8) & 0.7509 & & \\
\text{PH}_3 + X^+ & -441.291 171 & 0 + 0.7500 & & \\
\end{array}
\]

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

![Figure 14. SOMOs for the transition states for LUMO and HOMO approach on the \(r_s = 1.6\ \text{Å}\) surface.](image)

![Figure 15. LUMO-TS of the PH\(_3\) + H\(^-\) = HPH\(_3\) system. Calculated isotropic hyperfine coupling constants of this structure are \(a_{\text{iso}} = 144\), \(a_{\text{iso}} = 341\), and \(a_{\text{iso}} = 48\ \text{G}\).](image)

![Figure 16. LUMO-TS of the PH\(_3\) + F\(^-\) = FPH\(_3\) system. Calculated isotropic hyperfine coupling constants of this structure are \(a_{\text{iso}} = 144\), \(a_{\text{iso}} = 341\), and \(a_{\text{iso}} = 48\ \text{G}\).](image)

The energy of this transition state is 130.7 \(\text{kJ mol}^{-1}\) higher than the isolated PH\(_3\) and F\(^-\). The energy difference between FPH\(_3\) radical and transition state is only 9.8 \(\text{kJ mol}^{-1}\) indicating that the radical is rather unstable. In section III(1) of this paper we mentioned that for ClPH\(_3\) no stable geometry could be calculated. On attempted optimization all trial geometries revealed a HOMO-loose complex (PH\(_3\) + Cl\(_2\); distance 3.21 Å) or a LUMO-loose complex (PH\(_3\) + Cl\(_2\); distance 4.18 Å). The energies of these loose complexes are essentially the same as for the isolated PH\(_3\) and Cl\(_2\) (Table VII).

V. Conclusions

The calculations showed that all studied C\(_3\)\(_\text{p}\) X\(^\text{a}\)PX\(_{3}\) phosphoranyl radicals possess a TBP-a structure. The calculated electronic structure of these radicals is in good agreement with the experiments on the \(\text{P(OCH}_2\text{CH}_2)\text{N}^+\text{BF}_4^-\) radical. Geometry variations for HPH\(_3\) reveal a \(\sigma^*\)-arrangement, which, however, is unstable and dissociates directly into PH\(_3\) and H\(^-\). The cal-

\(\text{Values between brackets refer to differences relative to PH}_3 \text{ + X}^+ \text{ in kJ mol}^{-1}\).
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 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 bπ(π) and aπ(π) as the two highest occupied and bπ(π) and bπ(π) as the lowest unoccupied MOs of 2.

The structure of S₄N₄ (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 εₚ orbital of 1b (D₂h) is removed by forming two transannular S-S bonds in 1a (D₂h). 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.

The ring system prefers a planar monocyclic structure. *-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 bπ(π) and aπ(π) as the two highest occupied and bπ(π) and bπ(π) as the lowest unoccupied MOs of 2.

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

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<th>basis</th>
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<th>2b</th>
<th>2c</th>
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<tr>
<td></td>
<td>0</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.

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

2.428 Å, a value close to the transannular S-S distance found in S₄N₄ (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 films technique.

1 Universität Heidelberg.
2 Universität Köln.

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