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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I. Introduction

A number of single-crystal ESR studies have shown that phosphoranyl radicals (PX₃) can adopt different configurations depending on the ligands attached to phosphorus and steric constraints of ring structures.¹⁻⁴ Most frequently a C₃ᵥ geometry is encountered. The electronic structure of these C₃ᵥ phosphoranyl radicals is well established and may be described as a trigonal bipyramid (TBP) with the unpaired electron acting as a fifth ligand. The optimized PF₅⁻ radical is octahedral with the unpaired electron in an equatorial position.²⁻⁵⁻⁶ In contrast to the structure of C₃ᵥ phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C₄ᵥ geometry and phosphorane anion radicals with a C₄ᵥ geometry. The unpaired electron in the Ph₃PCI radical, which possesses a C₄ᵥ geometry, is believed to reside in a σ° P–Cl orbital,² accounting for the high spin density found on chlorine and the fact that the 3¹P tensor is parallel to the 3¹Cl tensor. By contrast the extensive studies on the C₃ᵥ radical, P(OCH₂CH₂)₃⁺BF₄⁻ show unambiguously that the unpaired electron resides in the apical position of a TBP (TBP-a).¹⁻⁸ The near isotropic ¹⁴N hyperfine coupling of 22 G

Structure of C₃ᵥ Phosphoranyl and C₄ᵥ Phosphorane Anion Radicals. A Quasi-Chemical Study

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Abstract: Ab initio molecular orbital calculations on various C₃ᵥ phosphoranyl radicals and the C₄ᵥ PF₅⁻ phosphorane anion radical are presented. By the unrestricted Hartree–Fock method with a 4-31G basis set the geometries for C₃ᵥ X₅PX₅⁻ (X₅ = apical ligand, X⁴ = equatorial ligand) radicals were optimized for X = H, F, and Cl. All C₃ᵥ radicals reveal a trigonal-bipyramidal structure with the unpaired electron in apical position. The optimized PF₅⁻ radical is octahedral with the unpaired electron acting as a ligand. The calculated isotropic hyperfine coupling constants are in good agreement with the experimental values. Variation of the apical–equatorial bond angle for HPH₃ and PF₅⁻ leads to σ°-arrangements. A detailed study of the C₃ᵥ, PH₃, and H₂P₃ potential energy surface is described. It appears that σ°-arrangements are not stable but leads to dissociation. The stability of X₅PH₃ with respect to dissociation into PH₃ and X₅ is described, and transition states are calculated. H₂PH₃ lies 43.2 kJ mol⁻¹ below its transition state, FPH₃ (9.8 kJ mol⁻¹), whereas CIPH₃ is unstable.

1. Introduction

A number of single-crystal ESR studies have shown that phosphoranyl radicals (PX₃) can adopt different configurations depending on the ligands attached to phosphorus and steric constraints of ring structures.¹⁻⁴ Most frequently a C₃ᵥ geometry is encountered. The electronic structure of these C₃ᵥ phosphoranyl radicals is well established and may be described as a trigonal bipyramid (TBP) with the unpaired electron acting as a fifth ligand in an equatorial position.²⁻⁵⁻⁶ In contrast to the structure of C₃ᵥ phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C₄ᵥ geometry and phosphorane anion radicals with a C₄ᵥ geometry. The unpaired electron in the Ph₃PCI radical, which possesses a C₄ᵥ geometry, is believed to reside in a σ° P–Cl orbital,² accounting for the high spin density found on chlorine and the fact that the 3¹P tensor is parallel to the 3¹Cl tensor. By contrast the extensive studies on the C₃ᵥ radical, P(OCH₂CH₂)₃⁺BF₄⁻ show unambiguously that the unpaired electron resides in the apical position of a TBP (TBP-a).¹⁻⁸ The near isotropic ¹⁴N hyperfine coupling of 22 G

GAUSSIAN80 program systems using the unrestricted Hartree-surface. The stability of D. J.; Schlegel, H. B.; Topiol, set was used. The structures were fully optimized with respect directed along the P-Cl linkage.12 The chlorine hyperfine coupling 11.

detailed study is made of the 139. entries and electronic structures of various ligand. The aim of this ab initio study is to shed some light on 13.

is discussed.

321. apical position, the 31P, 35Cl, and 37Cl tensors are coincident and 22.

The same structure has been proposed for PC1-80 and the isoelectronic SFS.11 For the C1P(02C6H4)- (PX3-) have been reported. The isotropic hyperfine pattern of 3.

indicates a small spin density on the apical nitrogen atom. Similar differences in the structure of phosphorane anion radicals (PX3-) have been reported. The isotropic hyperfine pattern of the PFP radical anion shows four equivalent equatorial fluorines with a large coupling and one with a small coupling arising from 4.

the unique apical fl~orine.~ The same structure has been proposed for C1P(02C6H4)- radical, which adopts a local C6 symmetry with chlorine in the 5.

Table I. Optimized Geometries, UHF Energies, and (S2) Values of the C6 X3PX3 Radicals

<table>
<thead>
<tr>
<th>X3PX3</th>
<th>P-X3</th>
<th>P-X3</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>-342.47245</td>
<td>0.8328</td>
</tr>
<tr>
<td>FP7</td>
<td>1.79</td>
<td>1.43</td>
<td>85.7</td>
<td>-441.245124</td>
<td>0.7579</td>
</tr>
<tr>
<td>CIP7</td>
<td>1.39</td>
<td>1.70</td>
<td>92.7</td>
<td>-638.782736</td>
<td>0.7787</td>
</tr>
<tr>
<td>FFP7</td>
<td>1.61</td>
<td>1.67</td>
<td>91.6</td>
<td>-737.549048</td>
<td>0.7798</td>
</tr>
<tr>
<td>CIPF</td>
<td>2.21</td>
<td>1.67</td>
<td>92.0</td>
<td>-1097.198494</td>
<td>0.7981</td>
</tr>
<tr>
<td>HPCI7</td>
<td>1.42</td>
<td>2.35</td>
<td>93.9</td>
<td>-1717.851382</td>
<td>0.9580</td>
</tr>
<tr>
<td>FPCI7</td>
<td>1.64</td>
<td>2.36</td>
<td>95.7</td>
<td>-1816.599229</td>
<td>1.0054</td>
</tr>
<tr>
<td>CIPC1</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 ρ(βNuc) and Isotropic Hyperfine Coupling Constants aNuc of the C6 X3PX3 Radicals

<table>
<thead>
<tr>
<th>P</th>
<th>X3</th>
<th>X4</th>
<th>X5</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH3</td>
<td>1.252</td>
<td>809</td>
<td>0.007</td>
</tr>
<tr>
<td>FP7</td>
<td>0.280</td>
<td>181</td>
<td>0.195</td>
</tr>
<tr>
<td>CIP7</td>
<td>2.032</td>
<td>1313</td>
<td>-0.013</td>
</tr>
<tr>
<td>FFP7</td>
<td>1.920</td>
<td>1241</td>
<td>-0.019</td>
</tr>
<tr>
<td>CIPF</td>
<td>2.006</td>
<td>1296</td>
<td>0.007</td>
</tr>
<tr>
<td>HPCI7</td>
<td>1.400</td>
<td>905</td>
<td>-0.005</td>
</tr>
<tr>
<td>FPCI7</td>
<td>1.218</td>
<td>787</td>
<td>-0.055</td>
</tr>
<tr>
<td>CIPC1</td>
<td>1.357</td>
<td>903</td>
<td>-0.027</td>
</tr>
</tbody>
</table>

aρ(βNuc) in electrons Bohr-3. bANuc in gauss.

apical position, the 31P, 35Cl, and 37Cl tensors are coincident and directed along the P-Cl linkage.12 The chlorine hyperfine coupling shows in sharp contrast to PFP a large spin density on the apical ligand. The aim of this ab initio study is to shed some light on these confusing differences and to examine the preferred geometries and electronic structures of various C6 an C4 radicals. A detailed study is made of the C6, PH3 + H+ potential energy surface. The stability of C6 radicals HPH3, FPH3, and CIP7 is discussed.

II. Quantum Chemical Methods

The calculations were performed with the GAUSSIAN76 and GAUSSIAN8044 program systems using the unrestricted Hartree–Fock (UHF) procedure. Throughout a split valence 4-31G basis set was used. The structures were fully optimized with respect to all bond lengths and bond angles within the symmetry constraints. Isotropic hyperfine coupling constants (aNuc) were calculated from the Fermi contact integrals (ρ(βNuc)):

\[
\rho(\beta_{Nuc}) = \sum_{\alpha \beta} P_{\alpha \beta} \delta_{\alpha \beta} \rho(\beta_{Nuc}) \phi_{\alpha}(\beta_{Nuc})
\]

(1)

where \( P_{\alpha \beta} \delta_{\alpha \beta} \) is the first-order spin density matrix and \( \phi_{\alpha} \) and \( \phi_{\beta} \) 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 UMPP) and by configuration interaction with all double substitutions (CID). Transition states were calculated with the GAUSSIAN80 saddle-point-search algorithm. At stationary points the second derivative matrix possesses a single negative value.

III. Geometry and Electronic Structure

(1) Optimized Geometries for C6 Radicals. The geometries of the radicals X3PX3 have been optimized for all combinations of X3 and X4 with X = H, F, or Cl within a C6 symmetry constraint.15 The optimized parameters for these radicals are collected in Table I together with the calculated UHF energies and the expectation values of S2. The geometric parameters for HPH3 and FPF3 differ slightly from those previously reported by Howell et al.,15 because in our study we included the apical–equatorial bond angle (φ) in the optimization. For CIPF3 no stable geometry could be calculated (vide infra). Characteristic for all these C6 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

(15) Without this symmetry constraint optimization would probably reveal C3v or C4 geometries (see, e.g., ref 2, 5, 7, and 10).


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Table III. Valence Orbital Spin Densities of the $C_{3v}$ $X^2pX^2$ Radicals$^a$

<table>
<thead>
<tr>
<th></th>
<th>$3s$</th>
<th>$3p_z$</th>
<th>$ns$</th>
<th>$np_x$</th>
<th>$np_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H\text{PH}_3$</td>
<td>0.08</td>
<td>0.20</td>
<td>-0.01</td>
<td>0.11</td>
<td>0.42</td>
</tr>
<tr>
<td>$F\text{PH}_3$</td>
<td>0.04</td>
<td>0.57</td>
<td>-0.01</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>$H\text{PF}_3$</td>
<td>0.31</td>
<td>0.37</td>
<td>0.04</td>
<td>-0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>$F\text{PF}_3$</td>
<td>0.31</td>
<td>0.33</td>
<td>0.00</td>
<td>-0.10</td>
<td>-0.01</td>
</tr>
<tr>
<td>$\text{HPCl}_3$</td>
<td>0.33</td>
<td>0.52</td>
<td>0.00</td>
<td>0.00</td>
<td>0.18</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>0.46</td>
</tr>
<tr>
<td>$\text{CIPCl}_3$</td>
<td>0.09</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.50</td>
</tr>
</tbody>
</table>

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

Figure 1. Schematic representation of the SOMOs of $C_{3v}$ phosphoranyl radicals. (A) $\text{HPH}_3$, (B) $\text{FPF}_3$, (C) $\text{FPH}_3$, (D) $\text{HPF}_3$.

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 $C_{3v}$ phosphoranyl radicals, we calculated the Fermi contact integrals ($\rho(\mathbf{R}_{\text{rad}})$) and the isotropic hyperfine coupling constants ($a_{\text{Nuc}}^{(1)}$) together with the valence orbital spin densities. These values are given in Tables II and III. The listed values for the three $X^2pX^2$ 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 $C_{3v}$ $\text{P(OC}_{2}H_{4})_3\text{N}^+\text{BF}_4^-$ radical and therefore confirms its assignment as TBP-a (vide supra).

In comparison with the other calculated $C_{3v}$ radicals the electronic structure of $\text{FPH}_3$ shows some remarkable differences. Relative to $\text{PH}_3$ 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 $\text{FPH}_3$, 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 $\text{HPP}_3$ the radial spin density distribution $\rho(r)$, 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 $X^2 = X^2$ ($\text{HPF}_3$, $\text{FPF}_3$, 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.$^{20}$ The same bond-length rule applies for TBP-e ($C_{2v}$) phosphoranyl radicals as was shown by Howell et al.$^7$ The question arises of why the TBP-a radicals form an exception and possess a short apical bond. To answer this question one must be aware of the fact that both phosphoranyl radicals and pentacoordinated phosphorus compounds are hypervalent species with more than eight electrons around phosphorus. To accommodate the extra electron(s) the HOMO$^1$ will possess some antibonding character. For phosphoranyl radicals this HOMO is identical with the SOMO. The HOMOs for the $\text{PH}_3$ molecule and the $C_{2v}$ and $C_{3v}$ $\text{PH}_3$ 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.
It is obvious that the increased bond length is a direct result of the antibonding character. The participation of d orbitals in pentavalent phosphorus compounds is still a subject of controversy. A number of ab initio studies on pentacoordinated phosphorus compounds and phosphoranyl radicals revealed that the principal concepts of the bonding are adequately described without the introduction of d functions. However, for numerically highly accurate results in the determination of bond lengths and bond energies they are found to be essential merely because their inclusion will increase the completeness of the basis set that is used. From Figure 3 it is clear that the symmetry of the HOMO of PH₅ fits exactly to the phosphorus 3d₂ orbital, when this is -3dz²


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

<table>
<thead>
<tr>
<th>expt²</th>
<th>calc'd</th>
</tr>
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<tbody>
<tr>
<td>aP⁵⁰</td>
<td>1356</td>
</tr>
<tr>
<td>aP⁵⁰</td>
<td>3</td>
</tr>
<tr>
<td>aP⁵⁰</td>
<td>197</td>
</tr>
</tbody>
</table>

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<tr>
<td>aP⁵⁰</td>
<td>197</td>
<td></td>
</tr>
</tbody>
</table>

(2) Optimized Structure for C₄v PF₅⁻. Optimization of PF₅⁻ within a C₂v symmetry constraint revealed an exact C₂v geometry. This optimized structure of PF₅⁻ is analogous to the C₂v optimized structure of FPF₃. The bond angle between the apical bond and the four equatorial bonds is 90.6°, and again the apical bond is substantially shorter than the equatorial bond (Figure 4). This is in accordance with the fact that the equatorial ligands contribute more to the antibonding SOMO than the apical ligand. The calculated isotropic hyperfine coupling constants are in good agreement with the experimental values (Table IV). The SOMO of the PF₅⁻ phosphorane anion radical indicates that this radical can be described as octahedral (O₆) with the unpaired electron acting as a sixth ligand. The electronic structure of PF₅⁻ 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 O₈ structure. This resulted in a small spin density on the apical ligand. In a σ* structure the unpaired electron occupies an an-
tribbing orbital and is located between phosphorus and the apical ligand. This structure has been assigned to the 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 \( \phi \) 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 \( \phi \approx 117° \). 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 \( \sigma^*-C_3 \). Figure 6 indicates that the \( \sigma^*-C_3 \) arrangement lies some 150 kJ mol\(^{-1}\) above the optimized \( C_3 \) structure. Attempts to optimize the \( \sigma^* \) structure were not successful, but led to the dissociation into PH3 and H- (vide infra). The most important difference between the TBP-a and the \( \sigma^*-C_3 \) radical is the distribution of the unpaired electron over the hydrogen atoms. The \( \sigma^*-C_3 \) 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 \( \sigma^*-C_3 \), 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 \( C_3 \) phosphoranyl radical gives no definite proof of a \( \sigma^*- \) arrangement. Nevertheless the calculated spin density distribution for the HPH3 \( \sigma^* \) structure is comparable with the experimental values of the \( \sigma^*-C_3 \) structure. This relative high spin density in the C1 axis of the PF3 radical anion possessing a \( \sigma^* \) arrangement is comparable with the experimental values of a \( \sigma^*-C_3 \) structure. This possibility was already recently suggested by Symons.31 Figure 10 gives a schematical representation of the SOMOs of \( \sigma^*- \) arrangements of HPH3 and PF3.

The energy difference between the optimized PF3 radical and its \( \sigma^*-C_3 \) arrangement is approximately 215 kJ mol\(^{-1}\). Analogue to the \( C_3 \) radicals, there is a difference in the electronic structure of the optimized PF3 radical and its \( \sigma^* \) arrangement. For the optimized octahedral structure the equatorial ligands possess a large spin density whereas the \( \sigma^*-C_3 \) 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 C1 axis of the PF3 radical anion possessing a \( \sigma^*- \) structure is comparable with the experimental values of the related \( C_3 \) CIP(O),C6H4)\(^+- \) 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),C6H4)\(^+- \) radical possesses a \( \sigma^*-C_3 \) structure. This possibility was already recently suggested by Symons.31 Figure 10 gives a schematical representation of the SOMO for the \( \sigma^* \) structures of HPH3 and PF3.

IV. Stability of \( X^* \)PH3 radicals

As we showed in section III(1) the optimized \( C_3 \) 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 distribution, very high (2.265 electrons Bohr$^{-1}$). The apical bond length is 1.5, and 1.6 $\alpha$, respectively. Cross sections were calculated for each P-H bond and the SOMO (Le., only the 3p, electrons). Attack of a hydrogen atom along the P-H axis leads to a barrier (135 kJ mol$^{-1}$) in favor of the dissociation. The HOMO of PH$_3$ and He. Using the saddle-point optimization method, we have optimized the LUMO-TS with respect to all geometric parameters. This LUMO-TS lies 178.3 $\alpha$, $\phi = 121.2^\circ$ and a LUMO-loose complex ($r_e = 4.17 \AA, \phi = 58.8^\circ$). Table V summarizes the energies of the various minima and transition state relative to the energy of isolated PH$_3$ and H- ($-342.523923$ au). From these potential surfaces it is clear that the TBP-a structure represents the only stable HP$H_3$ radical. None of the surface indicates a minimum that could belong to a stable $\sigma^*-\pi_3$ 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 $\AA$ for the LUMO and 3.86 $\AA$ 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$_3v$ HP$H_3$ radical. This demonstrates that the dissociation of PH$_3$ 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$_3v$ HP$H_3$ radical, the LUMO-TS, and both loose complexes we have calculated correlation energies by Müller-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 $\pi^*$-$\sigma_3$, 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>$r_e$ (\AA)</th>
<th>C$_{3v}$</th>
<th>LUMO-TS$^a$</th>
<th>HOMO-TS$^a$</th>
<th>LUMO-C$^c$</th>
<th>HOMO-C$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4 A</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 A</td>
<td>0.055675 (146.2)</td>
<td>0.089342 (182.1)</td>
<td>0.069342 (182.1)</td>
<td>0.004045 (10.6)</td>
<td>0.004016 (10.5)</td>
</tr>
<tr>
<td>1.6 A</td>
<td>0.158226 (238.9)</td>
<td>0.158226 (238.9)</td>
<td>0.158226 (238.9)</td>
<td>0.000106 (2.9)</td>
<td>0.000062 (2.8)</td>
</tr>
</tbody>
</table>

$^a$Energies are relative to PH$_3$ + H-. ($-342.523923$ au). Values between brackets refer to differences in kJ mol$^{-1}$. $^c$TS = transition state. $^c$LC = loose complex.

Figure 11. C$_3v$ optimized geometry for PH$_3$ ($\varepsilon$(UHF) = -342.025 690 au).

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

C$_3v$ HP$H_3$ radical. In principle it could be possible that there are more stable geometries for a C$_3v$ HP$H_3$ radical. Furthermore it is important to know the stability of the C$_3v$ HP$H_3$ 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 $\AA$, 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$_3v$ HP$H_3$ radical and the sum of isolated PH$_3$ and H- is 0.051449 au (135 kJ mol$^{-1}$) in favor of the dissociation. The HOMO of PH$_3$ contains the two nonbonding electrons. Attack of a hydrogen atom along the P-H C$_3$ axis leads to a C$_3v$ HP$H_3$ 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$_3v$ HP$H_3$ 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 $\AA$ and from 55$^\circ$ to 125$^\circ$, respectively. Cross sections were calculated for $r_a = 1.4$, 1.5, and 1.6 $\AA$ (Figure 13). The potential surfaces differ in the number of minima and transition states. For the $r_a = 1.6$ $\AA$ 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 ($r_a = 3.90; \phi = 123.4^\circ$) and LUMO approach ($r_a = 4.29; \phi = 56.6^\circ$). On this surface there are two transition states (TS). The HOMO-TS possesses a perfect tetrahedral geometry ($r_a = 1.60; \phi = 109.4^\circ$) and a symmetrical SOMO (Le., only the 3p 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$^{-1}$; $a_{3p} = 1698$ G), and a considerable amount of spin density is found on the four equivalent hydrogen nuclei (0.099 electrons Bohr$^{-1}$; $a_{3p} = 158$ G). The LUMO-TS ($r_a = 1.82; \phi = 73.9^\circ$) 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$^{-1}$; $a_{3p} = 238$ G) and a high value on the approaching hydrogen nucleus (0.216 electrons Bohr$^{-1}$; $a_{3p} = 345$ G). SOMOs of both transition states are depicted in Figure 14.

For the $r_a = 1.5$ $\AA$ surface again three minima were calculated. The TBP-a radical ($r_a = 1.44 \AA; \phi = 89.0^\circ$), the HOMO-loose complex ($r_a = 3.89 \AA; \phi = 122.5^\circ$), and the LUMO-loose complex ($r_a = 4.23 \AA; \phi = 57.5^\circ$). On this surface only one transition state, namely for the LUMO approach, is found ($r_a = 1.76 \AA; \phi = 78.6^\circ$). Its structure is comparable with the LUMO-TS on the $r_a = 1.6$ $\AA$ surface. Finally the $r_a = 1.4 \AA$ surface possesses only two specific points; a HOMO-loose complex ($r_a = 3.86 \AA; \phi = 121.2^\circ$) and a LUMO-loose complex ($r_a = 4.17 \AA; \phi = 58.8^\circ$).
Figure 13. Potential energy surfaces of the PH$_3$ + H system. Geometric parameters are $r_e$, $r_a$, 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.

(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 FPC$_3$. 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
of these loose complexes are essentially the same as for the isolated
the radical is rather unstable. In section III(
phoranyl radicals possess a TBP-a structure. The calculated
the experiments on the .P(OCH2CH2),N+BF4- radical. Geometry
LUMO-loose complex (PH,
radical and transition state is only
the isolated PH, and F.. The energy difference between FPH,
V. Conclusions
On attempted optimization all trial geometries revealed a
approach was calculated. Its structure (Figure 16) and
Figure 14. SOMOs for the transition states for LUMO and HOMO
Figure 15. LUMO-TS of the PH3 + H- = HPH3 system. Calculated
saddle-point optimization method the F-PH3 transition state for
LUMO approach 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
radical and transition state is only 9.8 kJ mol-1 indicating that
the radical is rather unstable. In section III(1) of this paper we
mentioned that for CIPh3 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, X4P3+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),N+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
Berczal et al. and therefore gives support to their σ*assignment.
The structure of C62PF5+ 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
PF5+ are in excellent agreement with the experimental values
reported by Morton et al. Variation 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), radical anion
indicates that the latter possibly possess a σ*C62 structure.
Despite many geometry variations and a number of different
radicals it was not possible to optimize the geometry of a σ*–C62
radical. This suggests that σ* structures are not stable.
Nevertheless the calculated electronic structures for the σ*arrange-
ments of HPH3 and PF5- are in correspondence with the
experimental values obtained for the Ph3PCI and CIP(O2C6H4),
radicals, respectively. It is possible that the apparent formation
and existence of a σ* structure for Ph3PCI and CIP(O2C6H4),
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), 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
Clark10 on the structure of H3PX4+ radical cations (X = H3, H2S,
HCl), which revealed a σ* structure for H3PPH3+. The H3PSH4+,
and H3PCI4+ 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>-342.472 475 (135.1)</td>
<td>-342.555 382 (114.8)</td>
<td>-342.572 836 (105.9)</td>
<td>-342.582 713 (96.8)</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>-342.456 009 (178.3)</td>
<td>-342.537 795 (160.9)</td>
<td>-342.554 448 (154.2)</td>
<td>-342.563 243 (147.9)</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>-342.523 978 ( -0.2)</td>
<td>-342.599 037 ( 0.0)</td>
<td>-342.613 133 ( 0.0)</td>
<td>-342.619 516 ( 0.0)</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>-342.524 016 ( -0.2)</td>
<td>-342.599 090 ( -0.1)</td>
<td>-342.613 186 ( -0.1)</td>
<td>-342.619 570 ( -0.2)</td>
</tr>
<tr>
<td>PH3 + H-</td>
<td>-342.523 923</td>
<td>-342.599 056</td>
<td>-342.613 152</td>
<td>-342.619 497</td>
</tr>
</tbody>
</table>

*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>FPH3</th>
<th>ClPH3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E(UHF)</td>
<td>(S2)</td>
</tr>
<tr>
<td>TBP-a</td>
<td>-441.245 124 (120.9)</td>
<td>0.7579</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>-441.241 399 (130.7)</td>
<td>0.7519</td>
</tr>
<tr>
<td>LUMO-LC</td>
<td>-441.291 240 ( -0.2)</td>
<td>0.7508</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>-441.292 633 ( -3.8)</td>
<td>0.7509</td>
</tr>
<tr>
<td>PH3 + X+a</td>
<td>-441.291 171</td>
<td>0 + 0.7500</td>
</tr>
</tbody>
</table>

*Values between brackets refer to differences relative to PH3 + X+a 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 bl(π) and a(π) as the two highest occupied and b2g(π) and b3g(π) as the lowest unoccupied MOs of 2.

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 exptl</td>
<td>-1076.99720</td>
<td>-1077.0465</td>
<td>6.1277</td>
<td></td>
</tr>
<tr>
<td>STO-3G STO-3G</td>
<td>-1077.0273</td>
<td>-1077.0684</td>
<td>-0.0411</td>
<td></td>
</tr>
<tr>
<td>4-31G STO-3G</td>
<td>-1088.0443</td>
<td>-1088.01958</td>
<td>0.0248</td>
<td></td>
</tr>
<tr>
<td>4-31G STO-3G</td>
<td>-1088.09202</td>
<td>-1088.04741</td>
<td>-0.0449</td>
<td></td>
</tr>
<tr>
<td>STO-3G+D exptl</td>
<td>-1077.53955</td>
<td>-1077.53750</td>
<td>0.0027</td>
<td></td>
</tr>
<tr>
<td>MNDO MNDO</td>
<td>-58.24313</td>
<td>-58.21361</td>
<td>-0.0269</td>
<td></td>
</tr>
<tr>
<td>MNDO MNDO</td>
<td>-58.24313</td>
<td>-58.21361</td>
<td>-0.0269</td>
<td></td>
</tr>
</tbody>
</table>

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

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

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Registry No. HPF2, 25530-87-4; FPF2, 14855-36-8; FPH2, 56360-19-1; HF2, 56360-18-0; PF, 8925-40-1; PH2, 7803-51-2; H2, 12385-13-6; CF2H, 89746-27-0; CIPF2, 89746-28-1; HPCIP2, 89746-29-2; FPCI, 89746-30-5; CIPCI, 20762-59-8.

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).

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