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

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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 sterically constrained ring structures.¹⁻¹⁻¹ Most frequently a C₂ᵥ geometry is encountered. The electronic structure of these C₃₆ phosphoranyl radicals is well established and may be described as a trigonal-bipyramidal structure with the unpaired electron in apical position.²⁻⁵ In contrast to the structure of C₃₆ phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C₄₆ geometry and phosphorane anion radicals with a C₄₆ geometry. The unpaired electron in the Ph₃P═Cls radical, which possesses a C₃₆ 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 C₃₆ radical ¹P(OC₂H₅)₃N⁺BF₄⁻ show unambiguously that the unpaired electron resides in the apical position of a TBP (TBP-a).³⁻⁸ The near isotropic ¹⁴N hyperfine coupling of 22 G

Structure of C₃₆: Phosphoranyl and C₄₆: 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 C₃₆ phosphoranyl radicals and the C₄₆ PF₅⁻ phosphorane anion radical are presented. By the unrestricted Hartree-Fock method with a 4-31G basis set the geometries for C₃₆ X₅PX₃ (X₅ = apical ligand, X₅ = equatorial ligand) radicals were optimized for X₅ = H, F, and Cl. All C₃₆ radicals reveal a trigonal-bipyrimidal 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 C₃₆, PH₃ + H₂ potential energy surface is described. It appears that a σ*-arrangement is 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. HPH₃ 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 sterically constrained ring structures.¹⁻¹⁻¹ Most frequently a C₂ᵥ geometry is encountered. The electronic structure of these C₃₆ phosphoranyl radicals is well established and may be described as a trigonal bipyramidal (TBP) with the unpaired electron acting as a fifth ligand in an equatorial position.²⁻⁵ In contrast to the structure of C₃₆ phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C₄₆ geometry and phosphorane anion radicals with a C₄₆ geometry. The unpaired electron in the Ph₃P═Cls radical, which possesses a C₃₆ 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

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

Finally, we briefly mention Prussian blue analogues. It has already been shown that iron-ruthenium cyanide (ruthenium purple; RP), Fe₄²⁺[RuII(CN)₆]₃, and iron-osmium cyanide, Fe₄²⁺[OsII(CN)₆]₃, can be prepared by an electrochemical method.¹⁵ It was found that both were active for the reduction of O₂. Applications as catalysts can be readily expected from the above results.

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

Registry No. Fe, 7439-89-6; Fe₂₃⁺[RuII(CN)₆]₃, 7722-84-1; H₂O₂, 7732-18-5; C, 7440-44-0; PB, 12240-15-2; Prussian white, 81681-39-2.
indicates a small spin density on the apical nitrogen atom. Similar
features in the structure of $C_6$ phosphorane anion radicals
($PX_3^-$) have been reported. The isotropic hyperfine pattern of
the $PX_3^-$ radical shows four equivalent equatorial fluorines with
a large coupling and one with a small coupling arising from
the unique apical fluorine. The same structure has been proposed
for $PCl_5$- and the isoelectronic $SFS$. For the $CIP(02C6H4)_2-
(PX,-)$ have been reported. The isotropic hyperfine pattern of
$ClPCl_5$ indicates a small spin density on the apical nitrogen atom. Similar
differences in the structure of $PCl_5$- and $ClPCl_5$ were calculated (vide infra). Characteristic for all these
radicals $XaPX$, $X=H, F$, or $Cl$ within a
symmetry constraint. Isotopic hyperfine coupling constants ($a_{Nuc}^{iso}$) were
calculated from the Fermi contact integrals ($\rho(\vec{R}_{Nuc})$):

$$\rho(\vec{R}_{Nuc}) = \sum_{\mu \nu} P_{\mu \nu}^a \phi_{\mu}(\vec{R}_{Nuc}) \phi_{\nu}(\vec{R}_{Nuc})$$ (1)

$$a_{Nuc}^{iso} = \frac{4\pi}{3} g \mu_B S J(r)\rho(\vec{R}_{Nuc})$$ (2)

in which $P_{\mu \nu}^a$ is the first-order spin density matrix and $\phi_{\mu}$ and $\phi_{\nu}$ are the atomic basis functions. Orbital spin densities were
obtained by performing a Mulliken population analysis on the
single determinant wave function. Correlation energies were
calculated by Möller–Plesset perturbation theory to second
and third order (UMP2 and UMP3) and by configuration interaction
with all double substitutions (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 $C_6$ Radicals. The geometries of the radicals $X^ePX_3^-$ have been optimized for all combinations
of $X^e$ and $X^e$ with $X = H, F$, or $Cl$ within a $C_6$ symmetry
constraint. The optimized parameters for these radicals are collected in Table I together with the calculated UHF energies and the expectation values of $S^2$. The geometric parameters for $HPH_3$ and $FPF_3$ differ slightly from those previously reported by Howell et al., because in our study we included the apical-equatorial bond angle ($\phi$) in the optimization. For $CIPH_3$ no stable geometry could be calculated (vide infra). Characteristic for all these $C_6$ radicals is the apical-equatorial bond angle $\phi$ that is near to 90°.

The singly occupied molecular orbital (SOMO) determines the distribution of the unpaired electron in the radical. The calculated

(15) Without this symmetry constraint optimization would probably reveal $C_2$ or $C_1$ geometries (see, e.g., ref 2, 5, 7, and 10).
the SOMO of the phosphorus equatorial hydrogen atoms. Simultaneously the contribution has been frequently suggested by various radicals (vide supra).

243, with the experimental values of the SOMOs. Table 11 and 111. Relative to HPH3 there is a serious decrease of the contribution SOMO. This calculated general structure is in perfect agreement because the possesses a near zero spin density, which is a direct result of the fact that its atomic orbitals do not contribute significantly to the radical and therefore confirms its assignment as TBP-a (vide 11). It appears that roughly speaking all TBP-a radicals have a considerable amount of contaminating higher multiplicities (Table 1). It seems 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 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. 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 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 PH3 molecule and the C3, PH3 radicals are depicted in Figure 3. The schematic representations indicate that, for the three examples, in the ligands that contribute most to the HOMO the bond length is increased, while the ligands with a smaller contribution possess a normal bond length (ca. 1.43 Å).

Figure 2. Radial spin density probability along the C3 axis for the HPH3 radical.

like FPH3, with one strongly electronegative ligand, preferentially occupies a tetrahedral geometry with the unpaired electron in an antibonding σ* orbital. However, our calculations show that for FPH3 the optimized value of φ (85.9°) does not confirm a tetrahedral geometry and that the electronic structure of FPH3 is clearly TBP-a (Figure 1). In order to get an indication of the distance between phosphorus and the point of the maximum probability of finding the unpaired electron along the C3 axis, we have calculated for HPH3 the radial spin density distribution \( r^2 p(r) \), where \( r \) is the radius centered on phosphorus and \( p(r) \) 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 \( X^* = X^* \) (HPH3, FPF3, and CIPCl3) is considerably shorter than the corresponding equatorial bond. In view of their TBP-a structures this is a remarkable result. It is a well-known fact that for pentacoordinated phosphorus compounds with a TBP geometry the axial bonds are longer than the equatorial bonds when identical ligands are involved. The same bond-length rule applies for TBP-e 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 PH3 molecule and the C3, PH3 radicals are depicted in Figure 3. The schematic representations indicate that, for the three examples, in the ligands that contribute most to the HOMO the bond length is increased, while the ligands with a smaller contribution possess a normal bond length (ca. 1.43 Å).

(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.

### Table III. Valence Orbital Spin Densities of the C3, X^*PX^* Radicals

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>X^*</th>
<th>X^e</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPH3</td>
<td>0.08</td>
<td>-0.10</td>
<td>0.42</td>
</tr>
<tr>
<td>FPH3</td>
<td>0.64</td>
<td>-0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>HPF3</td>
<td>0.31</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>FPF3</td>
<td>0.31</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>HPCl3</td>
<td>0.10</td>
<td>-0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>FPCl3</td>
<td>0.06</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CIPCl3</td>
<td>0.09</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*The listed values are summations over the inner and outer orbitals of the split valence 4-31G basis set. \( \nu_{np} \) is the equatorial contribution, calculated as \( \nu_{s_{np}} + \nu_{p_{np}} \).
1.141

Table IV. Experimentala and Calculated Isotropic Hyperfine Coupling Constants of PF5,b

<table>
<thead>
<tr>
<th>expcl,a</th>
<th>calc</th>
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<tbody>
<tr>
<td>1356</td>
<td>1323</td>
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<td>197</td>
<td>174</td>
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</table>

*See ref 9. Values in gauss.

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 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.

(2) Optimized Structure for C4v PF5-. Optimization of PF5- within a C4v symmetry constraint revealed an exact C4v geometry. This optimized structure of PF5- is analogous to the C4v 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 PFS- 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 O6 structure. This resulted in a small spin density on the apical ligand. In a σ* structure the unpaired electron occupies an

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

<table>
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<th>calc</th>
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<tr>
<td>1356</td>
<td>1323</td>
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<tr>
<td>197</td>
<td>174</td>
</tr>
</tbody>
</table>

*See ref 9. Values in gauss.

Figure 5. Calculated isotropic hyperfine coupling constants (σnucl) of HPH4 as a function of the apical-equatorial bond angle φ; values for σnucl are in gauss.

Figure 6. Energy of HPH4 as a function of the apical-equatorial bond angle φ 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 Ph3PCl radical in order to explain the high spin density on the apical chlorine.

For a further insight in these differences, we have calculated the effect of geometry variations on the spin density distribution. For the HPH3 radical the angle \( \phi \) between the apical and the three equatorial bonds was varied from 80° to 130°. During the variation of \( \phi \) all bond lengths were fixed at the optimized values. The calculated isotropic hyperfine coupling constants arising from the Fermi contact integrals at the phosphorus and hydrogen nuclei are given as a function of \( \phi \) in Figure 5. Figure 6 represents the corresponding UHF energy during this variation of \( \phi \) relative to the energy of the optimized radical (-342.472475 au). The phosphorus isotropic hyperfine coupling constant reaches a maximum value at \( \phi = 117° \). 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 \( \sigma^*-C_{3v} \). 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 Ph3H 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 HPH3 \( \sigma^* \) structure is comparable with the experimental values of the Ph3PCl radical and supports the \( \sigma^* \) assignment for Ph3PCl. For PF5\(^-\) we have performed a similar structure variation of the bond angle \( \phi \). Variation of \( \phi \) revealed a transition from \( O_4 \) to \( \sigma^*-C_{3v} \) at \( \phi = 108° \). The calculated parameters (\( \Delta E \), 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 \( \sigma^*-C_{3v} \) arrangement is approximately 215 kJ mol\(^{-1}\). Analogous to the \( C_{3v} \) radicals, there is a difference in the electronic structure of the optimized PF5\(^-\) radical and its \( \sigma^* \)-arrangement. For the optimized octahedral structure the equatorial ligands possess a large spin density whereas the \( \sigma^*-C_{4v} \) radical is characterized by a high spin density on the apical ligand. Both the \( O_4 \) and \( \sigma^* \) structure exhibit a large phosphorus isotropic hyperfine coupling. This relative high spin density in the \( C_1 \) axis of the PF5\(^-\) radical anion possessing a \( \sigma^* \)-arrangement is comparable with the experimental values of the related \( C_{4v} \) 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 anion possesses a \( \sigma^*-C_{4v} \) 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 PF5\(^-\).

IV. Stability of XPH3 radicals

As we showed in section III(1) the optimized \( C_{3v} \) HPH3 radical possesses a TBP-a structure. The question arises of whether this optimized structure represents the only stable structure for the

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a considerable amount of spin density is found on the four

constant while the apical bond length

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

bond angle

s

Figure 11. C₆ᵥ optimized geometry for PH₃ (E(UHF) = -342.025690 au).

Figure 12. Two possible routes for H- attack toward PH₃. Route A, LUMO approach; route B, HOMO approach.

C₆ᵥ HPH₃ radical. In principle it could be possible that there are more stable geometries for a C₆ᵥ HPH₃ radical. Furthermore it is important to know the stability of the C₆ᵥ HPH₃ radical, for example, with respect to the dissociation into PH₃ and H. 

(1) Potential Surface PH₃ + H. The PH₃ molecule is pyramidal and possesses a C₆ᵥ 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 C₆ᵥ axis is 58.3° (Figure 11).

The calculated energy difference between the optimized C₆ᵥ HPH₃ radical and the sum of isolated PH₃ and H is 0.051449 au (135 kJ mol⁻¹) in favor of the dissociation. The HOMO of PH₃ contains the two nonbonding electrons. Attack of a hydrogen atom along the C₃ axis leads to a C₆ᵥ HPH₃ radical. There are two possible routes for this attack (Figure 12): an approach of H toward the LUMO of the PH₃ molecule or an approach toward the HOMO. Likewise the dissociation of a C₆ᵥ HPH₃ radical can proceed along these two routes. To determine the route with the lowest energy barrier three cross sections through the multidimensional potential energy surface were calculated. For each cross section the equatorial bond lengths (rₑ) were kept constant while the apical bond length (rₐ) and the apical-equatorial bond angle (ϕ) were varied from 1.4 to 4.3 Å and from 55° to 125°, respectively. Cross sections were calculated for rₑ = 1.4, 1.5, and 1.6 Å (Figure 13). The potential surfaces differ in the number of minima and transition states. For the rₑ = 1.6 Å surface three minima were calculated, one for a stable TBP-a radical (rₑ = 1.43; ϕ = 89.5°) and two "loose complexes", for both HOMO approach (rₑ = 3.90; ϕ = 123.4°) and LUMO approach (rₑ = 4.29; ϕ = 56.6°). On this surface there are two transition states (TS). The HOMO-TS possesses a perfect tetrahedral geometry (rₑ = 1.60; ϕ = 109.4°) and a symmetrical SOMO (i.e., only the s orbitals of phosphorus and hydrogen are involved). The phosphorus Fermi contact integral is, due to the absence of 3p₅ contribution, very high (2.265 electrons Bohr⁻¹; aₚ₅ = 1698 G), and a considerable amount of spin density is found on the four equivalent hydrogen nuclei (0.099 electrons Bohr⁻¹; aₚ₅ = 158 G). The LUMO-TS (rₑ = 1.82; ϕ = 73.9°) lies 41.1 kJ mol⁻¹ below the HOMO-TS. The electronic structure of this LUMO-TS is characterized by a low phosphorus Fermi contact integral (0.368 electrons Bohr⁻¹; aₚ₅ = 238 G) and a high value on the approaching hydrogen nucleus (0.216 electrons Bohr⁻¹; aₚ₅ = 345 G). SOMOs of both transition states are depicted in Figure 14.

For the rₑ = 1.5 Å surface again three minima were calculated. The TBP-a radical (rₑ = 1.44 Å; ϕ = 89.0°), the HOMO-loose complex (rₑ = 3.89 Å; ϕ = 122.5°), and the LUMO-loose complex (rₑ = 4.23 Å; ϕ = 57.5°). On this surface only one transition state, namely for the LUMO approach, is found (rₑ = 1.76 Å; ϕ = 78.6°). Its structure is comparable with the LUMO-TS on the rₑ = 1.6 Å surface. Finally the rₑ = 1.4 Å surface possesses only two specific points; a HOMO-loose complex (rₑ = 3.86 Å; ϕ = 121.2°) and a LUMO-loose complex (rₑ = 4.17 Å; ϕ = 58.8°). Table V summarizes the energies of the various minima and transition state relative to the energy of isolated PH₃ and H (-342.523923 au). From these potential surfaces it is clear that the TBP-a structure represents the only stable HPH₃ radical. None of the surface indicates a minimum that could belong to a stable σ*-C₆ᵥ arrangement. The potential surface shows furthermore that the energy barrier for LUMO approach is smaller than for HOMO approach. We have calculated fully optimized structures for the HOMO- and LUMO-loose complexes. Their PH₃ fragments are identical with each other and with the optimized PH₃ molecule. The P-H distances differ: 4.18 Å for the LUMO and 3.86 Å for the HOMO. The energy of these loose complexes lies slightly below that of the isolated PH₃ + H. This difference has no physical significance and is probably due to a small calculated interaction between the outer 4-31G orbitals of PH₃ and H. Using the saddle-point optimization method, we have optimized the LUMO-TS with respect to all geometric parameters within C₆ᵥ symmetry (Figure 15). This LUMO-TS lies 178.3 kJ mol⁻¹ above the isolated PH₃ + H and 43.2 kJ mol⁻¹ above the optimized C₆ᵥ HPH₃ radical. This demonstrates that the dissociation of HPH₃ is not a wholly downhill process as previously suggested by Howell et al. Despite many trial geometries we were not able to calculate a saddle point that could be attributed to a HOMO-TS. All efforts led to nonoptimized structures with very short apical bonds and large values of ϕ or to the previously optimized LUMO-TS. For the C₆ᵥ HPH₃ radical, the LUMO-TS, and both loose complexes we have calculated correlation energies by Möller–Plesset perturbation theory (UMP2 and UMP3) and configuration interaction. These values are listed in Table VI. The post SCF calculations do not change the conclusions based on the UHF calculations. The energy difference between LUMO-TS and isolated PH₃ + H is lowered from 178.3 to 147.9 kJ mol⁻¹ after configuration interaction, while the stability of the C₆ᵥ 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 σ*-C₆ᵥ 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 of the Minima and Transition States on the Cross Sections of the Potential Surface

<table>
<thead>
<tr>
<th></th>
<th>rₑ = 1.6 Å</th>
<th>rₑ = 1.5 Å</th>
<th>rₑ = 1.4 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cₑ</td>
<td>0.051494 (135.2)</td>
<td>0.055675 (146.2)</td>
<td></td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>0.079576 (208.9)</td>
<td>0.069342 (182.1)</td>
<td></td>
</tr>
<tr>
<td>HOMO-TS</td>
<td>0.095208 (250.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LUMO-Rc</td>
<td>0.022120 (58.1)</td>
<td>0.004045 (10.6)</td>
<td>0.001106 (2.9)</td>
</tr>
<tr>
<td>HOMO-Lc</td>
<td>0.022094 (58.0)</td>
<td>0.004016 (10.5)</td>
<td>0.000626 (2.8)</td>
</tr>
</tbody>
</table>

*Energies are relative to PH₃ + H (-342.523923 au). Values between brackets refer to differences in kJ mol⁻¹. $TS = $transition state. $LC = $loose complex.
Figure 13. Potential energy surfaces of the PH$_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.

a $\sigma^*$ intermediate seems 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 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 variations for HPH, reveal a *-arrangement, which, however, of these loose complexes are essentially the same as for the isolated electronic structure of these radicals is in good agreement with phoranyl radicals possess a TBP-a structure. The calculated the experiments on the .P(OCH2CH2),N+BF4- radical. Geometry

V. Conclusions

Table VI. Correlation Energies* of HPH3 for the Optimized Structures and the Transition State

<table>
<thead>
<tr>
<th></th>
<th>E(UHF)</th>
<th>E(UMP2)</th>
<th>E(UMP3)</th>
<th>E(CID)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3p radical</td>
<td>-342.472475</td>
<td>(-135.1)</td>
<td>-342.555382</td>
<td>(-114.8)</td>
</tr>
<tr>
<td>LUMO-TS</td>
<td>-342.456009</td>
<td>(-178.3)</td>
<td>-342.537795</td>
<td>(-160.9)</td>
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<tr>
<td>LUMO-LC</td>
<td>-342.523978</td>
<td>(-0.2)</td>
<td>-342.599037</td>
<td>(0.0)</td>
</tr>
<tr>
<td>HOMO-LC</td>
<td>-342.524016</td>
<td>(-0.2)</td>
<td>-342.599090</td>
<td>(-0.1)</td>
</tr>
<tr>
<td>PH3 + H+</td>
<td>-342.523923</td>
<td>(--0.2)</td>
<td>-342.599056</td>
<td>(--0.1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-342.631652</td>
<td>(0.0)</td>
</tr>
</tbody>
</table>

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

Table VII. Energies* and (S²) Values of the Optimized Structures and the Transition State of FPH3 and CIPH3

<table>
<thead>
<tr>
<th></th>
<th>FPH3</th>
<th>CIPH3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E(UHF)</td>
<td>(S²)</td>
</tr>
<tr>
<td>TBP-a</td>
<td>-341.245124</td>
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<tr>
<td>LUMO-TS</td>
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<td>LUMO-LC</td>
<td>-341.291240</td>
<td>0.7508</td>
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<tr>
<td>HOMO-LC</td>
<td>-341.292633</td>
<td>0.7509</td>
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<tr>
<td>PH3 + X⁺</td>
<td>-341.291171</td>
<td>0+0.7500</td>
</tr>
</tbody>
</table>

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

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 X⁺PX³⁻ 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)3X⁺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 C6w 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 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)₂⁻ radical anion indicates that the latter possibly possess a σ*-C₆w arrangement. Despite many geometry variations and a number of different radicals it was not possible to optimize the geometry of a σ*–C₆w 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(O3C6H4)₂⁻ radicals, respectively. It is possible that the apparent formation and existence of a σ* structure for Ph3PCI and CIP(O3C6H4)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(O3C6H4)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 on the structure of H3PX⁺ radical. ange (X = Ph3, H3S, HCl), which reveal a σ* structure for H3PPhH⁺. The H3PShH⁺, and H3PClH⁺ 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⁺.

Electronic Structure of 1,5-Dithia-2,4,6,8-tetrazocine.  
Model Calculations and Spectroscopic Investigations

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

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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 bn(π) and an(π) as the two highest occupied and bn(σ) and bn(σ) 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 eg orbital of 1b (D3h) 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.

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 film technique.

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

<table>
<thead>
<tr>
<th>basis</th>
<th>geometrya</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>exp1</td>
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<td>-1077.06465</td>
<td>0.0675</td>
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<tr>
<td>STO-3G</td>
<td>STO-3G</td>
<td>-1077.02730</td>
<td>-1077.06884</td>
<td>-0.0415</td>
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<tr>
<td>4-31G</td>
<td>exp1</td>
<td>-1088.08443</td>
<td>-1088.01958</td>
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<tr>
<td>4-31G</td>
<td>STO-3G</td>
<td>-1088.09202</td>
<td>-1088.04741</td>
<td>-0.0447</td>
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<tr>
<td>STO-3G+d</td>
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<tr>
<td>MNDO</td>
<td>MNDO</td>
<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.

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2 Universitat Koln.


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