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Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja00218a004

Published: 01/01/1988

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

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A Single-Crystal ESR and Quantum Chemical Study of Electron-Capture Trialkylphosphine Sulfide and Selenide Radical Anions with a Three-Electron Bond

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Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands 5500 MB. Received September 4, 1987

Abstract: A low-temperature ESR study of electron-capture phosphoranyl radicals in X-irradiated single crystals of trialkylphosphine sulfides and selenides (R3PX: X = S, Se; R = CH3, C2H5, C3H7) is presented. The principal values and direction cosines of the g tensors and 31P and 77Se hyperfine coupling tensors are determined and correlated with the X-ray structure analysis of the parent compounds. All studied compounds reveal the formation of a R3PX radical anion, with a three-electron P–X bond in which the unpaired electron is nearly equally distributed over phosphorus and the substituent X. It is shown that the site symmetry of the radicals corresponds to the crystallographic point symmetry of the precursor molecules, resulting in pure trigonal (C3) radicals for (CH3)3PX+ and C2 symmetry for (C2H5)3PX+ and (C3H7)3PX+. Ab initio quantum chemical calculations (4-31G* SCF and CASSCF) on the model H3PS predict that the three-electron bond is unstable and dissociates into PH and S+. The calculations do not reproduce the experimental couplings and the observed spin density distribution, but tend to localize the unpaired electron entirely on sulfur. The origin of this deficiency appears to be predominantly due to a poor description of the negative charge of the nonbonding electron pairs of the sulfur atom. Via the introduction of a positive charge in the vicinity of the sulfur atom, the theoretical spin density distribution can be brought in accordance with the experimental data. The use of quantum chemical calculations for the simulation of trapped radicals in the solid state is discussed.

I. Introduction

The nature of two-center, three-electron bonds (A–B) has received much recent experimental1–7 and theoretical8–11 attention. The electronic structure of a three-electron bond is characterized by the combined effects of two bonding σ electrons and one antibonding, i.e., bond weakening σ* electron. Three-electron bonds can be formed via the addition of an electron to an existing σ bond or via an inter- or intramolecular interaction of a single occupied molecular orbital (SOMO) and a free electron pair. It has been argued by various authors that a three-electron bond is significantly stabilized when the energy levels of the two molecular fragments involved in the bonding are (nearly) degenerate.1,4–5 This is reflected in the relatively large number of symmetric three-electron bond radicals (A–A) which are known experimentally.5–7 Ab initio quantum chemical calculations on symmetric σσ* configurations invariant predict a stable three-electron bond.11,21,22 On the other hand, asymmetric three-electron bonds (A–B) are far less familiar.23–26 The asymmetry of the radical is likely to yield different energy levels for the overlapping SOMO and HOMO of the two constituents. Since stabilization due to three-electron (SOMO–HOMO) interaction falls off rapidly with increasing energy gap,12 an asymmetric σσ* configuration is expected to be less stable.

In the present paper we report a low-temperature single-crystal ESR study of trialkylphosphine sulfide and selenide electron-capture radical anions (R3PX−; X = S, Se; R = CH3, C2H5, and C3H7), containing a three-electron bond (Figure 1).

A prerequisite for the formation of a P–X three-electron bond is that the substituent X and the PX bond can accommodate the extra electron appreciably better than the ligands R and the PR bonds. Hence, its formation is closely related to the parent P=XR bond energy, because upon electron capture the antibonding component of the SOMO will tend to elongate the bond. Extensive experimental25,26 and theoretical27 studies have shown that the thiophosphoryl (PS) bond is weaker and contains less multiple bond character than does the phosphoryl (PO) bond. Typical dissociation energies of PS bonds are 443 versus 732 kJ mol−1 for the PO group.28 The quantum chemical estimate of the bond order of the PS bond in H3PS is 1.32, substantially less than the 1.58 bond order in H3PO.27 In consequence it can be expected that P–X three-electron bonds are more easily formed in phosphine sulfides and selenides than in the corresponding oxides.

From the ESR spectra of the R3PX− radicals and the observed 31P and 77Se hyperfine couplings it is concluded that the unpaired electron is approximately equally distributed over phosphorus and the chalcogen ligand. The orientation of the g tensor and the 31P and 77Se hyperfine coupling tensors is compared with the crystallographic bond directions of the parent compounds. It will be shown that the molecular symmetry adopted by the phosphoranyl...
II. Experimental Section

1. Synthesis. Trimethylphosphine sulfide (1) was obtained from the reaction of tetramethyldisulfide and methyl iodide. Tri- 
ethylphosphine sulfide (2), tricyclohexylphosphine sulfide (3), trimethylphosphine selenide (4), triocylohexylphosphine selenide (5), and tri- 
cyclohexylphosphine sulfide (7) and selenide (8) were synthesized from the correspond- 
ing phosphines and elemental sulfur or selenium. Triphenyl- 
phosphine sulfide (9) and selenide (10) were commercial materials (Janssen Chimica). All compounds were characterized with ‘H and 31P 
NMR and elemental analysis. Single crystals were prepared by slow 
evaporation or slow cooling of solutions of the desired compound in 
ethanol (1, 3, 4, 5, 6) or 1,4-dioxane (2, 8).

2. Irradiation and ESR. Single crystals were mounted on a quartz 
rod and subsequently sealed in a quartz tube. The samples were X-ir- 
radiated at 77 K using unfiltered radiation from a Cu source for 6 h. 
ESR measurements were performed using a Bruker ERZOOD spectrom- 
eter interfaced with a Bruker Aspect 3000 computer, operating with a X-band standard cavity. The single crystals were rotated perpendicular 
to the magnetic field with a single-axis goniometer in 10° steps. Tem- 
perature was controlled with the aid of a variable-temperature unit op- 
erating between 90 K and room temperature. ESR parameters were 
obtained from a second-order analysis of the spectra.

III. Results

1. Trimethylphosphine Sulfide (1). Trimethylphosphine sulfide 
(1) crystallizes in the monoclinic space group P2₁/m with unit 
cell parameters a = 6.266 Å, b = 7.588 Å, c = 6.642 Å, and β = 90.36°. Although the reported X-ray structure analysis is 
complete, the results suggest a small distortion of the molecules 
from C₂ to C₃ symmetry. One SPC angle is slightly larger than 
the other two.

The ESR spectrum obtained at 105 K of a X-irradiated single 
crystal of 1 (Figure 2a) shows a 31P doublet which can be at- 
tributed to the trimethylphosphine sulfide radical anion (1a). The 
high- and low-field transitions are broadened by a poorly resolved 
‘H hyperfine coupling. From some orientations of the single 
crystal with respect to the magnetic field this coupling can be 
determined to be approximately 0.4–0.5 mT. Since the unit cell 
angle β is very close to 90°, the three crystallographic axes were 
used as ESR reference axes. A complete single-crystal analysis 
of 1a was obtained from rotation of the crystal in the ab, ac, and 
bc planes. It was found that the principal hyperfine tensor and the 
g tensor share the same principal axes, and also coincide with the 
crystallographic axes (Table I).

...
The fact that the same axes system diagonalizes both the $^{31}\text{P}$ hyperfine tensor and the $g$ tensor for 1a as well as 1b, and the observation that the $^{31}\text{P}$ hyperfine tensors are essentially axially symmetric, indicates an overall $C_3v$ symmetry for the two radicals. Since the directions of the parallel hyperfine couplings also coincide with the $a$ axis, the $a$ axis must be the direction of the PS bond of the precursor molecule. This result is in accordance with the crystal structure analysis of trimethylphosphine selenide (section 3.4) which is isomorphous with that of the present compound.\textsuperscript{34} The $g$ tensor of 1a does not possess a $C_6v$ symmetry. The principal value in the $b$ direction is clearly different from those in the $ac$ plane.

2. Triethylphosphine Sulfide (2). Triethylphosphine sulfide (2) crystallizes as long needles in the hexagonal space group $P6_3mc$. The cell dimensions are $a = 8.98 \text{Å}$ and $c = 6.32 \text{Å}$\textsuperscript{35} The PS bond of the molecules is aligned along the $c$ axis which is parallel to the needle axis. The molecules possess a staggered conformation of the ethyl groups. One of the CH$_2$ hydrogen atoms is in a trans location with respect to the PS bond. The methyl groups and the remaining hydrogen atom are in the gauche positions. The molecules possess a $C_3$ symmetry.

X irradiation of a single crystal of 2 at 77 K generates an electron-capture phosphoranyl radical 2a. The ESR spectrum of 2a (Figure 3) clearly shows a large $^{31}\text{P}$ doublet with an additional splitting due to three equivalent $^1\text{H}$ nuclei. This splitting of 1.2 mT is essentially isotropic.

For all orientations of the crystal with the $c$ axis perpendicular to the magnetic field, identical spectra, giving $a$, $b$, and $g$, are observed. Rotation of the single crystal in the $ac$ plane reveals the parallel values of the $g$ and $^{31}\text{P}$ hyperfine coupling tensors (Table II). Both tensors are completely axially symmetric. From this observation it can be concluded that the irradiation process does not lead to any detectable distortion from $C_3v$ symmetry for 2a. The extra hyperfine splitting arises most likely from the three trans oriented $^1\text{H}$ nuclei. Radical 2a is irreversibly lost from the ESR spectrum at 170 K. No new species could be detected.

3. Tricyclohexylphosphine Sulfide (3). Crystals of tricyclohexylphosphine sulfide (3) are orthorhombic with $a = 10.906 \text{Å}$, $b = 15.836 \text{Å}$, and $c = 10.362 \text{Å}$\textsuperscript{36} The reported crystal structure parameters refer to the centrosymmetric space group $Pmna$. The four molecules in the unit cell lie on a mirror plane which is parallel to the ac plane. The PS bond directions are pairwise aligned, resulting in two different orientations, which are inclined by an angle of 15.8°. Recrystallization gives plate-like crystals ($b$ axis perpendicular to the plate face).

The ESR spectrum of a X-irradiated single crystal of 3, recorded at 105 K (Figure 4), exhibits a weak phosphorus doublet which can be attributed to the cyclohexylphosphine sulfide radical anion (3a). The low- and high-field transitions are broadened due to additional $^1\text{H}$ splitting. Upon rotation of a single crystal in the ac plane, two different sites are observed. The spectra of the two sites coalesce for all orientations in which the magnetic field direction is parallel or perpendicular to the $a$ or $c$ axis. The principal ESR parameters were determined by rotating the crystal in the $ac$, $ab$, and $bc$ planes (Table III). The principal hyperfine couplings and $g$ values of the two sites are identical within experimental error. The two hyperfine coupling tensors are inclined by an angle of 19.8°, which is close to the crystallographic angle of 15.8° between the two PS bonds. The directions of the ESR parameters of 3a correspond with the $C_3$ symmetry of the parent molecule. The signals of 3a are reversibly lost from the ESR spectrum at temperatures above 160 K.

4. Tricyclohexylphosphine Selenide (4). The crystal structure of trimethylphosphine selenide (4) is very similar to that of the corresponding sulfide. The compound crystallizes in the monoclinic space group $P2_1/m$ with unit cell parameters $a = 6.453 \text{Å}$, $b = 7.806 \text{Å}$, $c = 6.586 \text{Å}$, and $\beta = 90.46^\circ$\textsuperscript{34} The two molecules in the unit cell lie on a mirror plane with a staggered conformation of the methyl groups. The PSe bond directions of the two molecules are parallel and nearly directed along the crystallographic $a$ axis. The deviation is only 1°. Furthermore the crystallographic angle $\beta$ is close to 90°. This justifies the use of the $a$, $b$, and $c$ axes as orthogonal axes for the ESR experiments.

X irradiation of a single crystal of 4, and analysis of the ESR spectrum at 105 K, reveals the formation of two different phosphorus-centered radicals (Figure 5). The first species, 4a, exhibits a $^{31}\text{P}$ doublet broadened by $^1\text{H}$ splitting. The signals of the second radical product, 4b, are much weaker and consist of a $^{31}\text{P}$ doublet with an additional splitting of 1.38 mT. Raising the temperature

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
radical & temp (K) & total tensor & direction cosines & & \\
\hline
2a & 105 & $g$ & 2.006 & 0 & 0 & \\
 & & & 2.006 & 0 & 0 & \\
 & & & 2.002 & 0 & 0 & \\
31P & 1517 & 1 & 0 & 0 & \\
 & 1517 & 0 & 1 & 0 & \\
 & 1943 & 0 & 0 & 1 & \\
1H & $\sim 34$ & nearly isotropic & & & \\
\hline
\end{tabular}
\caption{g and Hyperfine Coupling (MHz) Tensors for 2a}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
radical & temp (K) & total tensor & direction cosines & & & \\
\hline
3a & 105 & $g$ & 2.004 & 0.986 & 0 & 0.169 \\
 & & $^{31}\text{P}$ & 1902 & 0.986 & 0 & 0.169 \\
 & & $^1\text{H}$ & <17 & nearly isotropic & & & \\
\hline
\end{tabular}
\caption{g and Hyperfine Coupling (MHz) Tensors for 3a}
\end{table}


Figure 3. Single-crystal ESR spectrum of radical 2a at 105 K. Lines marked H result from hydrogen atoms; magnetic field parallel to c axis.

Figure 4. Single-crystal ESR spectrum of radical 3a at 105 K; magnetic field parallel to c axis.
Electron-Capture R3PS- and -Se- Radical Anions

The maximum anisotropy of direction of the g tensor for 4b, along the 31P axis and hyperfine interaction in the radicals 4a, 4b and both 5a, 5b. The extra splitting of 4b, 5a, 5b could be clearly identified for most orientations of the single crystal with respect to the magnetic field. The anisotropic hyperfine tensors do not share the same principal axes for 4a, 5a, 5b. Rotation of a single crystal of 4b, 5b planes revealed the principal ESR parameters of 4a, 5a, 5b. The presence of the 77Se isotope in 4b, 5a, 5b offers a possibility for the determination of the Se hyperfine tensors. The determination of the perpendicular 77Se couplings was defined for both species. The intensity of the lines attributed to 31P, 77Se hyperfine coupling with an additional splitting from three equivalent 1H nuclei. This extra coupling is somewhat larger for 5a, and better resolved, than for 5b. The 77Se satellites are well defined for both species.

As for the corresponding sulfide 2a, a single-crystal ESR analysis of 5a, 5b reveals that both radicals possess axially symmetric g and hyperfine tensors. The parallel features coincide with the PSe bond. The ESR parameters of 5a, 5b indicate that their structures are rather similar. Two substantial differences, however, can be noted. First, the value of $\Delta g_a = (g_a - g_c)$ is much larger for 5b than for 5a. Second, the difference $A_{1s} - A_{1a} (3\beta)$ is for 5b (156 MHz) significantly smaller than for 5a (414 MHz). As for 2a the 1H splitting of 5a and 5b results from the trans located CH$_2$ hydrogen atoms. The signal intensity of 5b decreases rapidly upon warming, and the radical is irreversibly lost at 205 K. Further warming results in the loss of 5a at approximately 270 K.

6. Tricyclohexylphosphine Selenide (6). Single crystals of tricyclohexylphosphine selenide (6) are colorless well-defined

![Image of ESR spectrum](image)

**Figure 5.** Single-crystal ESR spectrum of 4a and 4b at 105 K; magnetic field parallel to the c axis.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Temp (K)</th>
<th>Total Tensor</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>105</td>
<td>g</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
<tr>
<td>4b</td>
<td>105</td>
<td>g</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
<tr>
<td>4b</td>
<td></td>
<td>31P</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
</tbody>
</table>

shows a decrease of signal intensity for both radicals. At 140 K, the small extra coupling of 4b coalesces into a normal 31P doublet. A further increase of the temperature results in the irreversible loss of 4b at 180 K and of 4a at approximately 220 K.

The presence of the 77Se isotope ($I = 1/2$, natural abundance 7.58%) in 4 offers a possibility for the determination of the Se hyperfine interaction in the radicals 4a, 4b. The intensity of a single 77Se satellite transition amounts to only 3.7% of the corresponding 31P transition. This weak intensity precluded the analysis of the 77Se satellites for 4b. For 4a, however, the 77Se satellites could be clearly identified for most orientations of the single crystal with respect to the magnetic field. The anisotropic ESR spectra reveal that the parallel 31P and 77Se couplings coincide. For perpendicular orientations the 77Se coupling is small and the satellite absorptions lie under the broad 31P transitions. The determination of the perpendicular 77Se couplings was achieved by a regression analysis of $A_{1s}$ versus cos$^2 \theta$.

Rotation of a single crystal of 4 in the crystallographic ab, ac, and bc planes revealed the principal ESR parameters of 4a, 4b, and their relative directions (Table IV). For 4a, the g tensor and both 31P and 77Se hyperfine tensors are aligned and directed along the a axis and thus along the PSe bond. The two hyperfine tensors possess a near-axial symmetry. These results lead to the conclusion that 4a has retained the original near C$_3$ symmetry. The g and 31P hyperfine tensors do not share the same principal axes for 4b. The type of symmetry is now C$_2$, because in the direction of the b axis, perpendicular to the ac mirror plane, the g and 31P tensor have a mutual principal axis. The direction of the maximum anisotropy of 4b forms an angle of 31° with the PSe bond. The C$_2$ symmetry leads to the suggestion that in 4b one of the methyl groups contributes more to the SOMO than the other two. The extra splitting of 1.25 mT could then be the result of the trans located CH$_2$ hydrogen atom in the mirror plane.

5. Triethylphosphine Selenide (5). The crystal structure of triethylphosphine selenide (5) is isomorphous with that of the corresponding sulfide (2). Triethylphosphine selenide crystallizes in the hexagonal space group $P6_3/mcc$ with unit cell dimensions $a = 9.06$ Å and $c = 6.54$ Å. All PSe bonds of the molecules in the unit cell are directed along the c axis, which is the elongation axis of the needle-shaped crystal.

After X irradiation at 77 K, the ESR spectrum of 5 at 105 K shows the features of two different phosphoranyl radicals 5a and 5b (Figure 6). The intensity of the lines attributed to 5b is appreciably larger than for 5a. Both radicals exhibit a large 31P hyperfine coupling with an additional splitting from three equivalent 1H nuclei. This extra coupling is somewhat larger for 5a, and better resolved, than for 5b. The 77Se satellites are well defined for both species.

![Image of ESR spectrum](image)

**Figure 6.** Single-crystal ESR spectrum of 5a and 5b at 105 K; magnetic field parallel to c axis. The positions of the Se satellites are marked.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Temp (K)</th>
<th>Total Tensor</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>105</td>
<td>g</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
<tr>
<td>5b</td>
<td>105</td>
<td>g</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
<tr>
<td>5b</td>
<td></td>
<td>31P</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
<tr>
<td>5b</td>
<td></td>
<td>77Se</td>
<td>a = 0.875</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c = 0.000</td>
</tr>
</tbody>
</table>
plates. No X-ray crystal structure analysis of this compound has been reported.

The ESR spectrum of an X-irradiated single crystal of 6 (Figure 7) shows the features of an electron-capture phosphoranyl radical (6a) together with a much weaker spectrum of a second radical product (6b). The spectrum of 6a exhibits additional hyperfine splitting from three $^3P$ nuclei with somewhat different coupling constants. The $^7Se$ satellites of 6a are well defined for most orientations.

The ESR reference $y$ axis was chosen perpendicular to the plate face, and the $x$ and $z$ axes were chosen, with the use of a polarization microscope, coincident with the extinction directions of the crystal perpendicular to $y$. When the single crystal is mounted with the $y$ axis parallel to the goniometer axis, a site splitting for 6a and 6b is observed. Coalescence of the differently oriented radicals occurs when the magnetic field direction is parallel to $x$ or $z$. The results of the single-crystal analysis of 6a and 6b are compiled in Table VI. The directions of the largest $^3P$ hyperfine coupling for the two orientations of 6a are inclined by an angle of 25.8° between the two principal $^3P$ hyperfine directions. Annealing of the crystal leads to the irreversible loss of 6b at 140 K and of 6a at 200 K.

**Figure 7.** Single-crystal ESR spectrum of 6a and 6b at 105 K; magnetic field parallel to $z$ axis.

**Table VI.** $g$ and Hyperfine Coupling (MHz) Tensors for 6a and 6b

<table>
<thead>
<tr>
<th>Radical</th>
<th>temp (K)</th>
<th>Total tensor</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>105</td>
<td>$g$</td>
<td>a 0.988 b 0.0 c 0.156</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^3P$</td>
<td>d 2.031 e 0.0 f 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^7P$</td>
<td>g 2.008 h 0.0 i 0.0</td>
</tr>
<tr>
<td>6b</td>
<td>105</td>
<td>$^1H$</td>
<td>j 0.987 k 0.0 l -0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^1H$</td>
<td>m 2.007 n 0.0 o 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^3P$</td>
<td>p 2.047 q 0.0 r 0.0</td>
</tr>
<tr>
<td>6b</td>
<td>105</td>
<td>$^7Se$</td>
<td>s 0.957 t 0.0 u 0.0</td>
</tr>
</tbody>
</table>

This result and the fact that the $^1H$ tensor for 6b is nearly isotropic, suggest that it is a center for a hyperfine interaction from three $^1H$ nuclei with somewhat different coupling constants. The $^7Se$ satellites of 6a are well defined for most orientations.

In the previous sections it was demonstrated that $X$ irradiation of trialkylphosphine sulfides and selenides at low temperature invariably yields a phosphoranyl radical anion with (approximately) $C_1$ symmetry. These anions are rather unstable and at temperatures above 200 K their signals irreversibly disappear from the ESR spectra.

Quantum chemical calculations can, in principle, give additional information on the structure of these radicals. It must be borne in mind that, in general, these calculations are performed on a single isolated radical and that effects of surrounding molecules in the single-crystal matrix are neglected. According to Clark, however, ab initio calculations with a restricted basis set can give a good simulation of radical anions in condensed phases.

**IV. Quantum Chemical Calculations**

In the previous sections it was demonstrated that $X$ irradiation of trialkylphosphine sulfides and selenides at low temperature invariably yields a phosphoranyl radical anion with (approximately) $C_1$ symmetry. These anions are rather unstable and at temperatures above 200 K their signals irreversibly disappear from the ESR spectra.

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**1. Computational Details**

The open-shell calculations were performed using several different quantum chemical techniques. Unrestricted Hartree–Fock (UHF) calculations have been carried out using the GAUSSIAN 80 program. The molecular geometries were optimized in an analytical gradient procedure with respect to all parameters within the symmetry constraints. After annihilation of the largest spin contaminant of the UHF wave function, the expectation value of the $S^2$ operator was always less than 0.7505. Isotropic and anisotropic hyperfine interactions ($A_{sp}$ and $B_{sp}$) were evaluated from the spin-annihilated wave function by computing the expectation values of the corresponding operators.

Additionally, hyperfine couplings were computed from the SOMO, neglecting all lower lying $\alpha$ and $\beta$ MOs. Alternatively, restricted open-shell Hartree–Fock (ROHF) calculations were performed using the GAMESS program package. Configuration interaction (CI) calculations have been carried out using the complete active space.

**References**

(22) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topol, S.; Kahn, L. R.; Popele, J. A. GAUSSIAN 91, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.
(24) Guest, M. F. GAMESS, Computational Science Group, SERC Daresbury Laboratory, Daresbury, Warrington. The calculations were performed on the Cyber 205 computer of the Stichting Academisch Rekencentrum Amsterdam.

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![Figure 8. Directions of the principal $^3P$ hyperfine couplings of 6a and 6b relative to the $x$ and $z$ axes.](image-url)

Figure 8. Directions of the principal $^3P$ hyperfine couplings of 6a and 6b relative to the $x$ and $z$ axes.
Electron-Capture R3PS'- and -Se- Radical Anions

Optimized self-consistently and employed in a full CI treatment using different computational methods.

A CASSCF algorithm of the GAMESS program. In this technique a selection is made of a set of orbitals which are optimized self-consistently and employed in a full CI treatment simultaneously. In all calculations we used a standard 4-31G basis set, augmented with a single set of second-order Gaussians on phosphorus and sulfur. In some calculations diffuse orbitals (s and p) were included in the basis set to allow for the accommodation of the negative charge on sulfur.

2. Results of the Calculations. Quantum chemical calculations were performed for H3PS+ as a model for the observed radical anions. Further, we studied the protonated species H3PSH, H3PSH2+, and H3PSH3+.

a. H3PS-. The UHF calculations predict that within C3v symmetry the three-electron P-S bond is unstable and that the radical dissociates into a neutral PH3 molecule and a S- radical.

At HF/4-31G level, the sum of the total energies of isolated PH3 (E = -341.089 83 au) and S- (E = -396.709 59 au) was 1726 kJ mol-1 below the alternative electron distribution of P3SH (optimized; PH = 1.384 Å, HPH = 112.6°, E = -341.075 48 au) and S- (E = -396.709 59 au). Such a large value for the single-electron transfer energy (ΔEet) implies a large difference between the energy levels of the HOMO of PH3 and SOMO of S- and accounts for the instability of the three-electron bond and its dissociation.

Since the stability of the experimentally observed radical anions may, in principle, be due to matrix interactions preventing dissociation at low temperature, we studied the electronic structure of H3PS- at fixed PS distances. Figure 9 shows the potential energy curves for H3PS- as a function of the PS distance (rps).

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b. H3PSH. Recent calculations by Gonbeau et al. show that a tetrahedral configuration of H3PSH is unstable and results in an immediate elongation of the PS bond, leading to rupture. Our calculations at 4-31G* UHF SCF level confirm this result. Similar to the potential energy curve of H3PS+ we determined the predicted; i.e., at rps = 2.6 Å, A<sub>p</sub> = 1615 MHz and 2B<sub>p</sub> = 87 MHz. The correspondence with experiment, however, remains unsatisfactory.

In order to improve the description of the nonbonding electron pairs on sulfur two sets of diffuse s and p orbitals (exponents 0.1 and 0.01) were added to the sulfur 4-31G* basis set (4-31G*++). This resulted in a lowering of the total UHF energy by ca. 0.05 au (Figure 9) but caused no substantial improvement of the spin density distribution. A similar result was obtained from CI calculations using the CASSCF routine of the GAMESS program on an ROHF wave function (Figure 9). The employed active space consisted of three doubly, one singly, and three unoccupied MOs resulting in 404 configurations. Despite the energy lowering no significant redistribution of spin density was observed.

Before returning to the H3PS+ model, it is worthwhile to study the successively protonated species H3PSH, H3PSH2+, and H3PSH3+. The introduction of one or more protons in the vicinity of the sulfur nucleus will increase the electronegativity of the sulfur ligand. Because of the antibonding character of the three-electron bond, the increased ligand electronegativity will result in a rise in the unpaired electron density near the phosphorus nucleus:

\[ \text{R}_{3}P: \quad \text{L} - \text{R}_{3}P\text{L}^{2}\text{L}^{-} \]

Increasing ligand electronegativity


Figure 9. Total energy of H3PS- within C3v symmetry vs rps using different computational methods.

Figure 10. Calculated isotropic phosphorus hyperfine interaction (A<sub>p</sub> \( ^{10} \)) MHz vs rps for H3PS+ (wave function and SOMO), H3PSH, H3PSH2+, and H3PSH3+.

Figure 11. Calculated dipolar phosphorus hyperfine coupling (2B<sub>p</sub>, MHz) vs rps for H3PS+ (wave function and SOMO) and H3PSH, H3PSH2+, and H3PSH3+.
total energy of $\text{H}_2\text{PS}^-$ as a function of $r_{\text{PS}}$ (Figure 12).

In these calculations the $\text{H}_2\text{P}$ fragment was constrained to a $C_2$ geometry and the sulfur nucleus was positioned in the $C_3$ axis. The sulfur proton was oriented at a fixed $\text{P}$-$\text{S}$ angle of $97^\circ$, one $\text{HSPH}$ dihedral angle being $180^\circ$. All other parameters (PH and SH distance, PH angle) were fully optimized. By computing the total energy of $\text{SH}$ ($\Sigma$ state optimized: $\text{SH} = 1.349 \text{ Å, } E = -397.654 \text{ au}$) and of $\text{SH}^-$ (optimized: $\text{SH} = 1.349 \text{ Å, } E = -397.653 \text{ au}$), and combining these with the energies of $\text{PH}_3$, $\text{PH}_{3}^+$ (vide supra), a value of $\Delta E_{\text{SET}} = 829 \text{ kJ mol}^{-1}$ for $\text{PH}_3 + \text{SH}^- \rightarrow \text{PH}_3^+ + \text{SH}^0$ is obtained. Although significantly smaller than the corresponding value for H$_2$S$^-$, this value of $\Delta E_{\text{SET}}$ is still too large to give rise to a stable three-electron bond. With respect to the spin density distribution, it appears that the isotropic phosphorus hyperfine coupling makes an angle of $31.3^\circ$ with the $\text{PS}$ bond.

d. $\text{H}_3\text{PS}^+$. The potential energy curve of $\text{C}_3\text{H}_2\text{PS}_3^+$ (Figure 12) reveals a rapid dissociation of the $\text{PS}$ bond, in agreement with the large calculated value of $\Delta E_{\text{SET}} = -1026 \text{ kJ mol}^{-1}$ for $\text{PH}_3 + \text{SH}_3^+ \rightarrow \text{PH}_3^+ + \text{SH}_3^+$ which is obtained from the total energies of $\text{PH}_3$ and $\text{PH}_3^+$ (vide supra) and those of $\text{SH}_3^+$ ($\text{C}_2$ optimized: $\text{SH} = 1.373 \text{ Å, } E = -397.832 \text{ au}$) and $\text{SH}_3^-$ ($\text{C}_2$ optimized: $\text{SH} = 1.331 \text{ Å, } E = -398.537 \text{ au}$). During the dissociation, the electronic structure of the complex is essentially equal to that of an isolated $\text{PH}_3^+$ radical, with a minor contribution from the sulfur orbitals.

From these calculations it appears that a stable three-electron bond is formed when the absolute value of $\Delta E_{\text{SET}}$ is small (Figure 13), i.e., for the $\text{H}_2\text{PS}^+$ radical cation. Unfortunately, no experimental analogue of this radical has been reported. In contrast, for the $\text{R}_2\text{PS}^+$ radical anions presented in this paper, and for the $(\text{CH}_3)_2\text{PS}$ and $(\text{CH}_3)_2\text{PSCH}_3$ radicals which are formed in liquid cyclopropane at 170 K, the model calculations predict a rapid elongation of the bond resulting in rupture.

e. $\text{H}_2\text{PS}^-$ in the Presence of Additional Charges. It is clear that the present calculations do not give an adequate simulation of the electronic structure and stability of $\text{R}_2\text{PS}^-$ and $\text{R}_2\text{PSR}$ radicals in condensed phases. A major drawback of the calculations seems to be the rather poor description of the nonbonding electron pairs on sulfur. For this reason we studied the spin density distribution and electronic structure of $\text{H}_2\text{PS}^-$ in the presence of additional point charges. In our ROHF calculations the sulfur 4-31G* basis set was augmented with a single set of diffuse s and p orbitals (exponent 0.1). The $\text{H}_2\text{PS}^-$ radical was placed between a positive and negative charge pair of the same absolute magnitude in the following fixed $\text{C}_3$ orientation:

From the calculated atomic spin density on sulfur and phosphorus as function of the charge $q$ (Figure 14), it appears that with increasing charge the unpaired electron shifts to the phosphorus nucleus. This is the result of the electron-withdrawing positive charge near sulfur, which induces a delocalization of the nonbonding electrons to the outer valence and diffuse orbitals. From Figure 14 it is clear that by an adequate placement of external charges the calculated spin density can be modulated to a range of spin density distributions between phosphorus and sulfur. For $q$ between 3 and 4 au the theoretical spin density distribution is in accordance with the experimental data. The improved correspondence between theory and experiment obtained via the introduction of point charges demonstrates some limitations of ab initio theory when applied to isolated radical anions as

Table VII. Isotropic and Dipolar Hyperfine Couplings (MHz) and Approximate Orbital Spin Densities (%)

<table>
<thead>
<tr>
<th>Radical</th>
<th>$^{31}$P</th>
<th>$^{77}$Se</th>
<th>$^{1}$H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A^{iso}$</td>
<td>$B$</td>
<td>$\rho_{s}$</td>
</tr>
<tr>
<td>1a</td>
<td>1776</td>
<td>245</td>
<td>13.3</td>
</tr>
<tr>
<td>1b</td>
<td>±917</td>
<td>±145</td>
<td>±6.9*</td>
</tr>
<tr>
<td>2a</td>
<td>1659</td>
<td>284</td>
<td>12.5</td>
</tr>
<tr>
<td>3a</td>
<td>1619</td>
<td>283</td>
<td>12.2</td>
</tr>
<tr>
<td>4a</td>
<td>1686</td>
<td>251</td>
<td>12.7</td>
</tr>
<tr>
<td>4b</td>
<td>1490</td>
<td>134</td>
<td>11.2</td>
</tr>
<tr>
<td>5a</td>
<td>1537</td>
<td>276</td>
<td>11.6</td>
</tr>
<tr>
<td>5b</td>
<td>1475</td>
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</tr>
<tr>
<td>6a</td>
<td>1474</td>
<td>300</td>
<td>11.1</td>
</tr>
<tr>
<td>6b</td>
<td>1474</td>
<td>88</td>
<td>11.1</td>
</tr>
</tbody>
</table>

*Calculated for valence orbital couplings (see text).

Figure 14. Atomic spin density on phosphorus and sulfur vs the charge $q$.

Figure 15. Possible TBP-e and $\sigma^*$ structures for $R_3PS^-$ radicals.

V. Discussion

Phosphoranyl radicals generated by radiation-induced electron capture of four-coordinated phosphorus compounds ($R_3P=X$) can, in principle, adopt several different structures. Two frequently observed structures are a trigonal-bipyrzidal configuration with the unpaired electron in an equatorial position (TBP-e) and a tetrahedral $\sigma^*$ structure containing a three-electron bond. Depending on the topology of the distribution of the substituents, two different TBP-e and two $\sigma^*$ configurations can result (Figure 15).

The formation of one of these structures, or an intermediate configuration, depends on the nature of the substituents $R$ and $X$. If the substituents $R$ are not identical, the number of possible configurations increases, and the relative site preference of the substituents $R$ is important. Structures of type I to III have been identified and investigated by single-crystal ESR. The present study on trialkylphosphine sulfide and selenide radical cations forms an angle of 20° with the parent As=S bond, indicating a deviation from $C_3$ symmetry, and the principal hyperfine couplings would not be found parallel to the original P-X bonds.

All the structural data lead to the conclusion that the radicals possess a three-electron PS or PSe bond in which the unpaired electron is located in an axial symmetric antibonding $\sigma^*$ orbital. It is noteworthy that upon annealing no dissociation from the $R_3PS^-$ and $R_3PSe^-$ radicals into $R_3P^+$ radical cations is observed, since rupture of a three-electron bond has been established for other $\sigma^*$ radicals. The trigonal symmetry of the $R_3PX$ radicals differs from the results of Geoffroy et al. on chalcogenetriphenylarsonoranyl radicals ($Ph_3AsX$, $X=O,S,Se$). A detailed study of these species, trapped in single crystals, has shown that the maximum $^{77}As$ coupling forms an angle of 20° with the parent As=S bond, indicating a deviation from $C_3$ symmetry.

Since the spin densities of 1a-3a and 4a-6a are not very sensitive to the nature of the irradiated compound, it can be concluded that a matrix effect is not an important factor for the structure of these radicals.
radicals. Nevertheless, the principal hyperfine couplings and g values reflect, in an elegant way, the symmetry properties of the precursor crystal structures. The complete axial symmetry of the A and g tensors of the radicals 2a and 5a is a result of the hexagonal space group of the crystals of 2 and 5. The radicals 1a, 3a, 4a, and 6a originate from the molecules of $C_2$ symmetry. Although the deviation of the geometry of 4 from $C_{3v}$ toward $C_2$ symmetry is very small and the corresponding phosphoranyl radical 4a possesses a principal axis along the PSe bond (near C3 axis), a very large difference is found for the two perpendicular g values. This must be the result of steric and electronic constraints imposed upon the radical by the surrounding crystal matrix. Similar effects are found for the radicals 1a, 3a, and 6a.

Until now no satisfying assignment can be made to the nature of radical 1b. This radical seems to be formed from 1a upon warming and is relatively stable. The single-crystal analysis and powder spectrum of 1b (Figure 2c) clearly indicate an opposite sign for $A^{14}$ and $B$. Because of the relatively large value of the hyperfine coupling, 1b must be a phosphorus-centered radical. Furthermore, the presence of additional $H$ splitting and the fact that the principal axes of the A and g tensor are parallel to the PS bond of the precursor molecule lead to the suggestion that the three methyl groups remain covalently bonded to the central phosphorus atom. It is unlikely that 1b is a trimethylphosphonium radical cation, since the $(CH_{3})_3P^+$ radical is known to possess approximately 10% 3s and over 90% 3p character. The absolute values of $A_{2p}$ and $B_{2p}$ of 1b are too large to be the result of spin polarization. The reason for a negative value of $A_{4s}$ or $B_{4s}$ remains unclear since there is no obvious explanation to justify extensive inner-shell polarization or a large contribution of a phosphorus 3p, contribution. As radicals 4b, 5b, and 6b are tentatively assigned to a $a^*$-like structure from the molecules of $C_3$ symmetry toward C3, because the direction of 2P and the parent P=Se bond form an angle of 31 and 26º, respectively. This indicates that 4b and 6b possess an intermediate structure between a $a^*$ and TBP-e configuration. The formation of only one orientation of 4b in a crystal of 4, of at least three possibilities, again emphasizes the subtle effects of matrix interactions. In contrast to 4b and 6b, 5b possesses an exact $C_3$ symmetry and can therefore not possess some TBP-e character. In principle, 5b could possess a apical position (TBP-a).

However, the large spin density on selenium (Table VII) argues against this possibility and favors a $a^*$ configuration. The orbital population of 5a and 5b indicate a nearly equal contribution of the selenium $4p_x$ and $4p_y$ orbitals to the SOMO. The large positive value of $\Delta g_2$ for 5b with respect to 5a must therefore originate from a relatively nearby filled e orbital which contains large contributions of the selenium $4p_z$, $4p_y$, and $4p_x$ orbitals. The quantum chemical calculations on an isolated $(H_SPSH)_{2+}$ radical have clearly shown that the three-electron P–S bond is unstable and dissociates into $H_P$ and $S^\cdot$. Even at fixed P distances the theoretical calculations do not reproduce the observed spin density distribution, but tend to localize the unpaired electron entirely on sulfur. It seems questionable that the large differences between computed and observed spin density distribution may be accounted for by the specific conditions inherent in matrix experiments because the nature of the irradiated compound does not seriously affect the experimental couplings. The origin of the deficiency of the theoretical calculations is predominantly due to a poor description of the negative charge on the sulfur atom, i.e., an inadequate description of the sulfur nonbonding electron pairs. This was demonstrated by introducing a positive point charge in the vicinity of the sulfur atom. In this way the theoretical spin density can be brought into accordance with the experimental data. Alternatively, the radical can be protonated ($H_SPSH_2^+$) resulting in a stable three-electron bond and an accurate description of experimental hyperfine couplings. The important effect of the positive charge is to shield the nonbonding electrons and cause a shift of unpaired electron density toward phosphorus.

In view of these results it appears that extreme caution must be used in employing theoretical calculations on isolated radical anions for the simulation of trapped radicals in condensed phases.

Acknowledgment. This investigation has been supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWo). We thank Mr. G. C. Groenenboom and Mr. J. van der Woerd for their assistance in the quantum chemical calculations.