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A Single-Crystal ESR Study on Radicals Derived from rac- and meso-1,2-Dimethyl-1,2-diphenylphosphine Disulfide: Stereochemical Selection in Radical Formation

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Abstract: An ESR study on electron-capture phosphorus centered radicals trapped in single crystals of rac- and meso-1,2-dimethyl-1,2-diphenylphosphine disulfide (MePhP(S)P(S)MePh) is reported. The principal values and axes of the g and hyperfine coupling tensors of the radical anions are determined. It is shown that X irradiation of the two diastereoisomeric compounds results in completely different radical products. The racemate yields a radical product in which the extra electron is asymmetrically distributed over the two phosphorus nuclei, whereas for the meso form exclusively asymmetric electronic configurations are detected.

For many years the formation and structure of free radicals, produced by ionizing radiation, has received much attention. Numerous ESR experiments have been performed to elucidate the principles that determine the electronic structure and molecular geometry of the formed doublet species. This has resulted in a detailed understanding of the role of the nucleus at the radical center and of the influence of the surrounding ligands. Stereochemical aspects, however, are not generally included in these analyses. In the present study we report the formation of phosphorus-centered radicals in single crystals of racemic (R,R and


The molecular conformation of diphosphine disulfides in the solid state is characterized by a trans orientation of the two sulfur nuclei:

\[
\text{S,S)} \quad 6002
\]

nuclei: solid state is characterized by a trans orientation of the two sulfur disulfides and ab initio quantum chemical methods, possesses a symmetrical distribution of the unpaired electron: unpaired electron occupies an antibonding orbital between the two we showed that the radiation process invariably results in the structure, which has been established by both single-crystal phosphorus nuclei, resulting in a three-electron bond. This structure, which has been established by both single-crystal ESR and ab initio quantum chemical methods, possesses a symmetrical distribution of the unpaired electron:

Depending on the nature of the substituents several other primary and secondary radical configurations were also identified. We will now show that the two diastereoisomeric forms of the title compound give rise to completely different radical products upon X irradiation. The radiation process of the racemate involves the formation of a symmetric species with a three-electron P-P bond as described above. The meso form, on the other hand, yields exclusively asymmetric radical configurations in which the unpaired electron is mainly localized on one of the two phosphorus nuclei. The electronic structure of these radicals as determined by an interpretation of the experimental single-crystal ESR results is presented and compared with theoretical calculations.

**Experimental Section**

**Synthesis.** 1,2-Dimethyl-1,2-diphenylphosphine disulfide was synthesized from dichlorophenylphosphine sulfide and methylmagnesium iodide following a procedure analogous to the one described by Maier. The two diastereoisomeric forms were easily separated by extraction of the crude reaction product with ethanol. The meso form, unsoluble in ethanol, was collected by filtration and recrystallized twice from chloroform. Single crystals of the meso form were prepared by slow evaporation of a chloroform solution in a stream of dry nitrogen. The racemic form was recrystallized several times from ethanol. Slow evaporation of an ethanolic solution of the racemate afforded needle-shaped crystals. Larger plate-shaped single crystals, more suitable for ESR experiments, were obtained from a slow evaporation of a pentane solution. Meso: \( \text{H NMR (CDCl}_3 \) \( \delta \) 1.97 (m, 3, CH\(_3\)), 7.58 (m, 3, PhH), 8.13 (m, 2, PhH); 31P NMR (CDCl\(_3\)) \( \delta \) 36.55; MS, m/e (rel intensity) 331 (93), 279 (6), 157 (100), 125 (48); mp 202 °C. Racemate: \( \text{H NMR (CDCl}_3 \) \( \delta \) 2.46 (m, 3, CH\(_3\)), 7.18-7.63 (m, 5, PhH); 31P NMR (CDCl\(_3\)) \( \delta \) 37.62; MS, m/e (rel intensity) 311 (11), 279 (11), 157 (100), 125 (42); mp 144 °C.

**Irradiation and ESR.** Single crystals of rac- and meso-1,2-dimethyl-1,2-diphenyl-phosphine disulfide were mounted on a quartz rod and subsequently sealed in a quartz tube. The crystals were X-irradiated in a glass Dewar vessel containing liquid nitrogen (77 K) with unfiltered radiation from a Cu source operating at 40 kV and 20 mA for 6 h. ESR experiments were performed with a Bruker ER200D spectrometer interfaced with a Bruker Aspect 3000 computer and operating with a X-band standard cavity. Microwave power was set as low as possible, being 2 mW in most experiments. The crystals were rotated perpendicular to the magnetic field with a single-axis goniometer in 10° steps.

**Results and Assignment**

**rac-1,2-Dimethyl-1,2-diphenylphosphine Disulfide (1).** Although there is no conclusive description of the crystal structure of rac-1,2-dimethyl-1,2-diphenylphosphine disulfide (1) it is known that the racemate crystallizes in the triclinic space group PI with two molecules (R,R and S,S) in the unit cell, centrosymmetrically related to each other. After X irradiation of a single crystal of the racemate at 77 K the ESR spectrum recorded at 105 K shows the weak transitions of at least two different radical species (Figure 1). The outermost features can be assigned to the \( m_1 = 1 \) and \( m_2 = -1 \) absorptions of a radical with a hyperfine coupling to two identical phosphorus nuclei (radical 1a). The large phosphorus hyperfine interaction results in a pronounced splitting between the two central \( m_1 = 0 \) lines, due to the non-degeneracy of the \( J = 1 \) doublet (second-order splitting). The second radical product (1b)


(5) The ESR spectra of Figures 1 and 4 were obtained from randomly oriented single crystals that were transferred after the X irradiation at 77 K to an unirradiated sample tube in order to remove the overlapping central absorptions due to the irradiated quartz.

Table I. Hyperfine Tensors of Radicals 1a and 1b in rac-1,2-Dimethyl-1,2-diphosphine Disulfide

<table>
<thead>
<tr>
<th>Radical</th>
<th>(MHz)</th>
<th>Isotropic (MHz)</th>
<th>Dipolar (MHz)</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>122</td>
<td>1213</td>
<td>-91</td>
<td>x: -0.013</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>y: 0.078</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>z: 0.997</td>
</tr>
<tr>
<td>1b</td>
<td>1143</td>
<td>-70</td>
<td>0.990</td>
<td>x: -0.136</td>
</tr>
<tr>
<td></td>
<td>1374</td>
<td>161</td>
<td>0.137</td>
<td>y: 0.988</td>
</tr>
<tr>
<td></td>
<td>803</td>
<td>-239</td>
<td>-0.311</td>
<td>z: 0.668</td>
</tr>
<tr>
<td></td>
<td>867</td>
<td>-175</td>
<td>0.950</td>
<td>x: 0.250</td>
</tr>
<tr>
<td></td>
<td>1456</td>
<td>414</td>
<td>-0.043</td>
<td>y: 0.701</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>z: 0.712</td>
</tr>
</tbody>
</table>

Table II. g Tensors of Radicals 1a and 1b

<table>
<thead>
<tr>
<th>Radical</th>
<th>g</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.994</td>
<td>x: 0.990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y: -0.140</td>
</tr>
<tr>
<td></td>
<td>2.007</td>
<td>z: 0.986</td>
</tr>
<tr>
<td>1b</td>
<td>2.012</td>
<td>x: 0.139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y: -0.086</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>z: 0.986</td>
</tr>
<tr>
<td></td>
<td>2.013</td>
<td>x: 0.139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y: -0.086</td>
</tr>
</tbody>
</table>

Radical 1b exhibits hyperfine interaction of the unpaired electron with a single phosphorus nucleus.

For all orientations of the single crystal with respect to the magnetic field direction only a single spectrum of the two radicals 1a and 1b is observed. This absence of site splitting is in accordance with the presence of a center of symmetry in the unit cell which results in a coalignment of the S-P-P-S linkages of planes (Figure 2). For that purpose one of the ESR reference axes was chosen perpendicular to the plate face, the remaining two (y, z) were directed parallel to the extinction directions in the plate face with use of a polarization microscope. A central absorption due to the irradiated quartz tube prevented the observation of the two m7 = 0 transitions for all orientations of the single crystal. For this reason the hyperfine coupling and g factor of radical 1a were evaluated from the m7 = ±1 lines, and when possible checked with the m7 = 0 position(s). The principal values and direction cosines of the a and g tensors of radicals 1a and 1b are compiled in Tables I and II. It appears that for both species the direction of the maximum A value (Amax) is close to that of the minimum g value. This is expected because it is the direction of the phosphorus 3p orbital contributing to the singly occupied molecular orbital (SOMO).

Radical 1a is attributed to a three-electron-bond radical (Figure 3), based on the hyperfine coupling to two identical phosphorus nuclei and the values of A^iso = 1213 MHz (A^iso = 1/3(Axx + Ayy + Azz) and B_2 = 161 MHz (B_2 = A_{yz} - A^iso)), which are close to the corresponding values of three-electron-bond radicals in X-irradiated tetramethyl-, tetraethyl-, and tetraphenyldiphosphine disulfides (1224 < A^iso < 1395 MHz, 155 < B_2 < 173 MHz). The values of the isotropic (A^iso) and dipolar (B_2) hyperfine couplings are commonly interpreted in terms of atomic valence s and p orbital contributions to the SOMO by comparing the experimental couplings to a set of calculated values for the free atom. This analysis, using the atomic parameters compiled by Morton and Preston, results in p_s = 9.1% and p_p = 21.9% (p/s = 2.4) for each phosphorus nucleus of 1a.

Radical 1b, exhibiting hyperfine irradiated to one phosphorus nucleus, is assigned to a dissociation product resulting from a rupture of the P-P linkage (Figure 3). The estimated spin densities p_s = 7.8% and p_p = 56.3% and the resulting p/s ratio of 7.2 indicate a large contribution of the phosphorus 3p, orbital and a considerable flattening of the original tetrahedral geometry. The experimental hyperfine couplings of 1b are in close agreement with those observed for Ph2PS formed in diphenylphosphine sulfide and with the values of Et2PS in X-irradiated tetraethylidiphosphine disulfide.

The spectrum of radical 1a is irreversibly lost upon annealing above 135 K. Further warming results in the loss of 1b at approximately 170 K.

rac-1,2-Dimethyl-1,2-diphosphine Disulfide (2). The meso form of 1,2-dimethyl-1,2-diphosphine disulfide crystallizes as lozenge-like crystals in the orthorhombic space group Pca with unit cell parameters a = 17.10 Å, b = 10.62 Å and c = 8.59 Å. The four molecules in the unit cell lie on a center of symmetry and are all differently oriented with respect to the crystallographic axes. The ESR spectrum of an X-irradiated single crystal of 2, recorded at 105 K (Figure 4), exhibits a few low-intensity transitions in the central region and strong absorptions in the lateral region. The large splitting between the two groups of signals undoubtedly results from the interaction of the unpaired electron with a phosphorus nucleus. An important difference between the spectra of the meso (Figure 4) and the racemic form (Figure 1) is the absence of two m7 = 0 transitions in the g = 2 region for the first. From this it can unambiguously be concluded that X-irradiation of the meso form, unlike the racemic form, does not result in the formation of a three-electron-bond radical with a symmetrical electron density distribution over the two phosphorus nuclei.

In order to obtain a more detailed analysis of the ESR spectrum, a single crystal of the meso form was rotated in three mutual orthogonal planes. The ESR reference axes were chosen as follows; the z axis points perpendicular from the plane face and the x and y axes coincide with the extinction directions of the crystal in the plate face. Rotation of the crystal in the xy, xz, or yz planes reveals the presence of two sites, symmetrically related to each other. The spectra of the two sites coalesce when the x, y, or z axis is parallel to the external magnetic field direction. In fact, there are four sites corresponding to the four molecules in the unit cell which reduce to two in a crystallographic plane (xy, xz, or yz) and to one site along a crystallographic axis (x, y, or z). Since there is

Figure 5. Angular dependence of the ESR signals due to radicals 2a, 2b, and 2c.

Figure 6. Structure of radicals 2a, 2b, and 2c.

Table III. Hyperfine Tensors of Radicals 2a, 2b, and 2c in meso-1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide

<table>
<thead>
<tr>
<th>Radical</th>
<th>Total Tensor (MHz)</th>
<th>Isotropic Dipolar (MHz)</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1201</td>
<td>1379 -178 -105</td>
<td>0.705 0.624</td>
</tr>
<tr>
<td></td>
<td>1231</td>
<td>1245 0.465 -0.516</td>
<td>0.719</td>
</tr>
<tr>
<td></td>
<td>1705</td>
<td>326 0.879 0.365 -0.306</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>1826</td>
<td>1934 -108 0.978 -0.203</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>1856</td>
<td>-78 0.099 0.683 0.723</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2120</td>
<td>186 0.186 0.701 -0.688</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>2103</td>
<td>2316 -213 0.371 0.357</td>
<td>0.857</td>
</tr>
<tr>
<td></td>
<td>2156</td>
<td>-160 0.844 -0.514 -0.152</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2689</td>
<td>373 0.387 0.780 -0.492</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-25</td>
<td>0.829 -0.559 0.018</td>
<td></td>
</tr>
<tr>
<td>222</td>
<td>83</td>
<td>0.533 0.781 -0.324</td>
<td></td>
</tr>
</tbody>
</table>


Table IV. g Tensors of Radicals 2a, 2b, and 2c

<table>
<thead>
<tr>
<th>Radical</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1.997 0.784 0.460</td>
</tr>
<tr>
<td>2b</td>
<td>2.010 -0.469 0.879</td>
</tr>
<tr>
<td>2c</td>
<td>2.025 0.407 0.126</td>
</tr>
</tbody>
</table>

a large number of signals, which are frequently overlapping, the elucidation of the angular variation of the hyperfine lines was not straightforward. For this reason the low and high field curves were determined as the best fit of a quadratic sine to the experimental magnetic field values, using a least-squares regression analysis. The resulting angular variation of the signals is presented in Figure 5. Going from one rotation experiment to another, there is an ambiguity in the relation between the curves in the two series. This ambiguity results in four possible assignments that are just the four orientations of the same radical in the crystal.

The ESR spectra of the X-irradiated meso form and the angular variation can be interpreted by assuming the presence of at least four different phosphorus-centered radicals. For three species a clear angular variation is observed; a fourth was undoubtably present but could not be analyzed in detail. A remarkable aspect of all radical species encountered in the meso compound is the fact that all hyperfine lines show an additional doublet splitting of 1.8 to 3.0 MHz, probably due to proton splitting. The hyperfine coupling and g tensors of the three species labeled 2a, 2b, and 2c are collected in Tables III and IV. The direction cosines in these tables are listed for only one of the four possible sites. The remaining three orientations are symmetry related to (x, y, z) via (x, -y, -z), (-x, y, -z), and (-x, -y, z).

Radical 2a is assigned to a three-electron-bond P-S radical (Figure 6). The estimated atomic orbital spin densities of the central phosphorus atom $\rho_3 = 0.103$ and $\rho_4 = 0.444$ are relatively close to the values found in recent studies on similar radicals generated in tetrasubstituted diphosphine disulfides and trialkylyphosphine sulfides and selenides.210 The isotropic hyperfine coupling (3s orbital contribution) of 2a (1379 MHz) is somewhat smaller than that for these related species (1619-1776 MHz), whereas the dipolar interaction (3p orbital contribution) is larger (326 MHz vs 245-315 MHz). This results in an increased p/s ratio of 4.3 for 2a, which is probably due to a small widening of the tetrahedral angle between the P-S bond and the bonds with the remaining three substituents.

Radical 2b is characterized by a high isotropic phosphorus hyperfine coupling ($A^{iso} = 1934$ MHz, $\rho_3 = 14.4\%$) and a relatively small dipolar interaction ($B^{iso} = 186$ MHz, $\rho_3 = 23.5\%$) resulting in a p/s ratio of 8.1. Similar species have not been encountered so far in X-irradiated diphosphine disulfides. This complicates the identification of a radical structure for 2b. The relatively low p/s ratio points to a trigonal-bipyramidal (TBP) radical structure, either with an equatorial (TBP-a) or an apical (TBP-a) location of the unpaired electron.13 TBP-a structures, identified in tetramethyl- and tetraethylidiphosphine disulfides, exhibit hyperfine coupling to two phosphorus nuclei and their magnitudes are clearly different from those of 2b.5 We therefore propose a TBP-like species with the SOMO pointing away from one to a second. The value of $m_1$ = 1 and $m_2$ = -1 lines of a phosphorus triplet can be ruled out since the expected $m_3$ = 0 transitions are absent. The weak absorptions in the g = 2 region of the ESR spectra of the meso form (Figure 4) are not related to the strong lateral absorptions because they are found to be much more persistent upon annealing the single crystal. A second possibility, that the large splitting is the result of a radical pair, one of whose components is a phosphoranyl type radical, seems unlikely because no transitions were observed in the half-field region between 70 and 260 mT. This leads to the conclusion that radical 2c is a phosphorus centered radical, exhibiting a large hyperfine coupling to one 31P nucleus and a small one to a second. The value of $A^{iso}$ for the central phosphorus atom is disproportionately low that for the other radicals encountered in X-irradiated diphosphine disulfides. We tentatively assign 2c to a radical with an asymmetric three-electron-P-P bond in which the unpaired electron is mainly localized on one of the two phosphorus nuclei (Figure 6). The spin density distribution, estimated from the hyperfine coupling parameters, amounts to 11.3 Hasegawa, A.; Ohnishi, K.; Sobage, K.; Miura, M. Mol. Phys. 1975, 30, 267.


Table V. Calculated Isotropic and Anisotropic Hyperfine Coupling Constants for R,R
rac- and meso-P3r inclined by an angle of 11.3°. Calculations have shown that the magnitude of the electron-bond phosphoranyl radical can vary strongly with the porting of the three-electron-bond assignment. Quantum chemical calculations show that the value of $A_{iso}$ in a three-electron-bond phosphonanyl radical can vary strongly with the angle between the three-electron bond and the remaining three substituents, possibly accounting for the large $A_{iso}$ of the central phosphorus atom.\(^{(14)}\)

The intensity of the ESR spectra of 2a, 2b, and 2c decreases slowly upon annealing and the signals are irreversibly lost above 240 K.

Quantum Chemical Calculations

In this section we present a quantum chemical description of symmetrical three-electron-bond radicals in racemic and meso diphosphine disulfide radical anions. Since a full calculation on the two diastereoisomeric forms of the title compound would be very time consuming the calculations were restricted to (R,R)- and meso-1,2-dimethylphosphine disulfide, thereby replacing the phenyl groups by hydrogen atoms. Unrestricted Hartree–Fock (UHF) calculations were performed in order to obtain a theoretical geometry at which the hyperfine coupling parameters could be evaluated. Throughout the calculations a split valence 4-31G basis set\(^{(15,16)}\) implemented with a single set of six second-order Gaussians on phosphorus and sulfur was used (radial exponents P 0.55, S 0.65).\(^{(17)}\) The UHF procedure was followed by removal of the last spin contaminant with use of the annihilation operator.\(^{(18)}\)

The molecular geometry of the two diastereoisomeric radical anions was constrained to the point symmetry of the precursor molecules: $C_2$ for R,R and $C_4$ for meso. Except for the CH bond lengths and the HCP bond angles which were simultaneously evaluated by using two variables, all molecular parameters were fully optimized in an analytical gradient procedure. This resulted in true energy minima for both the R,R and meso forms (Figure 7). Their structures are characterized by a relatively long P–P bond of 2.748 A and a SPP bond angle of 142.2°. This elongation of the SPP moiety is a direct result of the antibonding nature of the SOMO of these radicals. The isotropic and anisotropic (dipolar) hyperfine couplings were evaluated from the wave function by computing the expectation values of the corresponding operators.

$$A_{iso} = \frac{8\pi}{3} g\beta \mu_B S_z \left| \langle \Psi_0 | S_z | \Psi_0 \rangle \right|$$

$$B_i = -g\beta \mu_B S_i \left( \frac{r^2}{r^5} \right) \left| \langle \Psi_0 | S_i | \Psi_0 \rangle \right|$$


Resonance Raman Studies of Dioxygen Adducts of Cobalt-Substituted Heme Proteins and Model Compounds. Vibrationally Coupled Dioxygen and the Issues of Multiple Structures and Distal Side Hydrogen Bonding

Alan Bruha and James R. Kincaid*

Contribution from the Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233. Received September 22, 1987

Abstract: The resonance Raman (RR) spectra of the oxygen adducts of cobalt-substituted heme proteins have been carefully studied in the oxygen—oxygen stretching region. Included in the study are the cobalt analogues of myoglobin (MbCo), hemoglobin (HbCo), and its isolated subunits (αCo and βCo) as well as the iron/cobalt mixed heme hybrids, (αCoβFe)2 and (αFeβCo)2.

The spectra of the $^{16}$O$_2$, $^{18}$O$_2$, and scrambled oxygen ($^{16}$O$_2$$^{18}$O$_2$, 1:2:1) adducts have been measured in both normal (H$_2$O) and deuterated (D$_2$O) buffers for each of the proteins. Strong bands located at ~1135, ~1096, and ~1065 cm$^{-1}$ in H$_2$O solution are identified with v($^{16}$O=O), v($^{18}$O=O), and v($^{16}$=18O), respectively. Shifts of these bands in D$_2$O solution and the selective appearance of weaker features in the spectra of particular isotopic oxygen adducts are interpreted as the consequence of vibrational coupling of v(O=O) with internal modes of the proximal and/or the distal histidylimidazole.

The plausibility of this interpretation is supported by the observation of similar behavior in model compound systems which is documented here and in earlier studies. All of the major and minor features observed in the spectra of the proteins can be explained without requiring the existence of two liganded (O$_2$) conformers, in contrast to earlier interpretations. In addition, based on the results of model compound studies, the frequency observed for v(O=O) indicates that the bound dioxygen is hydrogen bonded to the distal histidylimidazole in these protein systems. However, the present interpretation argues that the frequency shifts of v($^{16}$O=O) observed upon replacement of H$_2$O by D$_2$O cannot be taken as evidence for this distal side hydrogen bonding. Finally, it is suggested that the spectroscopic consequences of such coupling not only complicate the interpretation of oxygen adduct spectra but also (in a positive light) may provide a powerful spectroscopic probe of subtle structural perturbations once they are more fully understood and properly calibrated.

The oxygen transport proteins, hemoglobin (Hb) and myoglobin (Mb), are perhaps the most thoroughly studied of all biomolecules. Despite extensive effort by many research groups and an extensive body of accumulated knowledge, questions remain unanswered, even at a rather fundamental level. In fact, knowledge of the details of O$_2$ structure and bonding at the heme site remains incomplete. Thus, issues such as the importance of distal side hydrogen bonding between the bound O$_2$ and the heme pocket remain controversial.

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 G. C. Groenenboom for assistance in the quantum chemical calculations.

Registry No. 1, 13639-75-3; 1a, 115181-91-4; Hb, 115093-24-8; 2, 13639-76-4; 2a, 115181-92-5.