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Citation for published version (APA):

DOI:
10.1021/ja00226a013

Document status and date:
Published: 01/01/1988

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

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Stereochemical Selection in Radical Formation

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

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Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. Received November 23, 1987

Abstract: An ESR study on electron-capture phosphorus centered radicals trapped in single crystals of rac- and meso-1,2-dimethyl-1,2-diphenyldiphenylphosphine 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 diastereoisomic compounds results in completely different radical products. The racemate yields a radical product in which the extra electron is symmetrically 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 (RR and
The molecular conformation of diphosphine disulfides in the solid state is characterized by a trans orientation of the two sulfur nuclei.\(^1\)

In a recent study on X-irradiated tetrasubstituted diphosphine disulfides \((R,P(S)P(S)R)\), also possessing a trans orientation, we showed that the radiation process invariably results in the formation of an electron-capture radical product in which the unpaired electron occupies an antibonding orbital between the two phosphorus nuclei, resulting in a three-electron bond.\(^2\)

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:

\[
\begin{array}{c}
\text{R} \quad \text{P} \quad \text{S} \quad \text{P} \quad \text{S} \quad \text{R} \\
\end{array}
\]

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-diphenyldiphosphine disulfide was synthesized from dichlorophenylphosphine sulfide and methylmagnesium iodide following a procedure analogous to the one described by Maier.\(^3\)

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 solution in a stream of dry nitrogen. The racemic form was recrystallized several times from ethanol. Slow evaporation of the crude reaction product with ethanol. The meso form, unsoluble in ethanol, was collected by filtration and recrystallized twice from 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. 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.

**Results and Assignment**

**rac-1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide (1).** Although there is no conclusive description of the crystal structure of rac-1,2-dimethyl-1,2-diphenyldiphosphine disulfide (1) it is known that the racemate crystallizes in the triclinic space group \(P\) with two molecules \((R,R\) and \(S,S\)) in the unit cell, centrosymmetrically related to each other.\(^4\)

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).\(^5\)

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 indetical 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 \(I = 1, m_1 = 0\) and \(I = 0, m_1 = 0\) energy levels (second-order splitting).\(^6\)

The second radical product (1b)

\[
\text{Mes} \quad \text{R} \quad \text{P} \quad \text{S} \quad \text{P} \quad \text{S} \quad \text{R} \\
\]

Temperature was controlled with the aid of a variable-temperature unit operating between 90 K and room temperature. ESR parameters were obtained from a second-order analysis of the spectra.

**References**


(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-diphenylphosphine Disulfide

<table>
<thead>
<tr>
<th>Radical</th>
<th>Total Tensor (MHz)</th>
<th>Isotropic (MHz)</th>
<th>Dipolar (MHz)</th>
<th>Direction Cosines</th>
<th>Direction Tensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1122 1213 91</td>
<td>-0.013 0.078 0.997</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>803 1042 -175</td>
<td>1.37 0.988 0.075</td>
<td></td>
<td></td>
<td></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>0.990 -0.140</td>
</tr>
<tr>
<td>1b</td>
<td>2.007</td>
<td>0.139 0.986</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.018 -0.086</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.655 0.751</td>
</tr>
<tr>
<td></td>
<td>2.021</td>
<td>-0.236 0.310</td>
</tr>
<tr>
<td></td>
<td>2.013</td>
<td>0.718 -0.583</td>
</tr>
</tbody>
</table>

Figure 3. Structure of radicals 1a and 1b.

Figure 4. Single-crystal ESR spectrum of X-irradiated meso-1,2-di- methyl-1,2-diphenylphosphine disulfide at 105 K.

Radical 1b, exhibiting hyperfine coupling 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 \( \rho_p = 7.8\% \) and \( \rho_p = 56.3\% \) 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 Ph3PS formed in diphenylphosphine sulfide\(^9\) and with the values of Et3PS in X-irradiated tetraethylphosphine disulfide\(^2\).

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.

Radical 1b in the racemic form, unlike the meso 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 plate 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 \( xy, xz, yz \) 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 (\( xy, xz, yz \) and \( z \) 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.

Table III. Hyperfine Tensors of Radicals 1a, 2b, and 2c in meso-1,2-Dimethyl-1,2-diphenylphosphine 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 -1370 -178</td>
<td>-1.05 -0.775 0.624</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>1826 1934 -108</td>
<td>0.978 -0.203 0.057</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>2103 2316 -213</td>
<td>0.371 0.357 0.857</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>2.018 0.887 0.148</td>
</tr>
</tbody>
</table>

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, $p_3p = 14.4\%$) and a relatively small dipolar interaction ($B_{pp} = 186$ MHz, $p_3p = 25.3\%$) resulting in a p/s ratio of 1.8. Similar species have not been encountered so far in X-irradiated diphenylphosphine 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-e) or an apical (TBP-a) location of the unpaired electron.11-13 TBP-e structures, identified in tetramethyl- and tetraethylphosphine disulfides, exhibit hyperfine coupling to two phosphorus nuclei and their magnitudes are clearly different from those of 2b.4 We therefore propose a TBP-a like species with the SOMO pointing away from the substituents (Figure 6).

The third species, radical 2c, exhibits hyperfine coupling to two distinct $I = 1/2$ nuclei. The central phosphorus nucleus apparently bears a large amount of spin density since both the isotropic and anisotropic hyperfine couplings are very large, viz., $A^{iso} = 2316$ MHz and $B_{pp} = 373$ MHz. In fact these values are approximately two times the values of the symmetrical three-electron-bond radical 1a, the racemate (vide supra). Nevertheless, the possibility that the large coupling is the result of a triplet of 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 $^{31}P$ nucleus and a small one to a second. The value of $A^{iso}$ for the central phosphorus atom is appreciably larger than that for the other radicals encountered in X-irradiated diphenylphosphine 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

Table V. Calculated Isotropic and Anisotropic Hyperfine Coupling Constants for \( R,R \) (C) and Meso (C) \( \text{HMeP(S)}(\text{S})\text{MePh}^+ \)

<table>
<thead>
<tr>
<th>radical</th>
<th>nucleus</th>
<th>( \alpha ) iomega MHz</th>
<th>( B )</th>
<th>direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R,R )</td>
<td>( P_1, P_2 )</td>
<td>0.602 1089</td>
<td>( -0.876 ) 189</td>
<td>( -0.402 ) 87</td>
</tr>
<tr>
<td>( )</td>
<td>( S_1, S_2 )</td>
<td>0.011</td>
<td>( 0.811 )</td>
<td>( -0.374 )</td>
</tr>
<tr>
<td>( )</td>
<td>( P_1, P_2 )</td>
<td>0.602 1091</td>
<td>( -0.876 ) 189</td>
<td>( -0.402 ) 87</td>
</tr>
<tr>
<td>}</td>
<td>( S_1, S_2 )</td>
<td>0.011</td>
<td>( 0.811 )</td>
<td>( -0.374 )</td>
</tr>
</tbody>
</table>

*Relative to the system axis in Figure 7.

\( \rho_m = 17.3\% \) and \( \rho_p = 50.8\% \) for the central atom, and \( \rho_m = 1.0\% \) and \( \rho_p = 1.3\% \) for the adjacent phosphorus nucleus. The directions of the dipolar hyperfine couplings of the two nuclei are inclined by an angle of 13° and therefore almost parallel, supporting the three-electron-bond assignment. Quantum chemical calculations have shown that the magnitude of \( \alpha^{\omega} \) in a three-electron-bond phosphoranyl radical can vary strongly with the angle between the three-electron bond and the remaining three substituents, possibly accounting for the large magnitude of \( \alpha^{\omega} \). Unrestricted Hartree-Fock calculations were performed in order to obtain a theoretical framework. The results of these calculations for the \( R,R \) and meso radical anions are compiled in Table V.

The hyperfine properties of the \( R,R \) 1,2-dimethylphosphine disulfide radical anion are in quantitative agreement with experiment. The two phosphorus nuclei hold most of the unpaired electron density. The value for \( \alpha^{\omega} \) is approximately 10% too small compared with radical 1a, whereas the dipolar couplings deviate approximately 17% from experiment. The direction of the largest principal value of the dipolar hyperfine coupling, corresponding to the direction of the phosphorus 3p orbital contributing to the SOMO, makes an angle of 29.1° with the P–P bond. From the direction cosines in Table V it appears that the dipolar couplings of the two phosphorus nuclei are inclined by a small angle of 5.6°. This is a consequence of the \( C_2 \) symmetry of the \( R,R \) radical and indicates that the two phosphorus nuclei are not strictly magnetically equivalent for all orientations of a magnetic field. Although the experiments do not reveal a symmetric three-electron-bond structure for the meso form, the calculations predict a stable geometry for the meso-1,2-dimethylphosphine disulfide radical anion. The hyperfine properties of this radical are very similar to the \( R,R \) couplings. However, by symmetry constraint \( (C_2) \) the principal directions of the dipolar couplings are now completely aligned and hence the phosphorus nuclei are magnetically equivalent.

Discussion

The present study reveals that there are major differences between the radicals generated in rac- and meso-1,2-dimethyl-1,2-diphenyldiphenylphosphine disulfide. It is noteworthy that, besides a difference in the nature of the radical configurations, stronger ESR absorptions are found for the meso form than for the racemate, indicating a more efficient electron-capture process. There is no doubt that some variations in the radical configurations between racemate and meso could be expected in advance, because in principle the two diastereoisomers are different compounds. However, their difference is small since it concerns merely the stereochemistry around the phosphorus nuclei. The formation of a specific radical product is usually explained by taking into account the different properties of the substituents such as electronegativity. These arguments cannot be used to account for
the present observations. The fact that no symmetrical three-electron-bond species are detected for the meso form can also not be explained by a possible wrong symmetry of the expected SOMO with respect to geometry of the parent molecule. In fact the $C_i$ point symmetry fits excellently to a hypothetical symmetric antibonding orbital. This is confirmed by the quantum chemical calculations that predict stable geometries for both the racemic and meso form.

Apparently, the addition process of an extra electron to the diposphine disulfides is able to discriminate between the several possible radical configurations in a highly selective way. It is conceivable that the differentiation in the formation of the various electronic and geometric radical configurations is a consequence of the kinetics of the electron-capture process, rather than the result of (small) differences in total energy between the final radical products. In general electron-capture will lead to detectable electron-gain centers provided there is a relatively fast relaxation of the electron acceptor. The relaxation may take the form of bond stretching or bending, or bond breaking, and it should lead to sufficiently deep traps to give detectable radical species. A possible explanation for the formation of a symmetric species in the racemate and asymmetric structures in the meso form can be obtained by assuming that the extra electron reacts with the parent molecules from a direction perpendicular to the plane of the phosphorus and sulfur nuclei. The electron will then first encounter one methyl and one phenyl group for the meso molecules and two methyl or two phenyl groups for the enantiomers $R,R$ and $S,S$. Discrimination between a symmetric and an asymmetric radical product can then be rationalized by a difference in the rate of molecular relaxation (e.g., bond bending) in the solid state between the small methyl group and the large phenyl substituent. For the meso form the electron adds preferentially to the side of the methyl group rather than to the side with the phenyl substituent, resulting in an asymmetric radical configuration. For the molecules of the racemate ($R,R$ and $S,S$), there is no difference between the relaxation rate of the two sides of the molecule and hence a symmetric electron-capture product is formed.

In the light of the present results further experimental and theoretical study on stereochemical selection in radical formation will be necessary.

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; Ib, 115093-24-8; 2, 13639-76-4; 2a, 115181-92-5.

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 23, 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 (aCO and $b_2$CO) as well as the iron/cobalt mixed heme hybrids, ($a_2$CO$b_2$) and ($a_2$CO$b_2$). The spectra of the $^{16}$O$_2$, $^{18}$O$_2$, and scrambled oxygen (30% $^{18}$O$_2$ and 70% $^{16}$O$_2$) adducts have been measured in both normal (H$_2$O) and deuteriated (D$_2$O) buffers for each of the proteins. Strong bands located at $\sim$1135, $\sim$1096, and $\sim$1065 cm$^{-1}$ in H$_2$O solution are identified with $\nu(\text{oxygen-oxygen})$ of $^{16}$O$_2$, $\nu(\text{oxygen-oxygen})$ of $^{18}$O$_2$, and $\nu(\text{oxygen-oxygen})$ of scrambled 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 $\nu$(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 $\nu$(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 $\nu$(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 intensive 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.