A single-crystal ESR study on radicals derived from rac- and meso-1,2-dimethyl-1,2-diphenyldiphosphine disulfide: stereochemical selection in radical formation

Janssen, R.A.J.; Woerd, van der, M.J.; Aagaard, O.M.; Buck, H.M.

Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja00226a013

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 author's 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.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 31. Jul. 2017


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 Selection in Radical Formation

René A. J. Janssen,* Mark J. van der Woerd, Olav M. Aagaard, and Henk M. Buck

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-diphenylphosphine Disulfide: Stereochemical Selection in Radical Formation

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 \( S,S \) phosphorus disulfides.

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

**René A. J. Janssen,* Mark J. van der Woerd, Olav M. Aagaard, and Henk M. Buck**

*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-diphenylphosphine disulfide (MePhP(S)S(P)(S)MePh) is reported. The principal values and axes of the hyperfine coupling tensors of the radical anions are determined. It is shown that X-ray radiation of the two diastereoisomeric phosphorus-centered radicals in single crystals of racemic (R,R) and (S,S) phosphorus disulfides 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.
S,S) and meso (R,S) 1,2-dimethyl-1,2-diphenylphosphine disulfide.

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

\[
\text{Solid state is characterized by a trans orientation of the two sulfur disulfides}
\]

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. 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:

\[
\text{In 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: \(\text{H NMR (CDCl}_3) \delta 1.97 (m, 3, CH\text{H}), 7.58 (m, 3, PhH), 8.13 (m, 2, PhH); \text{P NMR (CDCl}_3) \delta 36.55\) (rel intensity) 111 (93), 279 (6), 157 (100), 125 (42); mp 202°C. Racemate: \(\text{H NMR (CDCl}_3) \delta 2.46\) (m, 3, CH\text{H}), 7.18-7.63 (m, 5, PhH); \text{P 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-diphenylphosphine 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

\(\text{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 P\text{I}\text{I} 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 \text{ and } m_2 = -1 \text{ 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 \text{ lines, due to the non-degeneracy of the } J = 1, m_2 = 0 \text{ and } J = 0, m_2 = 0 \text{ energy levels (second-order splitting). The second radical product (1b) is presented and compared with theoretical calculations.}


(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.

The table of hyperfine tensors exhibits hyperfine coupling to one 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 the R,R and S,S planes (Figure 2). For that purpose one of the ESR reference positions was chosen as follows; rotation of the crystal in the (x,y) planes reveals the presence of two sites, symmetrically related to each other. The experimental hyperfine couplings of 1b are in close agreement with those observed for Ph3PS formed in diphenylphosphine sulfide and with the values of Et3PS in X-irradiated tetraethylphosphine disulfide.2

The spectrum of radical 1a is irreversibly lost upon aneeding above 135 K. Further warming results in the loss of 1b at approximately 170 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 \( \rho_3 = 7.8\% \) 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 coupling of 1b are in close agreement with those observed for Ph3PS formed in diphenylphosphine sulfide and with the values of Et3PS in X-irradiated tetraethylphosphine disulfide.2

The spectra of the two sites coalesce when the x, y, and 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

---

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 undoubtly 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 2.1 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 $\rho_{2a} = 10.3$ and $\rho_{3s} = 44.4$% are relatively close to the values found in recent studies on similar radicals generated in tetrasubstituted diphosphine disulfides and trialkylphosphine sulfides and selenides.\(^{(10)}\) The isotopic 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 ($A^{3p} = 1934$ MHz, $\rho_{2b} = 14.4$%) and a relatively small dipolar interaction ($B_{2b} = 186$ MHz, $\rho_{2b} = 25.3$%) resulting in a p/s ratio of 1.8. 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-e) or an apical (TBP-a) location of the unpaired electron.\(^{(11)}\) TBP-e structures, identified in tetramethyl- and tetraethyldiphosphine disulfides, exhibit hyperfine coupling to two phosphorus nuclei and their magnitudes are clearly different from those of 2b.\(^{(5)}\) 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 $I = \frac{1}{2}$ 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., $A^{3p} = 2316$ MHz and $B_{2c} = 373$ MHz. In fact these values are approximately two times the values of the symmetrical three-electron-bond radical 1a (vide supra). Nevertheless, the possibility that the large coupling is the result of the splitting of the $m_{I} = 1$ and $m_{I} = -1$ lines of a phosphorus triplet can be ruled out since the expected $m_{I} = 0$ 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 $^{31}$P nucleus and a small one to a second. The value of $A^{3p}$ for the central phosphorus atom is appreciably larger than 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

$$100 \times \sqrt{A_{i}^2 \rho_{i}^2 + \sum_{j=1}^{3} A_{j}^2 \rho_{j}^2}$$

where $A_{i}$ are the hyperfine coupling constants and $\rho_{i}$ are the spin densities for the phosphorus nuclei.


rac- and meso-MePhP(S)P(S)MePh

| Table V. Calculated Isotropic and Anisotropic Hyperfine Coupling Constants for $R,R$ (C) and Meso (C) HMeP(S)P(S)MeH$^+$ |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| radical nucleus | $A^{iso}$ au MHz | $B$ x y z au MHz | direction cosines$^a$ |       |       |       |
| $R,R$ P$_1$, P$_2$ | 0.602 1089 | -0.876 189 | 0.486 ±0.049 | 0.873 |       |       |
|                  |                | -0.402 -87 | -0.022 ±0.999 | -0.044 |       |       |
|                  |                | -0.474 -102 | -0.874 ±0.002 | 0.486 |       |       |
|                  |                | 0.811 0.170 | ±0.025 0.985 |       |       |       |
|                  |                | -0.374 -0.069 | ±0.997 0.013 |       |       |       |
|                  |                | -0.437 -0.983 | ±0.066 0.172 |       |       |       |
| meso S$_1$, S$_2$ | 0.011 | 0.811 0.169 | ±0.020 0.985 |       |       |       |
|                  |                | -0.374 -0.068 | ±0.998 -0.008 |       |       |       |
|                  |                | -0.437 -0.983 | ±0.065 0.170 |       |       |       |

$^a$Relative to the axis system in Figure 7.

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 diastereoismeric forms of the title compound would be very time consuming the calculations were restricted to $R,R$- and meso-1,2-dimethylidiphosphine 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 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 diastereoismeric radical anions was constrained to the point symmetry of the precursor molecules: C$_s$ for $R,R$ and C$_s$ 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 Å 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.

$A^{iso} = (8\pi /3)\sum g_{NN}\beta_N \left\langle \Psi_0 | \delta_{ij} \frac{r_i^3}{r_j^3} | \Psi_0 \right\rangle$

$B_{ij} = -\sum g_{NN}\beta_N \left\langle \Psi_0 | \frac{r_i^3}{r_j^3} \delta_{ij} | \Psi_0 \right\rangle$

After diagonalization of the $B$ matrix the three principal values are obtained, together with their directions relative to the molecular 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-dimethylidiphosphine disulfide radical anion are in quantitative agreement with experiment. The two phosphorus nuclei hold most of the unpaired electron density. The value for $A^{iso}$ 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$_s$ 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-dimethylidiphosphine disulfide radical anion. The hyperfine properties of this radical are very similar to the $R,R$ couplings. However, by symmetry constraint (C$_s$) 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-dimethylidiphosphine 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 nucleus. The formation of a specific radical product is usually explained by taking into account the different properties of the substrates such as electronegativity. These arguments cannot be used to account for
the present observations. The fact that no symmetrical triple-
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
point symmetry fits excellent to a hypothetical symmetric an-
tibonding 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
diphosphine 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
and geometric radial configurations is a consequence of a
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 sub-
stituent, 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 fi-
ncial aid from the Netherlands Organization for the Ad-
vancement of Pure Research (ZWO). We thank G. C. Groe-
nenboom 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 (αc and βc) as well as the iron/cobalt mixed heme hybrids, (αcβcPFe2) and (αcβcPFe2).
The spectra of the 16O2, 18O2, and scrambled oxygen (16O2·18O·18O·18O·2:1:1) adducts have been measured in both normal
(H2O) and deuterated (D2O) buffers for each of the proteins. Strong bands located near -1135, -1098, and -1065 cm⁻¹
in H2O solution are identified with v(16O2·18O2), v(18O2·18O2), and v(18O2·18O2), respectively. Shifts of these bands in D2O 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 (O2) 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(16O2·18O2) observed upon replacement of H2O by D2O 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 biomolec-
ules. Despite intensive effort by many research groups and an
extensive body of accumulated knowledge, questions remain un-
answered, even at a rather fundamental level. In fact, knowledge
of the details of O2 structure and bonding at the heme site remains
incomplete. Thus, issues such as the importance of distal side
hydrogen bonding between the bound O2 and the heme pocket


The oxygen transport proteins, hemoglobin (Hb) and myoglobin
(Mb), are perhaps the most thoroughly studied of all biomolec-
ules. Despite intensive effort by many research groups and an
extensive body of accumulated knowledge, questions remain un-
answered, even at a rather fundamental level. In fact, knowledge
of the details of O2 structure and bonding at the heme site remains
incomplete. Thus, issues such as the importance of distal side
hydrogen bonding between the bound O2 and the heme pocket

(1) Hemoglobin: Antonini, E., Rossi-Bernardi, L., Chiancone, E., Eds.;

(2) Mims, M. P.; Porras, A. G.; Olsen, J. S.; Noble, R. W.; Peterson, J.


(8) Potter, W. T.; Tucker, M. P.; Houichens, R. A.; Caughey, W. S.
Biochemistry 1987, 26, 4659.

0000-7863/88/1510-6006$01.50/0 © 1988 American Chemical Society