126.5, 90.1, 1.0 ppm. ^{1}H NMR (CCl_4); δ 7.33 (m, 5 H), 4.68 (s, 1 H), 0.20 (s, 9 H). Mass spectrum: *m/e* 223 (19%, $Mn(CO)_6^+$), 179 (68, $[CH(C_6H_5)(OSi(CH_3)_3)]^+$), 106 (91, $(C_6H_5CHO)^+$), 105 (100, $(C_6H_5CO)^+$).
(17) IR (cm^{-1}, $CHCl_3$): ν_{O-H} 3610–3260 (s, br); $\nu_{C\equiv O}$ 2116 (m), 2052 (m, sh), 2016 (vs); $\nu_{C=O}$ 1639 (m). ^{1}H NMR ($CDCl_3$): δ 7.5 (5 H), 6.2 (1 H), 5.0 (1 H).
(18) IR (cm^{-1}, hexane): 2118 (m), 2024 (vs), 2005 (s). ^{13}C NMR (CD_2Cl_2): 195.9, 129.9, 125.7, 123.0, 74.8, 1.1 ppm. ^{1}H NMR (CD_2Cl_2): δ 7.30 (s, 5 H), 6.07 (s, 1 H), 0.71 (s, 9 H). Mass spectrum: *m/e* 196 (8%, $HMn(CO)_5^+$), 195 (4, $Mn(CO)_5^+$), 179 (12, $[CH(C_6H_5)(OSi(CH_3)_3)]^+$), 106 (100, $(C_6H_5CHO)^+$).
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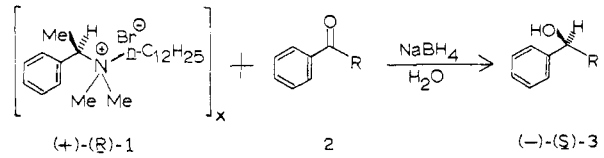
Micelle-Enzyme Analogy: Stereochemical and Substrate Selectivity

Sir:

Stabilizing forces, solution properties, and catalytic activities of aqueous micelles tend to parallel the corresponding characteristics of globular enzymes, thereby constituting the basis of an intriguing and potentially useful analogy.[1-4] The stereochemical component of the analogy, however, is not well established, although aqueous micellar systems have been observed to display manifestations of stereochemical effects consistent with enzymic behavior: the rate and stereochemical course of nitrous acid deamination of 2-aminooctane is significantly affected by micellization;[5a] rapid and selective hydrolyses of enantiomeric *p*-nitrophenyl esters are promoted by nonracemic micelles;[5b] and micelles formed from anionic surfactants materially alter the nonmicellar stereochemistry and hydrolysis rates of water-soluble sulfonates.[5c]

This communication describes some preliminary results which strengthen the micelle-enzyme analogy, for they clearly show the presence of the enzyme characteristics of stereochemical and substrate selectivity in the aqueous micellar system formed from enantiomerically pure (+)-(*R*)-*N*-dodecyl-*N*,*N*-dimethyl-α-phenylethylammonium bromide[6] (**1**) in a way different from previous examples.

Each of the phenyl ketones, **2**, (1×10^{-2} M), solubilized by **1** ($1\text{-}2 \times 10^{-2}$ M), was reduced slowly (~24 h) by the action of sodium borohydride (6×10^{-3} M) at room temperature to the corresponding carbinol, **3**, which was isolated, purified



(+)-(R)-1 2 (−)-(S)-3

(silicic acid chromatography), and identified by comparison with authentic material. Each carbinol was determined to be optically active, and the chiroptical data, which are given in Table I, show micellar **1** to possess the enzymic properties of stereochemical and substrate selectivity.

Stereochemical selectivity is manifest by the fact that the enriched enantiomer of each levorotatory nonracemic carbinol, **3**, possesses the same absolute configuration.[7-9] This suggests that solubilization (binding) of each prochiral ketone by micellar **1** is not only stereochemically ordered (on the time average) but ordered in the same absolute stereochemical sense, favoring reduction at the *re* face of each carbonyl plane. Substrate selectivity is indicated by the dependence of the level of stereoselectivity on the ketonic structure.

While the variation in enantioselectivity among the ketonic substrates is fairly large, ranging over a factor of 12, the absolute levels are all very low. Can such low levels of enantioselectivity have any significance? The fact that each ketone is reduced in the same absolute spatial sense appears to attest to the significance of the results, the low levels not withstanding. Micelles and their surfactant monomers exist in dynamic equilibrium,[4] making it remarkable perhaps that the effects of what must be a net, time-averaged stereochemical ordering in the molecular aggregates can be seen at all. The low levels of enantioselectivity may well be a true reflection of the ability of such dynamic associations to transfer stereochemical influence in the manner required by these experiments. We are, however, continuing to search for combinations of surfactants, substrates, and reactions conditions which will maximize the stereochemical features displayed by the present system.

Table I. Chiroptical Data

R	3, observed $[\alpha]^{22}_D$	*c*	solvent	3, maximum $[\alpha]_D$	*t*, °C	*c*	solvent	enantioselectivity, % $([\alpha]/[\alpha]_{max})$
Me	−0.075 ± 0.038	5.230	benzene	−50.6[a]	27	3.00	toluene	0.14 ± 0.08
Et	−0.200 ± 0.040	5.010	benzene	+40.05[b]	17–20	5.00	benzene	0.50 ± 0.10
Pr^n	−0.723 ± 0.042	4.980	benzene	+43.6[b]	17–20	5.00	benzene	1.66 ± 0.10
Pr^i	−0.194 ± 0.039	5.150	ether	+48.3[c]	23	6.7	ether	0.40 ± 0.08
Bu^t	−0.476 ± 0.048	4.200	acetone	+30.6[d]	23	3.593	acetone	1.56 ± 0.16

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10.12. Found: C, 66.10; H, 9.98. Critical micelle concentration = 4.3 ± 0.1 × 10^{-3} M (25 °C, surface tension).
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Structural Changes upon Oxygenation of an Iron(II)(porphyrinato)(imidazole) Complex

Sir:

Structural effects of metal ligation are a central theme of metalloporphyrin stereochemistry.[1] Of particular interest in interpreting structure/function relationships of hemoproteins are precisely determined, five-coordinate, imidazole porphyrinato iron(II) complexes and their dioxygen adducts. We report here the structure of such a five-coordinate complex[2,3] Fe(TpivPP)(2-MeIm)·C_2H_5OH, I (Figure 1), and its six-coordinate dioxygen adduct[3] $Fe(O_2)$(TpivPP)(2-MeIm)·C_2H_5OH, II, which provide the first direct observation of the structural changes occurring upon oxygenation.[4,5] Studies of I and II, which are models for the low affinity, "T", conformation of hemoglobin,[6] reveal the effects of axial base restraint in the binding of O_2 to metalloporphyrins. In solution, axial base restraint leads to decreased O_2 affinities.[7] We now show the structural effects, which include an increase in the Fe-O bond length (Figure 2).

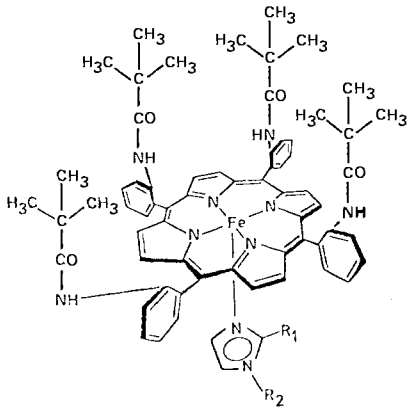

Figure 1. The "picket fence" metalloporphyrin: Fe(TpivPP)(1-MeIm). (R_1 = H, R_2 = H); Fe(TpivPP)(2-MeIm) (R_1 = CH_3, R_2 = H).

Several differences in the structures of the five-coordinate, high-spin, porphyrinato iron (II) complex I and the related Fe(TPP)(2-MeIm)·EtOH complex[1] are apparent. The Fe-N_{1m} separation is considerably shorter (by 0.066 Å) for I than for Fe(TPP)(2-MeIm).[1] This is attributable in part to the more nearly eclipsing conformation which the imidazole plane adopts with respect to the Fe-N_p bonds for the latter complex. In addition, the "doming" of the porphyrinato skeleton is much smaller for I than for Fe(TPP)(2-MeIm): 0.03 Å vs. 0.15 Å. There is, instead, considerable buckling of the porphyrinato skeleton to accommodate the 2-MeIm ligand: the mean displacement from the 24-atom least-squares porphyrinato plane is 0.056 Å in I.

The structural accommodation of the 2-MeIm ligand in the O_2 adduct, II, occurs in several ways. The 2-MeIm ligand causes lengthened axial bonds relative to the sterically undemanding 1-MeIm ligand; the sum of the Fe-N_{1m} and Fe-O separations is 4.005 Å in II, but only 3.813 Å in $Fe(O_2)$(TpivPP)(1-MeIm).[8] Of this 0.192-Å difference, most (0.150 Å) arises from the lengthening of the Fe-O bond to a value similar to that in unstrained Co-O_2 complexes.[9] This lengthened metal-oxygen distance may be correlated with the decreased O_2 affinities in solution which have been observed in Fe(Tpiv PP) systems with hindered imidazoles.[7] For II, the compromise between minimum destabilizing nonbonding contacts and maximum bonding results in the iron atom remaining 0.086 Å out of the plane *toward the imidazole ligand*, in contrast to $Fe(O_2)$(TpivPP)(1-MeIm)[8] where the Fe atom is displaced a slight 0.030 Å *toward the O_2 ligand*. The porphyrinato-dioxygen nonbonding contacts are not significantly different between II and $Fe(O_2)$(TpivPP)(1-MeIm).[10] Further adjustment for the steric hindrance of the 2-MeIm group is made by significant buckling of the porphyrinato skeleton: the mean displacement from the least-squares plane is 0.066 Å in II (0.010 Å larger than in I). The O_2 ligand is again[8] found coordinated in the bent, end-on fashion, with fourfold disorder (the occupancy ratio of the two crystallographically independent positions is 0.60:0.40 at room temperature). Lower bounds for the O-O bond lengths and upper bounds for the Fe-O-O bond angles are 1.21 (2) and 1.23 (2) and 129 (1) and 129 (2)°, respectively; these values are uncorrected for the effects of thermal motion and a possible, irresolvable disorder of the coordinated oxygen atom.

Distinct changes in the immediate coordination sphere occur upon oxygenation. There are the expected contractions in Fe-N_p and Ct··N_p separations, as well as a general contraction of the porphyrinato core (average change, 0.04 Å), attributable to a high-spin to low-spin transition of the iron atom. The iron atom moves 0.316 Å toward, *but not into*, the porphyrinato plane, while preserving the Fe-N_{1m} separation. Nonbonding porphyrinato-imidazole contacts show decreases of up to 0.27 Å—evidence for strong bonding in low-spin, six-coordinate, iron porphyrinato complexes. The 2-MeIm group adjusts for

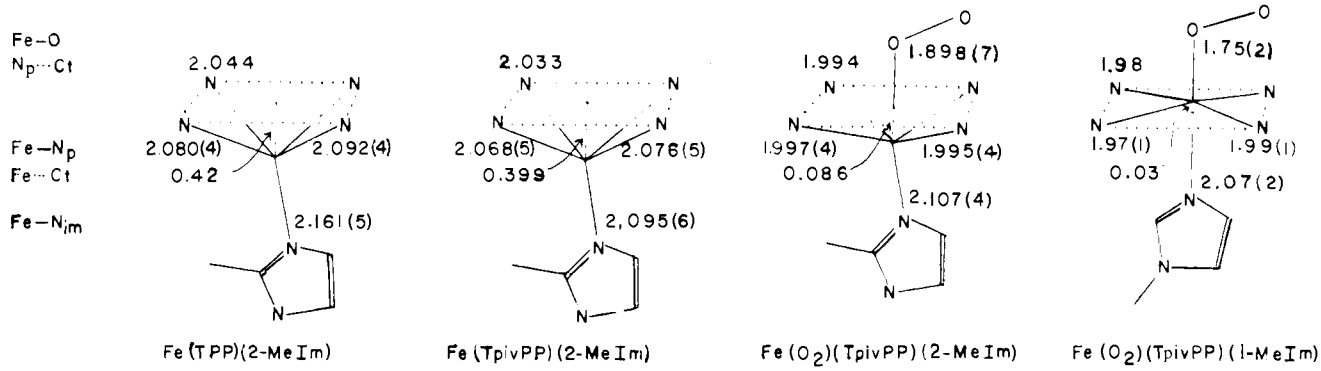

Figure 2. Selected distances (angstroms) in the coordination spheres of Fe(porphyrinato)(imidazole) and Fe(O)(porphyrinato)(imidazole) complexes.

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