mixing in an antibonding manner. In essence σ_2 has Co–C bonding and Co–N antibonding character. Finally σ_3, **4**, is both Co–C and Co–N antibonding. This latter MO may be also viewed as one member of the e_g set (z^2 and xy) of an octahedral complex.

In Figure 1A, the effects of Co–N bond elongation on the σ levels (Co–C maintained at 2.05 Å) are easily understood. In the lower energy region, below the populated octahedral t_{2g} set, σ_1 rises due to the loss of M–N bonding whereas σ_2 falls slowly because of its partial M–N σ^* character. For the same reason σ_3 also falls. The other e_g level (xy) is unaffected. Finally, two π^* combinations of the equatorial ligands,[9] located between t_{2g} and e_g, are unimportant for our considerations. What matters is that the total energy variation[10] is not large since σ_1 and σ_2 have opposite behavior and lie below the frontier region. In agreement with more sophisticated calculations,[3] a Co–N elongation from 2.1 to 2.4 Å costs only 6–8 kcal/mol. In terms of the σ interaction between the combining fragments L_5M[11] and CH_3,[12] **5**, the larger the p_z–z^2 mixing at the metal atom, the more developed is the σ lobe of L_5M and the better is the overlap with $\sigma(CH_3)$. The pd hybridization in L_5M increases with the amount of antibonding introduced by the axial ligand.[9] In the present case it depends on the relative position of the amide group and on its strength as a base, in agreement with point iii above.

Next the Co–C bond is elongated with Co–N set at 2.1 Å (Figure 1B). The level σ_1, Co–N bonding, is hardly affected, whereas σ_2 destabilizes because it loses Co–C bonding energy. The Co–C antibonding σ_3 MO stabilizes.[13] When the Co and C atoms are definitely separated (Co–C > 3.6 Å), the MOs σ_2 and σ_3 coincide with the CH_3 and L_5M lobes which combine in **5**. In other words, σ_2 and σ_3 correlate with the methyl and pd metal hybrids, respectively. As a consequence, the two Co–C bonding electrons in σ_2 become more and more localized in the methyl group. Were the process not obstructed by a significant energy increase (mainly that lost by the two electrons in σ_2), the Co–C cleavage would be heterolytic with formation of a methyl anion and a square-pyramidal d^6 metal complex.

As mentioned, the hybridization and energy of the L_5M σ orbital are strongly dependent on the position of the trans axial ligand. It may happen that for a certain Co–N elongation the final relative positions of σ_2 and σ_3 levels are reversed. Figure 1C shows the evolution of the MOs for the Co–C elongation, with Co–N fixed at 2.4 Å. Apparently, the solid lines behave similarly to Figure 1B but the smoothness of the σ_2 and σ_3 curves hides an essential feature: namely, a strongly *avoided crossing* region. According to electron transfer reaction theory,[14] this region accounts for the possibility of promoting a *sudden electron jump*. In other words, rather than having an ionic separation of the fragments (CH_3^- and L_5Co^{III}), the system may convert into a radical pair (CH_3^0 and L_5Co^{II}). In order to switch character the two levels, σ_2 and σ_3 must intermix. A Mulliken analysis of the atomic charges confirms that a major variation is associated with the dashed lines region. In fact, for the diamagnetic ground-state model with short Co–C and Co–N bonds, the charge of the carbon atom is somewhat negative and that of the metal slightly positive. As the Co–C bond lengthens, the carbon atom becomes smoothly more negative and the cobalt atom more positive. However, for a stretched Co–N bond (e.g., 2.4 Å), the carbon becomes more positive and the metal negative due to a progressively larger metal character in the doubly populated σ_2 orbital.

The monoelectronic wavefunctions in EHMO are inadequate in evaluating reliable energetics associated with the *sudden electron jump*. The energy of the diradical system is computed to be about 60–70 kcal/mol higher than that of the diamagnetic octahedral structure. However, in response to changes in relevant interelectronic effects, it may be profitable to promote an electron in a higher level so that the total energy loss is compensated. The process is probably analogous to the dissociation of Na–Cl into Na and Cl atoms.[15]

In conclusion, we have gained some idea of the conditions required for Co–C homolysis in coenzyme B_{12}. A weakening of the trans Co–N bond forces the carbon and metal orbitals to mix at nonbonding distances and is the necessary step for the genesis of the alkyl radical. The energetics required for such a Co–N weakening are low and the activation may be provided by minor conformational rearrangements introduced by the binding of coenzyme to apoenzyme or the binding of substrate to holoenzyme.[1]

Acknowledgment. L.G.M. thanks the NIH for support through Grant GM 29225.

(9) The levels are largely in-phase (S) and out-of-phase (A) combinations of a π^* orbital of the ligand HN=CH—CH=NH.

(10) The EHMO method assigns an absolute energy minimum at Co–C and Co–N distances both equal to 2.0 Å.

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(13) Crossings of σ_2 and σ_3 with t_{2g} and ligand π^* levels have no major consequences.

(14) The argument is exhaustively treated in the textbook: Salem, L. *Electrons in Chemical Reactions: First Principles*; Wiley-Interscience: New York, 1982. For a more specific theoretical treatment of electron-transfer reactions concerning metal elements, see: (a) Burdett, J. K. *Inorg. Chem.* **1978**, *17*, 2537. (b) Burdett, J. K. *Comments Inorg., Chem.* **1981**, *1*, 85.

(15) An MO treatment also leads to the wrong products (Na^+ and Cl^- ions) but the problem is solved at the VB level by mixing ionic and covalent contributions to the wavefunction.[12]

Probing the Binding Site of Bacteriorhodopsin with a Fluorescent Chromophore

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The discovery of bacteriorhodopsin (bR), the protein pigment of the purple membrane of the halophilic microorganism *Halobacterium halobium*,[1] had a significant impact on the field of bioenergetics and on the study of visual photochemistry.[2] It was found that photobiological activity of bR is due to a pigment consisting of a retinal (all-trans) chromophore covalently bound to a protein through a protonated Schiff base.

Electrostatic interactions in the binding site of bacteriorhodopsin play an important role in its function and properties. Its red-shifted absorption (relative to a protonated Schiff base in methanol solution) was attributed in part to a weaker interaction between the positively charged Schiff base nitrogen and its counteranion[3] and to electrostatic interaction of the retinal polyene with a dipole introduced by the protein in the vicinity of the β-ionone ring.[3d,4] The electrostatic interaction may also play a role in catalyzing the thermal isomerization of all-trans to 13-*cis*-bR in the dark adaption reaction and in the thermal isomerization of the M_{412} intermediate.[5] In addition, it was proposed[6] that the reduction

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Table I. Absorption and Emission Spectra of Chromophore **1** in Various Solvents

solvent	λ_{max}, nm	λ_{em}, nm[a]	$\Delta\bar{\nu}g$, cm^{-1} [b]
hexane	351	401	24752
chloroform	375	445	22222
acetone	356	455	21739
ethanol	372	510	19417
water	380	528	18867

[a] Excitation was carried out by using 360-nm light. [b] Center of mass of the emission.

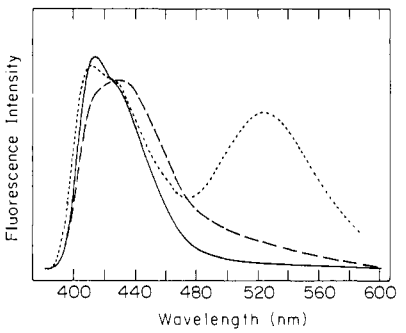
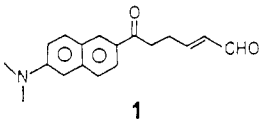


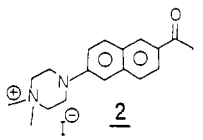
Figure 1. Emission spectra of chromophore **1**–bacterioopsin complex in 10 mM Hepes buffer (pH 6.5): (---) immediately after incubation of bacterioopsin with 1 equiv of chromophore **1**; (—) 30 min later; (- - -) incubation with 1.5 equiv of **1** for 1 h.

of the protonated Schiff base pK_a, taking place following light absorption, is a consequence of electrostatic interactions with the retinal polyene. The polarity of the binding site plays a major role in influencing these electrostatic interactions and its understanding is a prerequisite for their evaluation.

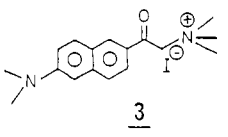
In the present work, we have studied the binding site using a fluorescent probe[7] whose emission spectrum is highly sensitive to solvent polarity. The red shift of a fluorescent spectrum with increasing solvent polarity has been extensively studied.[8] Various probes exhibit this phenomenon and recently Weber et al. introduced 2-(dimethylamino)-6-propionylnaphthalene (PRODAN) as a neutral species, highly sensitive to polarity (fluorescent at 530 nm with a lifetime of 3.2 ns in water and at 400 nm with a lifetime of 0.6 ns in hexane), and used an analogue of this chromophore for estimation of myoglobin haem pocket polarity.[9] In this study, we bound analogue **1**, which consists of two nonconjugated chromophores, to bacterioopsin and followed its



1



2



3

Table II. Absorption and Emission Spectra of Chromophores **2** and **3** in Chloroform and Methanol[a]

chromophore	λ_{abs}, nm	λ_{em}, nm
PRODAN	354 (362)	442 (505)
2	325 (328)	415 (460)
3	403 (392)	508 (557)

[a] In parentheses.

spectroscopic properties to probe the protein environment in the neighborhood of the naphthyl chromophore. Chromophore **1**[10] (whose absorption and emission spectra are summarized in Table I) was incubated with bacterioopsin at pH 6.5 (10 mM Hepes buffer) and the process was followed by emission spectrum. A band centered at 440 nm (22727 cm^{-1}) was detected immediately following the incubation which was replaced, after ca. 10 min, by another band centered at 425 nm (23529 cm^{-1}) with a shoulder at 440 nm (Figure 1). The absorption maximum of the complex was centered at 352 nm. Incubation at 0 °C inhibited the conversion of the 440-m band to 425 nm, which took place only after a few hours. The existence of a species with emission spectrum centered at 440 nm probably corresponds to a "prepigment" found previously in the reconstituted process of bacterioopsin with *all-trans*-retinal,[11] as well as with various retinal analogues.[12] The difference occurring in the emission spectra reflects two different kinds of interactions of chromophore **1** with the environment in the "prepigment" and in the final complex. Incubation with excess of chromophore (relative to bacterioopsin) resulted in the formation of an additional band which averaged at 532 nm (Figure 1), corresponding to an unbound species whose emission spectrum resembles the chromophore emission in water. A support for binding-site occupation by chromophore **1**, following incubation with bacterioopsin, is gained by competition studies. Formation of bR pigment was not observed following addition of *all-trans*-retinal to chromophore **1**–bacterioopsin complex, even after 6 h of incubation, but was, however, observed following 48 h of incubation. The bR pigment generation was monitored by following the disappearance of the 425 nm emission band (which was replaced by one of 532 nm) and by the formation of a 568 nm band in the absorption spectrum.

Time-resolved emission spectrum of the complex indicated the existence of one species with a lifetime of <1 ns. The fluorescence spectrum did not change, either following temperature variation between −50 and +50 °C or due to excitation with different wavelengths. The existence of only one species and the absence of a "red edge effect" (dependence of the fluorescence spectrum on the excitation wavelength) point to homogeneity of the probe interaction with its environment.

Several investigators[13,14] have indicated that the spectroscopic properties of fluorescence probes in the binding site of a protein should be interpreted carefully. The spectroscopic properties depend not only on the polarity of the environment but on its rigidity and ability to solvate the chromophore as well. Although the complex chromophore **1**–bacterioopsin exhibits a blue-shifted fluorescence spectrum closely resembling that of chromophore **1** in a relatively nonpolar solution, it is possible that this blue-shifted emission spectrum may have its origin in a polar rigid environment too. However, the absorption (352 nm), which is similar to the chromophore absorption in hexane solution (Table I), excludes the possibility of a polar rigid environment around the probe.

Furthermore, the blue-shifted emission spectrum of bacterioopsin–chromophore **1** complex may also originate from interaction through space with nonconjugated charges or dipoles in-

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troduced by the protein in the neighborhood of the chromophore. It was suggested previously that nonconjugated charges exist in the binding site of bacteriorhodopsin, influencing its absorption maximum.[3d,e,4,15] However, a significant effect on the emission spectrum of chromophore **1** by a nonconjugated charge should be accompanied by a considerable effect on the absorption maxima. This conclusion is borne out from studies of chromophores **2** and **3**, bearing nonconjugated positive charges in the vicinity of the chromophore. As outlined in Table II, both the absorption and the fluorescence spectra are shifted by similar magnitudes, due to the presence of the charge. The direction of the shift is determined by the charge location (blue in **2** and red in **3**, due to destabilization or stabilization of the excited state, respectively). Since the significant blue-shifted emission spectrum of the complex chromophore **1**-bacterioopsin (relative to the emission in water) is not accompanied by a similar magnitude of shift of the absorption, we conclude that the complex emission spectrum is not affected significantly by nonconjugated charges and that the blue-shifted fluorescence spectrum observed for the complex (centered at 23 529 cm^{-1}, relative to 18 867 cm^{-1} of the chromophore in water) points to the resultant field of the peptide bonds reaching a low value at the probe site.

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Enantioselective Hydrogenation of Allylic and Homoallylic Alcohols

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Homogeneous asymmetric hydrogenation of olefins with transition-metal-complex catalysts[2] offers an attractive tool for stereoselective organic synthesis. Recently much attention has been given to directing effects of hydroxyl functionality on the stereochemical course. Some cationic Rh and Ir phosphine complexes are known to catalyze diastereoselective hydrogenation of *chiral* allylic and homoallylic alcohols,[3] where the preexisting chirality of the sp^3-hybridized carbons induces new asymmetry on the neighboring olefinic diastereofaces through coordination of the hydroxyl group to the transition metals.[4] However, highly enantioselective hydrogenation of the *prochiral* substrates is still elusive.[5] This process is based on catalyst/substrate *intermolecular* asymmetric induction, holding potential for chemical multiplication of chirality. We disclose here that the new Ru(II) dicarboxylate complexes containing BINAP ligands,[6] **1**,[7] as catalysts exhibit high reactivity and excellent selectivity, thereby solving this important and difficult problem.

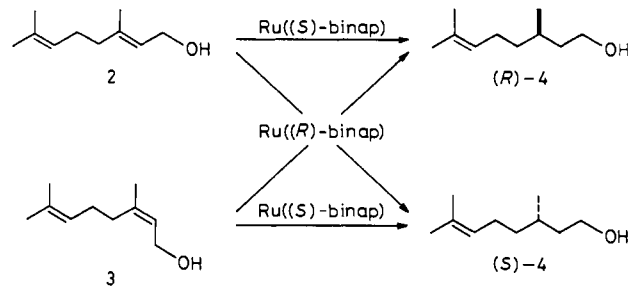
We selected stereochemically pure geraniol (**2**) and nerol (**3**) as substrates. Here the requirements for achieving a practically valuable asymmetric synthesis are (1) high chemical and optical yields of the citronellol product,[8] (2) regioselective reaction

Table I. Asymmetric Hydrogenation of Geraniol (**2**) and Nerol (**3**) Catalyzed by BINAP-Ru(II) Complexes[a]

substrate	catalyst	S/C	citronellol (**4**) optical purity[b]	% ee[c]	config-uration
2	(*S*)-**1a**	530	98	96	*R*
2	(*S*)-**1b**	500		98	*R*
2[d]	(*S*)-**1c**	10 000	99	96	*R*
2[d]	Ru((*S*)-binap)$(OCOCF_3)_2$[e]	50 000	96		*R*
2[d]	Ru((*S*)-tolbinap)$(OCOCF_3)_2$[e]	50 000	97		*R*
3	(*R*)-**1a**	540		98	*R*
3	(*S*)-**1c**	570		98	*S*

[a] The reaction was carried out with stirring in a stainless steel autoclave at 18-20 °C with a 0.35-0.61 M solution of the substrate in methanol with exclusion of air. After removal of the Ru complex by precipitation by adding pentane followed by filtration through Celite 545, the whole mixture was concentrated and distilled to give **4** in 97-100% yields. [b] Authentic sample of (*R*)-**4** in 98% ee exhibits $[\alpha]^{25}_D$ +5.12° (*c* 21.0, $CHCl_3$). [c] Determined by HPLC analysis (Chemco Nucleosil 100-3, 4.6 × 300 mm, 3:7 ether-hexane) of the diastereomeric amides prepared by condensation of citronellic acid, obtained by the Jones oxidation, and (*R*)-1-(1-naphthyl)-ethylamine.[10] [d] Reaction using 5.8 M solution of **2** in methanol at initial hydrogen pressure of 30 atm for 12-14 h. [e] These complexes (tentative structures) were prepared from **1a** and **1c**, respectively, by ligand replacement by addition of excess trifluoroacetic acid.

Scheme I



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(1) Visiting scientist from the Department of Applied Chemistry, Aichi Institute of Technology, Toyota 470-03, Japan.

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