phase transition. In the nematic phase, although the XZ scattering intensity is generally less than the XX intensity, the difference is within the experimental uncertainty. Therefore the depolarization ratio is nearly equal to 1 in most of the nematic phase. Except at the vicinity of T_λ', the unit depolarization ratio observed in the solid and nematic phases is probably associated with the scattering of the domain structure and indicates that the size of the single domain PPU in the nematic phase is less than the wavelength of light. Because of this limitation arising from the domain fluctuation, in order to obtain accurate information on the reorientational process associated with the phase transition by the depolarization study, it is necessary to increase the domain size by orienting the nematic liquid by an external electric field. The electric field dependent-Raman scattering is presently in progress and will be the subject of a future publication.

Finally, it should be pointed out under the identical experimental conditions, in contrast to the Raman experimental result, that the depolarization measurement of the Rayleigh scattered light in PPU does not reflect a quasi-discontinuous intensity at the nematic isotropic liquid-phase transition. The difference is mainly due to the presence of the interference of the scattering light from different molecules in the Rayleigh scattering, but the interference is absent in the Raman scattering. Consequently, for the purpose of obtaining the effect of short-range reorientation order, the Raman scattering technique is presumably more useful than the Rayleigh scattering.

Despite the fact that Raman scattering has been proclaimed to be insensitive to the study of the nematic liquid-phase transition in liquid crystals, we have demonstrated that Raman depolarization ratio studies do provide information about this type of phase transitions.

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Dynamics of Axial Ligation in Metalloporphyrins. I. Imidazole Exchange in Low-Spin Ferric Porphyrins

Sir:

The properties, structures, and reaction mechanisms, and their interrelation, of porphyrin complexes have been the subject of considerable interest recently[1-11] in light of their possible relevance as models for the structure–function relationships of the important class of iron hemoproteins[12,13] and cobalt corrinoids.[14] The frequent presence of an imidazole-coordinated residue in an axial position, coupled with the suggestions that metal–imidazole bond rupture may play a critical role in biological processes of coenzyme B_{12}[14] and the cytochrome *c* system,[13] indicates that a detailed characterization of the structure and dynamics of the imidazole–metal bond in such porphyrin complexes could have significant biological implications.

To date, relatively few studies have concerned themselves with the lability of the coordinated imidazole moiety.[1,3,14b] A number of studies have characterized the lability of the nitrogenous bases in ruthenium(II) carbonyl porphyrin complexes with imidazole[1,3] and pyrazoles,[2] as well as some six-membered ring ligands.[2] However, comparable data for the biologically functional iron systems are lacking, though some investigations of the substitution reactions of axially coordinated hemin have been reported.[6-8] Axial ligand substitution reactions for a number of other metal porphyrins have also appeared,[15,16] but the paucity of experimental data precludes any generalizations of the factors which govern the mechanism and rate of such reactions.

We report here one of the initial aspects of a systematic investigation of the kinetics and mechanism of axial ligation and ligand lability in iron porphyrin complexes. The complexes of interest here are the bisimidazole adducts of ferric porphyrins[5,11,17] (*meso*-tetraphenylporphyrin = TPP, octaethylporphyrin = OEP, protoporphyrin IX dimethyl ester = PPDME), which in the case of TPP has been characterized by Mossbauer[17] and esr and nmr,[11] as well as X-ray[5] spectroscopy. Analyses[17] was well as X-ray data[5] substantiate a 2:1 adduct which magnetic data[17] reveal to be in the low-spin ($S = {}^1/_2$) state. The bis adduct of *N*-methylimidazole,[18] NMIm, with TPPFeCl in $CDCl_3$ exhibits the proton nmr spectrum shown in Figure 1. The peaks labeled LS (low spin) arise[11] from TPPFe $(NMIm)_2^+$; the 6:8 ratio peak intensities for the coordinated $N-CH_3$ and the pyrrole-H clearly establish the 2:1 stoichiometry of this species in solution. Of particular interest is that the $N-CH_3$ peaks exhibit dynamic line broadening due to exchange between free and coordinated NMIm according to (1). The rates

$$\mathrm{TPPFe(NMIm)_2^+ + NMIm^*} \underset{\tau_{-1}^{-1}}{\overset{\tau_1^{-1}}{\rightleftarrows}} \mathrm{TPPFe(NMIm)(NMIm^*)^+ + NMIm} \quad (1)$$

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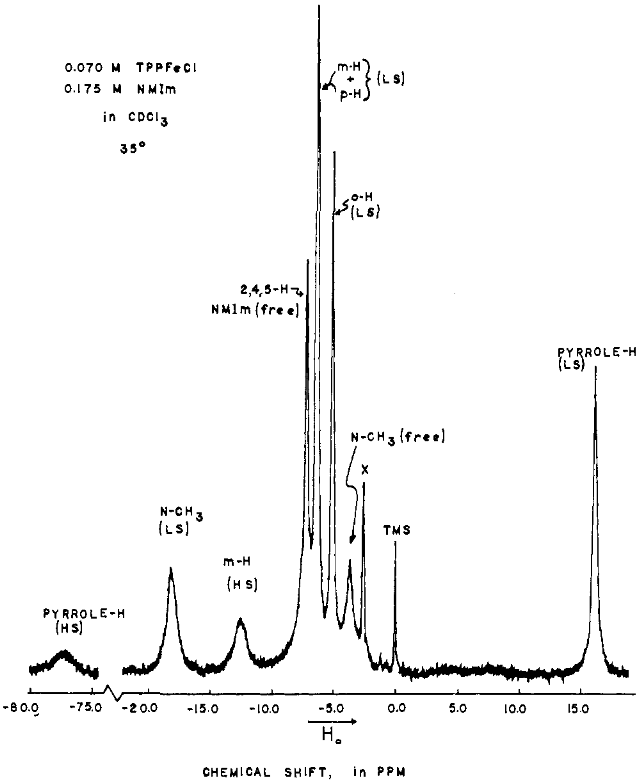

Figure 1. Proton nmr spectrum of a $CDCl_3$ solution, 0.070 *M* in TPPFeCl and 0.175 *M* in NMIm, at 35°. The peaks for [TPPFe-$(NMIm)_2{}^+$]Cl^- are indicated by LS (low spin), and the peaks for TPPFeCl are designated by HS (high spin). The remaining phenyl resonance for the HS species is obscured by the LS spectrum as well as by the free NMIm peak in the region −4 to −7 ppm.

for this reaction are obtained by standard line width analysis.[19] The preliminary conclusions from the analysis of the effect of temperature on the proton nmr spectra are as follows.

There are two dominant ferric porphyrin species present in solution whose relative amounts depend on the porphyrin concentration and the imidazole–porphyrin ratio. The major component is the 2:1 adduct described above (peaks labeled LS in Figure 1); the minor component is the high spin (HS) complex, TPPFeCl (peaks labeled HS in Figure 1), readily identified by the previously reported[20] spectrum for this complex. For a solution 0.070 *M* in TPPFeCl and 0.175 *M* in NMIm, integration of the pyrrole-H peak for the two species reveals that ~20% of the porphyrin is present in the high-spin form. The resulting $K_{eq} \sim 10^3$ at 35° is significantly smaller than that reported[7] for the analogous imidazole complex with hemin ($K_{eq} \sim 10^6$). The preexchange lifetimes for the coordinated NMIm in the LS form are essentially independent of the TPPFeCl and NMIm concentrations, indicating that bond rupture is the rate-determining step, as also found for the ruthenium(II) system,[2,3] and as suggested for the substitution reactions of the hemin complexes.[6–8] Rate data for (1) are: $\tau_1{}^{-1} = k_0{}^{298} \sim 60\ sec^{-1}$, $E_a \sim 17$ kcal/mol, log $A \sim 14$, indicating a small (~7 eu) entropy of activation. These kinetic parameters are surprisingly similar to those reported for the ruthenium(II) system with pyrazoles[2] and imidazole.[3]

The lability of the coordinated NMIm depends on the porphyrin substituents, with the rate of exchange an order-of-magnitude faster in $OEPFe(NMIm)_2{}^+$. This increase in axial lability may be expected due to the more basic porphyrin ligand.[21] For PPDMEFe(NM-$Im)_2{}^+$, the porphyrin methyl signals[9] overlap seriously with the coordinated $N–CH_3$ peak, making line width analysis difficult; however, a rate intermediate to that of TPP and OEP is suggested.

At high temperatures, $\gtrsim 50°$, we have obtained indirect evidence for a third species in solution which is in dynamic equilibrium with both free NMIm and TPPFe$(NMIm)_2{}^+$, as indicated in (2), which we tentatively

$$TPPFe(NMIm)_2{}^+Cl^- \rightleftharpoons TPPFe(NMIm)^+Cl^- + NMIm \quad (2)$$

suggest to be a high-spin mono-NMIm complex. These preliminary conclusions are based on the observation that, in this temperature range, the pyrrole–H peak in $TPPFe(NMIm)_2{}^+$ begins to broaden with increasing temperature (reversibly), with a simultaneous increase in the free NMIm line width in excess of that consistent with the kinetic data for reaction 1. This increasing pyrrole–H line width can be suppressed by increasing the NMIm concentration, which is consistent with driving the equilibrium in (2) to the left. The kinetic data reported for (1) were obtained at a NMIm–TPPFeCl ratio of 10:1, and only in the temperature region where the pyrrole–H resonance line width indicates only a single imidazole complex.

Preliminary results from investigations in progress indicate that the present and related systems are excellent candidates for the elucidation of the influence of a variety of factors, such as imidazole or porphyrin substituent, solvent, counterions, on the dynamics and thermodynamics of (1) and (2), and may therefore serve as useful models for understanding the dynamics and thermodynamics of the imidazole–metal bond in metalloporphyrins.

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The Wittig Modification of the Hofmann Elimination Reaction. Evidence for an α',β Mechanism

Sir:

Wittig and Polster[1] reported that trimethylcyclooctylammonium bromide (**1**) reacted with phenyllithium to give trimethylamine and *cis*- and *trans*-cyclooctene in a ratio of 81:19. They suggested that the mechanism in-

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