# Proton NMR Studies of the Interaction of Metalloporphyrins with $\pi$ Acceptors and Donors. I. Effect of $\pi$-Complex Formation on the Electronic Structure of Low-Spin Cobalt(II)

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**Abstract:** The porphyrin proton NMR shifts of low-spin tetra-*p*-tolylporphinatocobalt(II) have been investigated upon the addition of various aromatic $\pi$ acceptors and donors. The interactions are described by the formation of 1:1 adducts, and in the case of 1,3,5-trinitrobenzene, TNB, the thermodynamic parameters are reported. Sizable changes in dipolar shifts upon complex formation are observed, with the magnetic anisotropy increasing markedly in the presence of $\pi$ acceptors, and decreasing significantly in the presence of a donor. The increase in magnetic anisotropy requires that the adducts are peripheral $\pi$ complexes. Similar characteristic changes in porphyrin line widths are also recorded. The changes in magnetic anisotropy and proton relaxation times are analyzed in detail in terms of the changes in electronic structure of the metal and in metal-porphyrin bonding. The changes in electronic structure of the cobalt are shown to arise primarily from changes in the metal-porphyrin $\sigma$ bond.

The continuing interest in porphyrins $\pi$-$\pi$ interactions stems from the importance of these interactions in characterizing a number of physical properties of porphyrins in simple solutions[1-6] as well as in their biological role in hemoproteins.[7,8] The tendency for aggregation in solution for both porphyrins and metalloporphyrins is well-documented.[1-3] One system where $\pi$ interactions may be relevant is cytochrome $c_3$, which possesses at least three, probably four, porphyrins per 12 000 molecular weight; heme-heme $\pi$ stacking has been suggested[9] as a possibility in this unusual molecule. Close stacking ($\leq$5 Å) of heme $\pi$ planes has recently been demonstrated[2] by proton relaxation studies. The possible existence of $\pi$ complexes between steroids and the heme of cytochrome P450 has also been suggested.[10] Similar $\pi$ interactions have also been postulated[3,7] to provide important stabilization in heme-protein linkages. Recent studies indicated[5,6] that $\pi$ interactions with aromatic acceptors and donors can modulate the thermodynamics and kinetics of axial ligations. However, very little is known about the manner in which these $\pi$-$\pi$ interactions affect the metal-porphyrin, M-P, bond and the electronic structure of the metal.

The recent literature has witnessed several reports which demonstrate[5,6,10-14] the occurrence of significant complex formations between porphyrins and aromatic $\pi$ acceptors and donors. The effect of low-spin cobalt(II) mesoporphyrin dimethyl ester, MPCo, on the chemical shifts of a variety of substrates has confirmed[10-13] the $\pi$ nature of the complexes, for which structural analysis focused on the role of MPCo as a "shift reagent".[15] However, the complexity of the substrates[10,12] precluded the determination of a unique structure largely because the system contained too many parameters. In one study, the effect of a $\pi$ acceptor on the MPCo chemical shifts was monitored[13] in order to characterize the changes in porphyrin electronic structure due to complex formation. Although an increase in the dipolar shifts was noted,[13] a detailed interpretation of the shift changes was not presented due to the extensive aggregation of MPCo which precluded determination of the shifts for pure MPCo.

Walker has reported[14] on a low-temperature ESR investigation of frozen glasses of cobalt(II) tetraphenylporphyrin, TPPCo, in the presence of a variety of $\pi$ donors and acceptors. The spectra yielded unambiguous evidence for the formation of $\pi$ complexes as characterized by changes in both $g$ values and coupling constants. However, since the low-temperature ESR $g$ values of TPPCo have been shown[16,17] to depend critically on solvent, temperature, and phase due to axial solvation of the planar cobalt even in weak solvents such as $CHCl_3$, it was not possible to compare $g$ values of TPPCo in the presence and absence of a $\pi$ substrate without the complication of axial solvation.

We have shown previously,[16] however, that proton NMR can be used successfully to characterize the electronic structure of *p*-$CH_3$-TPPCo, and that the solution structure at ambient temperatures is free from the problems of axial solvation of the metal and porphyrin aggregation. It should therefore be possible to determine directly by NMR the effect of $\pi$ complex formation on the porphyrin chemical shifts.

The advantageous use of NMR is based on the demonstrated dominance of magnetic anisotropy as the sole origin of the isotropic shifts[18] for the phenyl resonance. In the limit of Curie behavior, these shifts are given by the familiar equation:[18]

$$\left(\frac{\Delta H}{H}\right) = -\frac{K}{T}(g_{\parallel}^2 - g_{\perp}^2)\left(\frac{3\cos^2\theta - 1}{r^3}\right) \qquad (1)$$

where $\theta$ and $r$ describe the usual axial geometric factor, and $K = \beta^2 S(S+1)/9k$. The relative shifts for two nonequivalent phenyl positions are given by

$$\left(\frac{\Delta H}{H}\right)_i \Big/ \left(\frac{\Delta H}{H}\right)_j = (3\cos^2\theta_i - 1)r_i^{-3}/(3\cos^2\theta_j - 1)r_j^{-3} \qquad (2)$$

This relation has been confirmed[16] for pure *p*-$CH_3$-TPPCo in both chloroform and toluene. A knowledge of the dipolar shift, $(\Delta H/H)_i$, the geometric factor, and $K/T$ permits the determination of $g_{\parallel}^2 - g_{\perp}^2$, which can be correlated with the electronic structure of the metal.

In this study we investigate the effect of interaction of aromatic $\pi$ acceptors and a donor[19] on the paramagnetic shifts of *p*-$CH_3$-TPPCo. The most important molecules will be one of the strongest $\pi$ acceptors, trinitrobenzene, TNB, and one of the strongest $\pi$ donors, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, TMPD. We will be interested in determining how the electronic structure of the metal is altered, and whether the changes are transferred to the metal primarily by $\pi$ or by $\sigma$ bonding effects. In the companion

Table I. Effect of Concentration on $p$-$CH_3$-TPPCo Chemical Shifts[a]

| [$p$-$CH_3$-TPPCo][b] | Chemical shift | | |
|---|---|---|---|
| | $o$-H | $m$-H | Pyrr-H |
| 7.72 | −12.90 | −9.78 | −16.9 |
| 3.86 | −12.90 | −9.79 | −16.9 |
| 1.93 | −12.90 | −9.79 | −16.9 |
| 0.96 | −12.90 | −9.79 | −16.9 |

[a] Shifts in ppm from internal TMS. [b] Concentration in millimolar.

article,[20] we will use some of the conclusions reached in this report in conjunction with the induced shifts and line broadening of the substrate TNB to arrive at a quantitative description of the solution structure of the 1:1 $p$-$CH_3$-TPPCo:TNB complex. That structural analysis will confirm our conclusion reached here that the $\pi$-$\pi$ interaction occurs exclusively at the periphery of the porphyrin and does not involve the metal directly.

## Principles

The observation of the effect of the $\pi$ substrates on the NMR shifts and line width will yield data which can be used to determine the shifts and line widths for the pure $\pi$ complex. Since chemical exchange of the aromatic substrate between the free and complexed form is rapid on the NMR time scale, the exchange-averaged observed shift, for the porphyrin, $\langle \Delta H/H \rangle_{obsd}$, is given by

$$\left\langle \frac{\Delta H}{H} \right\rangle_{obsd} = f_f \left(\frac{\Delta H}{H}\right)_f + f_c \left(\frac{\Delta H}{H}\right)_c \quad (3)$$

where $f_f$ and $f_c$ are the mole fraction of $p$-$CH_3$-TPPCo in the free and complexed form, and $(\Delta H/H)_f$ and $(\Delta H/H)_c$ are the porphyrin chemical shifts for the free and complexed cobalt porphyrin. In the cases of interest here, as has been found in the other ambient temperature studies, we need consider only a 1:1 complex of the form

$$P + S \rightleftarrows P{:}S \quad (4)$$

where P = $p$-$CH_3$-TPPCo and S is the $\pi$ substrate, for which the equilibrium constant is given by

$$K = [P{:}S]/[P][S] \quad (5)$$

Equations 5 and 4 can be combined and, with some rearrangement, yield

$$\left\langle \frac{\Delta H}{H} \right\rangle_{obsd} = \Delta\left(\frac{\Delta H}{H}\right)\left[\frac{P_0 + S_0}{2P_0} + \frac{1}{2P_0K} - \frac{1}{P_0}\sqrt{\left(\frac{P_0 - S_0}{2}\right)^2 + \left(\frac{P_0 + S_0}{2K}\right) + \frac{1}{4K^2}}\right] \quad (6)$$

where $P_0$ and $S_0$ are the total amounts of $p$-$CH_3$-TPPCo and substrate added, and where we define $\Delta(\Delta H/H) = (\Delta H/H)_c - (\Delta H/H)_f$ as the change in shift for a porphyrin peak upon formation of the 1:1 complex with the substrate. The equation can be simply solved by iterative computer methods which yield both $\Delta(\Delta H/H)$ and hence $(\Delta H/H)_c$, and $K$. The knowledge of $K$ from eq 6 and the line width as a function of $S_0$ directly yields the porphyrin line widths for the 1:1 complex. In the limit that both $(\Delta H/H)_f$ and $(\Delta H/H)_c$ can be shown to be dominated by the dipolar interaction,[16,18] the change in shift, $\Delta(\Delta H/H)$, directly yields the change in the magnetic anisotropy $(g_\parallel^2 - g_\perp^2)$.

Following our earlier model,[16] the $g$ values of planar low-spin $d^7$ are given, to first order,[21] by

$$g_\parallel = 2.0 \quad (7a)$$

$$g_\perp = 2.0 + \frac{6\xi}{\Delta E(a_1 - e)} \quad (7b)$$

where $\Delta E(a_1 - e)$ is the gap between $d_{z^2}$ and the $d_{xz}$,$d_{yz}$ orbitals (or, more correctly, the $A_1$ and E states). Hence eq 7 indicates that the anisotropy is dominated[16,21] by the magnitude of $\Delta E(a_1 - e)$, i.e., dramatic increases (or decreases) in $(g_\parallel^2 - g_\perp^2)$ reflect predominantly decreases (or increases) in $\Delta E(a_1 - e)$.

It has also been noted[16] that the energy gap $\Delta E(a_1 - e)$ controls the rate of electron spin relaxation via spin-orbit coupling.[22] Hence, $T_{1e}$ will increase with $\Delta E(a_1 - e)$, and therefore the proton NMR line widths will increase with $\Delta E(a_1 - e)$. Thus it is predicted[16] that decreases in the magnetic anisotropy are accompanied by a broadening of the NMR signals, while increases in the magnetic anisotropy parallel a narrowing of the NMR signals. The changes in $g$ tensor anisotropy and line width therefore provide independent evidence for changes in the energy gap $\Delta E(a_1 - e)$.

## Experimental Section

*meso*-Tetra-$p$-tolylporphyrin was prepared by the method of Adler et al.[23] The crystalline product was chromatographed on dry silica gel (J.T. Baker reagent, 60–200 mesh). The purity of the ligand was confirmed by its proton NMR spectrum. The Co(II) complex was prepared by the method of Adler et al.[24] The reaction was followed to completion (~45 min) spectrophotometrically; the purple crystalline products were dissolved in reagent grade chloroform and chromotographed on silica gel. The high degree of purity of the complex was confirmed by its proton NMR spectrum.

The $\pi$ substrates used in the study were obtained commercially and used as supplied except for trinitrobenzene, TNB, and trinitrotoluene, TNT, which were recrystallized several times from absolute ethanol and dried several hours in vacuo. TNT was further purified by vacuum distillation at 80–100 °C. The purities of all $\pi$ substrates were also confirmed by their proton NMR spectra.

Proton NMR spectra were obtained on a JEOL PS100 pulsed FTNMR spectrometer interfaced with a Digilab NMR-3 disk data system. Up to 2000 transients were accumulated using ~20 $\mu$s 90° pulses over a 2 kHz bandwidth. TMS was used as internal reference, and unless noted otherwise, the temperature was maintained at 25 °C. For variable temperature runs, calibration was effected both before and after recording spectra by a thermocouple wire within a NMR tube. Shifts are reported in ppm, and line widths in Hz at 100 MHz.

All quantitative spectra were carried out at fixed porphyrin concentration in $CDCl_3$ solution, with the amount of $\pi$ substrate made variable over a wide range. The amount of $\pi$ substrate added was determined by careful weighing of the NMR tubes prior and after adding the substrate. The effect of incremental additions of $\pi$ substrates on porphyrin shifts and line widths were recorded at several fixed porphyrin concentrations.

The values of $K$ and $\Delta(\Delta H/H)$ in eq 6 were obtained by computer fit to the experimental data using an iterative least-squares minimization procedure using a Burroughs B6700 computer. The optimum values of $K$ and $\Delta(\Delta H/H)$ were independent of the initial guesses for these parameters.

## Results

The chemical shifts for $p$-$CH_3$-TPPCo as a function of concentration in $CDCl_3$ are found in Table I. The invariance of shifts with concentrations attests to the absence of significant aggregation. The changes in porphyrin shifts and line widths upon the addition of increasing amounts of TNB are illustrated in Figure 1, while Figure 2 exhibits the changes in porphyrin shifts upon the addition of TMPD. The solid lines represent the theoretical curves for the optimum fit of the experimental data to eq 5. The resulting equilibrium constants for the 1:1 complex formation with several acceptors and a donor are given in Table II, along with thermodynamic data on the $p$-$CH_3$-TTPCo:TNB system.

The relative values of the isotropic shifts for $p$-$CH_3$-TPPCo as a function of added TNB and TMPD are listed

**Table II.** Equilibrium Constants and Thermodynamic Parameters for 1:1 Complexes of $p$-$CH_3$-TPPCo with Donors and Acceptors

| Substrate | Donor or acceptor | Limiting $m$-H shift[a] | $K$[b] | $\Delta H°$, kcal/mol | $\Delta S°$, eu |
|---|---|---|---|---|---|
| TNB | A | −3.18 | 17.5 ± 0.5 | 5.7 ± 0.4 | −14 ± 2 |
| TNT | A | −2.60 | 3.3 ± 0.3 | | |
| DNB | A | −2.47 | 2.9 ± 0.3 | | |
| None | | −2.23 | | | |
| TMPD | D | −1.3 | 10.2 ± 0.9 | | |

[a] Computed shift for pure 1:1 complex; referenced against diamagnetic $p$-$CH_3$-TTPNi. [b] Determined by computer fit to aryl resonance shifts as a function of [substrate]/[$p$-$CH_3$-TPPCo] ratio; at 25 °C in $CDCl_3$.

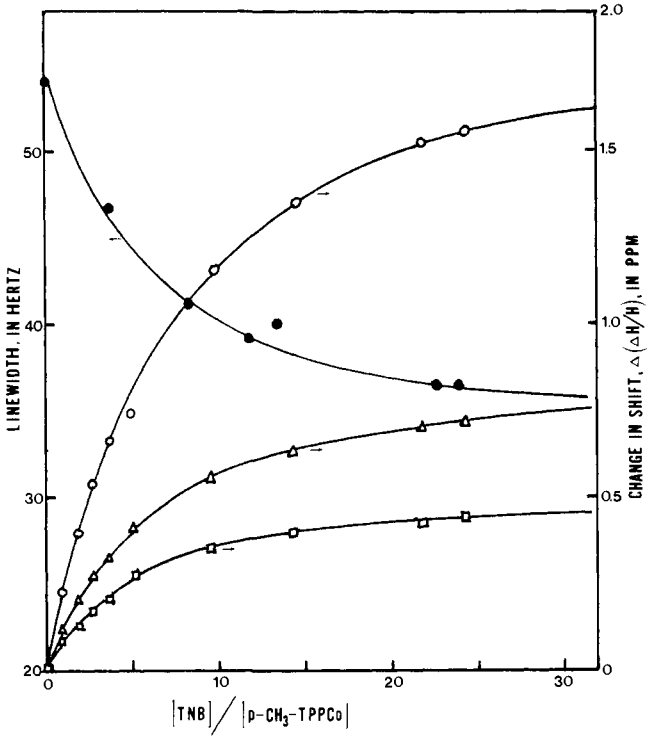


**Figure 1.** Plot of the observed averaged porphyrin isotropic shifts (○, $o$-H; △, $m$-H; □, $p$-$CH_3$) and $o$-H averaged line width (●) vs. the mole ratio of TNB to $p$-$CH_3$-TPPCo; [$p$-$CH_3$-TPPCo] = 7.12 × $10^{-3}$ M, and $T$ = 25 °C. The solid lines are the optimum computer fits to eq 6.

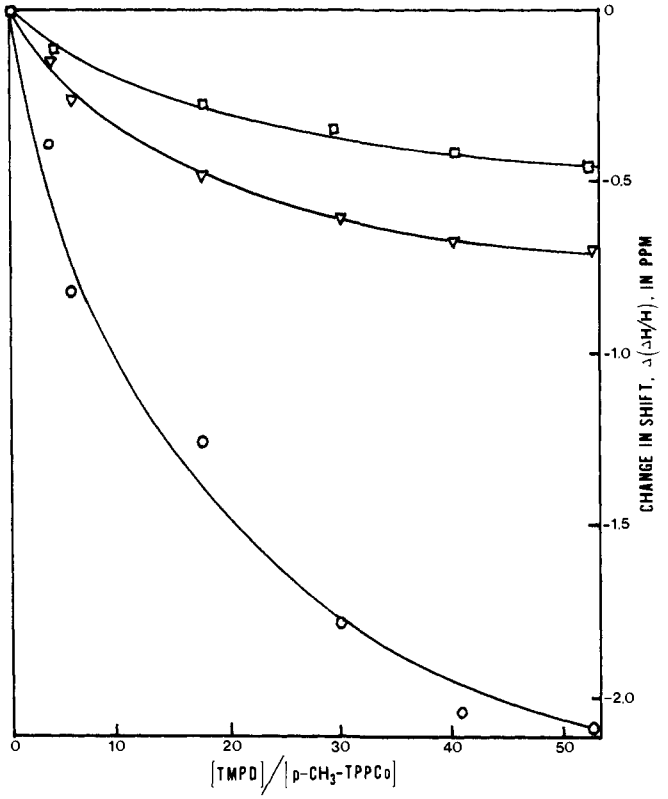


**Figure 2.** Plot of the observed averaged porphyrin isotropic shifts (○, $o$-H; △, $m$-H; □, $p$-$CH_3$) vs. the mole ratio of TMPD to $p$-$CH_3$-TPPCo; [$p$-$CH_3$-TPPCo] = 6.34 × $10^{-3}$ M, and $T$ = 25 °C. The solid lines are the optimum computer fits to eq 6.

**Table III.** Isotropic Shift Ratios for $p$-$CH_3$-TPPCo as a Function of TNB Concentration[a]

| | Position | | | |
|---|---|---|---|---|
| [TNB] | $o$-H[b] | $m$-H | $p$-$CH_3$ | Pyrr-H |
| 0.000 | −10.0 | −4.36 | −2.95 | −13.8 |
| 0.053 | −10.0 | −4.48 | −2.90 | −12.2 |
| 0.101 | −10.0 | −4.42 | −2.87 | −11.4 |
| 0.151 | −10.0 | −4.40 | −2.84 | −11.1 |
| 0.181 | −10.0 | −4.43 | −2.84 | −11.0 |
| 0.249 | −10.0 | −4.43 | −2.81 | −10.7 |
| 0.299 | −10.0 | −4.40 | −2.84 | −10.7 |
| Average | −10.0 | −4.42 | −2.86 | |
| Predicted[c] | −10.0 | −4.63 | −3.04 | −18.9 |

[a] In $CDCl_3$ solution, at 25 °C; referenced against diamagnetic $p$-$CH_3$-TPPNi; [$p$-$CH_3$-TPPCo] = 8.5 × $10^{-3}$ M. [b] The $o$-H shift is normalized to −10.0. [c] Based on calculated relative geometric factors as reported in ref 16.

**Table IV.** Isotropic Shift Ratios for $p$-$CH_3$-TPPCo as a Function of TMPD Concentration[a]

| | Position | | | |
|---|---|---|---|---|
| TMPD | $o$-H[b] | $m$-H | $p$-$CH_3$ | Pyrr-H |
| 0.000 | −10.0 | −4.36 | −2.95 | −13.8 |
| 0.024 | −10.0 | −4.43 | −2.93 | −14.4 |
| 0.037 | −10.0 | −4.56 | −3.53 | −14.5 |
| 0.111 | −10.0 | −4.37 | −2.96 | −15.0 |
| 0.186 | −10.0 | −4.84 | −3.35 | −14.7 |
| 0.260 | −10.0 | −5.02 | −3.42 | −15.8 |
| 0.336 | −10.0 | −5.06 | −3.24 | −15.2 |
| Average | −10.0 | −4.66 | −3.19 | |
| Predicted[c] | −10.0 | −4.63 | −3.04 | −18.9 |

[a] In $CDCl_3$ solution, at 25 °C; referenced against diamagnetic $p$-$CH_3$-TPPNi. [b] The $o$-H shift is normalized to −10.0. [c] Based on calculated relative geometric factors as reported in ref 16.

in Tables III and IV, respectively. In Table V we give the porphyrin isotropic shifts and line widths for $p$-$CH_3$-TPPCo and its 1:1 complexes with TNB and TMPD, as determined from the computer fit of the data in Figures 1 and 2. The line widths were obtained using the value of $K$ obtained from the shifts and the averaged line width at low-to-moderate [TNB]/[$p$-$CH_3$-TPP] ratios.

## Discussion

**Stoichiometry of the π Complexes.** The fits of the experimental shifts to the predicted equation (eq 6) for a 1:1 complex are very good. In the case of the $p$-$CH_3$-TPPCo:TNB complex, the equilibrium constant has been independently obtained[20] from an analysis of the induced shifts of TNB,

Table V. Isotropic Shifts and Line Widths for $p$-$CH_3$-TPPCo and Its 1:1 Complexes with TNB and TMPD[a]

| | $p$-$CH_3$-TPPCo | | $p$-$CH_3$-TPPCo:TNB | | $p$-$CH_3$-TPPCo:TMPD | |
|---|---|---|---|---|---|---|
| Position | Shift[b] | Line width[c] | Shift[b] | Line width[c] | Shift[b] | Line width[c] |
| $o$-H | −5.12 | 54 ± 3 | −7.46 | 36 ± 2 | −2.6 | ~90 |
| $m$-H | −2.23 | 8.1 ± 0.5 | −3.18 | 6.3 ± 0.6 | −1.3 | ~20 |
| $p$-$CH_3$ | −1.48 | 2.9 ± 0.2 | −2.09 | 1.8 ± 0.2 | −0.8 | ~5 |
| Pyrr-H | −6.5 | 68 ± 5 | −7.5 | 41 ± 1 | −5.0 | ~200 |

[a] In $CDCl_3$ solution at 25 °C. [b] Shifts in ppm, referenced against diamagnetic $p$-$CH_3$-TPPNi. [c] Line widths in Hz at 100 MHz.

with $K = 16.7 \pm 0.6$, which is in excellent agreement with the present data in Table II. Hence the interaction can be explained by the formation of only 1:1 complexes. The 1:1 adducts have also been characterized for TNB with a variety of porphyrins[11,25,26] and chlorin-type[27] complexes. The 1:1 complex of MPCo with TNB has been isolated and its composition confirmed by elemental analysis.[11] Low-temperature ESR spectra also reflected[14] primarily 1:1 complexes with both $\pi$ donors and acceptors, though the existence of a 1:2 complex was noted. However, these measurements were made at 77 K, where a 1:2 complex may be stabilized.

$K$ for $p$-$CH_3$-TPPCo:TNB is $\frac{1}{7}$ as large as that for MPCo:TNB.[11] This probably reflects the steric influence of the meso-aryl groups which are essentially perpendicular to the heme plane.[28] This steric interference is also observed in the significantly reduced tendency of TPP complexes[16] to aggregate relative to those of natural porphyrin derivatives.[13] The decrease in $K$ for dinitrobenzene, DNB, and trinitrotoluene, TNT, is due to their weaker $\pi$ acceptor properties.[19] The fact that $K$ for the interaction with a strong $\pi$ donor, TMPD, is almost as large as with a strong $\pi$ acceptor (TNB) confirms the ability of metalloporphyrins to act as either $\pi$ acceptors or $\pi$ donors under the appropriate circumstances.

The thermodynamic parameters for formation of $p$-$CH_3$-TPPCo:TNB, obtained from a plot of log $K$ vs. $T^{-1}$ for the $K$'s determined over a temperature range +30 to −20 °C, yield a $\Delta H°$ which is very close to values reported for TNB complexes with a number of porphyrins[25,26] and chlorophylls.[27] The negative $\Delta S°$ is consistent with an associative equilibrium.

**Analysis of Shift Changes.** The data in Figures 1 and 2 clearly show that the porphyrin shifts are highly sensitive to $\pi$ complex formation. All of the shifts increase upon addition of TNB (or any acceptor), and decrease upon adding the donor, TMPD. We have already demonstrated[16] that for pure $p$-$CH_3$-TPPCo, the phenyl shifts arise solely from the dipolar interaction since the relative shifts follow closely the pattern predicted by the relative values of the calculated geometric factors.

In Tables III and IV we tabulate the relative values of the observed isotropic shift as a function of increasing TNB and TMPD concentration, respectively. For TNB, it is abundantly clear that the phenyl shift ratios are totally invariant with TNB concentrations, and therefore originate solely from the dipolar interaction in both $p$-$CH_3$-TPPCo and $p$-$CH_3$-TPPCo:TNB. In the case of adding TMPD (Table IV), there is a very slight change in shift ratios, but the final phenyl ratios are still consistent with >95% dipolar shifts in $p$-$CH_3$-TPPCo:TMPD.[29]

Since the phenyl shifts in both the pure complex and in the adducts with either a $\pi$ donor or $\pi$ acceptor are dipolar in origin, the *changes* in the magnitudes of the dipolar shifts directly reflect changes in the magnetic anisotropy, $g_\parallel^2 - g_\perp^2$. Table V gives the values for the dipolar shifts for the pure 1:1 complexes of TNB and TMPD. At 25 °C, the shifts for both the pure complex[16] and the adducts[30] obey the Curie law, so that the increase in shift for the TNB complex reflects an ~40% increase in $g_\parallel^2 - g_\perp^2$, where the decrease in shifts for the TMPD complex indicates a ~50% decrease in $g_\parallel^2 - g_\perp^2$. Assuming that $g_\parallel = 2.0$ in all cases, the changes in $g_\parallel^2 - g_\perp^2$ are consistent with $g_\perp \sim 3.2$ for the pure complex, increasing to 3.5–3.6 for the TNB complex,[31] and decreasing to ~2.6 for the TMPD complex. The shifts increase for all acceptors (i.e., see Table II), but the anisotropy is increased less for weaker $\pi$ acceptors. The significant increase in $g_\perp$ for the TNB complex is comparable to that reported[13] for MPCo:TNB ($g_\parallel = 1.8$, $g_\perp = 3.6$) while the decrease in $g_\perp$ for the TMPD complex is similar to that found by ESR[14] ($g_\parallel = 2.0$, $g_\perp = 2.4$); the solution structure at ambient temperature, however, does not necessarily correspond to the solid-phase structure at 77 K.

The dramatic increase in $g_\parallel^2 - g_\perp^2$ for the TNB (or any acceptor) complex must reflect a decrease in $\Delta E(a_1 - e)$. Since it has been shown[16] that solvation at the metal necessarily increases the $d_{z^2}$ energy and thereby increases $\Delta E(a_1 - e)$, the interaction between the acceptor and the porphyrin must occur at the porphyrin periphery. This proposed site of interaction is consistent with the suggestion of others.[11] In the companion study,[20] analysis of the porphyrin-induced shifts and relaxation of TNB confirms this proposal and provides a detailed solution structure for the complex.

The decrease in dipolar shifts for $p$-$CH_3$-TPPCo:TMPD requires that $\Delta E(a_1 - e)$ increase. Although this could arise from simple solvation[16] of the metal by TMPD, it is deemed unlikely by analogy to the TNB complex. If the amine group were capable of coordination, a much larger decrease in $g_\parallel^2 - g_\perp^2$ would be expected, comparable in magnitude to that observed[14] upon the coordination of heterocyclic or aliphatic amines. It is also considered very unlikely that tertiary amines can bond due to severe steric hindrance. We conclude that the increase in $\Delta E(a_1 - e)$ upon interaction with TMPD reflects a peripheral $\pi$ interaction as in the case of TNB (vide infra).

**Analysis of Line Width Changes.** Our model indicated[16] a parallel between increased anisotropy ($g_\parallel^2 - g_\perp^2$) and decreased NMR line width due to decreases in $\Delta E(a_1 - e)$. The data in Figure 2 and Table V demonstrate that the 40% increase in $g_\parallel^2 - g_\perp^2$ for the TNB complex is accompanied by a ~30% decrease in line width, while the 50% decrease in $g_\parallel^2 - g_\perp^2$ for the TMPD complex is accompanied by an increase in line width of a factor ≥2.5. It may be noted that small (~10–20%) increases in line width could be expected simply on the basis of a decrease in the rotational correlation[22] time of the larger complex. However, the decrease in porphyrin line width on forming the TNB complex demands that the changes in line width reflect directly changes in $T_{1e}$. Hence, changes in line width similarly indicate that $\Delta E(a_1 - e)$ is increased in the TMPD complex and decreased in the TNB complex, as was found from the changes in shifts.

**Changes in Co–P Bonding.** Since the interaction with substrates occurs at the porphyrin periphery, the changes observed for the metal must be transmitted through the bonding framework. Although interactions of the porphyrin

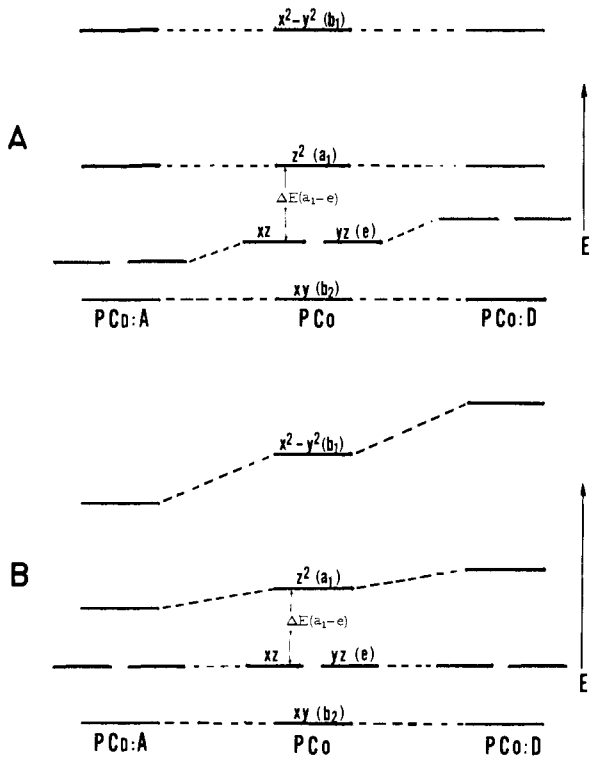


**Figure 3.** Energy levels of the d orbitals in PCo and the expected changes upon interaction with a $\pi$ acceptor, PCo:A, and a $\pi$ donor PCo:D. In A, only changes in $\pi$ bonding ($d_{xz}$,$d_{yz}$) are considered, while in B, changes solely in $\sigma$ bonding ($d_{z^2}$ and $d_{x^2-y^2}$) are considered.

$\pi$ system with the aromatic donor or acceptor $\pi$ electrons will certainly alter the Co-P $\pi$ bonding, it is not necessary that the changes in $\Delta E(a_1 - e)$ reflect changes primarily in $\pi$ bonding. In fact, the $\pi$-$\pi$ interaction can also modulate the $\sigma$ basicity of the porphyrin pyrrole nitrogens. It is of interest to inquire which of these two factors dominate in altering the electronic structure of the metal.

The effect of $\pi$ complex formation on M-P bonding will depend on whether we consider $\sigma$ or $\pi$ bonding, and whether the $\pi$ bonding involves M $\rightarrow$ P$\pi^*$ or P $\rightarrow$ M$\pi$ charge transfer.[32] In the following analysis we make the reasonable assumption that complexation with a $\pi$ acceptor will increase M $\rightarrow$ P$\pi^*$ charge transfer, decrease P $\rightarrow$ M$\pi$ charge transfer, and decrease the strength of P $\rightarrow$ M$\sigma$ bonding. Complexation with a $\pi$ donor will reverse each of these changes. In order to determine which type of changes dominate we will consider first changes arising solely from $\pi$ bonding changes, and then changes due solely to $\sigma$ bonding alterations.

Changes in $\pi$ bonding alone can only affect[32] the energy of $d_{xz}$,$d_{yz}$(e); the other orbital energies remain fixed. For M $\rightarrow$ P$\pi^*$ back-bonding, the spin is in the bonding linear combination, so that the acceptor will increase M $\rightarrow$ P$\pi^*$ charge transfer and stabilize $d_{xz}$,$d_{yz}$, thereby increasing $\Delta E(a_1 - e)$, as depicted in (A) of Figure 3. A donor will thus decrease $\Delta E(a_1 - e)$. In the case of P $\rightarrow$ M$\pi$ bonding, interaction with the acceptor will decrease P $\rightarrow$ M$\pi$ charge transfer, and since the spin is now in the antibonding orbital, decrease the energy of $d_{xz}$,$d_{yz}$, thereby also increasing $\Delta E(a_1 - e)$ (see Figure 3A). These predictions are totally inconsistent with the observed changes in $\Delta E(a_1 - e)$ upon interactions with either a donor or an acceptor. We therefore conclude that the changes in $\Delta E(a_1 - e)$ are not dominated by changes in Co-P$\pi$ bonding.

For changes solely in $\sigma$ bonding, the energy of $d_{xz}$,$d_{yz}$ remains fixed while $d_{z^2}$ (as well as $d_{x^2-y^2}$) will vary with changes in $\sigma$ bonding.[32] Interaction with the acceptor will lower the ligand basicity, decrease $\sigma$ bonding, and hence lower $d_{z^2}$; the reverse is true for a donor. As illustrated in (B) of Figure 3, lowering $d_{z^2}$ will decrease $\Delta E(a_1 - e)$, consistent with the observations of an increase in $g_\parallel^2 - g_\perp^2$ and a decrease in proton line width. Interaction with a $\pi$ donor will similarly increase $\sigma$ bonding, raise the $d_{z^2}$ energy, and hence increase $\Delta E(a_1 - e)$, which accounts for the observation in the presence of TMPD. Since the expected change in $\sigma$ bonding accounts for the change in $\Delta E(a_1 - e)$ with donor and acceptor while the changes in $\pi$ bonding do not, we conclude that the dominant changes in the cobalt energy levels due to $\pi$ complex formation are transmitted through the $\sigma$ system. From the magnitude of the change in the magnetic anisotropy, our results suggest that peripheral $\pi$ interactions such as those present in heme-protein linkage in myoglobins, hemoglobins,[33] and cytochromes[34] could play some role in modulating the electronic structure of heme iron.

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## References and Notes

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(30) In the presence of excess TNB, such that the 1:1 complex is complete-

ly formed, the porphyrin shifts obey the Curie law in the range +50 to −30 °C. The extended range over which the Curie law holds for the adduct indicates that the π-complex formation inhibits axial solvation of the $CDCl_3$, as noted in ref 14 and 15.

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# Proton NMR Studies of the Interaction of Metalloporphyrins with π Acceptors and Donors. II. Solution Structure of the 1:1 Adduct of 1,3,5-Trinitrobenzene with Tetra-*p*-tolylporphinatocobalt(II)

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**Abstract:** The isotropic shifts and relaxation induced in 1,3,5-trinitrobenzene, TNB, by tetra-*p*-tolylporphinatocobalt(II) are analyzed in terms of the formation of a 1:1 adduct. The induced TNB shift is separated into its ring current and dipolar contributions by determining the TNB shift for the related complex with a diamagnetic nickel(II) porphyrin. By assuming parallel π planes and scaling the known dipolar shift and line width for the *o*-H of the porphyrin by the ratio of known geometric factors for *o*-H to the computed geometric factors for TNB in various configurations, the solution structure of the 1:1 adduct is uniquely determined. This determination required the use of both the shift and relaxation geometric factors. The structure is consistent with a peripheral complex indicating purely π-π contacts, with the interplane spacing 3.2 ± 0.2 Å, and with TNB centered approximately over a pyrrole. The nitro groups are found not to interact with the cobalt in any manner.

Although the existence of π interactions of metalloporphyrins with aromatic donors or acceptors in the formation of molecular complexes is well documented,[2-9] to date there has not appeared an x-ray crystal structure which clearly defines the point of contact between the two π systems. The formation of an adduct between a metalloporphyrin and π substrate does not necessarily derive its stabilization primarily from π-π interaction. Thus chlorophyll dimerization[10] has been shown to involve primarily bonding forces where a carbonyl group of one molecule provides the axial base for the Mg ion in the other molecule. In the case of Co(II) porphyrin interaction with a transition metal complex acceptor, covalent bonds are formed[11] even though a π charge-transfer transition is observed.

Establishing π-π interactions as dominant sources of stabilization therefore depends on demonstrating that the interaction between a metalloporphyrin and π substrate occurs at the periphery of the porphyrin where the π-electron density is centered. The characterization of the factors contributing to such stabilization is central to understanding the important π-π heme–protein linkages which stabilize the tertiary structure of hemoproteins.[12,13]

Hill and co-workers[7-9] have carried out extensive proton NMR studies on the interaction of natural porphyrin cobalt(II) complexes with a variety of π substrates. They employed the proposed "shift reagent" properties[7-9] of low-spin Co(II) to induce dipolar shifts in the substrate which were then analyzed in terms of the orientation of the substrate relative to the metal and heme plane. However, most of the substrates[8] studied were highly complex and unsymmetrical, often containing functional groups capable of bonding to the metal. The low symmetry of the substrates as well as the porphyrin therefore afforded an undetermined system for which it was not possible to offer unique solution structures but rather families of approximate structures consistent with the available data.[8] In some cases, the substrate was so large that it totally overlapped the porphyrin plane,[8] making it difficult to estimate the dominant sources of stabilization for the complex. In a study using trinitrobenzene, TNB, it was suggested[7,9] that TNB resided over the pyrrole ring, but no evidence was presented to support this hypothesis. The reasonableness of this suggestion, however, is indicated by the x-ray characterization[14] of a series of TNB adducts with divalent metal complexes of salicylidinimine, salen, where the TNB was located exclusively over the ligand π system.

With the definitive characterization[15] of the origin of the phenyl isotropic shifts in the 1:1 complex of TNB with *p*-tolylporphinatocobalt(II), *p*-$CH_3$-TPPCo:TNB, as wholly dipolar,[16] as reported in the preceding paper, hereafter referred to as I, it should be possible to unambiguously determine the solution structure of the complex if there are available as many independent pieces of data as there are parameters necessary to describe the structure. TNB complexed with a synthetic porphyrin should provide the ideal case for determining the point of π-π contact which would be free from most of the problems[8] of aggregation and substrate and porphyrin symmetry.[17] TNB is axially symmetric so that its orientation relative to the porphyrin can be defined accurately with very few parameters (at least for the expected case of parallel π planes, vide infra).

In this study we will analyze the dipolar[16] shifts of TNB induced by *p*-$CH_3$-TPPCo in terms of the solution structure of the complex. In order to maximize the amount of experimental data and to improve the quality of the resulting structure, both shift and relaxation data[18] will be employed.