

- 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  $\pi$ -complex formation inhibits axial solvation of the  $\text{CDCl}_3$ , as noted in ref 14 and 15.
- (31) A more realistic set of  $g$  values for the TNB complex are  $g_{\parallel} = 1.8$ ,  $g_{\perp} = 3.5$ , which are very similar to the values reported for the 1:1 TNB complex with  $\text{MPCo}$  (ref 14).

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## Proton NMR Studies of the Interaction of Metalloporphyrins with $\pi$ 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  $\pi$  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  $\pi$ - $\pi$  contacts, with the interplane spacing  $3.2 \pm 0.2 \text{ \AA}$ , 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  $\pi$  interactions of metalloporphyrins with aromatic donors or acceptors in the formation of molecular complexes is well documented,<sup>2-9</sup> to date there has not appeared an x-ray crystal structure which clearly defines the point of contact between the two  $\pi$  systems. The formation of an adduct between a metalloporphyrin and  $\pi$  substrate does not necessarily derive its stabilization primarily from  $\pi$ - $\pi$  interaction. Thus chlorophyll dimerization<sup>10</sup> 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<sup>11</sup> even though a  $\pi$  charge-transfer transition is observed.

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

Hill and co-workers<sup>7-9</sup> have carried out extensive proton NMR studies on the interaction of natural porphyrin cobalt(II) complexes with a variety of  $\pi$  substrates. They employed the proposed "shift reagent" properties<sup>7-9</sup> 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<sup>8</sup> 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 undeter-

mined system for which it was not possible to offer unique solution structures but rather families of approximate structures consistent with the available data.<sup>8</sup> In some cases, the substrate was so large that it totally overlapped the porphyrin plane,<sup>8</sup> making it difficult to estimate the dominant sources of stabilization for the complex. In a study using trinitrobenzene, TNB, it was suggested<sup>7,9</sup> 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<sup>14</sup> of a series of TNB adducts with divalent metal complexes of salicylidinimine, salen, where the TNB was located exclusively over the ligand  $\pi$  system.

With the definitive characterization<sup>15</sup> of the origin of the phenyl isotropic shifts in the 1:1 complex of TNB with *p*-tolylporphinatocobalt(II), *p*-CH<sub>3</sub>-TPPCo:TNB, as wholly dipolar,<sup>16</sup> 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  $\pi$ - $\pi$  contact which would be free from most of the problems<sup>8</sup> of aggregation and substrate and porphyrin symmetry.<sup>17</sup> 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  $\pi$  planes, *vide infra*).

In this study we will analyze the dipolar<sup>16</sup> shifts of TNB induced by *p*-CH<sub>3</sub>-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<sup>18</sup> will be employed.

## Principles

Analysis of the TNB shift first requires obtaining the shift in the 1:1 complex, i.e.,  $(\Delta H/H)_c$ . Based on eq 3-5 in I, eq 6 in I can be rewritten<sup>15</sup> for the observed substrate (TNB) shift or line width:

$$\langle X \rangle_{\text{obsd}} = \Delta(X_c - X_f) \left[ \frac{P_0 + S_0}{2S_0} + \frac{1}{2S_0K} - \frac{1}{S_0} \sqrt{\left(\frac{P_0 - S_0}{2}\right)^2 + \frac{P_0 + S_0}{2K} + \frac{1}{4K^2}} \right] \quad (1)$$

where  $\langle X \rangle$ ,  $X_c$ ,  $X_f$  are the averaged, complexed and free observables (shift,  $\Delta H/H$ , or line width,  $\delta$ ), respectively, and  $P_0$  and  $S_0$  are the total amounts of *p*-CH<sub>3</sub>-TPPCo and TNB in the solution. A two-parameter complex fit of the experimental data to eq 1 will provide two more independent determinations of  $K$  to compare with the value obtained from porphyrin shifts in I.

Since the relative dipolar shifts of two nonequivalent protons are given by eq 2 of I, the geometric factor for the TNB protons in the 1:1 complex with *p*-CH<sub>3</sub>-TPPCo can be obtained directly by:

$$\langle (3 \cos^2 \theta - 1)r^{-3} \rangle_{\text{TNB}} = \langle (3 \cos^2 \theta - 1)r^{-3} \rangle_{o\text{-H}} \left( \frac{\Delta H}{H} \right)_{\text{dip}}^{\text{TNB}} / \left( \frac{\Delta H}{H} \right)_{\text{dip}}^{o\text{-H}} \quad (2)$$

$(\Delta H/H)_{\text{dip}}^{o\text{-H}}$  was determined in I and  $\langle (3 \cos^2 \theta - 1)r^{-3} \rangle_{o\text{-H}}$  has been computed<sup>19,20</sup> from x-ray data. Determination of  $(\Delta H/H)_{\text{dip}}^{\text{TNB}}$  via eq 1 will yield the geometric factor for TNB which can then be compared with values for a variety of structures.

Additional structural information can be obtained by analyzing the substrate line broadening. Paramagnetic relaxation of the TNB protons by the cobalt spin occurs exclusively by the dipolar mechanism,<sup>21</sup> for which the applicable equation for the axially symmetric  $g$  tensor is:<sup>18,22</sup>

$$\pi\delta = T_2^{-1} = Kr^{-6}[\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta]f(\tau) \quad (3)$$

where  $K = \gamma^2\beta^2S(S+1)/15$ ,  $f(\tau)$  is a function which is identical for all spins in the intact complex, and  $\bar{g}^2 = \frac{1}{3}(g_{\parallel}^2 + 2g_{\perp}^2)$  ( $\theta$  and  $r$  are as defined for the shift geometric factor in eq 1 of I). Hence the ratio of line widths for two nonequivalent protons in the 1:1 complex depends only on the relative values of  $(\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)r^{-6}$ , and leads to the equation:<sup>22</sup>

$$\langle (\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)r^{-6} \rangle_{\text{TNB}} = \langle (\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)r^{-6} \rangle_{o\text{-H}} \delta_{\text{TNB}} / \delta_{o\text{-H}} \quad (4)$$

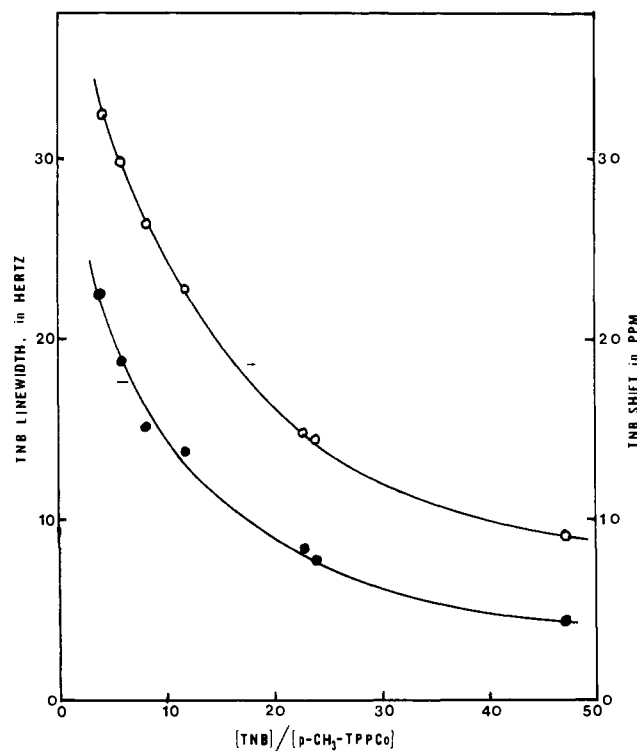
Since the term in brackets can be computed accurately for *o*-H,  $\delta_{o\text{-H}}$  is known,<sup>15</sup> and  $\delta_{\text{TNB}}$  is obtained by the fit to eq 1,  $\langle (\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)r^{-6} \rangle_{\text{TNB}}$  can be obtained and compared with values computed from various structures.

Furthermore, it will be shown that, while a unique structure cannot be determined using either only shift or only line width data, the simultaneous use of the data will provide a structure which clearly demonstrates the peripheral  $\pi$ - $\pi$  interaction.

## Experimental Section

The samples of *p*-CH<sub>3</sub>-TPPCo and TNB used in this study are those reported in I. *meso*-Tetraisopropylporphyrin and its Ni(II) complex, *p*-*i*-Pr-TPPNi, were prepared by the methods of Adler et al.<sup>23</sup> The shifts and line width for TNB in the presence of *p*-CH<sub>3</sub>-TPPCo and *p*-*i*-Pr-TPPNi were obtained from samples containing fixed amounts of porphyrin, and variable, carefully weighed amounts of TNB in CDCl<sub>3</sub> solutions.

Proton NMR spectra were recorded on a JEOL PS-100



**Figure 1.** Plot of the averaged TNB isotropic shift (O) and line width (●) as a function of the mole ratio TNB to *p*-CH<sub>3</sub>-TPPCo: [*p*-CH<sub>3</sub>-TPPCo] =  $6.74 \times 10^{-3}$  M, and  $T = 25^\circ\text{C}$ . The solid lines are the optimum computer fits to eq 1.

**Table I.** Equilibrium Constants, Shifts, and Line Widths for *p*-R-TPPM(II):TNB  $\pi$  Complexes<sup>a</sup>

Method	R	M	$K$	$(\Delta H/H)^b$	$\delta_c^c$
Porphyrin shift	CH <sub>3</sub>	Co	$17.5 \pm 0.5^d$	+7.46 ( <i>o</i> -H) <sup>d</sup>	
TNB shift	CH <sub>3</sub>	Co	$16.7 \pm 0.6$	+47.5	
TNB line width	CH <sub>3</sub>	Co	$21 \pm 4$		330
TNB shift	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	Ni	$12.7 \pm 0.7$	+7.35	

<sup>a</sup> At  $25^\circ\text{C}$ , in CDCl<sub>3</sub> solution. <sup>b</sup> Chemical shift difference between the proton in the 1:1 complex and either *p*-CH<sub>3</sub>-TPPM(II) or free TNB, in ppm. <sup>c</sup> Line width in Hz at 100 MHz. <sup>d</sup> Taken from I.

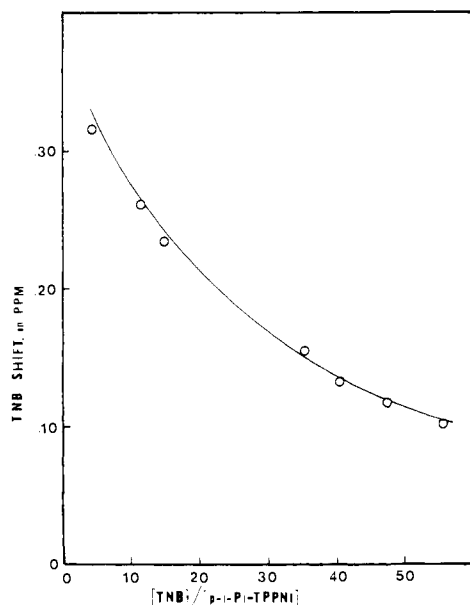
FTNMR spectrometer as described in I. Shifts are reported in ppm and line widths in Hz at 100 MHz. Computer calculations were carried out on a Burroughs B6700 computer. Fits to eq 1 were determined by an iterative least-squares minimization procedure. The geometric factors in eq 6 and 7 were computed using known TPPM(II)<sup>20</sup> and TNB geometry.<sup>24</sup>

## Results

Figure 1 illustrates a set of experimental data for the averaged TNB shift for fixed [*p*-CH<sub>3</sub>-TPPCo] and variable [TNB]. The solid line indicates the optimum computer fit, with  $K = 16.7 \pm 0.6$ . In this same figure we also present an example of the averaged [TNB] line width as a function of [TNB]. The optimum fit to eq 1, indicated in the solid line, yielded  $K = 21 \pm 4$ . The value for the coordinated shift and line width are given in Table I. The effect of *p*-*i*-Pr-TPPNi on the TNB shift is depicted in Figure 2, and the solid line reflects the computer fit, with  $K = 12.7 \pm 0.7$ . The TNB shift in the 1:1 complex is shifted 7.35 ppm upfield from the free TNB signal (9.39 ppm below TMS).

## Discussion

The equilibrium constant for formation of the 1:1 complex of Co(II) obtained from the TNB shifts and eq 1,  $K =$



**Figure 2.** Plot of the averaged TNB shifts as a function of the mole ratio of TNB to *p-i-Pr-TPPNi*:  $[p-i-Pr-TPPNi] = 4.73 \times 10^{-3}$  M,  $T = 25$  °C. The solid line represents the optimum computer fit to eq 1.

$16.7 \pm 0.6$ , is in excellent agreement with the value obtained in I from the porphyrin shifts,  $K = 17.5 \pm 0.5$ . Even  $K$  obtained from the TNB line width and eq 1 yields a  $K = 21 \pm 4$ , which is within experimental error of the much more accurate values from shift data. The large uncertainty in  $K$  from the line width data is due to difficulties in determining TNB line widths in the presence of the *p-CH<sub>3</sub>-TPPCo* signals at a number of TNB concentrations. Also, quantitative corrections from diffusional relaxation could not be made. Hence we choose to use the much more reliable average value from shift data,  $K = 17.5 \pm 1.0$ , to obtain  $\delta_c$ , the TNB line width in the 1:1 complex from accurately determined line width at low  $[TNB]/[p-CH_3-TPPCo]$  ratios. The values for  $\delta_c^{TNB}$ , as well as  $(\Delta H/H)_c^{TNB}$ , are listed in Table I.

**Analysis of TNB Shifts.** The TNB shift in *p-CH<sub>3</sub>-TPPCo:TNB*,  $(\Delta H/H)_c^{TNB}$ , however is not solely paramagnetic in origin, since it was referenced against free TNB, and therefore does not correct for any diamagnetic ring currents.<sup>25</sup> Such ring currents for  $\pi$  substrates have been reported,<sup>2,6-10</sup> so that the ring current contribution to  $(\Delta H/H)_c^{TNB}$  must be determined in order to obtain the dipolar contribution,  $(\Delta H/H)_{dip}^{TNB}$ , i.e.,

$$\left(\frac{\Delta H}{H}\right)_c^{TNB} = \left(\frac{\Delta H}{H}\right)_{rc}^{TNB} + \left(\frac{\Delta H}{H}\right)_{dip}^{TNB} \quad (5)$$

$(\Delta H/H)_{rc}^{TNB}$  can be determined from the TNB shift from the free TNB position in an analogous 1:1 complex of a diamagnetic nickel(II) porphyrin. A TPP-type complex of Ni(II) should serve as an excellent model for obtaining the ring current contribution, since the structural similarity of the pure complexes should produce very similar 1:1 complexes with TNB.<sup>26</sup> Due to the improved solubility, *p-i-Pr-TPPNi* was selected and its effect on TNB shifts determined. The data and computer fit to eq 1 are given in Figure 2, and the resulting  $K$  and  $(\Delta H/H)_{rc}^{TNB}$  are listed in Table I.

The value of  $(\Delta H/H)_c^{TNB}$  in the Co(II) complex and  $(\Delta H/H)_{rc}^{TNB}$  from the Ni(II) complex and eq 5 yield  $(\Delta H/H)_{dip}^{TNB} = +40.1$  ppm, as recorded in Table II. The paramagnetic contribution to  $(\Delta H/H)_c^{TNB}$  can be attributed solely to the dipolar interaction since our analysis in I

**Table II.** Dipolar Shifts and Calculated Geometric Factors for TNB and *o*-H Protons in *p-CH<sub>3</sub>-TPPCo:TNB*<sup>a</sup>

	TNB	<i>o</i> -H
$(\Delta H/H)_c$ , ppm	+47.5	+7.46 <sup>b</sup>
$(\Delta H/H)_{rc}$ , ppm	7.35	0 <sup>b</sup>
$(\Delta H/H)_{dip}$ , ppm	+40.1	+7.46 <sup>b</sup>
$\delta_c$ , Hz	330	36 <sup>b</sup>
$\langle (3 \cos^2 \theta - 1)/r^3 \rangle$ , Å <sup>-3</sup>	$1.97 \times 10^{-2}$ <sup>c</sup>	$3.62 \times 10^{-3}$ <sup>c</sup>
$\langle (\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)r^{-6} \rangle$ , Å <sup>-6</sup>	$6.7 \times 10^{-3}$ <sup>e</sup>	$7.32 \times 10^{-4}$ <sup>f</sup>

<sup>a</sup> At 25 °C in CDCl<sub>3</sub> solution. <sup>b</sup> Taken from I. <sup>c</sup> Computed via eq 6. <sup>d</sup> Computed in ref 19. <sup>e</sup> Computed via eq 7. <sup>f</sup> Computed using same parameters as for  $(3 \cos^2 \theta - 1)r^{-3}$ , and  $g_{\parallel} = 1.8$ ,  $g_{\perp} = 3.5$ .

indicated that TNB does not interact with the metal ion (vide infra), and there is no delocalized  $\pi$  spin density<sup>19</sup> in cobalt(II) porphyrins. Also, both the aromatic proton and methyl protons in the trinitrotoluene complex were found to be upfield in I, as expected from the dipolar shift. Contact shift from  $\pi$  spin density would have resulted in shifts of opposite sign for the proton and methyl group.<sup>27</sup>

Using  $(\Delta H/H)_{dip}^{TNB} = +40.1$  ppm from Table II,  $(\Delta H/H)_{dip}^{o-H} = +7.46$  ppm from I, and the computed *o*-H geometric factor reported earlier,<sup>19,28</sup> eq 3 yields

$$\left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle_{TNB} = (1.97 \pm 0.2) \times 10^{-2} \text{ \AA}^{-3} \quad (6)$$

Similarly, inserting  $\delta_c^{TNB}$  from Table I,  $\delta_c^{o-H}$  from I, and the computed value for  $\langle (\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)r^{-6} \rangle_{o-H}$  into eq 4 yields:

$$\langle \bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \rangle_{TNB} r^{-6} = (6.71 \pm 0.6) \times 10^{-3} \text{ \AA}^{-6} \quad (7)$$

The appropriate values of  $g_{\parallel}$  and  $g_{\perp}$  to use are those determined by the upper limits of magnetic anisotropy, as estimated in I, namely  $g_{\parallel} = 1.8$  and  $g_{\perp} = 3.5$ . Such  $g$  values have been reported<sup>9</sup> for the 1:1 TNB complex with *meso*-porphyrin dimethyl ester cobalt(II). Since the geometric factors for both TNB and *o*-H are affected similarly for changes in  $g$  values, small changes of 0.1–0.2 affect the ratio insignificantly. These two experimentally determined geometric factors will permit determination of the structure if it can be described by at most two independent parameters.

**Structure Determination.** The problem of effecting a structure determination based on the data in eq 6 and 7 is made tractable when we make the reasonable assumption that if a  $\pi$ - $\pi$  interaction occurs at the porphyrin periphery, then the TNB and porphyrin  $\pi$  planes should be essentially parallel. This appears a sound assumption based on the high symmetry of TNB and the observation of parallel  $\pi$  planes in previously characterized TNB  $\pi$  complexes.<sup>29</sup> Failure to make this assumption leads to too many parameters and an insoluble structure. The validity of this assumption is also strongly supported by the physical reasonableness of the resulting studies (vide infra).

Upon assuming parallel planes, the structure is described by two parameters  $Q$  and  $Z$ , as illustrated in Figure 3. The axial symmetry of the porphyrin renders both TNB geometric factors independent of the rotational angle in the  $x,y$  plane. However, inspection of space-filling molecular models<sup>30</sup> clearly indicates that the perpendicular orientation of the *meso*-aryl groups<sup>20</sup> precludes an approach of TNB for  $Z \leq 4$  Å unless the approach is with the center of TNB along a vector passing through the trans nitrogens, i.e., along either the  $x$  or  $y$  axes, as shown in Figure 4. Since our calculations show that the computed  $\langle (3 \cos^2 \theta - 1)/$

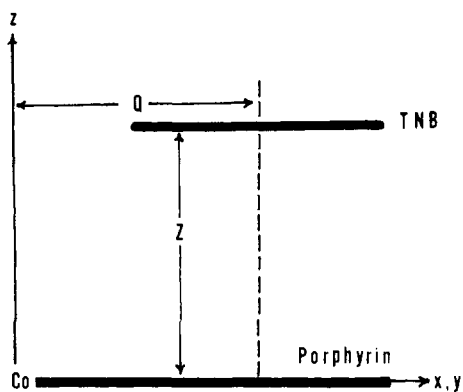


Figure 3. Definition of the two structural parameters for the 1:1 adduct with parallel  $\pi$  planes;  $Z$  is the interplane spacing, and  $Q$  is the radial distance of the center of TNB from the  $Z$  axis.

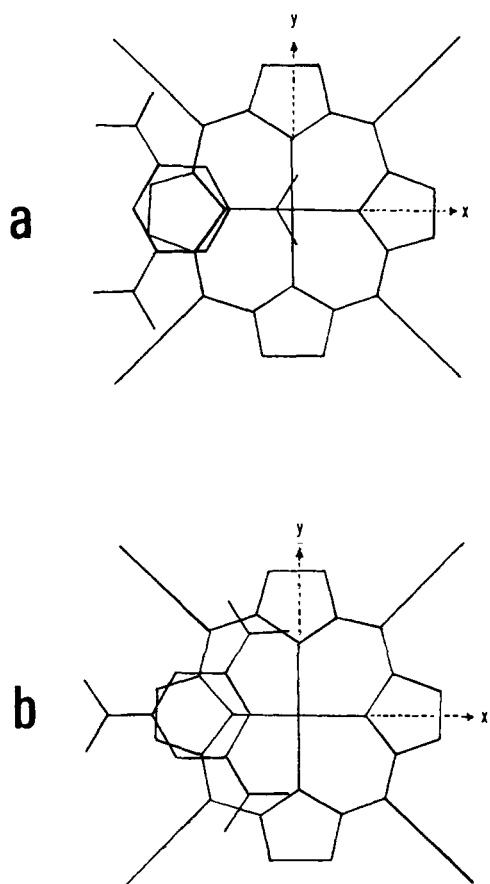


Figure 4. Structural models depicting possible rotational orientations of TNB relative to the  $x$  axis. In (a), a nitro group points toward the metal (case (ii) in text), while in (b), the nitro group points away from the metal (case (iii) in text).

$r^3)_{\text{TNB}}$  for  $Z \geq 4$  cannot account for the observed value in eq 6, we proceed based on interaction with the center of TNB along the  $x$  (or  $y$ ) axis.

Molecular models indicate<sup>30</sup> that van der Waals contact between TNB and the porphyrin plane can occur under the above conditions with no serious steric interactions, but that TNB would not be free to rotate about the  $C_3$  axis in the 1:1 complex. This latter observation leads us to consider three models: (i) a centrosymmetric model with the TNB center directly over the cobalt, (ii) the TNB center on the  $x$  axis with an  $\text{NO}_2$  pointing toward the metal, i.e. (a) in Figure 4, and (iii) same as (ii) except that the  $\text{NO}_2$  is pointing away from the metal, as depicted in (b) of Figure 4. The interconversion between models (ii) and (iii) in the complexed form

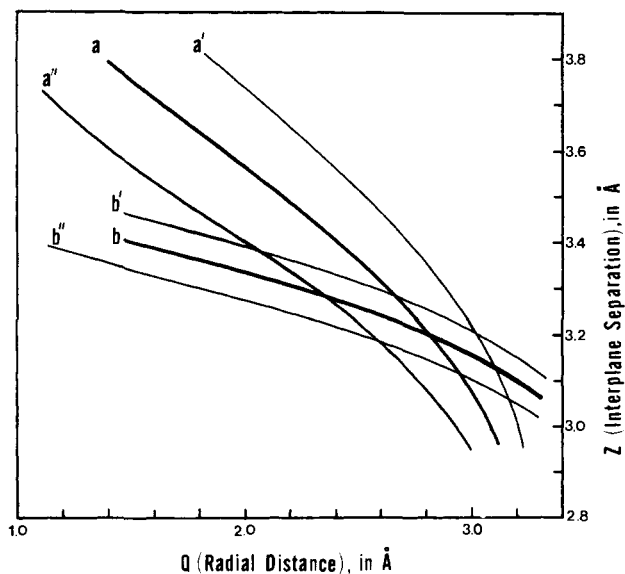


Figure 5. Graph of the possible combinations of  $Z$  and  $Q$  which satisfy the shift data in eq 6 (line a), and the line width data in eq 7 (line b). Lines  $a'$ ,  $a''$ ,  $b'$ , and  $b''$  indicate the 10% error limits in the determined geometric factors.

is prevented by the meso-aryl groups and can only occur via dissociation of the complex. Computer calculations were carried out for the geometric factors in eq 6 and 7 as a function of  $Q$  and  $Z$  for each of the three models, and the results were compared with the experimentally determined values. Since there are two sets of nonequivalent TNB protons in each of models (ii) and (iii) which are averaged by rapid exchange with free TNB, the computed average geometric factor, (GF) for the three TNB protons, is given by

$$\langle \text{GF} \rangle_{\text{av}}^{\text{TNB}} = \frac{1}{3} \sum_{i=1}^3 (\text{GF})_i \quad (8)$$

For model (i), the centrosymmetric case, the largest value of  $\langle (3 \cos^2 \theta - 1)r^{-3} \rangle_{\text{TNB}} \leq 0.017$  was found at  $Z = 3.0$  Å. However, this maximum value<sup>31</sup> is still 15% smaller than the experimentally determined value, and the predicted line width is too large by a factor of 2. For the interplane spacing for which eq 7 is satisfied,  $\langle (\cos^2 \theta - 1)r^{-3} \rangle_{\text{TNB}}$  is too low by a factor of 2. Hence this model can be discarded. The lack of direct axial interaction was also indicated by the increase in magnetic anisotropy, as discussed in I.

In the case of model (ii) where the  $\text{NO}_2$  group is pointing toward the metal, it is again found that the maximum positive<sup>31</sup> value for the geometric factor, independent of  $Q$  and  $Z$ , is  $\langle (3 \cos^2 \theta - 1)r^{-3} \rangle_{\text{TNB}} \leq 0.017$ , which occurs at  $Z = 3.2$  and  $Q = 0.3$  Å. This value is again 15% too low, reflecting the inappropriateness of this model. Furthermore, the value of  $Q = 0.3$  Å places the TNB essentially over the metal, which is totally inconsistent with the changes in magnetic anisotropy characterized in I. The inability to predict the geometric factor given in eq 6 leads us to reject this model as unrealistic.

The computed geometric factors for model (iii) are given in Figure 5. The combinations of  $Z$  and  $Q$  consistent with eq 6 are line a, while those combinations consistent with eq 7 are labeled line b. Lines  $a'$  and  $a''$  represent the error limits for line a, while  $b'$  and  $b''$  serve the same purpose for b. As seen in Figure 5, a precise fit to both eq 6 and 7 is obtained at  $Z = 3.2$  Å and  $Q = 2.8$  Å. Within the error limits of the two geometric factors, structures consistent with the data are found in the area bounded by lines  $a'$ ,  $a''$ ,  $b'$ , and  $b''$ , with ranges of  $3.1 \leq Z \leq 3.4$  Å and  $2.2 \leq Q \leq 3.3$  Å. We therefore conclude that the solution structure repre-

sents a peripheral  $\pi$  complex with an interplane spacing of  $3.2 \pm 0.2 \text{ \AA}$  and the TNB over the pyrrole with its center displaced  $0.4 \pm 0.4 \text{ \AA}$  from the center of the pyrrole ring toward the cobalt, and a proton pointing toward the metal. The schematic structure (b) of Figure 3 is drawn to scale and depicts the structure as determined above.

This structure based on model (iii) is consistent with other x-ray crystallographically characterized  $\pi$  complexes of TNB for which interplane spacings in the range 3.2–3.5  $\text{\AA}$  have been obtained.<sup>14,25</sup> For the related salen-metal complexes  $Z = 3.25 \text{ \AA}$  prevailed.<sup>14</sup> The location of the TNB over a pyrrole is also consistent with expectations for a  $\pi$ - $\pi$  complex in that this is the location of the maximum  $\pi$  electron density in the porphyrin. The apparent greater stabilization of the orientation with the  $\text{NO}_2$  pointing away rather than toward the cobalt probably arises from steric interaction of the two equivalent  $\text{NO}_2$  groups with the adjacent meso-aryl groups, as shown in (a) of Figure 4. The preference for the orientation of the  $\text{NO}_2$  group away from the metal underscores the absence of important stabilizing effects from substrate-functional-group interactions with the metal and confirms the dominance of  $\pi$ - $\pi$  interaction.

In addition to providing a definitive description of the solution structure of the *p*- $\text{CH}_3$ -TPPCo:TNB complex, the present analysis demonstrates the utility of employing relaxation data to complement shift data in effecting meaningful quantitative structural determination by NMR.

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## References and Notes

- (1) Fellow of the Alfred P. Sloan Foundation.
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