Correlations between Raman Frequencies and Structure for Planar and Nonplanar Metalloporphyrins

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Resonance Raman spectra were obtained for two series of metalloporphyrins, and frequencies of structure-sensitive Raman lines are correlated with structural changes in the porphyrin macrocycle. In the first series, metal derivatives of tetracyclohexenyltetraphenylporphyrin (TC_6TPP), the porphinato core size is varied by varying the metal (Ni < Co < Cu), causing little change in the planarity of this nonplanar porphyrin. In the second series, nickel complexes of tetracyclo*pentenyl*-, tetracyclo*hexenyl*-, and tetracyclo*heptenyl*tetraphenylporphyrin ($NiTC_xTPP$, where x = 5–7), the size of the alkyl ring at the β-carbon positions of the pyrrole rings is varied. In the $NiTC_xTPP$ series, the porphyrin macrocycle becomes significantly more nonplanar as the alkyl ring becomes larger and steric crowding increases. As a consequence of the increasing nonplanarity, the porphyrin core contracts. Correlations between Raman frequencies and structural parameters, including core size and C_α–N–C_α angle (obtained from molecular mechanics calculations), are found for both series of porphyrins. These new correlative relationships are compared to similar relationships previously observed for metal octaalkylporphyrins, metal tetraphenylporphyrins, and a series of Ni octaalkyltetraphenylporphyrins. Most importantly, by comparing the metal series (Ni, Co, Cu, Zn, etc.) for differing porphyrin ligands, we find a trend toward weaker frequency dependence on core size for the more nonplanar porphyrins. Thus, the applicability of this useful structural correlation is extended to both planar and nonplanar porphyrins. Finally, the differences between these correlative relationships are traced to more fundamental (Badger's rule) relationships between vibrational frequencies and the length of bonds contributing to the total potential energy of the vibrational modes corresponding to the structure-sensitive Raman lines.

Introduction

The nonplanar conformation of metalloporphyrins may play a role in determining the biological properties and function of tetrapyrrole cofactors of proteins. Of ultimate interest are the relationships between macrocycle planarity and reactivity in tetrapyrrole-containing biological systems such as the special pair in the photosynthetic reaction center, heme (Fe porphyrins) in hemoproteins, and cofactor F_{430} in methanogenic bacteria. Resonance Raman spectroscopy has proven useful for investigating the nonplanar distortions of metalloporphyrins;[1–5] however, a more precise interpretation of how the shifts of structure-sensitive Raman lines correlate with the structure of metalloporphyrins is needed. A better understanding of the relationships between vibrational frequencies and structure can lead to new structure–function relationships and their more reliable application to the proteins. These relationships can then be applied to developing a better understanding of the biological reactions and can also be used in the design of biomimetic metalloporphyrin catalysts.[1,6]

To obtain improved structure–frequency relationships that are applicable when nonplanar macrocycle distortions are present, we have used resonance Raman spectroscopy to investigate two series of nonplanar metalloporphyrins. The structural parameters for these correlations are calculated using a molecular mechanics force field which has been highly successful in predicting X-ray crystal structures.[1,2] The relationships found for these two new series are then compared to corresponding relationships noted previously for other porphyrin series[1,2,8–14] with the objective of reaching the stated goals of obtaining more universally applicable relationships and improving the Raman technique as a probe of tetrapyrrole-containing proteins.

It is well-known that the frequencies of certain Raman lines are especially sensitive to the metalloporphyrin core size.[2,7–11] The core size, δ, which is defined hereinafter as the length of the projection of the metal–nitrogen bond into the average plane of the heavy atoms of the porphyrin macrocycle, is particularly sensitive to the type of metal atom and its oxidation, spin, and axial ligation states.[11] The correlations with metalloporphyrin core size have mostly been determined for planar porphyrins that are prototypical of biological cofactors such as most hemes. In particular, the metal protoporphyrins (PP),[12] octaethylporphyrins (OEP),[13,14] and tetraphenylporphyrins (TPP),[10,14] have been examined extensively with regard to the mechanism of core expansion or contraction. However, in a recent study,[1] we found that systematic insertion of a particular series of metal ions into a nonplanar porphyrin results in an expanded core, an increased

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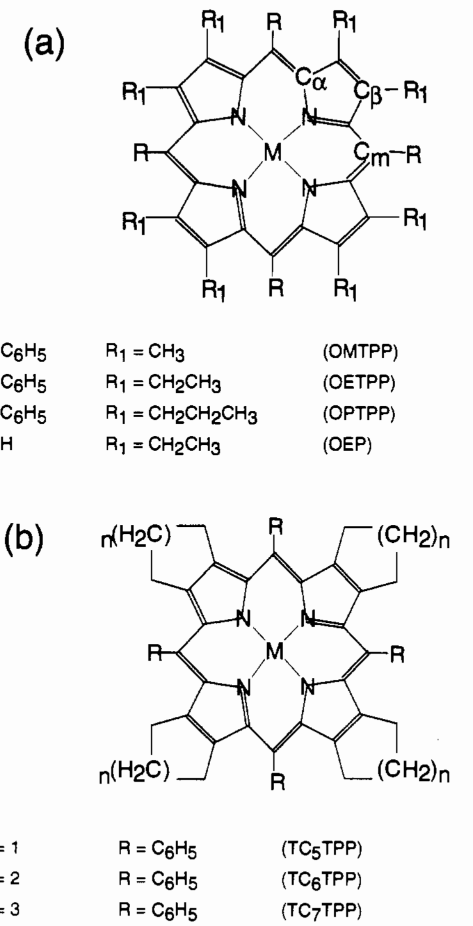
pyrrole C_α–N–C_α angle (θ), and systematic changes in several other structural parameters. A detailed examination of these structural variations shows that for metal substitution many structural parameters change in a correlated fashion, although it was originally thought that the pyrrole rings remained relatively rigid while most movement occurred in the C_m bridges.[12,15] (See Figure 1a for porphyrin atom labels.) For example, a good correlation between δ and θ is usually observed, but the correlations differ depending on the type of perturbation of the structure of the porphyrin (*e.g.*, increasing nonplanarity or increasing metal size).[1,2,8] Prendergast and Spiro have examined the dependence of vibrational frequencies on several structural parameters such as the C_α–C_m, C_α–C_β, C_β–C_β, and C_α–N bond lengths and the C_α–C_m–C_α angle.[14]

There are several ways in which δ may be intentionally altered to allow investigation of the relationship between δ and frequency. As already stated, incorporation of small metals like Ni decreases δ by a combination of in-plane and out-of-plane distortions. Hoard[7] noted that the porphyrin core size decreases as the degree of nonplanarity is increased. Shelnutt *et al.*[2] verified this trend using a series of nickel octaalkyltetraphenylporphyrins (OATPP) which exhibit different degrees of nonplanarity depending upon the amount of steric crowding of the peripheral substituents. Further, the relationships between Raman frequencies and δ for this series of porphyrins with increasing nonplanarity are very different from those observed for the planar porphyrins.[2] In particular, the Raman frequency versus δ correlation for the series of NiOATPPs has a positive slope (correlation) while for the planar porphyrins a negative slope (anticorrelation) is observed. That is, as the degree of nonplanarity of the porphyrin macrocycle increases, δ *decreases* and the structure-sensitive modes ν_4, ν_3, and ν_2 shift to *lower* frequencies, contrary to the conventional anticorrelation observed for metal complexes of planar porphyrins.[2]

The core size of nonplanar porphyrins can also be altered by substitution of different metals in the same way that led to the conventional core-size anticorrelation.[8] For example, for the metal series (Zn(II), Cu(II), Co(II), and Ni(II)) of OEPs and octaethyltetraphenylporphyrins (OETPPs), variation of the central metal ion *decreases* δ for this metal order and *increases* the frequencies of the modes ν_4, ν_3, and ν_2 (anticorrelation).[1] However, while the dependence on δ for the highly nonplanar MOETPP series is also an anticorrelation, the dependence on δ is much weaker (smaller slope magnitude) than for the planar MOEPs. Therefore, the observed relationship between Raman frequency and δ seems to depend on the type of systematic distortion imposed upon the macrocycle (*e.g.*, metal-induced core expansion) and on whether or not the macrocycle is distorted from planarity (*e.g.*, by steric crowding). Clearly, a better understanding of the origin of these correlations is necessary for their reliable application to biological systems.

In this study, new relationships between δ and frequency are found for the two series of highly substituted porphyrins shown in Figure 1—the porphyrin series of Ni(II) tetracyclo*alkenyl*tetraphenylporphyrins (NiTC$_x$TPP where x = 5–7) and the metal series of tetracyclo*hexenyl*tetraphenylporphyrins (Ni^{II}-, Co^{II}-, and Cu^{II}TC$_6$TPP). The structural parameters used in obtaining these new relationships are obtained from molecular mechanics calculations that have been validated by extensive comparison with X-ray crystal structures. Comparing the core-size relationships for these two series with the correlations determined previously, we find systematic differences in the correlations that are related to structure. Further, we discover more direct (Badger's rule) relationships between Raman frequencies and the length of the bonds whose force constants contribute to the structure-sensitive normal modes.



1:	$R = C_6H_5$	$R_1 = CH_3$	(OMTPP)
2:	$R = C_6H_5$	$R_1 = CH_2CH_3$	(OETPP)
3:	$R = C_6H_5$	$R_1 = CH_2CH_2CH_3$	(OPTPP)
4:	R = H	$R_1 = CH_2CH_3$	(OEP)

5:	n = 1	$R = C_6H_5$	(TC$_5$TPP)
6:	n = 2	$R = C_6H_5$	(TC$_6$TPP)
7:	n = 3	$R = C_6H_5$	(TC$_7$TPP)

Figure 1. (a) Structures of octaethylporphyrin (OEP) and the octaalkyltetraphenylporphyrins (OATPPs) including octamethyl-, octaethyl- and octapropyltetraphenylporphyrins. (b) The metal TC$_x$TPP series, tetracyclopentenyl- (x = 5), tetracyclohexenyl- (x = 6), and tetracycloheptenyltetraphenylporphyrin (x = 7).

Materials and Methods

Synthesis. The syntheses of TC$_5$TPP, TC$_6$TPP, and TC$_7$TPP have been described elsewhere.[16a] The metal complexes were prepared using the standard metal acetate procedure.[16b]

Resonance Raman Spectroscopic Studies. Resonance Raman spectra were obtained using either the 413.1-nm line from a krypton ion laser or the 457.9-nm line from an argon ion laser (Coherent, Inc.) as the excitation source. Details of the Raman instrument are given elsewhere.[17] For solution spectra, the metalloporphyrins were dissolved in carbon disulfide and ~150-μL aliquots were added to each side of a two-compartment Raman cell. Laser power was typically ~100 mW at the sample, and sample concentrations were in the range 1×10^{-4} to 1×10^{-5} M. NiOETPP was added to the reference chamber, and resonance Raman spectra of pairs of metalloporphyrins were obtained simultaneously. Frequencies were obtained from the peak positions of the lines in fast-Fourier-transform smoothed spectra. The Raman modes were assigned on the basis of previous normal-coordinate analyses[18] and recent isotopic substitution and normal-coordinate studies of NiOETPP.[19]

Sample integrity was monitored by UV–visible absorption spectroscopy before and after the Raman spectrum was obtained and by examination

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Table 1. Frequencies of Structure-Sensitive Raman Lines and Selected Structural Parameters[a] for the $NiTC_xTPP$ and MTC_6TPP Series

	line frequencies (cm^{-1})			bond lengths (Å)					angles (deg)		
porphyrin	ν_4	ν_3	ν_2	δ[b]	M–N	C_m–C_α	N–C_α	C_β–C_β	θ[c]	C_α–C_m–C_α	N–M–N
$NiTC_5TPP$[d]		1526	1587	1.969	1.969	1.380	1.407	1.287[e]	105.3	121.7	180.0
$NiTC_6TPP$[d]	1371	1513	1577	1.919	1.933	1.391	1.393	1.335	106.0	122.3	165.6
$NiTC_7TPP$[d]	1369	1505	1564	1.882	1.907	1.395	1.387	1.342	106.1	122.2	161.6
$NiTC_6TPP$[d]	1371	1513	1577	1.919	1.933	1.391	1.393	1.335	106.0	122.3	165.6
$CoTC_6TPP$	1366	1507	1575	1.961	1.973	1.395	1.392	1.337	106.8	123.2	167.6
$CuTC_6TPP$	1366	1503	1570	1.983	1.994	1.397	1.392	1.339	107.3	123.7	168.5

[a] Data obtained from molecular mechanics calculations. [b] Core size, δ, is defined as the length of the projection of the M–N bond into the mean porphyrin plane. [c] The pyrrole or C_α–N–C_α angle (see Figure 1). [d] Raman frequencies from ref 2. [e] C_β–C_β bond length is probably underestimated (see caption for Figure 4).

of individual 20-min scans of the Raman spectrum. Porphyrin photodegradation was not noted during the 5–10 scans required to obtain Raman spectra.

Molecular Mechanics Calculations. Molecular mechanics calculations were performed using BIOGRAF software (Molecular Simulations, Inc.) and a specialized porphyrin force field developed by Shelnutt *et al.*[2] for nickel and subsequently modified for other metals.[1] The force field was formulated on the basis of a recent NiOEP normal-coordinate analysis,[18d] the DREIDING force field,[20] and the crystal structure of planar triclinic B NiOEP.[4] Specifically, the force constants for bond stretching, angle bending, and bond torsions were obtained from the normal-coordinate analysis of nickel octaethylporphyrin.[18d] For substituents other than alkyl groups, the DREIDING force constants and structural parameters were used.[20] The nonbonding parameters for the van der Waals potentials and partial atomic charges for all atoms were taken from the DREIDING force field.[20]

The conjugate-gradient minimization technique[21] was used to obtain the energy-minimized metalloporphyrin structures. It was important that the convergence criterion was set to 0.001 kcal/(mol Å) for the root-mean-square force to ensure convergence of the structure. Calculations were performed on a MicroVAX II computer (Digital Equipment Corp.) and displayed on a PS390 graphics workstation (Evans & Sutherland, Inc.), a Personal Iris 4D35, or a 4D210 Power Series workstation (Silicon Graphics, Inc.).

Results and Discussion

Although the correlations between δ and the frequencies of a group of Raman lines called the "core-size marker lines" have been used extensively,[8-11] the origin and the range of applicability of these empirical correlations are not well understood, especially with regard to nonplanar porphyrins. The nonplanar porphyrins in both series that were examined are similar in that they have phenyl substituents at the methine bridge carbons and alkyl substituents at the β-carbons of the pyrroles. However, the systematic perturbations on the conformation of these porphyrins are different for the two series, *i.e.*, variation of the metal or variation of the steric crowding at the periphery. It has already been established that the nickel complexes of TC_5TPP, TC_6TPP, and TC_7TPP have increasing degrees of nonplanarity as a result of the steric requirements of the larger alkyl rings (Table 1).[2] $NiTC_5TPP$ is calculated to be planar, and $NiTC_6TPP$ and $NiTC_7TPP$ are predicted to be saddle shaped, with $NiTC_7TPP$ being the most distorted. These predictions have been confirmed by NMR,[22] X-ray,[23] and EXAFS[23] measurements.

Structural data from the molecular mechanics calculations are listed in Table 1, including θ, δ, and the C_m–C_α and C_β–C_β bond distances. The M–N and N–C_α bond distances and the C_α–C_m–C_α and N–M–N angles are also given. The N–M–N angle of interest here extends across the porphyrin ring (two opposing nitrogens) and indicates the magnitude of the saddle-type distortion of the porphyrin macrocycle. For a strictly planar porphyrin, this angle is 180°, but for saddle-shaped porphyrins, this angle is reduced as for the highly distorted $NiTC_7TPP$ (162°).

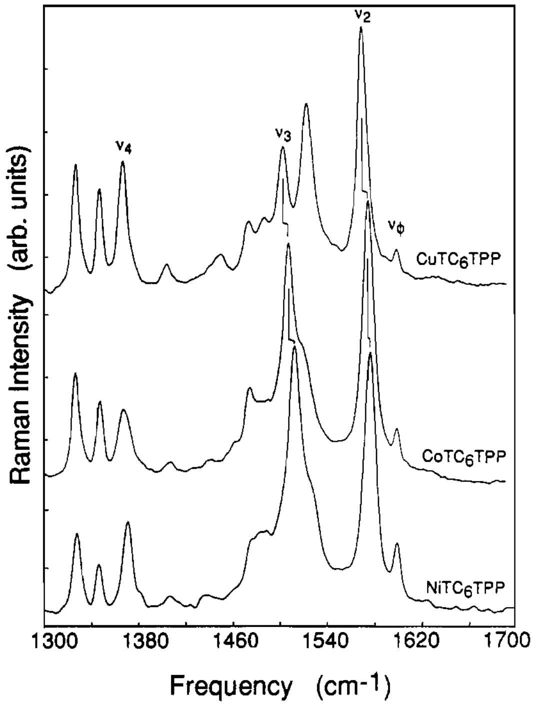

Figure 2. Raman spectra of the MTC_6TPP (M = Ni, Co, Cu) series. Upshifts in the frequencies of ν_2 and ν_3 upon core contraction are indicated. Excitation wavelengths were 413.1 nm (Cu and $CoTC_6TPP$) and 457.8 nm ($NiTC_6TPP$), and all samples were dissolved in carbon disulfide.

Resonance Raman spectra of the MTC_6TPP series are shown in Figure 2, and the Raman frequencies of the main structure-sensitive modes for both series are listed in Table I. As the metal–nitrogen bond distance decreases (Cu > Co > Ni) for the MTC_6TPP series, the modes ν_3 and ν_2 shift to higher frequency by 10 and 7 cm^{-1}, respectively. Similar shifts are observed for these modes in the MOEPs and MOETPPs[1] for the same series of metals. Raman spectra of the $NiTC_xTPP$ series have been published previously.[2] In the $NiTC_xTPP$ series, the frequencies of ν_3 and ν_2 decrease by up to 21 and 23 cm^{-1}, respectively,[2] as x and the macrocyclic distortion from planarity increase (and δ decreases). The spectrum of $NiTC_5TPP$ is of significantly poorer quality due to the low solubility of this compound, and definite assignment of ν_4 was not possible.[2] Raman lines in the region of this oxidation-state marker line are weak and may be shifted due to mixing with vibrational modes of the five-membered ring. Interestingly, there are two additional strong Raman modes in the vicinity of ν_4 (Figure 2) that are not usually observed in spectra of planar porphyrins (such as the OEPs) lacking the alkyl rings at the β-carbons of the pyrroles. Polarized spectra of $NiTC_6TPP$ indicate that both new lines are a_{1g} modes.[2]

In Figure 3, the frequencies of the structure-sensitive Raman lines, ν_2 and ν_3, are plotted versus δ (a) and θ (b). Slopes and intercepts from the least-squares fits are listed in Table 2 for the $NiTC_xTPP$ series and the MTC_6TPP series; also included in Table

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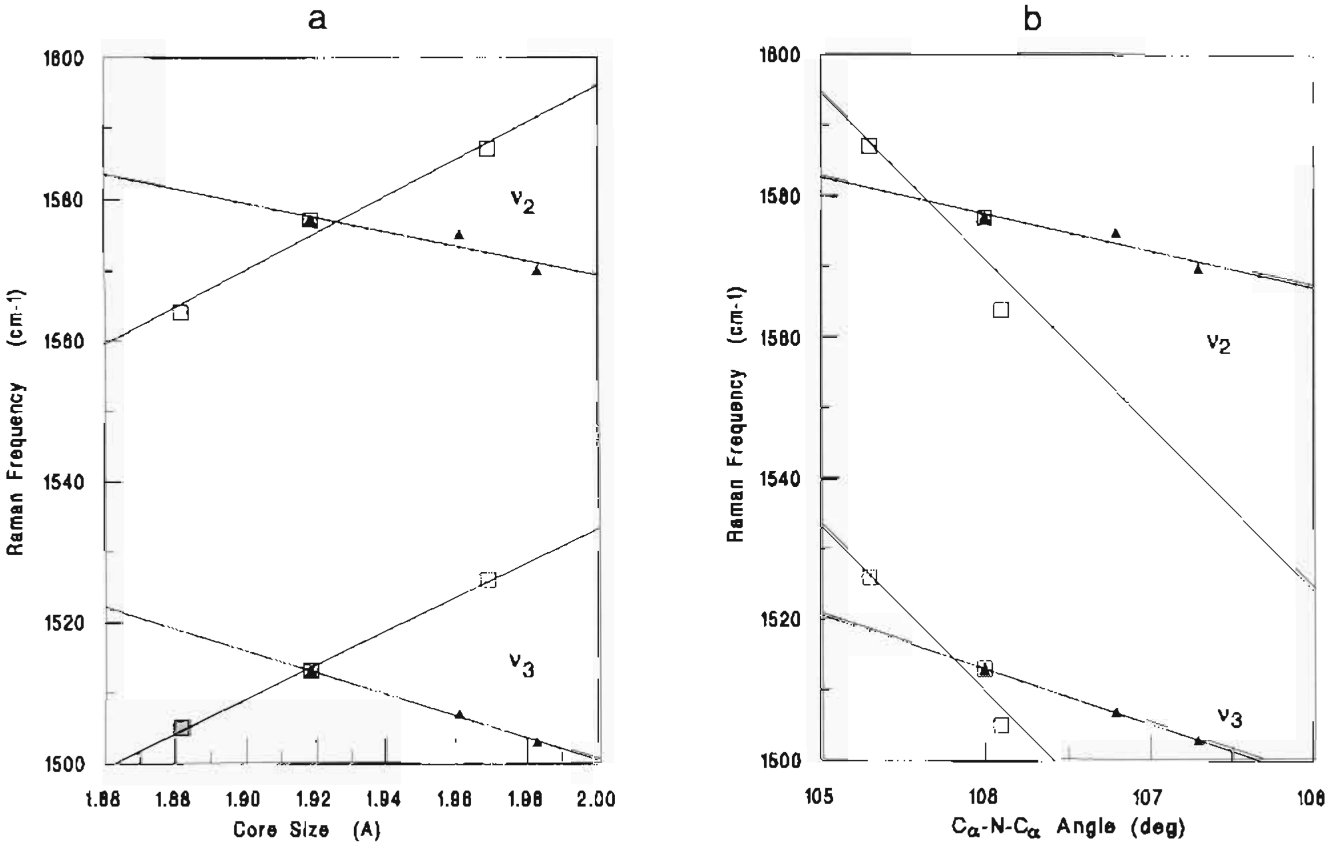

Figure 3. (a) Plot of the relationship between the Raman frequencies of ν_2 and ν_3 and the core size. Note the opposite slopes of the lines for the two perturbations: positive for increased degree of ruffling (squares: NiTC$_x$TPP, x = 5–7) and negative for increased metal size (triangles: MTC$_6$TPP, M = Ni, Co, Cu). (b) Relationship between the Raman frequencies of ν_2 and ν_3 and the C$_\alpha$–N–C$_\alpha$ angle. In this case, the slopes of the best fit lines for both series are negative.

Table 2. Slopes (–K) and Intercepts (*A*) for the Linear Relationships between Core Size (δ) and Raman Frequencies and between the C$_\alpha$–N–C$_\alpha$ Angle (θ) and Frequencies for the Structure-Sensitive Raman Lines ν_3 and ν_2

	δ				θ			
	ν_3		ν_2		ν_3		ν_2	
	K^a	A^a	K	A	K^a	A^a	K	A
	Nickel Porphyrin Series							
NiTC$_x$TPP^b	–242	–4.3	–261	–4.1	23.4	170	23.4	173
NiOATPP (four points)^c	**–271**	**–3.7**	**–703**	**–0.3**	**8.7**	**279**	**22.5**	**175**
NiOATPP (seven points__	–213	–5.2	–351	–2.6	11.1	242	23.7	172
	Metal Series							
MOETPP	**48**	**33.0**	**97**	**18.1**	**3.1**	**595**	**6.6**	**342**
MOETPP	48	33.1	84	20.4	2.4	738	4.2	476
MTC$_6$TPP^d	155	11.7	101	17.5	7.7	303	5.1	414
MOEP^e	**410**	**5.7**	**234**	**8.8**	**16.1**	**199**	**9.3**	**277**
MOEP^e	443	5.4	255	8.3	12.5	226	7.2	327
MPP^f	**488**	**5.4**	**391**	**6.0**				
MTPP^g	**410**	**5.5**	**262**	**8.0**				

[a] K is the slope (cm^{-1}/Å or cm^{-1}/deg) and *A* is the intercept (Å or deg) for the relation $\nu = K(A - \delta)$, where ν is the Raman frequency and δ is the core size (Å). [b] "*x*" indicates the series in which five-, six-, and seven-membered rings connect the two β-carbons on each pyrrole ring. [c] **Bold** text indicates correlations using structural data taken from X-ray crystal structures; normal text indicates structural data taken from molecular mechanics calculation. [d] The central metal ions, M, in this series are Ni(II), Co(II), and Cu(II). [e] Metals are Ni, Co, Cu, and Zn; data from ref 27. [f] Data from ref 24. [g] Data from ref 9.

2 are slopes and intercepts for the metal complexes of OEP, OETPP,[1] PP,[24] and TPP.[9] Comparison of cases for which the relationships are known from both X-ray structural data and molecular mechanics data suggest that the molecular mechanics results are accurate.

The NiTC$_x$TPP series shows a correlation between Raman frequency and core size with a slope that is *positive* (*K* is negative in $\nu = K(A - \delta)$). The relationship is similar to that observed for a series of NiOATPPs, which consisted of a wider range of dodecasubstituted porphyrins (four porphyrins for X-ray data; seven porphyrins for molecular mechanics data) in addition to the NiTC$_x$TPP series. The slopes for the NiOATPP series are also listed in Table 2. In contrast with the slopes of these series in which the degree of planarity is varied, a *negative* slope (*K* is positive) is seen for the mostly planar metal complexes of OEP and TPP where the metal is varied.[2] Thus, δ correlates with frequency differently for these series of porphyrins, implying that δ is not the determining factor for the marker line frequencies.

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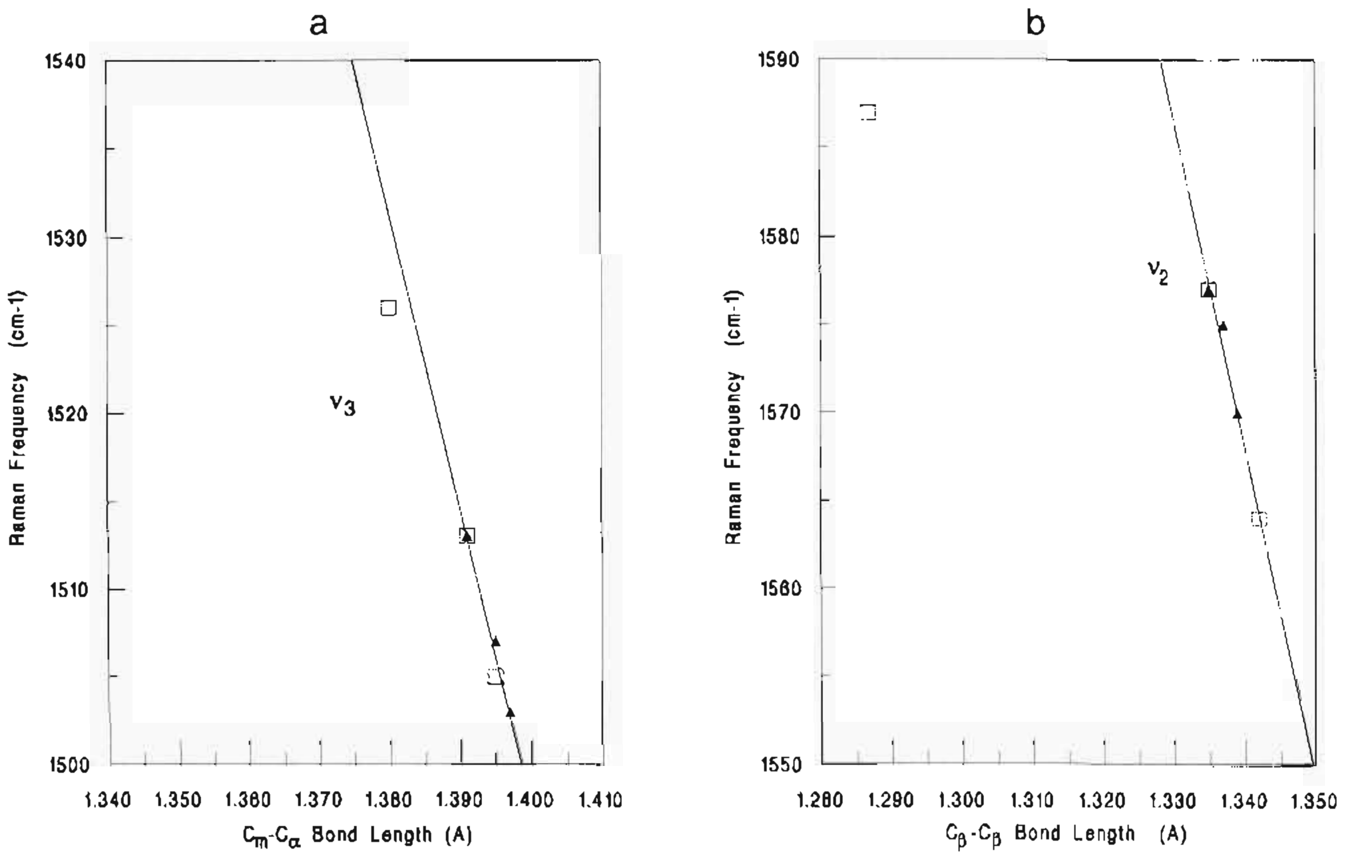

Figure 4. Relationships between the Raman mode and the bond whose vibration (stretching motion) is the primary component of the mode for the (squares) NiTC$_x$TPP (x = 5–7) and (triangles) MTC$_6$TPP (M = Ni, Co, Cu) series: (a) plot of the relationship between ν_3 and the C$_m$–C$_\alpha$ bond distance (slope= 1694 cm^{-1}/Å); (b) plot of the relationship between ν_2 and the C$_\beta$–C$_\beta$ bond distance (slope = 1869 cm^{-1}/Å). The slopes given are determined by omitting the unrealistic distances given by the calculations for the five-member-ring porphyrin; without omitting this point the slopes are 1352 and 310 cm^{-1}/Å for ν_3 and ν_2, respectively. X-ray data for NiTC$_5$(3,4,5-MeO-P)P show that the C$_\beta$–C$_\beta$ bond length is only 0.023 Å shorter for this NiTC$_5$TPP analog than for NiTC$_6$TPP. However, we calculate the C$_\beta$–C$_\beta$ bond length of NiTC$_5$TPP to be 0.048 Å smaller than for NiTC$_6$TPP. Using the smaller decrease in bond length would place the point for NiTC$_5$TPP closer to the least-squares lines through the other data points.

The different correlations with δ reflect the different types of structural perturbations of the porphyrin macrocycle. As systematic structural perturbations such as these are imposed on the porphyrin macrocycle, *all* structural parameters such as the bonds, angles, ϑ, and δ will most likely vary in a more or less systematic fashion. However, from a theoretical viewpoint, only the structural parameters that contribute to the potential energy distribution (PED) of a particular mode will determine its vibrational frequency. Specifically, correlations of the "Badger's rule" type[25,26] for the conjugated bonds of the macrocycle, which contribute to the structure-sensitive normal modes, are expected to determine their frequencies.

In the present case, we are fortunate enough to be able to observe these more fundamental relationships. Figure 4 shows the correlations between normal modes ν_3 (a) and ν_2 (b) and the length of the bond that is the major contributor to the PED of each of these normal modes. The percentage contributions to the PED for NiOEP indicate that the C$_m$–C$_\alpha$ and C$_\beta$–C$_\beta$ bond stretches are the primary components of ν_3 (28%) and the C$_\beta$–C$_\beta$ bond stretch is the primary component of ν_2 (45%).[18d] This type of correlation is more direct[26] than that between Raman frequency and δ, which is a secondary parameter that does not have a force constant or normal mode associated with it. Using the structural parameter that predominantly contributes to the PED of the structure-sensitive normal mode, we find that both sets of data (NiTC$_x$TPP and MTC$_6$TPP series) can be fit with the *same line* as shown in Figure 4a,b.

The least-squares fit of the line for the C$_m$–C$_\alpha$ bond distance (r^2 = 0.99) shows better agreement with all of the data points than that in Figure 4b for the C$_\beta$–C$_\beta$ bond distance (r^2 = 0.81). A better fit is obtained (shown in Figure 4b) if the outlying point for the five-membered-ring porphyrin is ignored. The better overall agreement in Figure 4a can be partially explained on the basis of peripheral substitution. In NiTC$_x$TPP, the C$_m$ substituents remain the same (all phenyl groups), while the C$_\beta$ substituents change from a five-membered ring to a seven-membered ring. One would therefore expect a higher degree of structural perturbation of ν_2 (C$_\beta$–C$_\beta$ stretch) than of ν_3 (C$_m$–C$_\alpha$ stretch) in the NiTC$_x$TPP series. Another possibility is that the molecular mechanics calculation may not be accurate enough for the strained five-membered ring of NiTC$_5$TPP. (See the caption of Figure 4).

Assuming that deformation of the contributing bond length(s) determines the frequency as Figure 4 implies, then the correlations between frequency and structural parameters like δ and θ must result from ancillary relationships between these bond lengths and δ or θ. Further, these coincidental relationships differ depending on the type of systematic perturbation imposed on the porphyrin conformation because different perturbations may affect the secondary parameter and the C$_m$–C$_\alpha$ and C$_\beta$–C$_\beta$ bond lengths differently. Ancillary relationships like those between the δ and the Raman frequencies may often be found, but they are largely fortuitous since these parameters are not directly related to the force constants that contribute to the normal modes. Further, the bond length–frequency relationships are rarely found for a high-frequency mode because the bond length variation is small (~0.01 Å) for strong bonds and errors in experimental

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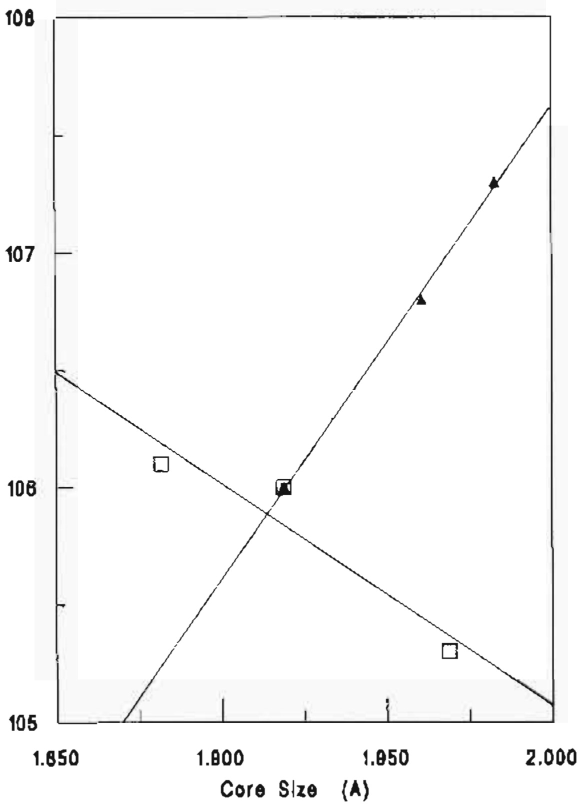

Figure 5. Plot of the relationship between core size and the C_α–N–C_α angle for (squares) the NiTC$_x$TPP (x = 5–7) and (triangles) MTC$_6$TPP (M = Ni, Co, Cu) series.

determinations of bond length may obscure the presence of these relationships. On the other hand, correlations with parameters like δ and θ are more likely to be observed because these parameters are more deformative (~0.1 Å), but they are still indirect in nature. Moreover, these ancillary relationships will vary with the type of systematic distortion imposed upon the molecule as illustrated in Figure 3.

Because both δ and θ correlate with ν_3 (or ν_2) (Figure 3) and with the length of the C_α–C_m (C_β–C_β) bond (Figure 4), we must also conclude that δ and θ are each linearly related to one another. However, δ and θ may not be related to bond lengths in the same way for each different structural perturbation. Thus, one might expect that the correlations between δ and θ for the two series might differ also, and this is the case as shown in Figure 5. For the MTC$_6$TPP series, θ opens up as δ increases. However, in the NiTC$_x$TPP series (x = 5–7), increasing nonplanar distortion causes θ to increase, while δ decreases. The dissimilar effects of these two types of structural perturbations on the two ancillary parameters δ and θ are made obvious by the slopes of the lines in Figure 5; nevertheless, both of these relationships arise from the same Badger's rule[25,26] relationships shown in Figure 4.

Conclusions

The two porphyrin series NiTC$_x$TPP (x = 5–7) and MTC$_6$TPP (M = Ni, Co, Cu) in which δ was systematically altered in different ways have provided an opportunity to investigate how the relationships between metalloporphyrin structural parameters and the frequency of Raman lines vary when nonplanar distortions come into play. Comparison of these new structure–frequency relationships to those of several previously studied metalloporphyrin series (Table 2) aids in determining the effects of nonplanarity on these correlations. For metal variation series, we find that the observed relationship between Raman frequency and δ is dependent on the magnitude of the nonplanar distortion of the macrocycle (in this case as measured by the N–M–N angle).

On the other hand, we find that a more direct (Badger's rule) relationship exists between the frequency of a specific Raman mode and the length of the bond that contributes to the Raman mode. Furthermore, this relationship holds regardless of the type of distortion, *i.e.*, for both series. Correlations between frequency and secondary structural parameters like δ must result from ancillary relationships between these bond lengths and δ. The question arises as to how these incidental relationships should be used in the structural interpretation of Raman spectra.

Fortunately, we are beginning to see trends in the relationships between frequency and structure that may make these empirical relationships more useful in the analysis of tetrapyrrole conformation in protein environments, the stated goal of the work. Examination of Table 2 shows a trend toward a *strong* (large K) core-size dependence for the more *planar* porphyrins; *i.e.*, the magnitude of the slope, K (cm^{-1}/Å), is large if the degree of nonplanar distortion brought about by the steric crowding at the periphery is small. The strength of the dependence (magnitude of K) decreases in the order MPP ≥ MOEP ≈ MTPP > MTC$_6$TPP > MOETPP. Thus, the planar metal porphyrins (PP, OEP, TPP) have large K's, metal OETPPs have small K's, and metal TC$_6$TPPs, which have intermediate nonplanarity, have intermediate dependence on δ.

Structurally, the decrease in K with the degree of nonplanar distortion is most easily understood by realizing that the more nonplanar porphyrins have a smaller optimal core size than do the planar porphyrins. Thus, insertion of a small metal like Ni (which has smaller unconstrained M–N bond lengths than the optimal core sizes of both planar and nonplanar porphyrins) results in a smaller core for a nonplanar porphyrin than for a planar one. On the other hand, for large metals like zinc, the metal–nitrogen bonds are larger than the optimal core sizes of both planar and nonplanar porphyrins. Apparently, the M–N bonds contract less readily than they expand, and the result is that the core sizes are nearly the same for the planar and nonplanar Zn porphyrins. The outcome is that δ varies over a wider range for nonplanar porphyrins. Meanwhile, the Raman frequencies vary over a smaller range for the more nonplanar porphyrins and, consequently, the magnitude of K in the core-size correlations is smaller.

How might this new understanding about the core-size correlations be used to obtain structural information for a porphyrin in its protein environment? Suppose for example that a hemoprotein induces a nonplanar distortion in the macrocycle, as is the case for cytochromes c.[28] The protein can be reconstituted with Ni, Co, Cu, and Zn and the resonance Raman spectra obtained. Then, the frequencies of the structure-sensitive lines can be plotted versus the *unconstrained metal–nitrogen distances* for these metals (given in Table 2 of ref 1). The slope of the linear regression can then be compared with similar slopes for other series of metal porphyrins with known degrees of nonplanarity. These slopes are linearly related to the degree of nonplanarity. Thus, by using this slope–nonplanarity relationship, the slope obtained for the metal-reconstituted hemoproteins can be used to estimate the degree of nonplanarity of the porphyrin in its protein environment. We are currently attempting such a study for mitochondrial cytochrome c.[29]

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