Substituent Effects on the Electronic Structure of Metaiioporphyrins: A Quantitative Analysis in Terms of Four-Orbital-Model Parameters

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Substituent Effects on the Electronic Structure of Metalloporphyrins: A Quantitative Analysis in Terms of Four-Orbital-Model Parameters

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The effects of substituents at the periphery of the porphyrin ring on its $\pi \rightarrow \pi^*$ absorption spectrum are determined in a quantitative fashion by using a new approach based on the four-orbital model. To accomplish this we systematically investigated with UV–visible absorption spectroscopy the Mg (Sn), Zn, Cu, Ni, and Pt series of metals incorporated into porphyrins with different substituents at the periphery of the macrocycle. The metal dependence of the UV–visible spectrum is used to determine relative energy splittings of the frontier orbitals, intensity parameters for $\pi \rightarrow \pi^*$ transitions, and configuration interaction energies for metalloporphyrins with a variety of patterns of peripheral substitution (P, OEP, UroP, CoproP, ProtoP, and TPP). Differences in these MO parameters for distinct porphyrins are related to inductive and conjugative effects of the substituents. In particular, a good correlation between the splitting of the α-band and the Soret band for a series of copper porphyrins and the Hammett constants for the substituents is explained by a relationship between the electron-withdrawing ability of substituents and the strength of the configuration interaction that mixes one-electron excited states of the porphyrin. Variations among the porphyrins in the configuration interaction energy result from delocalization of ring charge caused by increased mixing of p-orbitals of the substituent α-carbons with ring orbitals as the "electronegativity" of the substituents increases. Delocalization of ring charge onto substituent carbons lowers the electron–electron repulsion, and therefore the configuration interaction. Anomalous features of the spectra of the metalloporphines and metalloprotoporphyrins are also explained. The spectra of the metalloporphines are unusual because suitable substituent p-orbitals are not available on the hydrogens for mixing with ring π-orbitals. The spectra of the metalloprotoporphyrins are of biological interest and are found to be only mildly anomalous. The unusual features can be traced to enhanced mixing with and delocalization of ring charge onto the π-system of the two vinyl substituents. For a complete understanding of substituent effects on the absorption spectra, changes in the configuration interaction, orbital energies, and transition dipoles must all be considered.

Introduction

The rates of many desired catalytic and photoassisted reactions mediated by metalloporphyrins are controlled to a varying extent by the electronic properties of the macrocyclic ligand of the metal. The electronic properties of the ring and metal can be controlled by selecting a suitable porphyrin structure or by selecting the environment with which the metalloporphyrin interacts. One simple example is in the control of redox reactions. The oxidation or reduction potential of the ring can be selected by a suitable choice of the metal incorporated into the porphyrin's core or subtituents at the periphery of the ring.[1,2] These changes in the porphyrin's structure will affect rates of reactions that proceed via a ring oxidation or reduction mechanism.

The electronic structure of the porphyrin ring can be influenced by perturbations other than metal and peripheral substitution. Electronic properties of the ring are influenced by such perturbations as π–π[3–11] and axial ligand complexes,[12–14] aggregation,[15–18]

polymerization,[19,20] adsorption onto surfaces,[19,20] and incorporation into micelles to name a few.

It is of special interest to determine the effects of these perturbations on the π-electron system of the ring, the ring's interaction with the metal ion, and the relationship between these electronic properties and reactivity of the metalloporphyrin. To accomplish this goal a method of quantitatively determining the effect of a perturbation on the π-electron system is needed.

The four-orbital model of metalloporphyrin electronic states[12,21] provides a basis for quantitatively evaluating the changes in the frontier π-orbitals that are brought about by environmental and structural perturbations. In previous work it has been shown that differences in the optical absorption spectra of a series of metalloporphyrins can be quantitatively evaluated in terms of the four-orbital model.[8,15] The four-orbital model in essence parameterizes the interaction of one-electron states (or MO configurations) that give rise to the $\pi \rightarrow \pi^*$ absorption spectrum of metalloporphyrins. The four parameters of the model are the energies and dipoles of the excited-state MO configurations. The excited configurations result from promotion of one electron from the nearly degenerate highest filled a_{1u} and a_{2u} orbitals to the lowest unoccupied e_g orbital. Electron–electron repulsion causes the MO configurations to interact and gives rise to a 2×2 matrix, whose elements are the parameters of the model, that can be diagonalized in general. Exact diagonalization of the Hamiltonian matrix provides expressions for the eigenstate energies (E_B and E_Q) and the transition dipoles (q_B and q_Q) of the observed Soret band and α band, respectively, in terms of the four MO parameters.[15,21]

The parameters are the matrix elements A_{1g} and A_{1g}' which define the energies of the excited MO configurations, the off-diagonal configuration-interaction (CI) element A_{1g}'' which de-

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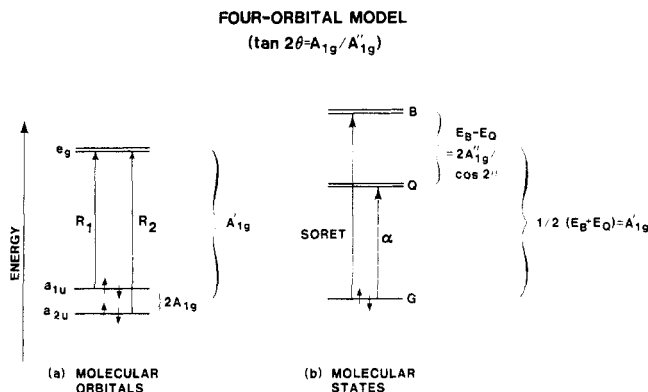(21) Gouterman, M. *J. Chem. Phys.* **1959**, *30*, 1139.

FOUR-ORBITAL MODEL
$(\tan 2\theta = A_{1g}/A_{1g}'')$

Figure 1. Definitions of the parameters of the four-orbital model. The parameters are A_{1g}, A_{1g}', A_{1g}'', and R_1/R_2.

Figure 2. Separation of the 0–0 transitions of the Q and B states ($E_B - E_Q$) vs. the ratio of their dipole strengths (q_Q^2/q_B^2) for the Mg (Sn), Zn, Cu, Ni, and Pt series of metalloporphyrins: porphines ($\bullet$), uroporphyrins ($\odot$), octaethylporphyrins ($\square$), protoporphyrins ($\triangle$), and *meso*-tetraphenylporphyrins ($\bigcirc$). Curves are fits by eye to the data points using the theoretical expressions given in ref 15. Values of θ defined by B = $^1/_2 \tan^{-1} (A_{1g}/A_{1g}'')$ are indicated along the curves.

scribes mixing of the one-electron configurations, and the final parameter R_1/R_2 (or equivalently $r/R = (R_1 - R_2)/(R_1 + R_2)$) which is the ratio of the transition dipoles for the one-electron states. The parameters are defined graphically in Figure 1.

If one of the parameters is varied continuously while the three remaining ones are held constant, various relationships between spectral properties of the porphyrin result. Therefore, provided a series of metalloporphyrins can be found for which only one of the parameters varies in the series, the four-orbital model predicts relationships between the spectral properties for the series.

In an earlier investigation[15] it was shown that incorporation of a series of divalent metals including Mg, Zn, Cu, Ni, and Pt into the uroporphyrin ring resulted in a relationship between the splitting of the 0–0 excited-state levels ($E_B - E_Q$) and the ratio of their intensities (or, alternatively the ratio of the transition dipoles squared, q_Q^2/q_B^2). This energy–intensity relationship for the α band and the Soret band is useful because it eliminates one of the parameters (A_{1g}') from consideration. A curve relating the two experimental quantities is generated when A_{1g} is varied and A_{1g}'' and r/R are held constant. The relationship correctly predicts the observed trend in the energy–intensity plot for the series of metals.[15]

The matrix element $2A_{1g}$ is the energy splitting of the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals; therefore, we are led to the conclusion that the metals alter the splitting of the highest occupied orbitals of the porphyrin. Furthermore, the experimental data for the series of metals could be fit by a curve generated by varying A_{1g} with reasonable values for the other two parameters. This leads to an estimate of the CI matrix element (A_{1g}'') and r/R for the porphyrin studied, i.e., uroporphyrin I, and for a value of the a_{1u}–a_{2u} splitting for each of the metals.

For the same series of metallouroporphyrins [M(UroP)], a different relationship between $E_B - E_Q$ and q_Q^2/q_B^2 is found for the π–π dimers.[15] Nevertheless, that data also is fit by varying A_{1g}; however, a value of r/R is required that is different from the monomer value. The splitting of the a_{1u} and a_{2u} orbitals in the dimers is larger by a constant amount, but the relative effect of the metals on A_{1g} is about the same for monomers and dimers.

To obtain a detailed understanding of the relationship between electronic structure and reactivity, it is desirable to apply the theoretical method to as many systematic perturbations of the ring as possible. With this goal in mind the method was extended to an analysis of the effects of π–π complex formation between aromatic acceptors and metallouroporphyrins.[8] A sound understanding of the electronic spectra of the non-hyper porphyrins obtained by application of the method to many ring perturbations may also lead to improved relationships between vibrational spectra and electronic structure.

The present investigation applies the new method to metalloporphyrins with other patterns of peripheral substitution. Uroporphyrin I (UroP) has alternating propionic and acetic acid groups around the macrocycle at the eight β-carbons of the pyrroles. Altered energy–intensity relationships are found for the series of metal derivatives of porphine (P), octaethylporphyrin
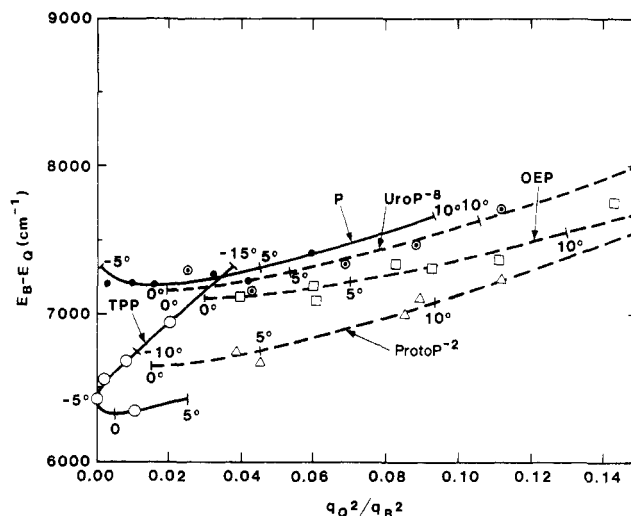
(OEP), protoporphyrin IX (ProtoP), and *meso*-tetraphenylporphyrin (TPP). By curve fitting each of these data sets the values of the MO parameters are determined for each porphyrin.

The differences in the parameter values in each case define the perturbation on the porphyrin's π-electron system that is brought about by the substituents. Further, the parameters in some cases represent relative orbital energies, but by taking into consideration the charge distributions in the π-orbitals, differences in the MO parameters can be understood in terms of substituent effects on the individual orbitals. For example, in this way, A_{1g}, which gives the splitting of the a_{1u} and a_{2u} levels, can be interpreted in terms of shifts in the a_{1u} and a_{2u} levels themselves. From further analysis of the spectral data, the effect of peripheral substituents on the e_g orbital and CI energy are evaluated as well.

It is found that substitution cannot be treated purely as a simple inductive charge effect on the π-electron system. Mixing of ring orbitals and p-orbitals on the α-carbons of the substituents (i.e., hyperconjugation) is of prime importance.

Materials and Methods

All metalloporphyrins were obtained from Porphyrin Products and used without further purification. Solvents used are as follows: UroP, 0.1 M NaOH; OEP, TPP, and porphine, toluene; ProtoP, 0.1 M NaOH with cetyltrimethylammonium bromide (CTAB) added.

Absorption spectra were taken on a Perkin-Elmer Model 330 spectrophotometer. All spectra agreed with those reported in the literature. Possible errors in band maxima are typically ± 0.5 nm. Integrated intensities of the absorption bands are estimated from $f \sim A\Delta\nu$, where A is the maximum absorbance and $\Delta\nu$ is the width at half-maximum in wavenumbers. The transition dipole q is related to the oscillator strength f by $q^2 \sim f/E$.

Results

Table I gives the relevant absorption spectral data for the metalloporphyrins. Figure 2 shows a plot of $E_B - E_Q$ (the splitting between the α or Q(0–0) band and the Soret or B(0–0) band) and q_Q^2/q_B^2 (the ratio of the α-to-Soret-band dipole strengths) for the Mg (or Sn), Zn, Cu, Ni, and Pt derivatives of each porphyrin. The lines represent theoretical analysis of the data generated by varying A_{1g} for constant values of r/R and A_{1g}''. The dashed curves are for pyrrole-substituted porphyrins; the solid curves are for porphine and the *meso*-phenyl-substituted porphyrin. The parameters of the fits by eye to the data are listed in Table II. In Figure 4 the experimental values of $^1/_2(E_B + E_Q)$ are

TABLE I: Energies and Dipole-Strength Ratios of Metalloporphyrin Absorption Bands

porphyrin	metal	q_Q^2/q_B^2	$E_B - E_Q$, cm⁻¹	$\frac{1}{2}(E_B + E_Q)$, cm⁻¹	$2A_{1g}$, cm⁻¹	$2A_{1g}(cor)$,[b] cm⁻¹
OEP	Mg	0.0399	7119	20771	372	380
	(Sn)	(0.0365)	(7088)	(21026)		
	Zn	0.0602	7180	21164	973	1030
	Cu	0.0825	7332	21460	1561	1700
	Ni	0.1110	7370	21764	2171	2420
	Pt	0.1458	7764	22643	2840	3240
UroP	Mg	0.0250	7298	20876	250	250
	Zn	0.0421	7105	20960	931	980
	Cu	0.0646	7397	21543	1707	1820
	Ni	0.0955	7468	21919	2191	2430
	Pt	0.1121	7698	22608	2750	3120
ProtoP	Mg	0.0385	6749	20266	958	1010
	Zn	0.0452	6682	20582	1149	1230
	Cu	0.0887	7117	21072	2342	2480
	Ni	0.1115	7237	21444	2823	3240
	Pt					
TPP	Mg	0.0203	6946	20057	-2874	-2520
	Zn	0.0078	6690	20352	-2107	-1910
	Cu	0.0019	6559	20701	-1720	-1500
	Ni	~0	6429[a]	20990[a]	-890	-900
	Pt	0.0103	6350	21763	376	370
P	Mg	<0.002	7198	21339		
	(Sn)	(0.0093)	(7208)	(21210)	(-450)	(-460)[c]
	Zn	0.0157	7205	21523	20	30[c]
	Cu	0.0320	7263	21814	800	890[c]
	Ni	0.0419	7219	22231	1140	1880[c]
	Pt	0.0590	7402	22895	1710	2250[c]

[a]Estimated from a plot of E_B vs. E_Q for series of metals. [b]Corrected for A_{1g}'' dependence on top filled orbital shifts ($f = 0.3$). [c]$f = 1.0$.

TABLE II: Parameters of the Four-Orbital Model for Metalloporphyrins with Various Peripheral Substituents[a]

porphyrin	$2A_{1g}''$, cm⁻¹	r/R	$2A_{1g}^{Cu}$, cm⁻¹	$A_{1g}'^{0,c}$ cm⁻¹
OEP	7100	-0.173	1561	20595
UroP	7165	-0.141	1707	20677
	(7250)	(-0.173)		
ProtoP[b]	6650	-0.122	2342	19815
P	7190	-0.122	800	21500
TPP	6335	-0.071	-1720	21447

[a]Values in parentheses are from earlier work in which more metals were included. [b]Average over the series of metals excluding Pt. [c]Taken from intercept in Figure 4.

plotted vs. the values of $2A_{1g}$ obtained from the theoretical analysis the data in Figure 2. The values of $2A_{1g}$ are given in Table I.

Discussion

Differences in the parameters result from substituent perturbations of the MO energies and dipoles and the configuration interaction energy. Differences in the parameter A_{1g} are easiest to interpret because of the particular charge distributions of the a_{1u} and a_{2u} orbitals. The a_{1u} orbital has nodes at the meso carbons and (at zeroth order) is not expected to be influenced by meso substitution. The a_{2u} orbital, on the other hand, places considerable charge on the meso carbons and should be strongly affected by meso substituents. In contrast, the a_{2u} orbital puts less charge at the β-carbons of the pyrrole rings than does the a_{1u} orbital. Thus, primarily the a_{1u} level is shifted when comparing pyrrole-substituted metalloporphyrins. However, when comparing meso-substituted metalloporphyrins only the a_{2u} level is shifted.

The orbital energies for each porphyrin (relative to porphine) are illustrated in Figure 3. The levels are shown for the a_{2u} orbital for each of the metals of the series. The shifts are derived from the values of $2A_{1g}$ given in Table I. The a_{2u} levels for all metals are represented by dashed lines in Figure 3; for a given porphyrin the a_{1u} level is the same for all metals.

Less electronegative metals shift a_{2u} to higher energies; more electronegative metals stabilize a_{2u}. Only the a_{2u} orbital is affected by metal substitution because a_{1u} has nodes through the nitrogens and cannot interact directly with the metal. MO calculations show that the a_{2u} level is influenced by the metal via the symmetry allowed interaction with an empty metal p_z orbital.[14] As the electronegativity of the metal increases, the p_z orbital becomes
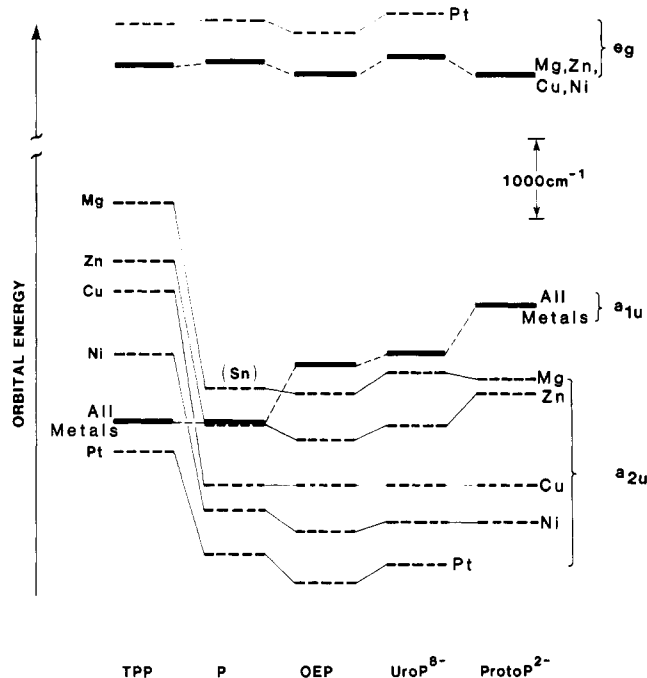

Figure 3. Energy levels of the frontier molecular orbitals for metalloporphyrins with various patterns of substitution. The a_{2u} levels for the series of metals are indicated by dashed lines; at first order only the a_{2u} level is affected by metal substitution for the series of metals investigated. Energy levels are derived from the molecular orbital parameters given in Tables I and II that were obtained by fitting the spectral data in Figure 2. The upward shift in the e_g level for Pt results from enhanced interaction with $e_g(d_\pi)$ levels for this third-row transition metal (see ref 15). The a_{2u} levels of the Cu derivatives have been arbitrarily assumed to lie at the same energy for pyrrole-substituted porphyrins; levels for other metals include the scatter in the parameter values and are not quite equal. The a_{1u} level for exo-substituted porphyrins is determined from the splitting ($2A_{1g}$) for Cu derivatives (a_{2u} levels held constant). Finally, the e_g level is determined from A_{1g}' after the contribution from the shift in the a_{1u} (or a_{2u}) level is removed. (See ref 8 and 15.)

increasingly conjugated with the ring, stabilizing the a_{2u} orbital with which it primarily mixes. The relative spacing of the a_{2u} levels for the metals remains approximately the same for different
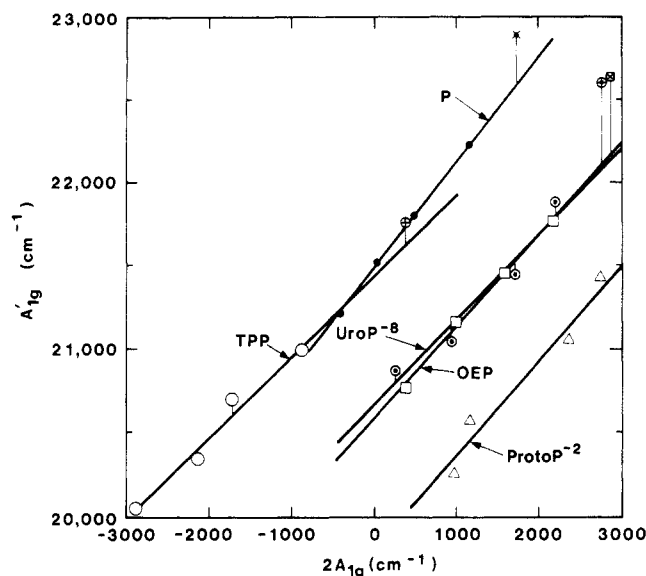
Figure 4. Average MO transition energy A_{1g}' [$=^1/_2(E_B + E_Q)$] vs. the separation of the two highest occupied molecular orbitals $(2A_{1g})$ for the metalloporphyrins represented in Figure 2. $A_{1g}'^0$ in Table II is the intercept of the least-squares straight line for the corresponding metalloporphyrin. The Pt point is not included in the least-squares fits because there is an additional interaction with the e_g orbital for this third-row transition metal (see ref 15). The value of $2A_{1g}$ for each metal is estimated from its position along the theoretical curves in Figure 2.

porphyrins, but the levels are shifted as a group as indicated in Figure 3. A closer examination shows that the TPP levels have larger spacing and span a larger energy than the pyrrole-substituted porphyrins. Porphines, on the other hand, exhibit a smaller spacing than pyrrole-substituted porphyrins.

Relative energies of the a_{1u} and a_{2u} orbitals for distinct porphyrins agree well with those derived qualitatively from arguments based on the four-orbital model.[22] However, the present analysis is quantitative and, further, it predicts the effect of the substituents on the e_g orbital as well. The energy of the $e_g(\pi^*)$ orbital in Figure 3 is determined from Figure 4.

Figure 4 is obtained by first estimating a value of $2A_{1g}$ for each metal from its position along the curve in Figure 2 for each porphyrin type. Then, A_{1g}', the average energy of the Q and B transition, is determined from the spectra and plotted vs. the estimated value of $2A_{1g}$ as shown in Figure 4. The intrinsic separation of the π and π^* porphyrin orbitals is given by the intercept. $A_{1g}'^0$ in Table II is the energy separating the LUMO's and HOMO for the hypothetical "metal" for which the a_{1u} and a_{2u} orbitals are degenerate. The relative energies of the e_g orbital shown in Figure 3 are obtained by assuming that only a_{2u} is affected by meso-substitution and only a_{1u} is shifted by pyrrole-substitution relative to porphine (vide infra). Otherwise, a shift of the a_{1u} and a_{2u} orbitals that maintains their relative spacing could not be separated from the e_g orbital shift.

An interesting conclusion derived from the levels given in Figure 3 is that, even for the alkyl substituents, the effect of the substituents is not purely inductive. The simplest treatment of the inductive effect assumes that a substituent induces a change in the Coulomb integral $\delta\alpha_i$ for only the atom (i) to which the substituent is bonded. In this case the change in the energy of an orbital a is given by[21]

$$\delta a = \sum_i C_{ai}{}^2 \delta\alpha_i \qquad (1)$$

where the sum is over all atoms at which substituents are introduced. Thus, the relative shifts of two orbitals for a substituent at atom i is fixed by the ratio of the MO coefficients squared $(C_{ai}{}^2/C_{bi}{}^2)$.
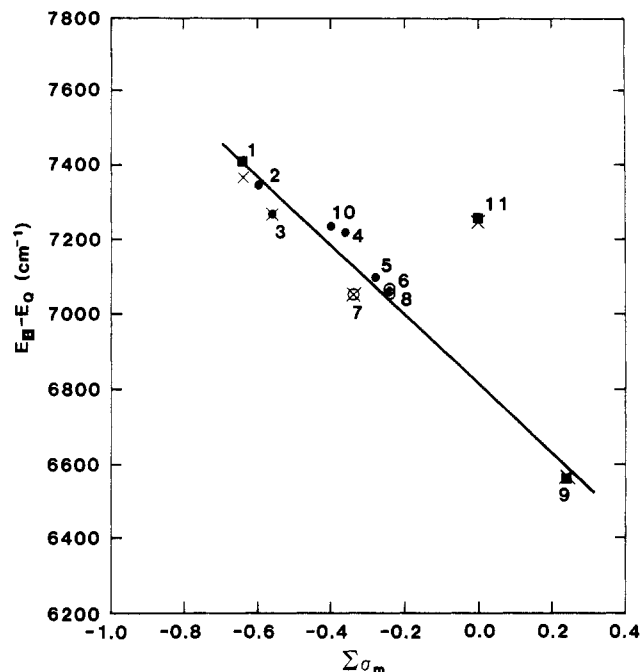
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Figure 5. Energy separation of the α band and Soret bands vs. the sum of the Hammett constants for meta substitution for the ring substituents of copper porphyrins, 1, uroporphyrin I/0.1 M NaOH; 2, coproporphyrin I/0.1 M NaOH + CTAB; 3, octaethylporphyrin/toluene; 4, pentacarboxylporphyrin pentamethyl ester/toluene; 5, heptacarboxylporphyrin heptamethyl ester/toluene; 6, uroporphyrin I octamethyl ester/toluene; 7, protoporphyrin IX/0.1 M NaOH + CTAB; 8, protoporphyrin IX dimethyl ester/toluene; 9, tetraphenylporphyrin/toluene; 10, coproporphyrin I tetramethyl ester/toluene; 11, porphine/toluene. Line is a least-squares fit ($r = -0.98$) without the porphine data point included. The Hammett constants, taken from ref 23, are methyl and ethyl, −0.07; vinyl, 0.05; acetate and propionate, −0.08 (estimated from methyl, ethyl, and CO_2^-); proton, 0.00; phenyl, 0.06; acetic acid ester and propionic acid ester, −0.03 (taken to be the same as the acids).

For example, for the substitution of four phenyl substituents for four protons at the meso positions (P → TPP) we would expect

$$\frac{\delta e}{\delta a_2} \approx \frac{\left(C_{e_g}^{meso}\right)^2}{\left(C_{a_2}^{meso}\right)^2} = \frac{(0.2933)^2}{(0.3423)^2} = 0.73 \qquad (2)$$

where the values of the molecular orbital coefficients are taken from previous work[14] and overlaps have been neglected. Hence, the shift in the $e_g(\pi^*)$ orbital is predicted to be in the same direction as the a_{2u} orbital and almost $^3/_4$ as large. Instead, what is observed (Figure 3) is a small shift in the opposite direction. It is apparent that the conventional treatment of the inductive effect can never give a shift in the opposite direction for the a_{2u} and e_g orbitals.

The same kind of argument applies for pyrrole substituents; therefore, the effect of modifying the ring substituents is more complicated than a simple inductive charge effect. For the phenyl and vinyl substituents, which have π-electron systems that might conjugate with the ring, this result might have been anticipated.

This result might also cause some concern that the assumed lack of effect of meso-substitution on the a_{1u} orbital and of pyrrole substitution on the a_{2u} orbital is an oversimplification. It appears that we should view the absolute orbital levels in Figure 3 with less confidence than the relative energy parameters A_{1g} and A_{1g}'.

In spite of apparent problems in understanding the absolute orbital shifts illustrated in Figure 3 in terms of a very simple treatment of the inductive effect, it is obvious from Figure 5 that an inductive effect is at work. The energy separation of the 0–0 transitions of the Q and B states clearly correlates well with the sum of the Hammett constants of the substituents for a wide variety of copper porphyrins. The Hammett constants σ_m are a measure of the inductive electron donating/withdrawing ability of the substituents.[23,24] The correlation is quite good ($r = 0.98$)

if the copper porphine point (11) is omitted. A relationship such as that in Figure 5 can be understood in terms of the MO parameters if the configuration interaction matrix element (A_{1g}'') is linearly related to the electron-withdrawing ability of the substituents. This statement follows from the 4-orbital-model expression for $E_B - E_Q$, which is

$$E_B - E_Q = 2A_{1g}''[1 + (A_{1g}/A_{1g}'')^2]^{1/2} \qquad (3)$$

Because $A_{1g} \ll A_{1g}''$, a correlation of A_{1g}'' with $\sum \sigma_m$ is sufficient to force $E_B - E_Q$ to be linearly related to $\sum \sigma_m$ as well.

Figure 6a shows that a relationship between the CI matrix element and the Hammett constants is observed (again omitting the point of copper porphine). A more positively charged ring may shrink the molecular orbitals concomitantly increasing the electron–electron repulsion, and, therefore, A_{1g}''. This mechanism does not explain our result because it predicts an increase, not a decrease, in the CI energy with increasing electron-withdrawing ability. The explanation also does not account for the anomalous copper porphine point in Figure 6a.

Another mechanism that explains the relationship and its anomalous features assumes mixing of p-orbitals of the α-carbons of the substituents with orbitals of the ring. Mixing delocalizes charge onto the carbons and results in lowering the electron-electron repulsion. The more "electronegative" (electron withdrawing) a substituent the more the substituent carbons become conjugated with the ring and the more charge is delocalized, thus explaining the observed correlation (Figure 6a). This mechanism of interaction with the substituents also accounts (1) for the anomalous lowering of the CI for ProtoP and (2) for the high value for $2A_{1g}''$ for porphine. Strong conjugation of the π-electron system of the vinyls with the ring enhances delocalization of ring charge beyond the α-carbons of the vinyls and provides an additional lowering of the CI for ProtoP. In the case of porphine, substituent carbons are replaced by protons which do not permit delocalization beyond the macrocycle because suitable p-orbitals are not available. The high value for A_{1g}'' for porphine is seen to be related to the anomalously high value of $E_B - E_Q$ for porphine (Figure 5).

Conjugation of the substituents with the ring can also account for the relatively large shifts in the π-orbitals compared to the π^*-orbitals (Figure 3). The $e_g(\pi^*)$ level is apparently far from empty or filled p-orbitals of the substituent α-carbons, but the filled $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals are relatively close to the filled p-orbitals. Therefore, the filled ring orbitals are destabilized by mixing with substituent-carbon p-orbitals that lie at lower energy than a_{1u} and a_{2u}; the e_g level is less affected by the far away filled p-orbitals. Apparently the unfilled p-orbitals are at high energy, forcing the e_g level down, but the interaction is weaker than that between filled p-orbitals and filled ring orbitals.

The hypothesis that mixing of substituent-carbon p-orbitals increases with $\sum \sigma_m$ has the corollary that the energy of the affected a_{1u} or a_{2u} orbital should increase with $\sum \sigma_m$ as well. In addition, we again expect porphine to be anomalous because it lacks filled p-orbitals.

Figure 6b shows the shift in the affected orbital for each of the copper porphyrins relative to its level for copper porphine. Remember that only one orbital, either a_{2u} for meso substitution or a_{1u} for pyrrole substitution, is affected because of the particular charge distributions of the orbitals. In plotting the orbital–energy shifts in Figure 6b we are also assuming substituents of a given electron-withdrawing ability have the same effect on the a_{2u} orbital for meso substitution as on the a_{1u} orbital for pyrrole substitution.

The required linear relationship between orbital energy and $\sum \sigma_m$ is observed and, as expected, the more electron-withdrawing substituents cause a larger destabilization of the affected orbital; i.e., the slope is positive as predicted. The copper porphine point is predicted to be low because there is no mixing and, indeed, it is anomalously low in Figure 6b.
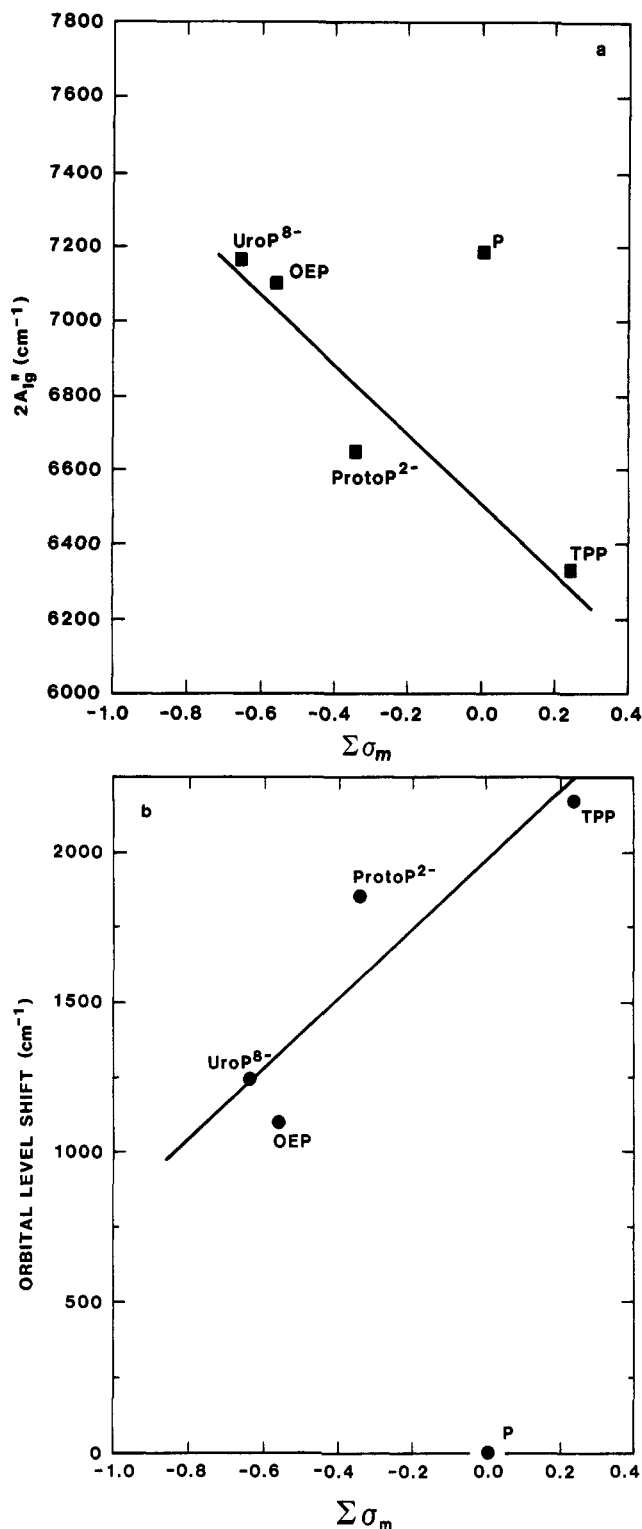
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Figure 6. (a) Configuration interaction matrix element $(2A_{1g}'')$ vs. sum of the Hammett constants for ring substituents. Line is from a least-squares fit ($r = -0.95$) excluding porphine data point. $2A_{1g}''$ (from Table II) is obtained by fitting data in Figure 2. (b) Shifts in the a_{1u} and a_{2u} molecular orbitals vs. sum of the Hammett σ_m's. Shifts are calculated from $2A_{1g}^{Cu}$ for each porphyrin by subtracting the value of $2A_{1g}^{Cu}$ for porphine. Hammett constants are given in legend of Figure 5.

Since $2A_{1g}''$ and the shift in the affected orbital's energy are both correlated with $\sum \sigma_m$, they are also correlated ($r = -0.98$) with each other. The linear relationship is given by

$$2A_{1g}'' = 2A_{1g}''^0 - 0.75\delta a \qquad (4)$$

where $2A_{1g}''^0 = 8011$ cm^{-1} and δa is the shift in the a_{2u} orbital for meso substitution and δa is the shift in the a_{1u} for pyrrole substitution.

This relationship implies that $2A_{1g}''$ and $2A_{1g}$ are related. The change in the orbital splitting $2A_{1g}$ is given by

$$\Delta(2A_{1g}) = \delta a_1 - \delta a_2 \qquad (5)$$

where for pyrrole substitution $\Delta(2A_{1g})$ approximately equals δa_1. Therefore, eq 4 can be rewritten as

$$\Delta(2A_{1g}'') = -0.75\Delta(2A_{1g}) \qquad (6)$$

where $\Delta(2A_{1g}'') = 2A_{1g}'' - 2A_{1g}''^0$.

At first glance it is disturbing to find that $2A_{1g}''$ depends so strongly on the splitting of the top filled orbitals, especially since we have assumed that $2A_{1g}''$ is a constant for the series of metals in our treatment of metal dependence in the relationship between energy and intensity expressed in Figure 2. However, we know that as the metal is varied the degree of metal conjugation with the ring changes and ring molecular orbitals become delocalized onto the metal—the a_{2u} orbital in particular. The degree of delocalization increases with metal electronegativity and the a_{2u} level is also progressively stabilized by the interaction with the empty metal p_z orbital. That is, the configuration interaction (A_{1g}'') is expected to decrease as the a_{2u} orbital is stabilized (A_{1g} increases) by more electronegative metals. Thus, A_{1g}'' and A_{1g} are expected to be related for the series of metals, but the sense of the relationship between A_{1g}'' and a_{1g}, i.e., the sign of the slope, is expected to be reversed from that for substituent effects because the filled ring orbital interacts with a metal p-orbital at higher, not lower, energy.

Fortunately, fitting the data in Figure 2 allows us to determine whether A_{1g}'' is dependent on A_{1g} or not for the series of metals. If A_{1g}'' is linearly related to A_{1g} the curves in Figure 2 remain the same except that the values of A_{1g} along the curves shown would be changed. The value of A_{1g} for each metal would, therefore, be underestimated or overestimated. Further, the values of A_{1g}'' at $A_{1g} = 0$ and r/R still determine the shape of the curve, however.

Because the shape of the curve is not affected when A_{1g}'' depends on A_{1g}, values of A_{1g} for the series of metals must be compared for distinct porphyrins to determine the metal dependence. As noted the spacing of the a_{2u} levels for the series of metals is larger for TPPs than for pyrrole-substituted porphyrins. Because the π-orbital shifts resulting from differences in substituents are small compared to shifts in the metal p_z orbital for distinct metals, it is reasonable to expect that the spacing of the a_{2u} orbitals for the series of metals should be the same regardless of the substituents. The pyrrole-substituted porphyrins themselves exhibit about equal spacing of the a_{2u} levels. The difference in spacing for pyrrole-substituted and meso-substituted porphyrins results from the metal dependence of the CI energy on the metal-dependent shifts of the a_{2u} orbital and allows us to determine explicitly the metal dependence.

Figure 7 shows the effect of several linear relationships between A_{1g}'' and A_{1g} on the theoretical curves shown in Figure 2. Three cases are illustrated ($f = 0.75, 0, -0.75$) where

$$2A_{1g}'' = 2A_{1g}''^0 + f(2A_{1g}) \qquad (7)$$

The case where $f = 0$ is the case for which A_{1g}'' is independent of A_{1g}, i.e., $2A_{1g}'' = 2A_{1g}''^0 = 6335$ cm^{-1}. The values of the parameters are those used to fit the TPP data in Figure 2.

Values of A_{1g} at 1000-cm^{-1} intervals are indicated by tick marks along the theoretical curves in Figure 7. Positive values of f expand the A_{1g} scale for the upper branch of the curves and contact the lower branch relative to the $f = 0$ case. Conversely, negative f contracts the A_{1g} scale for the upper branch and expands the lower branch. It is clear that the values of A_{1g} given in Table I can be strongly affected if f is on the order of unity. Since the spacing of the levels for different porphyrins is known, we can adjust the parameter f so that the level spacing for the M(TTP)s is equal to the spacings for M(UroP)s and M(OEP)s. In doing so we are making the reasonable assumption that the effect of the metal is independent of the porphyrin's substituents. The value of f that satisfies this condition is found to be 0.3. Therefore, metal dependence of A_{1g}'' on shifts in the top filled orbitals is somewhat
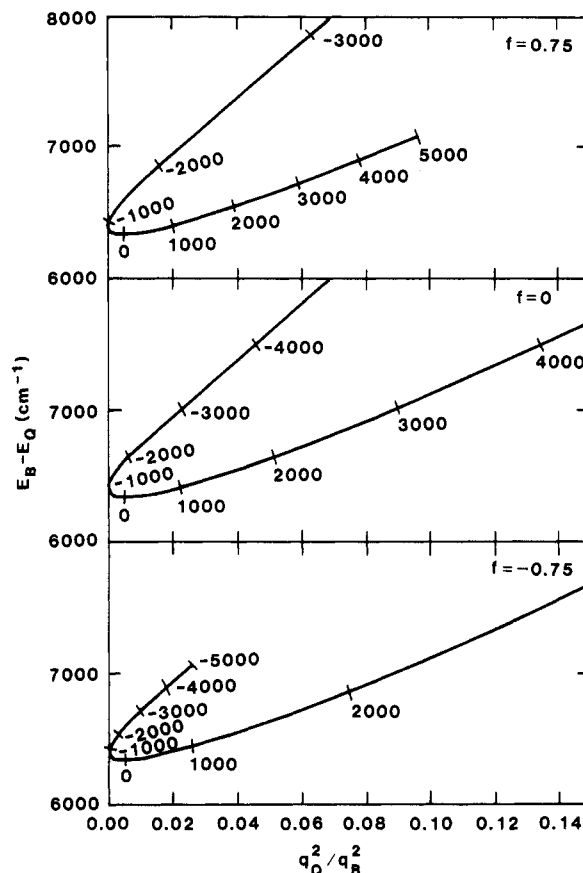

Figure 7. Effect of linear relationships between A_{1g}'' and A_{1g} on the theoretical curves shown in Figure 2.

weaker and has the opposite sign compared to the substituent dependence. Remember that the opposite slope for the relationship was expected and is a consequence of the a_{2u} orbital mixing with a metal orbital at higher energy than itself.

The metal dependence of A_{1g}'' on A_{1g} is only about 40% (0.3/0.75) as strong as for peripheral substitution. A plausible argument suggests that CI dependence on $2A_{1g}$ should be weaker for the metal data. Because only one p-orbital is involved in the metal interaction with a_{2u}, delocalization is extended over only one additional atom for conjugation with the metal. In contrast, conjugation extends ring charge over four or eight extra atoms for peripheral substitution. Because the strength of the electron–electron repulsion is inversely related to the volume containing the electrons, interaction with the substituents has the larger effect on CI.

The value of A_{1g} corrected for A_{1g}'' dependence on the shifts in the top filled orbitals ($f = 0.3$) is given in Table I alongside of the value obtained when A_{1g}'' is assumed to be independent of the orbital shifts. We see that the effect of the relationship between A_{1g}'' and the orbital levels is to increase the separation of the top filled orbitals for the pyrrole-substituted porphyrins and decrease the spacing of the levels for the TPPs. Figure 3 should then be replaced by one reflecting the corrected spacing of the a_{2u} orbitals for the different metals. In this new figure the spacing of the levels for M(TPP), M(OEP), M(UroP), and M(ProtoP) will be approximately the same. Figure 4 should also be corrected; the slope of the TPP line will increase relative to that of the pyrrole substituted porphyrins.

For the metalloporphines, however, the spacing of the a_{2u} levels will still be smaller even after the correction. A different value of f is required to give the same spacing as for the substituted porphyrins. A value of f near 1.0 will suffice. The strong metal dependence of the CI on the top filled orbital shifts for the porphines can be rationalized as follows. First, ring charge is not delocalized beyond the macrocycle because p-orbitals of the hydrogens are not near enough to the top filled orbitals to mix. Therefore, there is *more* π charge in the ring to be transferred

to the metal for porphines relative to the substituted porphyrins. Thus, there can be more delocalization of charge in the porphine case for an equivalent mixing of metal and porphyrin orbitals.

Finally, from Table II and the definition of r/R in terms of R_1 and R_2, it is apparent that delocalization of charge onto α-carbons of the pyrrole substituents causes R_1 to decrease relative to porphine; delocalization of charge at the meso positions decreases R_2.

In summary, we have found that the four-orbital model predicts relationships among spectroscopic properties that we have observed (Figures 2 and 4). In deriving these theoretical expressions we have assumed that the pattern of substitution at the periphery is totally symmetric, that is, that the substituents do not lower the symmetry (D_{4h}) of the macrocycle. This is not rigorously true, but is probably a good approximation. Fitting the spectroscopic data with the theoretical expressions provides a quantitative measure of the energy and intensity parameters of the model. These parameters quantify electronic differences in porphyrins with different patterns of peripheral substitution and with distinct metals. In particular, we find that for each porphyrin the configuration-interaction energy and the splittings of the top filled molecular orbitals are related to each other and to the inductive power of the substituents. In addition, the metal dependence of the CI energy on a_{2u} energy is determined and found to be less than half as strong as for substituent dependence of CI energy on level shifts. Also, the sign of the slopes of these two linear relationships differ.[25]

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(25) In previous work (ref 8, 15, and 21) metal dependence of the CI energy was ignored; therefore, the values of the MO parameters quoted require a simple correction. Corrections are also probably required for vibronic effects and systematic errors in determining absorption-band intensities and positions.

Conjugation of the α-carbons of the substituents with ring orbitals accounts for variation of the four-orbital-model parameters, if the electron-withdrawing ability is viewed as the "electronegativity" of the substituents and if this property controls the degree of α-carbon conjugation. An interpretation based on conjugation with the substituent carbons explains the empirical relationships between the MO parameters and the substituent constants and, additionally, the anomalous values for the metalloporphyrins. The metalloprotoporphyrins, which are of biological interest, have only mildly unusual values for the parameters; that is, the data points for M(ProtoP) do not fall significantly off the lines in Figures 5 and 6. On the other hand, the vinyl groups might have been expected to strongly conjugate with the porphyrin ring. Apparently, the vinyl substituent constant adequately accounts for the effect of the vinyls on the porphyrin's π-system.

Potential Energy Surfaces and Tunnelling Dynamics of Some Jahn–Teller Active Molecules

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Potential energy surfaces and rates of tunnelling have been calculated for degenerate rearrangements of cyclopropane radical cation, cyclopropenyl radical, cyclopropenyl anion, and cyclooctatetraene, using MNDO or MNDO/HE/CI. Heavy atom tunnelling (HAT) plays an important role.

Introduction

Carpenter's seminal suggestion[2] concerning the mechanism of the automerization of cyclobutadiene (**1**) has generated an upsurge

1 　　　　　　　　 *2*
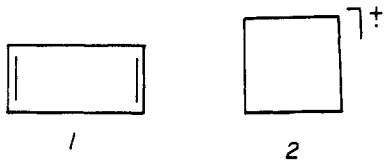
of interest in heavy atom tunnelling (HAT), i.e., tunnelling involving atoms other than the hydrogen isotopes. Using a procedure superior to Carpenter's, we have shown[3] that the rate of tunnelling in **1** is indeed even greater than the value calculated by Carpenter,

suggesting that HAT may play a much more important role in chemistry than had been previously supposed.

For tunnelling to occur at a significant rate, the displacements of the atoms involved must not be much greater than the de Broglie wavelengths[4] of the atoms. In the case of the "organic" elements (C,H,O,N), these are of the order of 10 pm, so tunnelling involving them can occur only if the geometries of the interconverting isomers resemble one another closely. It is also necessary that the barrier separating them be small.[5] These conditions are most easily met by bond switch isomerizations and the examples so far claimed[3,6] have been of this type. Another process likely to meet the required conditions is the interconversion of Jahn–Teller (JT)

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