is oxidized to $Fe^{III}(P)$ by CCl_4 (eq 3), which is reduced to Cl^- and the $^{\bullet}CCl_3$ radical. In turn, $Fe^{III}(P)$, depending on its stability, can react with ethanol, giving the original catalyst, or undergo destroying attack by free-radical species. The $CH_3CH_2O^{\bullet}$ radical rapidly reacts, as expected, with ethanol to give the $CH_3\dot{C}HOH$ radical (eq 5). The rapid scavenging of this radical by CCl_4 (eq 7) prevents the secondary reduction of $Fe^{III}(P)$, which is observed to occur in the absence the carbon tetrachloride (process 7 in Scheme I). The higher value of Φ_{Cl} (2.7×10^{-2}) (Table II) as compared with the Φ_{red} obtained in the presence of a radical scavenger (0.8×10^{-2}) (Table I) indicates that the reaction of CCl_4 with ethanol (eq 1) occurs to a great extent (70%) via thermal processes initiated by $CH_3\dot{C}HOH$ and $^{\bullet}CCl_3$ radicals (eqs 5–7). The free-radical thermal processes are suppressed by adding a suitable amount of pbn. Accordingly, acetaldehyde and chloroform are formed in negligible amounts. Thus, since in the presence of scavengers the reduction of CCl_4 occurs only by reaction with $Fe^{II}(P)$ (eq 2), $\Phi_{Cl} = \Phi_{red}$.[32]

Conclusions

The results obtained from the investigation on the photoredox properties of iron *meso*-tetraarylporphyrins in ethanol show that the substituents on the meso-phenyl groups are observed to have negligible influence on the energy and reactivity of the excited state responsible for the primary photoreduction process. In cyclohexane–ethanol mixed solvent, important effects of the microsolvation in proximity to the central iron are observed.

The irradiation of an iron porphyrin can induce an intramolecular photoredox reaction giving rise to the formation of reactive species, $Fe^{II}(P)$ and $CH_3CH_2O^{\bullet}$ radical, which are capable of initiating a catalytic cycle leading to the reduction of CCl_4 to Cl^- and $CHCl_3$ and the oxidation of CH_3CH_2OH to CH_3CHO.

The phenyl substituents play an important role in protecting the porphyrin ring against free-radical attacks, when iron arylporphyrin compounds are used as catalysts for the photoreduction of CCl_4 by ethanol. Chlorine atoms and methyl groups exhibit the most efficient protection due to their steric hindrance on the meso positions.

Acknowledgment. This research was supported by the Consiglio Nazionale delle Ricerche, Progetto finalizzato Chimica Fine II, and by the Ministero per la Università e la Ricerca Scientifica e Tecnologica. Thanks are expressed to Mr. Luciano Righetti for his contribution to the experimental work.

Registry No. Fe(TPP)(Cl), 16456-81-8; Fe(TPFPP)(Cl), 36965-71-6; Fe(TDCPP)(Cl), 91042-27-2; Fe(TMP)(Cl), 77439-21-5; Fe(TTP)(Cl), 52155-50-7; CCl_4, 56-23-5; CH_3CH_2OH, 64-17-5; Cl^-, 16887-00-6; CH_3CHO, 75-07-0; $CHCl_3$, 67-66-3.

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[32] The slightly higher value of Φ_{Cl} with respect to Φ_{red} could be ascribed to an incomplete trapping of the $CH_3CH_2O^{\bullet}$ radicals by pbn.

Contribution from the School of Chemistry,
The University of Sydney, NSW 2006, Australia

Modulation of Valence Orbital Levels of Metalloporphyrins by β-Substitution: Evidence from Spectroscopic and Electrochemical Studies of 2-Substituted Metallo-5,10,15,20-tetraphenylporphyrins

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A new approach for obtaining information about the electronic structure and, in particular, the relative ordering of the frontier and subfrontier orbitals in metalloporphyrin systems is presented. This treatment involves a combination of electrochemical and spectral data. A series of 2-substituted copper(II) 5,10,15,20-tetraphenylporphyrins (**2–11**), in which the electronic nature of the substituent has been significantly varied, have been studied. The substituent has a considerable effect on the energies of the two highest occupied molecular orbitals, the a_{2u} and the a_{1u} orbitals, and can even cause the relative order of these orbitals to change. Substantial modulation of the a_{2u}/a_{1u} orbital energies is achieved by variation of the nature of a pyrrolic β-substituent. The effect is, as expected, felt much more strongly on the a_{1u} orbital, which has significant electron density associated with the pyrrolic β-position of metalloporphyrins. Indeed, the relative energy of the a_{1u} orbital in the nitroporphyrin **2** and the aminoporphyrin **11** differs by 0.71 eV; the corresponding difference in the energies of the a_{2u} orbitals is 0.14 eV. In cases where there is a good electron-donating 2-substituent (NH_2, OCH_3, SPh), the "normal" ordering $a_{2u} > a_{1u}$ is reversed. These observations have important consequences in metalloporphyrin systems as their patterns of reactivity, influenced by the electron distribution in the highest filled molecular orbital, will be particularly sensitive to the relative a_{1u}/a_{2u} separation and ordering. A role for pyrrolic β-substituents in the fine tuning of energy levels in porphyrin-based molecular electronic logic and memory devices is suggested.

Introduction

The physical properties and reactivities of metalloporphyrins are widely variable. These differences result from a combination of electronic and steric factors. While steric factors are generally well understood and arise mainly from the environment in which the metalloporphyrin interacts, and from bulky peripheral substituents in the case of 5,10,15,20-tetraarylporphyrins, the electronic structure of the porphyrin ring is subject to a number of influences. For a given metalloporphyrin, however, the major effects on electronic structure should result mainly from the coordinated metal (together with its axial ligands) and the peripheral substituents.[2] Other factors have been noted to give rise to relatively small perturbations of the metalloporphyrin electronic structure. These factors include the effects of aggregation, solvent, polymerization, adsorption onto surfaces, and incorporation into micelles.[3]

It is of particular interest, therefore, to determine how a given metal or peripheral substituent modifies the electronic structure of the porphyrin ring. Several theoretical investigations that involved extensive all-valence electron calculations on porphyrin systems of D_{4h} symmetry have been reported.[4] For more complex systems of this size, however, such calculations are not generally practicable. Fortunately, it is usually found sufficient, for porphyrins of approximate or exact D_{4h} symmetry, to focus attention on the π-electron structure of the ring, and in particular the frontier

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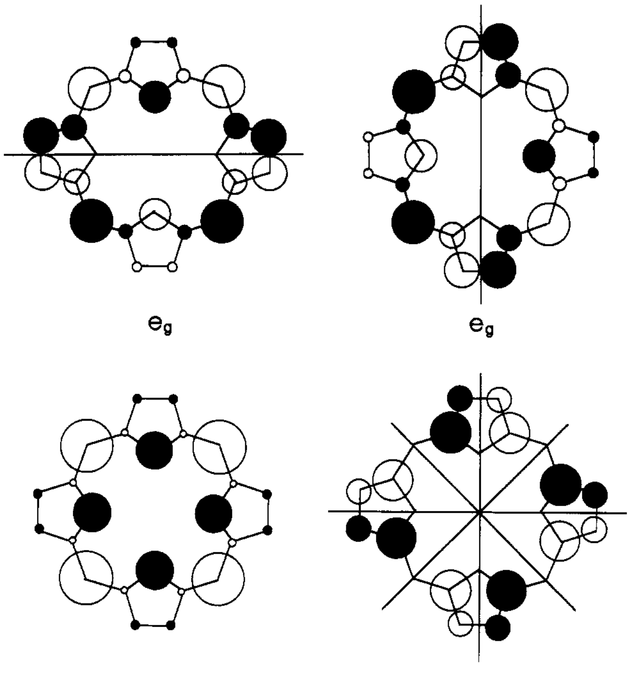


Figure 1. Schematic representation of the two highest filled π-orbitals (a_{1u} a_{2u} symmetry) and lowest virtual π-level (e_g) in the D_{4h} porphyrin ring. [Size of circles proportional to atomic orbital coefficients with filled circles representing negative coefficients.] Values were obtained by Hückel tight-binding calculations with $\alpha_N - \alpha_C = 0.66\beta_{CC}$ and $\beta_{CC} = \beta_{CN}$; these data differ slightly from those of Gouterman (ref 4, p 93), which were calculated assuming that $\alpha_N = \alpha_C$.

orbitals, in order to obtain insight into the principal mechanisms involved, as calculations concerned only with the π-framework have yielded essentially the same results as the more extensive treatments.[4] Thus, in D_{4h} symmetry, the highest occupied and lowest virtual canonical π-levels are calculated (in the π-electron approximation) to have the same symmetry for a wide range of central metal substituents. The lowest unoccupied (virtual) level is invariably degenerate and of e_g (e_g*) symmetry. The highest two occupied levels are of a_{1u} and a_{2u} symmetry (the latter having the symmetry corresponding to translation along the vertical axis), respectively. These two orbitals are separated from the next occupied orbital by a large energy gap (>3 eV).

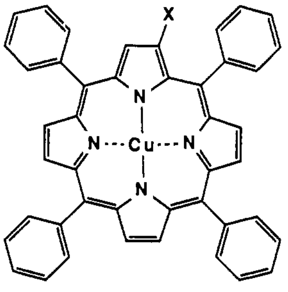
The electron density associated with the a_{1u} orbital is nonvanishing only on the pyrrolic α- and β-carbons ($\alpha > \beta$), while that associated with the a_{2u} orbital is concentrated mostly on the meso carbons and the nitrogen centers, with a small component from the pyrrolic β-carbons; orbital representations are shown in Figure 1. The precise composition of these orbitals (which may include contributions from metal orbitals of appropriate symmetries) will show some variation with the electronic structure of the central metal. However, the three orbitals referred to are believed to retain essentially the above symmetry characteristics, with the proviso that if the metal moves out of the molecular plane, thus destroying the inversion symmetry, the u–g distinction is formally lost. In practice the effects of loss of exact symmetry appear to be generally small.

There is one important property of the "frontier" orbital set that may well vary from one molecule to another: this is the relative ordering of the highest lying a_{2u} and a_{1u} π-orbitals, which are calculated to be nearly degenerate in most metalloporphyrins. Variation in or inversion of the relative energies of the two very closely separated highest filled π-orbitals will be expected to have significant effects on physical properties and on reactivities of porphyrins and their π-cations. Patterns of reactivity influenced by the electron distribution in the highest filled orbital will also be particularly sensitive to the relative a_{1u}/a_{2u} separation.

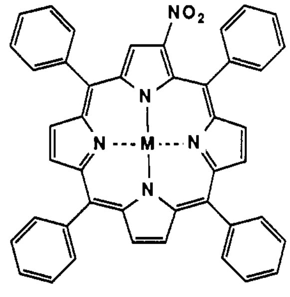
Previous studies of modulation of porphyrin ring electronic structure have mainly focused on effects that have a direct influence on the energy of the a_{2u} orbital: changes in coordinated metal, axial substituents, and *meso*-aryl substituents. A number of systematic studies of the effect that different metals and axial ligands have on porphyrin electronic structure, monitored by changes in electronic spectra, have been reported.[2,3,5-7] In an important earlier study, Gouterman and co-workers have estimated the a_{1u}/a_{2u} separation in several porphyrin systems by analysis of the electronic absorption intensities.[8]

In contrast, studies on the effect of peripheral substituents on the electronic structure of metalloporphyrins have been extremely limited. Indeed, there has been no report of a systematic study of orbital interactions in metalloporphyrins where a single pyrrolic ring substituent has been significantly varied. Such changes should mainly influence the energy of the a_{1u} orbital, although the energy of the a_{2u} orbital should also be affected.

In this paper, we describe a new approach for obtaining information about the electronic structure and, in particular, the relative ordering of the frontier and subfrontier orbitals in metalloporphyrin systems. The approach involves a treatment of a combination of electrochemical and spectral data. The development of new methods for efficient functionalization of the porphyrin periphery in our laboratory has made available a number of 2-substituted porphyrins. The compounds used in this study are copper(II) 2-substituted 5,10,15,20-tetraphenylporphyrins [Cu(TPP)'s] **2**–**11** in which the substituents are chosen to cover a significant range of electronic effects. We report here the UV/vis spectral data and successive one-electron oxidation and reduction potentials of these compounds and show that the pyrrolic β-substituent has a considerable effect on the energies of the frontier orbitals, in particular the a_{1u} orbital, and can even cause the relative order of the a_{1u} and a_{2u} orbitals to change.



1, X = H
2, X = NO_2
3, X = CHO
4, X = CN
5, X = SOPh
6, X = Cl
7, X = $NHCOCH_3$
8, X = CH_2OH
9, X = SPh
10, X = OCH_3
11, X = NH_2



12, M = Mg
13, M = Zn

Experimental Section

Porphyrins. Copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**2**),[9] copper(II) 2-(phenylsulfinyl)-5,10,15,20-tetraphenylporphyrin (**5**),[10] copper(II) 2-chloro-5,10,15,20-tetraphenylporphyrin (**6**),[10] copper(II) 2-acetamido-5,10,15,20-tetraphenylporphyrin (**7**),[11] copper(II) 2-(hydroxymethyl)-5,10,15,20-tetraphenylporphyrin (**8**),[12] copper(II) 2-(phenylthio)-5,10,15,20-tetraphenylporphyrin (**9**),[10] copper(II) 2-methoxy-5,10,15,20-tetraphenylporphyrin (**10**),[13] copper(II) 2-amino-5,10,15,20-

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Table I. Electrochemical Half-Wave Potentials vs Ag/0.01 M $AgNO_3$ for 2-Substituted Cu(TPP) Complexes in CH_2Cl_2/0.1 M $TBA(PF_6)$[a]

		$E_{1/2}$, V			
porphyrin	substituent	ox2	ox1	red1	red2[c]
1	–H (parent)	+1.045	+0.670	−1.640[c]	−2.05
2	$-NO_2$	+1.165	+0.783	−1.269	−1.54
3	–CHO	+1.105	+0.737	−1.411	−1.74
4	–CN	+1.145	+0.804	−1.415	−1.80
5	–SOPh	+1.075	+0.747	−1.483	−1.83
6	–Cl	+1.06	+0.710	−1.581	−1.96
7	$-NHCOCH_3$	+0.915[c]	+0.662	−1.624	−2.005
8	$-CH_2OH$	+1.01	+0.657	−1.638[c]	irrev[b]
9	–SPh	+0.97	+0.632	−1.615[c]	−1.945
10	$-OCH_3$	+0.96	+0.608	−1.659[c]	−2.06
11	$-NH_2$	+0.825[c]	+0.463[c]	−1.695[c]	−2.08

[a] All measurements were made at 20–22 °C. Solutions were purged by bubbling with argon. [b] Irreversible for scan rates up to 10 V/s. [c] Quasi-reversible only at high scan rate (10 V/s).

Table II. Electrochemical Half-Wave Potentials vs Ag/0.01 M $AgNO_3$ for M(TPP) and Corresponding M(2-NO_2–TPP) Complexes in CH_2Cl_2/0.1 M $TBA(PF_6)$[a]

	$E_{1/2}$, V			
porphyrin	ox2	ox1	red1	red2
Cu(TTP) (**1**)	+1.048	+0.689	−1.64[b]	−2.05[b]
Cu(2-NO_2–TPP) (**2**)	+1.166	+0.782	−1.269	−1.54[b]
Mg(TPP)	+0.702	+0.367	irrev	irrev
Mg(2-NO_2–TPP) (**12**)	+0.807	+0.487	irrev	irrev
Zn(TPP)	+0.825	+0.565	−1.670	−2.04
Zn(2-NO_2–TPP) (**13**)	+0.940	+0.696	−1.291	irrev

[a] All measurements were made at 20–22 °C. Solutions were purged by bubbling with argon. [b] Quasi-reversible only at high scan rate (10 V/s).

Table III. Electronic Spectral Data for 2-Substituted Cu(TPP) Complexes in CH_2Cl_2

		λ, nm			
		B band	Q band		Q–B center[a] of gravity,
porphyrin	substituent	(Soret)	β	α	10^{-3} cm^{-1}
1	–H (parent)	414.0	537.5	570.0 sh	20.850
2	$-NO_2$	421.5	547.5	589.5	20.345
3	–CHO	427.0	550.0	590.0	20.184
4	–CN	422.0	546.0	583.5	20.418
5	–SOPh	421.0	543.5	580.0	20.497
6	–Cl	416.25	539.5	573.0 sh	20.738
7	$-NHCOCH_3$	418.0	541.0	577.5	20.620
8	$-CH_2OH$	414.5	538.0	570.0	20.835
9	–SPh	420.0	544.0	572.5 sh	20.638
10	$-OCH_3$	416.0	538.5	578.5	20.662
11	$-NH_2$	416.0	546.0	595.5	20.415

[a] Electronic center of gravity is defined as $(E_{\text{Soret}} + E_\alpha)/2$.

tetraphenylporphyrin (**11**),[11] magnesium(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**12**),[9] and zinc(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**13**)[9] were prepared in the course of other work in our laboratories and were all analytically pure samples. Cu(TPP) (**1**),[14] Mg(TPP),[14] Zn(TPP),[14] copper(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (**3**),[15] and copper(II) 2-cyano-5,10,15,20-tetraphenylporphyrin (**4**)[16] were prepared by literature methods.

Materials. Tetrabutylammonium hexafluorophosphate (TBAH) was prepared by metathesis from tetrabutylammonium bromide (Fluka, puriss) and ammonium hexafluorophosphate (Merck, LAB) in warm water (distilled from $KMnO_4$) and was purified by two recrystallization steps from hot, absolute ethanol followed by drying in vacuo at 110 °C. Dichloromethane (Merck, AR) was purified by refluxing over P_4O_{10} for 2 h and then distilling at a moderate rate. The fraction boiling in the range 39.5–40 °C was collected and stored over 3A molecular sieves that had been dried at 350 °C.

Electrochemical Equipment and Methods. Electrochemical half-wave potentials, $E_{1/2}$, were obtained by cyclic voltammetry using a precision triangle wave generator[17] and an operational amplifier based potentiostat with positive feedback IR compensation[18] in conjunction with a Hewlett-Packard 7015B X-Y chart recorder and a Tektronix 5103N storage oscilloscope. All measurements were made at room temperature (20–22 °C) in CH_2Cl_2/0.10 M TBAH by using a Teflon-shrouded gold disk working electrode,[19] platinum wire auxiliary electrode, and a Ag/$AgNO_3$ (0.01 M in CH_3CN) reference electrode. This reference electrode was found to have a potential of +0.354 V vs SCE by using the ferrocene/ferrocinium couple in CH_3CN/0.10 M TBAH. The reference and auxiliary electrodes were separated from the sample solution with bridges of CH_2Cl_2/0.10 M TBAH using a three compartment cell with medium porosity glass frits. Solutions were deoxygenated by bubbling with argon, which had been purified by passage through a column of BASF R3-11 catalyst.

Electronic Spectra. Spectrophotometric measurements were made on CH_2Cl_2 solutions of porphyrins in 1.000 cm path length silica cuvettes using a CARY 171 spectrophotometer. The wavelength accuracy of the CARY 171 was checked versus the emission lines of a mercury pencil lamp. The reported peak maxima are accurate to within ±0.25 nm.

Results

Electrochemical Studies. Electrochemical half-wave potentials of the parent metalloporphyrin [Cu(TPP)] and its 2-substituted derivatives are summarized in Table I. Except for the $-NHCOCH_3$ and $-NH_2$ derivatives, compounds **7** and **11**, the cyclic voltammograms revealed two reversible oxidation processes for each of the Cu(X-TPP) complexes with peak separations, ΔE_p, in the range 60–75 mV, which were substantially independent of sweep rate (v = 50–500 mV/s), while the peak currents i_{pa} and i_{pc} increased linearly with $\sqrt{v}$ and their ratio i_{pa}/i_{pc} was close to unity, as expected for one-electron waves. For the $-NHCOCH_3$ derivative **7**, the first oxidation was reversible while the second oxidation appeared to be only quasi-reversible. In the case of the $-NH_2$ derivative **11**, the oxidative electrochemistry was irreversible in an air-saturated solution even at a sweep rate of 10 V/s. Reproducible reversible data were obtained when oxygen was completely excluded from the cell.

The reductive electrochemistry of the metalloporphyrins was similar with the observation of two reduction processes within the solvent limits. The first reduction process was reversible for those metalloporphyrins most easily reduced while the others were observed to be reversible only at fast sweep rates (1–10 V/s). In all cases the second reduction process could only be observed reversibly at the maximum sweep rate of 10 V/s, indicating rapid reaction of the ions with solvent or solvent impurities. The nature of the chemistry following reduction was not investigated further.

Electrochemical half-wave potentials of the Cu(II), Mg(II), and Zn(II) complexes of 2-NO_2–TPP, compounds **2**, **12**, and **13**, and the corresponding parent M(TPP)'s are collected in Table II.

Electronic Spectroscopy. The absorption spectra of the 2-substituted Cu(TPP) molecules are typical, containing only the strong Soret or B band near 415 nm and a weaker pair of components (α- and β-bands) of the electronically forbidden Q transition in the visible. The lower energy α-band is the 0–0 component of the Q transition, while the β-band is an envelope of vibronically allowed Q-band peaks.[4] The positions of the α-, β-, and the Soret-band maxima for the 2-substituted Cu(TPP) molecules were measured in CH_2Cl_2 and are listed in Table III. The center of gravity (E^{cg}) of the Q–B system [considering only the 0–0 electronic transitions],[20] defined as

$$E^{cg} = \tfrac{1}{2}\{E(B) + E(\alpha)\} \tag{1}$$

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Table IV. Spectroscopic Energy Shifts vs Redox Potential Shifts for 2-Substituted Cu(TPP) Complexes in CH_2Cl_2 Solution

		ΔE, eV					
porphyrin	substituent	center of gravity[a]	ox1	red1	$\delta\epsilon_i$, eV	$\delta\epsilon_j$, eV	$\delta\epsilon_k$, eV
1	-H	0	0	0	0	0	0
2	$-NO_2$	−0.0638	0.113	0.371	−0.503	−0.113	−0.371
3	-CHO	−0.0826	0.067	0.229	−0.226	−0.067	−0.229
4	-CN	−0.0536	0.134	0.225	−0.209	−0.134	−0.225
5	-SOPh	−0.0438	0.077	0.157	−0.149	−0.077	−0.157
6	-Cl	−0.0139	0.040	0.059	−0.050	−0.040	−0.059
7	$-NHCOCH_3$	−0.0285	−0.008	0.016	+0.009	+0.008	−0.016
8	$-CH_2OH$	−0.0019	−0.013	0.002	−0.013	+0.013	−0.002
9	-SPh	−0.0263	−0.038	0.025	−0.035	+0.038	−0.025
10	$-OCH_3$	−0.0233	−0.062	−0.019	+0.023	+0.062	+0.019
11	$-NH_2$	−0.0539	−0.207	−0.055	+0.011	+0.207	+0.055

[a] Electronic center of gravity is defined as $(E_{\text{Soret}} + E_\alpha)/2$.

where $E(i) = [\lambda(i)]^{-1}$ is also listed; the units are 10^3 cm^{-1}. Again it was necessary to rigorously protect solutions of the amino derivative **11** from exposure to oxygen; otherwise additional peaks at longer wavelengths were observed in the spectrum.

Theory

We interpret the trends seen in redox potentials and spectral shifts in terms of one-electron energy level shifts. While this is undoubtedly a highly simplified approach, it provides a firmer basis for correlating trends than those that rely entirely on the analysis of electronic spectra.

We consider the 2-substituted Cu(TPP) series and use the data of the unsubstituted Cu(TPP) (**1**) as reference. Thus for the effect of substituents on the nth oxidation or reduction potential, E_0^n, we write

$$\Delta E_0^n(\text{s}) = E_0^n(\text{s-CuTPP}) - E_0^n(\text{CuTPP}) \qquad (2)$$

For a given reference electrode, these quantities are related to ionization potentials (I), electron affinities (A), and solvation energies ($\sigma^\pm$), as follows:

$$\delta E_0^{\text{red1}}(\text{s}) = (A - \alpha^-)(\text{s-CuTPP}) - (A - \alpha^-)(\text{CuTPP}) \qquad (3)$$

$$\delta E_0^{\text{ox1}}(\text{s}) = (I - \alpha^+)(\text{s-CuTPP}) - (I - \alpha^+)(\text{CuTPP}) \qquad (4)$$

At this level of approximation, we neglect differences in solvation energy between substituted and unsubstituted cations and simplify eqs 3 and 4 to

$$\delta E_0^{\text{red1}}(\text{s}) = A(\text{s-CuTPP}) - A(\text{CuTPP}) \qquad (5)$$

$$\delta E_0^{\text{ox1}}(\text{s}) = I(\text{s-CuTPP}) - I(\text{CuTPP}) \qquad (6)$$

In terms of the one-electron scheme of Figure 2, we then write

$$\delta E_0^{\text{red1}}(\text{s}) = -\delta\epsilon_k(\text{s}) \qquad (7)$$

$$\delta E_0^{\text{ox1}}(\text{s}) = -\delta\epsilon_j(\text{s}) \qquad (8)$$

where for the right-hand side of eqs 5 and 6 we have substituted the appropriate shifts of one-electron levels resulting from β-substitution by s. We expect that orbital k will invariably be the doubly degenerate e_g level (Figure 2), whereas orbital j may be of either a_{1u} or a_{2u} symmetry; however, we also anticipate that the "normal" (unsubstituted) ordering is probably $a_{2u} > a_{1u}$. The values of $\delta\epsilon_k$, $\delta\epsilon_j$ so obtained are listed in Table IV. We have assumed that differences between half-wave potentials $E_{1/2}$ and standard potential E_0 can be ignored here when potential shifts are considered.

We interpret the spectral shifts also in terms of the four-orbital model of Figure 2. In this treatment, the Soret (or B) band and the α- and β- (or Q) bands in the visible region of metalloporphyrin spectra can be considered as arising, in the first approximation, from excitations localized on the macrocycle involving the frontier π-orbitals. Because of the degeneracy of the two e_g orbitals, the excitations $a_{1u}(\pi)/a_{2u}(\pi) \rightarrow e_g(\pi^*)$ gives rise to four (i.e., two doubly degenerate) excited configurations. These undergo pairwise configuration interaction to give the excited molecular states corresponding to the B and Q excitations. Parameters of the four-orbital model that define the molecular orbitals and molecular states are shown graphically in Figure 2. It should be noted that the only parameter that is independent of the extent of configurational interaction is the center of gravity of the energy, or E^{cg}, of the Q and B bands.

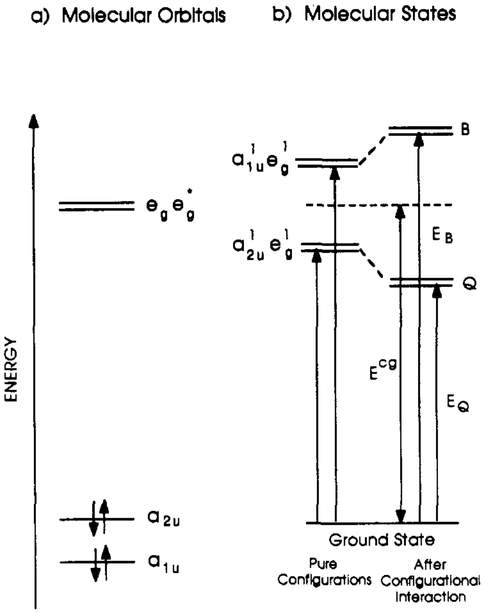

Figure 2. Origin of Q and B excited states in D_{4h} porphyrins, assuming four-orbital model (see text): (a) active π-orbitals, (b) molecular states. We have assumed the ordering $E(a_{1u}e_g) > E(a_{2u}e_g)$ in constructing this figure. This is in agreement with, for example, calculations of Weiss et al.[32] However, the conclusions of this paper are independent of this ordering.

The center of gravity E^{cg} of the Q and B bands of a metalloporphyrin, with the model employed here, is given in a usual notation[21] by

$$E^{\text{cg}} = [\epsilon_k - \tfrac{1}{2}(\epsilon_i + \epsilon_j)] - \tfrac{1}{2}[J_{ik} + J_{jk} - 2K_{ik} - 2K_{jk}] \qquad (9)$$

We assume that the second term in eq 9, involving the two-electron coulomb and exchange integrals, is essentially invariant under β-substitution. In fact, from the data of Table I, we find $E(\text{B}) - E(\alpha) = (6.63 \pm 0.21) \times 10^3$ cm^{-1}, which supports this assumption. Thus, the shift of the Q–B center of gravity $\Delta E^{\text{cg}}(\text{s})$ under β-substitution by substituent s is given by

$$\delta E^{\text{cg}}(\text{s}) = \delta\epsilon_k - \tfrac{1}{2}(\delta\epsilon_i + \delta\epsilon_j) \qquad (10)$$

where

$$\delta\epsilon_i = 2(-\delta E^{\text{cg}} + \delta\epsilon_k - \tfrac{1}{2}\delta\epsilon_j) \qquad (11)$$

The values for $\delta\epsilon_i$ so obtained are also listed in Table IV.

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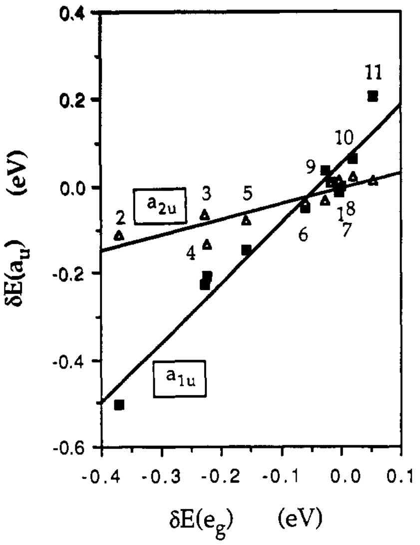

Figure 3. Shifts of the highest occupied π-level energies [(■) $\delta E(a_{1u})$ and (△) $\delta E(a_{2u})$] under substitution plotted against corresponding shifts for the lowest virtual level [$\delta E(e_g)$]. Values are from Table III, in eV, where $\delta\epsilon_i = \delta E(a_{1u})$ and $\delta\epsilon_j = \delta E(a_{2u})$ (these assignments are reversed for porphyrins **9–11**, see text) and $\delta\epsilon_k = \delta E(e_g)$. The absolute value of the a_{1u}/a_{2u} shift is relative to the assumption that $\epsilon(a_{1u}) = \epsilon(a_{2u})$ in unsubstituted Cu(TPP) (cf. ref 22).

Discussion

The changes in M(TPP) redox potential and in energies of the singlet Q and B bands under substitution are evidently substantial. The effect of the pyrrolic β-substituent on the first reduction potential through this series of compounds is qualitatively similar to that found in a series of β-substituted free-base porphyrincarboxylic esters.[22] For 2-substituted Cu(TPP)'s, the effect of changing the pyrrolic β-substituent from nitro, compound **2**, to amino, compound **11**, for example, is to decrease the first reduction potential by 0.415 V, increase the first oxidation potential by 0.32 V, and cause a red shift of the Q–B center of gravity by 0.05 eV (Tables I and II). The Q–B center of gravity is shifted more substantially in some of the other derivatives.

It is clear from the data of Table IV that, insofar as these do indeed reflect energy shifts in the frontier orbitals, there are interesting parallel trends under substitution. In Figure 3, we plot the energy shifts of highest occupied orbitals i and j against that of the lowest virtual orbital k. Our treatment does not lead to an unequivocal assignment of the orbital symmetry of the highest occupied molecular orbital in any given case; $\delta\epsilon_i$ may be the energy difference of a_{1u} or of a_{2u} orbitals between the given 2-substituted Cu(TPP) and Cu(TPP). It is evident, however, when the data of the whole series of compounds are considered that it may be fitted to two straight lines when $\delta\epsilon_i$ and $\delta\epsilon_j$ assignments are reversed in the case of porphyrins **9–11**, which have electron-donating substituents.

It is also evident that the shifts in levels i and k are quite similar, whereas those for level j are significantly smaller (about $^1/_4$ that of i). This is in qualitative accordance with results of calculations on the form of these orbitals; while the details vary according to the method of calculation, the densities C_β^2 are generally largest and about equal for the e_g and a_{1u} orbitals (somewhat larger for e_g) and smaller for a_{2u}.[4] Assuming that the β-substituent effect is approximately proportional to the β-density, the above trends can be rationalized provided that i and j are identified respectively with the a_{1u} and a_{2u} levels: this is in keeping with the normal ordering $a_{2u} > a_{1u}$.[4] It will be noted that the predicted separation of a_{1u} and a_{2u} levels in 2-substituted Cu(TPP) molecules is relative to that in Cu(TPP) itself. There is, however, convincing evidence from UV photoelectron spectroscopy that, at least in Cu and Ni(TPP)'s, the separation between a_{1u} and a_{2u} levels is below the usual level of resolution for large molecules—i.e., 20–30 meV.[23] Thus, for example, the first two π-ionizations of the octaethylporphyrin complex Ni(OEP) are of equal intensity and separated by 0.48 eV while the corresponding ionizations in Ni(TPP) overlap essentially completely to give one band of twice the single ionization intensity [relative to the first one-electron ionization of Ni(II)]. The results for Cu(TPP) and Cu(OEP) are almost identical with these, but slightly less well resolved.[23] Thus, the predicted separation of a_{1u} and a_{2u} levels in Figure 3 can also, on this assumption, be taken to be absolute within approximately ±20 meV. We note that Gouterman and co-workers deduce that, in Cu(TPP), the a_{1u} and a_{2u} levels are indeed practically degenerate, the a_{2u} level being very slightly higher.[8] It is not, however, possible to quantify this exactly.

The energy gap between a_{1u} and a_{2u} orbitals increases markedly for substitution by energy-lowering β-substituents (e.g., NO_2); thus the a_{2u} symmetry of the highest occupied orbital in molecule and monocation will be increasingly favored under such substitution. For energy-raising substituents, however (e.g., OCH_3 and NH_2), this trend is inverted, so that such substituents increasingly favor the order $a_{1u} > a_{2u}$. By selective β-substitution, it thus appears possible to modulate the magnitude and sign of the a_{1u}/a_{2u} energy gap in metalloporphyrins.

Support for the conclusion that there is a inversion in the ordering of the a_{1u}/a_{2u} orbitals in progressing from those 2-substituted Cu(TPP)'s with strongly electron-withdrawing substituents, porphyrins **2–5**, to the 2-substituted Cu(TPP)'s, **9–11**, with electron-donating substituents is found in consideration of the ratio $(\epsilon_\alpha/\epsilon_\beta)$ of the extinction coefficients of the α- and β-bands, which is a minimum in the vicinity of the crossing point in Figure 3 [0.10 for Cu(TPP) (**1**)] and increases as the distance from the crossing point increases in either direction [0.66 for Cu(NO_2–TPP) (**2**) and 0.54 for Cu(NH_2–TPP) (**11**)]. Furthermore, the relative intensity of the B band falls off as the distance from the crossing point increases in each direction. Both of these observations are in qualitative accord with the earlier treatment of Gouterman and his colleagues[8] and in line with the tenet of the four-orbital model that the extent of configuration interaction increases with decreasing a_{1u}/a_{2u} energy separation. We are currently investigating the effects in detail.

The effect of the substituents on the half-wave potential for the first oxidation and the first reduction showed a parallelism between the order of the substituent effect and empirical linear free energy parameters. Linear regressions were determined by using empirical substituent parameters and the first oxidation half-wave potential of the 2-substituted Cu(TPP)'s. The best fit for the data was obtained for correlations with Swain and Lupton resonance (R) values[24] (correlation coefficient 0.97) (Figure 4); when the data for the 2-aminoporphyrin (**11**) are excluded, an even better fit is obtained (correlation coefficient 0.99_4). Correlation of the data with the Hammett σ_p also provided a good fit (correlation coefficient 0.96), although the $E_{1/2}$ value for **11** was again lower than would be predicted by using the line of best fit. Correlation with other substituent parameters (σ_m, σ_{m^+}, σ_{p^+}, σ_I, σ_R, σ_{R°, σ_{R^+})[25] was poor as those compounds with electron-donating substituents, especially **11**, deviated significantly from the line of best fit of the other compounds. Indeed, in the case of the correlation of σ_I with the half-wave potential for the first oxidation, the data can be fitted to straight lines in two sets, the compounds **2–8** ($\rho_I = 0.25$, correlation coefficient 0.87) and the compounds **9–11** ($\rho_I = 0.95$, correlation coefficient 1.0). These data are also in accord with an inversion of the normal ordering so that $a_{1u} > a_{2u}$ in the case of the 2-substituted Cu(TPP)'s **9–11** with electron-donating substituents.

The possibility that the amino group in compound **11** is somehow "abnormal" can be discounted. The substituent in this compound exists entirely in the amino form. A study of tautomeric

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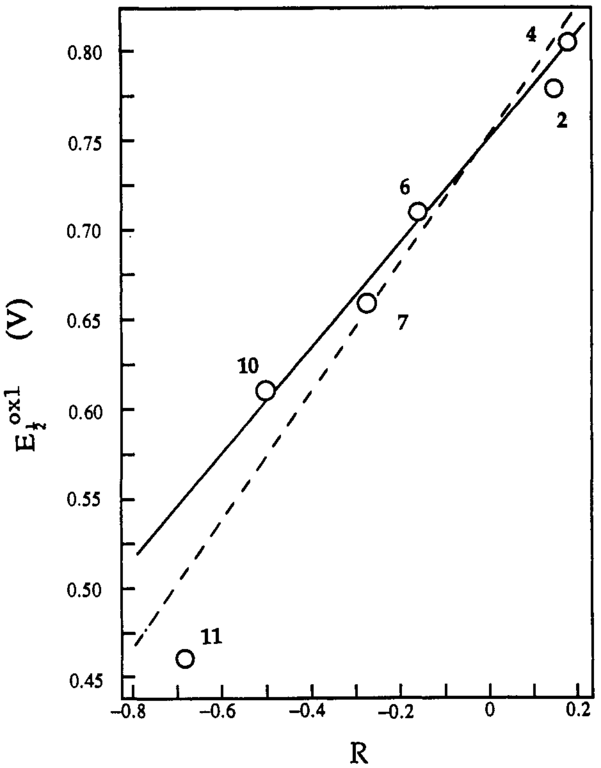

Figure 4. First oxidation half-wave potential for copper(II) 2-substituted tetraphenylporphyrins as a function of the Swain and Lupton[24] *R* empirical parameter of the substituent. The line of best fit of all the data is shown as a broken line and as a solid line when the amino compound **11** is excluded.

processes of substituents in free-base porphyrins and metalloporphyrins found no evidence for the existence of the tautomeric imino–chlorin forms in 2-aminoporphyrins.[26] The amino group is also completely precluded from acting as a ligand toward the metal in a second metalloporphyrin molecule because of the shielding provided by the adjacent *meso*-phenyl group.

Some electrochemical data for tetraphenylporphyrins containing metals other than Cu are given in Table II. Comparisons can be made for the influence of β-NO_2 substitution for magnesium, copper, and zinc tetraphenylporphyrins. For the first and second oxidation steps (producing in each case mono- and dications, respectively), the shifts $\delta E_{1/2}$ are nearly independent of the central metal ($\delta E^{ox1} \approx \delta E^{ox2} \approx +0.12$ V). For the reduction step, δE^{red1} caused by β-NO_2 substitution is identical for the Zn and Cu complexes (Mg values irreversible). It appears from those results that, at least for the TPP complexes of Mg, Cu, and Zn, the modulation of valence level energies by β-substitution is nearly independent of the nature of the central metal.

The only previous studies on the effect of pyrrolic substituents on electronic structure of metalloporphyrins have been limited to observations of spectral differences in several, structurally very similar, metal complexes of 2,3,7,8,12,13,17,18-octasubstituted porphyrins[2,3] and of metal complexes of 5,10,15,20-tetraphenylporphyrin (TPP).[3] The considerable differences between the two classes of metalloporphyrin were attributed mainly to the nature of the porphyrin peripheral substituents, leading to the closer approach to degeneracy of excited configurations in the M(TPP) cases.[2] Only small differences in behavior were found among the 2,3,7,8,12,13,17,18-octasubstituted porphyrins (octaethylporphyrin, uroporphyrin, coproporphyrin, mesoporphyrin, and protoporphyrin),[3] which is not surprising given the similarity of the substituents (alkyl or substituted-alkyl groups, together with a vinyl group in the case of protoporphyrin) and, thus, the relatively small perturbation of the system expected on variation of them.

The present work, however, demonstrates that pyrrolic β-substituents, particularly those that are either strongly electron-donating or electron-withdrawing, may have a large influence on the π-orbital energies in porphyrin systems.

A brief comment on the relevance of these results to the design of proposed molecular electronic logic or memory devices, in which there is a current surge of interest,[27] in which porphyrins or polyporphyrin systems[28] could play a role in electron/hole or energy transmission, is in order. It is clear that in general *fine tuning* of relevant energy levels will be necessary to optimize, for example, the threshold electrical bias voltage[29] and/or time constant[30] in a "molecular switch". Similarly, the projected photoactivated molecular memory shift registers composed of chains of electron-transfer molecules suggested by Hopfield, Onuchic, and Beraton[31] require built-in electrochemical potential gradients. Where porphyrins are involved in the design of such devices, it should be possible to incorporate and predict sensitive tuning by appropriate pyrrolic β-substitution employing the principles outlined above.

Concluding Remarks

A new approach for obtaining information about the relative ordering of the frontier and subfrontier orbitals in metalloporphyrin systems has been presented in this paper. These values are obtained by consideration of a combination of electrochemical and spectral data. The treatment, although undoubtedly a highly simplified approach, provides a firmer basis than previous treatments involving only absorption spectral data for correlating trends in sets of metalloporphyrins that retain approximate D_{4h} symmetry. The new treatment allows the separation of the a_{1u} and a_{2u} orbital energies and enables them to be quantified relative to the orbitals in an appropriate parent porphyrin system.

The series of 2-substituted Cu(TPP)'s used in this work was chosen to minimize effects of aggregation and ligand complexation and to maximize the range of substituent electronic effects. This work has revealed that substantial modulation of the a_{2u}/a_{1u} orbital energies is achieved by variation of the nature of a pyrrolic β-substituent. The effect is, as expected, felt much more strongly on the a_{1u} orbital, which has significant electron density associated with the pyrrolic β-position of metalloporphyrins. Indeed, the relative energies of the a_{1u} orbital in the nitroporphyrin **2** and the aminoporphyrin **11** differ by 0.17 eV; the corresponding difference in the energies of the a_{2u} orbitals is 0.14 eV. This work has also revealed that, in favorable cases, the "normal" ordering $a_{2u} > a_{1u}$ can be reversed by the use of electron-releasing substituents on the pyrrolic β-position to destabilize the a_{1u} orbital with respect to the a_{2u} orbital.

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