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Comparative Study of the Visible Spectra of the Iron(III) Complexes of *para*-Substituted Tetraphenylporphyrins. Electronic Effects of Substituents and Axial Ligands

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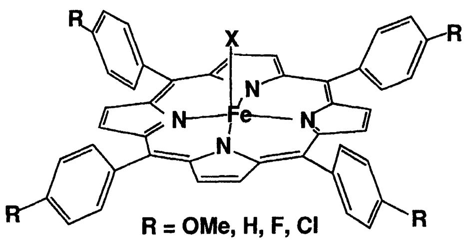
The visible absorption spectra of the high-spin iron(III) complexes of the tetra-*para*-substituted derivatives of 5,10,15,20-tetraphenylporphyrin, Fe(*p*-Rtpp)X (R=OMe, H, F or Cl; X=Cl, Br or I), have been compared with each other in order to clarify the electronic effects of the phenyl substituents and axial ligands. Two charge-transfer bands shift to higher energy as the electron-withdrawing ability of the substituents increases. This is attributed to a stabilization of the porphyrin $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals involved in the electronic transition. These bands shift to lower energy in the order $X = Cl < Br < I$; the energies of these bands for I are the lowest of the three. By considering the predominantly ionic character of the bond between Fe and X, it has been proved that the iron d_{yz} and d_{zx} levels are lowered in this order, thereby causing a red shift. The Q_v porphyrin transition shifts to lower energy in the order $X = Cl < Br < I$, and the Q_0 transition exhibits the same trend to a less extent. These results are explained by taking into consideration two kinds of effects of axial ligands: the electron–electron repulsion in the porphyrin ring and the porphyrin skeletal vibrations.

The diverse biological functions of heme proteins are associated with varying degrees of change in the local heme environment, from subtle conformational variations to changes in the axial ligands, spin states and oxidation states. A number of recent studies of model heme compounds have demonstrated the importance of substituent effects in porphyrins.[1—9] Electron-withdrawing substituents directly attached to porphyrins significantly affect the catalytic properties of their metal complexes.[8] Substituents even on the phenyl rings in tetraphenylporphyrin have been found to modulate the electronic properties of the central region of the porphyrin macrocycle.[1c,5c] Although the met-forms of myoglobin and hemoglobin, which contain the most commonly known high-spin iron(III) heme complexes, are physiologically not active, the high-spin iron(III) state is also found in several heme enzymes, particularly in the resting form of peroxidases and catalases, and in the substrate complex of native cytochrome P-450.



R = OMe, H, F, Cl

X = Cl, Br, I

Fig. 1. Complexes Fe(*p*-Rtpp)X studied.

In the study reported here, we measured the visible absorption spectra of model heme complexes, the high-spin iron(III) complexes of a series of tetra-*para*-substituted derivatives of 5,10,15,20-tetraphenylporphyrin, Fe(*p*-Rtpp)X (R = OMe, H, F or Cl; X = Cl, Br or I), shown in Fig. 1. During the course of the study using Mössbauer spectroscopy of this series of complexes,[10] we became conscious of the fact that the optical spectra of these compounds show a regular variation with the axial and porphyrin ligands. In particular, two bands at longer wavelengths characteristic of high-spin iron(III) complexes of porphyrins greatly change their peak positions. We examined the effects of the electron-withdrawing and -releasing phenyl substituents, and of the axial ligands in a systematic way.

Experimental

The porphyrins were synthesized from pyrrole and aldehydes in refluxing propionic acid according to the usual method.[11] The complexes, Fe(*p*-Rtpp)X, were prepared from the porphyrins and finely powdered iron metal[12] or iron(II) chloride[13] via the acetato or chloro and the μ-oxo complexes.

The electronic absorption spectra of benzene solutions were taken on a Hitachi U-3300 spectrophotometer. The concentration was about 80 and 16 $\mu mol\,dm^{-3}$ for measurements at longer wavelengths and in the Soret region, respectively.

Results and Discussion

The dominant contribution to the visible and near-ultraviolet absorption bands of metalloporphyrins arises from π,π^*-transitions of the porphyrin macrocycle:[14] $a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(\pi^*)$ transitions in point group D_{4h}. For high-spin iron(III) heme complexes, since the porphyrin $a_{1u}(\pi), a_{2u}(\pi) \rightarrow$ iron $e_g(d_{yz}, d_{zx})$ charge-transfer transitions are estimated to be in the visible region, a number of excited states arising from a coupling of the singlet and triplet porphyrin π,π^*-configurations with the $a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(d_{yz}, d_{zx})$ charge-transfer configurations are expected[15,16] in the visible and near-infrared regions. Makinen and Churg[16] have used polarization and intensity data for identifying and assigning the spectral bands of a variety of hemoproteins. Although the origin of the near-infrared broad band at around 10000 cm^{-1} of several high-spin iron(III) complexes has been assigned to a configuration interaction mixture, virtually pure porphyrin π,π^*-transitions and porphyrin $\pi \rightarrow$iron d charge-transfer transitions have been assigned to the visible bands of the complexes. The present data were analyzed according to their assignment. Although the analyses were not of complete quantitative accuracy, they are being employed with reasonable success to qualitatively delineate the factors that affect the visible spectra.

Five visible bands were observed for the complexes, Fe(*p*-Rtpp)X. They are hereinafter designated as a, b, c, d, and e in order of decreasing energy. Typical electronic spectra are shown in Figs. 2 and 3. Bands a, b, and c arise from the porphyrin $a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(\pi^*)$ transitions, and correspond to the Soret, vibronically excited Q_v and Q_0 bands (in Gouterman's notation[14]), respectively. On the other hand, bands d and e are assigned to the $a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(d_{yz}, d_{zx})$ charge-transfer transitions.[1c,16] The energy levels of the frontier orbitals relevant to these transitions are illustrated schematically in Fig. 4. The spectral data are summarized in Table 1. The band energies were found to be affected by the electronic nature of the axial ligands and substituents, bands e and d being the most affected ones.

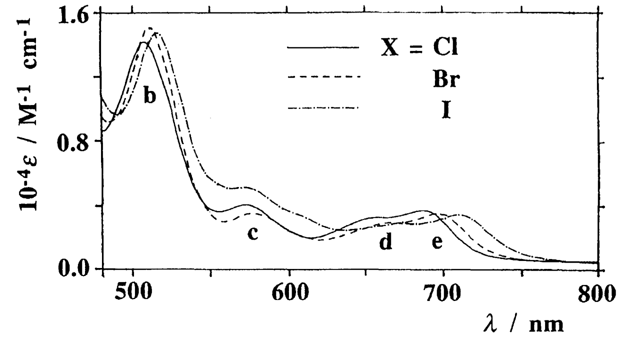


Fig. 2. Absorption spectra of Fe(tpp)X. Symbols b to e correspond to absorption bands as defined in the text. Soret bands are not shown.

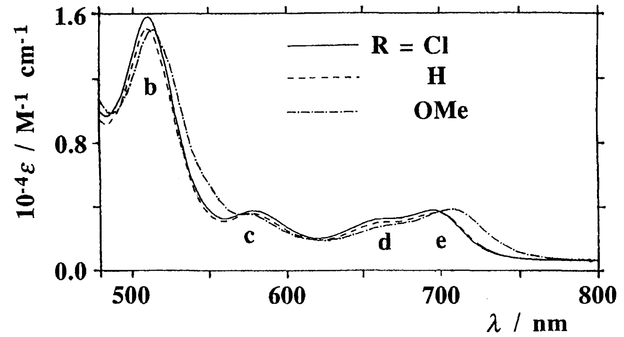


Fig. 3. Absorption spectra of Fe(*p*-Rtpp)Br. Symbols b to e correspond to absorption bands as defined in the text. Soret bands are not shown.

Columns 8 and 9 of Table 1 give the energy differences between bands a and c ($E_a - E_c$) and between bands b and c ($E_b - E_c$). The energy separation ($E_a - E_c$) is the splitting of of the 0–0 excited-state levels, and is expressed[14,17] on the basis of the four-orbital model of the metalloporphyrin electronic states as

$$E_a - E_c = 2A''_{1g}[1 + (A_{1g}/A''_{1g})^2]^{1/2}, \tag{1}$$

where $2A_{1g}$ is the energy splitting of the nearly degenerate highest filled a_{1u} and a_{2u} orbitals and A''_{1g} is the off-diagonal configuration-interaction element, which is attributed to the electron-electron repulsion. Because $A_{1g} \ll A''_{1g}$, $E_a - E_c$ approximately equals $2A''_{1g}$. The Q_v band is the envelope of the 0–1 vibronic transitions;[18a] the energy difference ($E_b - E_c$) is then a measure of the average frequency of the mixing modes.

Effects of the Axial Ligands. We first discuss the dependence of the peak positions of the charge-transfer bands d and e on the axial ligands. Figure 2 and Table 1 show that the absorption maxima of these bands shift to longer wavelengths as the atomic number of the halide axial ligand increases. These bands are assigned to the $a_{1u}(\pi), a_{2u}(\pi) \rightarrow e_g(d_{yz}, d_{zx})$ charge-transfer transitions;[1c,16] this result is explained by considering the effects of the axial ligands on the energies of the iron e_g (d_{yz},d_{zx}) orbitals. Although the Fe–N binding is largely covalent in these systems, the bonds between the halide axial ligands and the iron were found[10] to be predominantly ionic. We can properly apply the point-charge model within the framework of a crystal field treatment[19] to extract the effects of the axial ligands on the energies of the d orbitals.

A crystal field of tetragonal symmetry splits the originally fivefold degenerate d orbitals into four distinct energy levels: three singly and one doubly degenerate levels (Fig. 4). A tetragonal field parameter (δ) is defined as the splitting between the $b_{2g}(d_{xy})$ and $e_g(d_{yz}, d_{zx})$ orbitals. We consider an iron ion at the origin of the *x*, *y*, and *z* coordinate axes, replacing the axial ligand with an effective point charge of

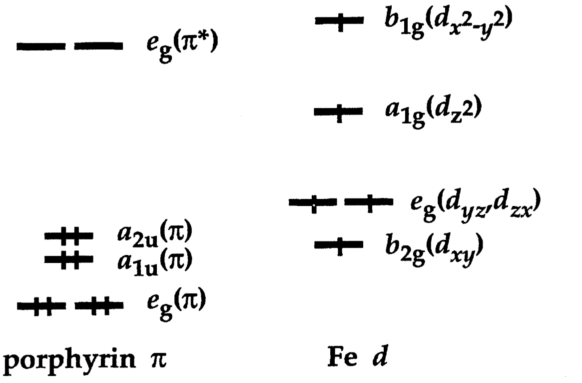


Fig. 4. Energy levels of the frontier orbitals.

Table 1. Absorption Spectral Data for Fe(p-Rtpp)X

R	X	$E/10^4$ cm^{-1}					$E_a - E_c$	$E_b - E_c$	$E_d - E_e$
		a	b	c	d	e	10^3 cm^{-1}	10^3 cm^{-1}	10^2 cm^{-1}
OMe	Cl	2.351	1.956	1.743	1.504	1.437	6.07	2.13	6.7
	Br	2.342	1.944	1.734	1.486	1.416	6.08	2.10	7.0
	I	2.402	1.928	1.729	1.468	1.390	6.73	1.99	7.8
H	Cl	2.388	1.970	1.745	1.514	1.453	6.43	2.25	6.1
	Br	2.380	1.956	1.730	1.493	1.432	6.50	2.26	6.1
	I	2.437	1.938	1.747	1.479	1.403	6.90	1.91	7.6
F	Cl	2.388	1.969	1.745	1.520	1.457	6.43	2.23	6.3
	Br	2.393	1.958	1.742	1.503	1.441	6.51	2.16	6.2
	I	2.397	1.940	1.733	1.483	1.410	6.64	2.07	7.3
Cl	Cl	2.379	1.966	1.740	1.527	1.469	6.38	2.26	5.8
	Br	2.373	1.955	1.729	1.499	1.438	6.44	2.26	6.1
	I	2.407	1.937	1.729	1.485	1.412	6.78	2.08	7.3

$-ae$ (axial), placed at Z along the z-axis, and replacing the four in-plane porphyrin ligands with an effective point charge of $-he$ (horizontal) placed at $\pm R$ along the x and y axes. Then, the expression for δ is derived[20)] in units of $e^2/(4\pi\varepsilon_0)$ as

$$\delta = (5/21)(2h/R^5 - a/Z^5)\langle r^4\rangle - (3/7)(2h/R^3 - a/Z^3)\langle r^2\rangle, \quad (2)$$

where $\langle r^n\rangle$ is the expectation value of r^n taken over an iron 3d orbital. Although the out-of-plane displacement of the iron atom is not taken into consideration for simplicity, the following conclusion is qualitatively valid.

The electronegativity of the halogen atom, and, hence, the absolute value (a) of the negative charge of the axial halide ion decreases in the order Cl > Br > I. This means that the value of a, not the extent of the decrease in the value, is smallest for I. The tetragonal splitting parameter (δ) is partially differentiated by a to give

$$\partial\delta/\partial a = [3\langle r^2\rangle/Z^2 - (5/3)(\langle r^4\rangle/Z^4)]/(7Z). \quad (3)$$

We note that $\langle r^n\rangle/Z^n < 1$, and that the value decreases with increasing n. Hence, the first term in Eq. 3 is greater than the second; i.e., $\partial\delta/\partial a > 0$. A more detailed treatment which takes into consideration that Z should be shorter for a larger a,[21)] gives qualitatively the same conclusion. The energy of the $b_{2g}(d_{xy})$ orbital is not affected by the axial ligand in the first approximation, or if any, it shifts to lower energy as the absolute value a of the negative charge of the axial ligand decreases. Thus, the less electronegative axial ligand causes a larger stabilization of the $e_g(d_{yz},d_{zx})$ orbitals. In the $a_{1u}(\pi)$,$a_{2u}(\pi)$$\rightarrow$$e_g(d_{yz},d_{zx})$ charge-transfer transitions, the orbital to which an electron is promoted is stabilized in the order Cl < Br < I: the stabilization is largest for I. Of the lower orbitals involved in the transitions, a_{1u} is believed not to be affected by the axial ligand in the first approximation, and a_{2u} is expected to shift to a higher energy in the same order (as discussed in the next paragraph). Therefore, the transition energy decreases in this order.

Since the $a_{2u}(\pi)$ orbital has a higher energy than the $a_{1u}(\pi)$ orbital in iron complexes of tetraphenylporphyrin,[14c,17,22)] band e is assigned to the transition from the $a_{2u}(\pi)$ orbital, and band d to the transition from the $a_{1u}(\pi)$ orbital. Hence, the energy separation ($E_d - E_e$) corresponds to the energy splitting of the nearly degenerate highest occupied a_{1u} and a_{2u} orbitals. Table 1 indicates that $E_d - E_e$ tends to increase in the order Cl < Br < I: with R = OMe, for example, the values are 6.7, 7.0, and 7.8×10^2 cm^{-1} for X = Cl, Br and I, respectively. MO calculations show[17)] that the a_{2u} level of a metalloporphyrin is influenced by the metal via the symmetry-allowed interaction with an empty metal p_z orbital, while the a_{1u} orbital has nodes through the pyrrole nitrogens and cannot interact directly with the metal. As the electronegativity of the metal increases, the p_z orbital becomes increasingly conjugated with the ring, stabilizing the a_{2u} orbital with which it primarily mixes; more electronegative metals shift the a_{2u} to a lower energy. In the present case, the "effective electronegativity" of the iron is considered to depend on the electronegativity of the axial ligand; the a_{2u} level is expected to shift to a higher energy in the order Cl < Br < I. This mechanism accounts for the higher dependence of E_e on the axial ligand than that of E_d.

The energy ordering of the porphyrin HOMO's (a_{1u} and a_{2u}) is reversed[14c,17,22)] in iron(III) octaethylporphyrin (oep) complexes relative to the present complexes. Thus, there should be qualitative differences in the halide axial ligand effects on the transition energies of the CT bands: the energy difference between these two bands should be smallest for I, and it should be the higher energy band that shows larger dependence on the axial ligand than the other. Although we measured the optical spectra of oep complexes, it was impossible to assign the two CT bands. And although an absorption maximum assigned to a CT band was observed around 650 nm, the other peak was missed, possibly because it overlapped with the Q bands.

Secondly, we direct out attention to the fact that the energy difference between bands a and c ($E_a - E_c$) increases in the same order (Table 1). This energy separation approximately equals $2A''_{1g}$ (Eq. 1), which is attributed to an electron–electron repulsion. An electronegative axial ligand pulls electrons from the central iron; the electron-attracting effect is considered to be transmitted to the porphyrin core to some extent. This effect diminishes the electron-electron repulsion in the porphyrin core, concomitantly decreasing $E_a - E_c$. The less electronegative is an axial ligand, the less effect is expected, thus explaining the observed result.

Lastly, attention should be called to the result that the energy separation $E_b - E_c$ decreases in the order $Cl > Br > I$; $E_b - E_c$ is smallest for I (Table 1). The energy difference is a measure of the average frequency of the mixing modes which cause the 0–1 vibronic transitions. The resonance Raman frequencies of metalloporphyrins have been noted to be sensitive to the oxidation state, coordination number, and spin state of the central metal ion.[18,23—25] It was shown[18] that all of the porphyrin skeletal modes above 1450 cm^{-1} exhibited negative correlations with the porphyrin core size, i.e., the porphyrin-ring center to pyrrole–nitrogen distance. The porphyrin core size is larger for iron(II) complexes than for iron(III) complexes within each of high- and low-spin states.[18a] An ab initio MO study has revealed[26] that a reduction of the iron ion decreases the covalent character of the iron-ligand bonds: The total overlap populations between iron $d_{x^2-y^2}$ orbital and the four pyrrole–nitrogen orbitals were found to be smaller for iron(II) states than for iron(III) states, the contribution from a typical bonding MO being smaller for iron(II) states, while the contribution from a typical antibonding MO being almost independent of the oxidation state. The decreased covalent character for the iron(II) states is believed to cause the larger core size and lower vibrational frequencies than for the iron(III) states. In the present case all of the complexes have iron in the iron(III) high-spin state. The "effective oxidation number" of the iron, however, varies with the axial ligand and decreases in the order $Cl > Br > I$ to accommodate their electronegativity; the "effective oxidation number" of the iron is smallest for I. Thus, the variation of the energy separation ($E_b - E_c$) is attributed to a variation of the electronegativity of the axial halide. This conclusion has been drawn from a model in which the frequencies of the porphyrin core modes should be changed as the axial ligand is varied from Cl to Br to I. It is desired that the validity of this model be demonstrated through a resonance Raman study.

The preceding discussions can be put together to predict the dependence of the E_b on the axial ligand; E_c decreases in the order $Cl > Br > I$ as a result of the less diminished electron–electron repulsion in the porphyrin core for the latter halide, while $E_b - E_c$ decreases in the same order, reflecting the weaker covalent character of the porphyrin ligand bonds for the latter halide. Consequently, E_b should decrease in the same order to a larger extent than E_c. Table 1 and Fig. 2 indicate that this is the case; with R=F, for example, from X=Cl to I E_b and E_c decrease by 2.9 and 1.2×10^2 cm^{-1}, respectively.

Effects of the Phenyl Substituents. A pronounced influence of the phenyl substituents on the charge-transfer bands (d and e) is seen in Fig. 3 and Table 1. In describing the electronic effect of the substituents, it is common to separate the effect into the inductive and resonance contributions.[27] This can readily be done by using the dual substituent parameter,[28] a linear combination of the inductive and resonance substituent parameters (σ_I and σ_R). In our attempt to correlate the observed values discussed below and the Mössbauer quadrupole-splitting values[10] and these substituent parameters, it was shown that neither of these two parameters is superior to the other, but they both have nearly equal contributions. The sum of σ_I and σ_R is equal[27] to the well-known Hammett substituent constant (σ_p), which is commonly used as a measure of the electron-withdrawing ability of the substituents; the values of σ_p are -0.28, 0, 0.06, and 0.22 for OMe, H, F, and Cl, respectively.[27] The absorption maxima of bands d and e shift to shorter wavelengths as the electron-withdrawing nature of the substituent increases. With W=I, for example, the values of E_d are 1.468, 1.479, 1.483, and 1.485×10^4 cm^{-1} for these substituents, respectively; the values of E_e are 1.390, 1.403, 1.410, and 1.412×10^4 cm^{-1}, respectively. Walker and co-workers have reported[1c] a similar result for band e, band I in their notation, for high-spin Fe(tpp)Cl derivatives.

It seems most likely that electron-releasing OMe shifts the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals to higher energies through both inductive and resonance effects, and that F and Cl shift them to lower energies. In the $a_{1u}(\pi),a_{2u}(\pi) \rightarrow e_g(d_{yz},d_{zx})$ charge-transfer transitions, the orbital from which an electron is promoted is increasingly stabilized as the electron-withdrawing ability of the substituent increases. The higher orbitals, d_{yz} and d_{zx}, involved in the transitions are believed to not be affected by the phenyl substituent in the first approximation. Therefore, the transition energy increases with the electron-withdrawing ability of the substituent.

The effects of the phenyl substituents on the a_{1u} and a_{2u} levels are different because of the particular charge distributions of these orbitals. The a_{1u} orbital has nodes at the *meso* carbons and is expected to be slightly influenced by phenyl substitution. The a_{2u} orbital, on the other hand, places considerable charge on the *meso* carbons, and should be strongly affected by the phenyl substituents. Thus, the stabilization of the a_{2u} orbital by a given electron-withdrawing substituent is predicted to exceed that of the a_{1u} orbital. In support of this conclusion, Table 1 indicates that the energy difference ($E_d - E_e$) is smaller for electron-withdrawing F and Cl than for electron-releasing OMe; with X=Cl, for example, the values are 6.7, 6.3, and 5.8×10^2 cm^{-1} for R=OMe, F and Cl, respectively.

Conclusions

For high-spin iron(III) complexes, Fe(*p*-Rtpp)X, five visible bands were observed and designated as a, b, c, d, and e. Bands a, b, and c correspond to the Soret, Q_v and Q_0 bands, respectively; bands d and e are assigned to the $a_{1u}(\pi),a_{2u}(\pi) \rightarrow e_g(d_{yz},d_{zx})$ charge-transfer transitions. The absorption maxima of the latter two bands shift to longer wavelengths as the atomic number of the halide axial ligand increases. This is attributed to the larger stabilization of the $e_g(d_{yz},d_{zx})$ orbitals by a less electronegative axial ligand. Conjugation of empty iron p_z orbitals with $a_{2u}(\pi)$ accounts for the larger dependence of band e on the axial ligand than band d.

The extent of diminishing the electron–electron repulsion in the porphyrin core depends upon the electronegativity of the axial ligand, and leads to increasing $E_a - E_c$ in the order $Cl < Br < I$. The energy separation ($E_b - E_c$) decreases in the order $Cl > Br > I$; $E_b - E_c$ is smallest for I. This dependence is probably caused by the difference in the vibrational frequencies of the porphyrin skeletal modes that arise from the difference in the "effective oxidation number" of the iron and the resulting difference in the porphyrin core size.

The phenyl substituents influence bands d and e. The absorption maxima of these bands shift to shorter wavelengths as the electron-withdrawing ability of the substituent increases. This phenomenon occurs because the electron-withdrawing substituents shift the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals to lower energies. The a_{2u} orbital is more strongly affected by the phenyl substituents than the a_{1u} orbital because of the particular charge distributions of these orbitals. This explains the observed result that the energy difference ($E_d - E_e$) is smaller for electron-withdrawing F and Cl than for electron-releasing OMe.

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