SPECTROSCOPIC CHARACTERIZATIONS OF *MESO*-PHENYL SUBSTITUTED TETRABENZOPORPHYRIN ZINC COMPLEXES[1]

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Abstract----- Zinc complexes of tetrabenzoporphyrin with mono-, di-, tri-, and tetraphenyl substituents at *meso*-position show electronic spectra with progressive red shifts from those of tetrabenzoporphyrin zinc complex, and these shifts may be related to ruffling of the macrocycle revealed by crystal structure determination. Fluorescence emissions and basicities of these compounds are also effected by this nonplanarity.

Porphyrins have attracted intense research interest not only for their well-established biological importance, but also for the opportunity they offer in studying structure-bonding-reactivity interrelationships.[2] Among the many variations of the basic porphyrin structure, tetrabenzoporphyrin (TBP) is uniquely different. TBP has been claimed as a structural intermediate between porphyrin and phthalocyanine.[3] The extension of the π-electron system in TBP has the effect of drastic lowering of the redox potentials.[4] Currently our knowledge on the coordination chemistry of metalloTBP is rather limited due to the poor solubility of this porphyrin system in most non-coordinating solvents.[5] In order to enhance the solubility of TBP, we studied the possibility of introducing phenyl substituents to the *meso*-positions. There are two synthetic routes reported to make *meso*-tetraphenyltetrabenzoporphyrin (TPTBP). Method 1 developed by Remy employs isoindole and benzaldehyde as starting materials.[6] Method 2 reported by Kopranenkov chooses 3-benzylidenephthalimidine as starting material.[7]

In our hands we discovered that instead of obtaining a single product as reported, the reactions always yielded a complex mixture. Similar results have been noticed by other laboratories.[8] The mixture can be separated by hplc (Dynamax C8, 300 Å, 12 μ column eluted with 95% acetonitrile aqueous solution) to give four major products (I, II, III, and IV sequentially). Data of the corresponding mass[9] and electronic spectra

Table I. Summary of mass and electronic spectra data of the major components from hplc

	TBPZn	I	II@	III	IV
mass(m/z)#	572	648	724	800	876
Soret(nm)*	433.5(8.3)	438.5(8.9)	445.0(10.0)	454.5(13.3)	473.0(18.9)

@ Compound II comprised two randomers with two phenyls substituted at 5,10- or 5,15-positions.
# Spectra taken by FAB technique with suspension matrix CH_2Cl_2+NBA or dithiol.
* Spectra taken in pyridine. The numbers in parentheses are the half-line-width of the corresponding Soret peaks.

are collected in Table I. While the Soret bands of these compounds indicate a clear red shift from I to IV, the mass numbers show a constant difference of 76, the mass difference between phenyl and hydrogen.

^{1}H Nmr spectra of IV and III are shown in Figure 1. The spectrum of compound (IV) is basically consistent with that of the reported TPTBPZn complex, but with different peak assignments.[6,10] In contrast, the spectrum of compound (III) shows a distinct lack of fourfold symmetry. The spectrum is very much solvent dependent, and peaks are better resolved in CD_2Cl_2. Together with the mass of complex (III), spectrum 1(b) can be assigned successfully as *meso*-triphenyltetrabenzoporphyrin. Peak assignments were accomplished by comparison with the spectra of TBPZn and TPTBPZn, and based on the concept of ring current effect. The assignments of peaks of α_1, β_1, β_2, and α_2 were further confirmed by the cross peaks shown in the 2DCOSY spectrum. Similarly, the ^{1}H nmr spectra of II and I, together with their mass spectra, are consistent with *meso*-diphenyltetrabenzoporphyrin and *meso*-monophenyltetrabenzoporphyrin, respectively.[11] As expected, from the two *meso*-proton peaks of compound (II) and the two overlapping peaks of the chromatogram that compound (II) comprised two randomers with two phenyls substituted at 5,10- or 5,15-positions.

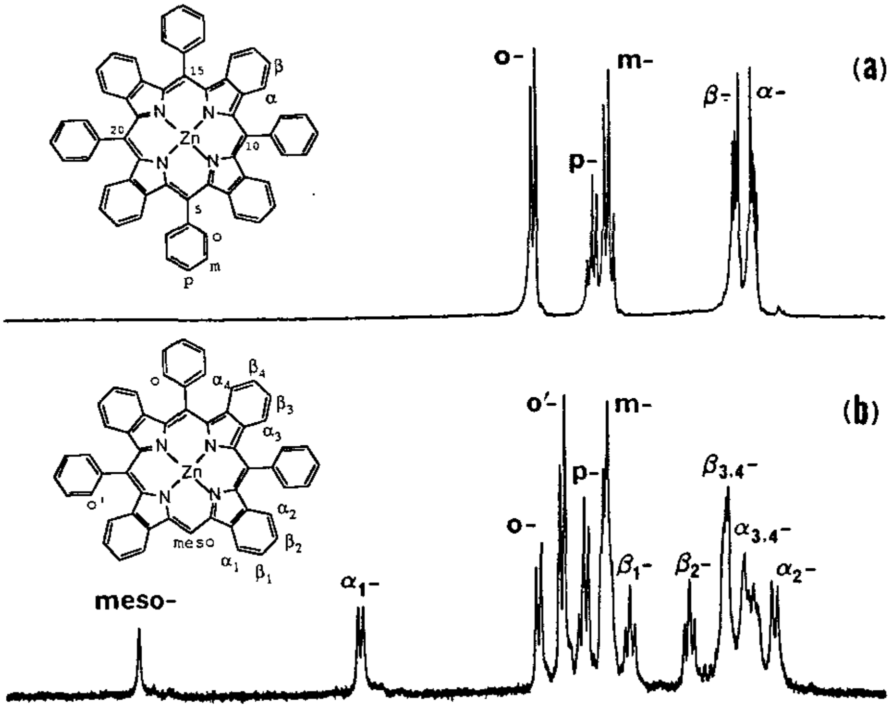

Figure 1: 300 MHz ^{1}H nmr spectra of (a) TPTBPZn, and (b) triphenyltetrabenzoporphyrin zinc complexes in CD_2Cl_2.

In order to avoid the influence of aggregation, we measured the electronic spectra of the complexes in pyridine. It is clear from the data of Table I that the magnitude of the red shift of the Soret peak increases with the number of phenyl substituent, so is the width of the absorption peaks. As can be seen from the X-ray crystallographic structure (Figure 2), the macrocycle plane of TPTBPZn is severely saddle-shaped with the β carbons of adjacent isoindole rings displaced by ~±1.7 Å relative to the plane of the four nitrogens.

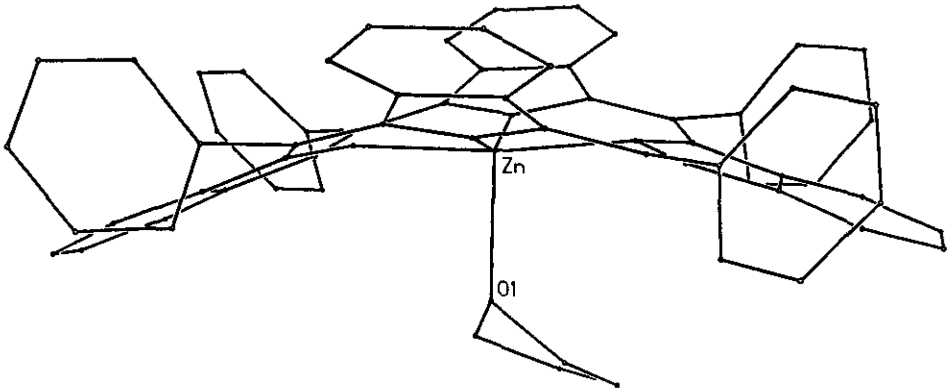

Figure 2 : Perspective view of TPTBPZn(THF) from X-ray crystal structure determination.

VT ^1H nmr studies established that the puckered conformation is retained in solution.[11] The distortion from planarity is believed to arise from the steric hindrance caused by phenyl substituents. Although the structure data of III, II, and I are presently unavailable, it is our expectation that the degree of ruffling should depend on the number of phenyl-substituent. Based on IEH MO calculations of Shelnutt for OEPNi, the primary effect of ruffling is decreasing the separation between the HOMOs and LUMOs.[12] This should account for the progressive red shifts observed in our TBP series. Furthermore, the lowering of the symmetry due to ruffling also may account for the increase of the absorption line-width. Of course, while the electronic effect of the phenyl substituents might be responsible for part of the red shifts, it should have nothing to do with the line-broadening. In addition to the characteristic red shift, this series of compounds *also show unusual emission properties* and different basicities. While TBPZn shows strong red fluorescence under long wavelength uv light, the intensity of the red emission is weakest in TPTBPZn. The fluorescence quantum yield of TPTBPZn is a factor of ~30 less than that of TBPZn in benzene. Different basicities of this series of compounds have been reflected by the conditions necessary to demetalate their zinc complexes. While TPTBPZn can be demetalate by 15% HCl, TBPZn has to be treated with conc. H_2SO_4. When comparing the pyridine affinities of the corresponding nickel complexes, a basicity sequence IV>III>II>I is obtained.

The above two synthetic routes gave quite different product distributions. Based on hplc, the yields for method 1 were of the order *IV>III>II>I*, and for method 2, *II>III>I, with almost no product IV detected.*[8a] Except for the *meso* mono-, di-, and tetraphenyl substituted etioporphyrins,[13] we have the first well characterized porphyrin system containing a complete series of 1~4 *meso*-phenyls. The modulation of porphyrin conformation by controlling *meso*-phenyl substituents should prove useful in studying porphyrin properties. As noted previously by Fajer "conformational variations provide an attractive mechanism for fine-tuning the redox, optical, and charge transfer properties of the chromophores in vitro and in vivo."[14] Recent publicatons of Smith further confirm the effect of non-planarity on the light absorption properties.[15]

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