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TETRACYCLOALKENYL-MESO-TETRAPHENYLPORPHYRINS AS MODELS FOR THE EFFECT OF NON-PLANARITY ON THE LIGHT ABSORPTION PROPERTIES OF PHOTOSYNTHETIC CHROMOPHORES

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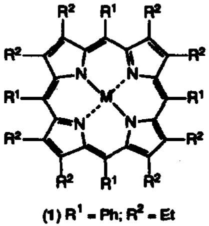
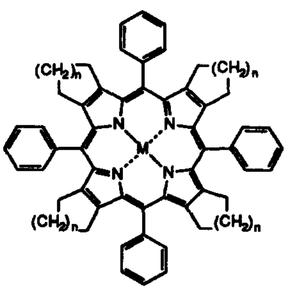
Abstract: *As the size of the cycloalkenyl ring in synthetic C_5-C_7 tetracycloalkenyl-meso-tetraphenylporphyrins (TC_nTPP) is increased the porphyrin core changes from planar to non-planar, showing that porphyrins with well-defined degrees of ruffling can be synthesized for use in systematic studies to determine the effects of non-planarity.*

Non-planar porphyrin molecules are currently a source of considerable interest, as it has been suggested that non-planar conformational distortions may serve to modify the optical and redox properties of photosynthetic chromophores.[1,2] Theoretical calculations on the effects of non-planarity indicate that the highest occupied molecular orbital should be destabilized with respect to the lowest unoccupied molecular orbital, resulting in a red shift of the first visible absorption band.[2] For zinc 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin (ZnOETPP) [(1) M=Zn], which is known from X-ray diffraction data to adopt a very non-planar saddle conformation, the first visible absorption band is red-shifted (637 nm) when compared to ZnTPP [(2) M=Zn] (586 nm) and ZnOEP [(3) M=Zn] (569nm).[2] Resonance Raman spectra of NiOEP [(3) M=Ni] in dichloromethane solution also show an enhanced contribution from Soret band of the ruffled form at 406.7 nm, compared with an absorption maximum for the planar form, in solution, of 393 nm.[3] Clearly, a series of porphyrins possessing varying degrees of ruffling, but little other perturbation of the macrocycle, would be most useful in a detailed study of the effects of non-planarity on light absorption, redox, and other properties of the porphyrin macrocycle. We now describe the synthesis and spectroscopic characteristics of a series of compounds with these properties.



(1) R^1 = Ph; R^2 = Et
(2) R^1 = Ph; R^2 = H
(3) R^1 = H; R^2 = Et



(4) n = 1-3

The non-planar conformation of OETPP results from the considerable steric repulsion that exists between the ethyl and phenyl groups. This suggested that the macrocyclic non-planarity could be modified by replacing the alkyl chains with a cycloalkenyl ring (4). We therefore proceeded to synthesize porphyrins with C_5-C_7 rings starting from the corresponding 1-nitrocyloalkenes. These were prepared in 60-73% yield using the nitroselenylation reaction of Tomoda et al.,[4] except for 1-nitrocyclohexene which was obtained commercially. Reaction with ethylisocyanoacetate using the procedure of Barton and Zard[5] gave the 2-ethoxycarbonyl-3,4-cycloalkenylpyrrole in 45-80% yield, with hydrolysis and steam distillation then giving the α-free pyrrole in 43-76% yield. Subsequent condensation with benzaldehyde in the presence of a $BF_3.OEt_2$ catalyst and oxidation with DDQ or chloranil, according to the procedure of Lindsey,[6] gave the porphyrins in 12-61% yield (unoptimized). The porphyrins were purified by column chromatography using a Brockmann Grade III neutral alumina column with 2% methanol in dichloromethane as eluent, followed by recrystallisation from alcoholic KOH solution. The free base porphyrins and nickel complexes were soluble in dichloromethane, except for $NiTC_5TPP$ which was completely insoluble in all the solvents tried, and H_2TC_5TPP, which was only sparingly soluble and formed a mixture of the free base and dication. The dications were soluble in a range of organic solvents.

Molecular mechanics calculations[7] (Figure 1) and preliminary crystal structures[8] support the suggestion that these porphyrins have different degrees of non-planarity. The porphyrin core of $NiTC_5TPP$ [(4), n = 1] is calculated to be essentially planar, whereas $NiTC_6TPP$ [(4) n =2] and $NiTC_7TPP$ [(4) n = 3] are calculated to adopt non-planar saddle conformations. The RMS displacement of the core atoms (C_α, C_β, C_{meso} and N) of $NiTC_7TPP$ is 0.66 Å with respect to $NiTC_5TPP$. $NiTC_6TPP$ is of intermediate non-planarity, with a RMS displacement of 0.57 Å, and NiOETPP is the most non-planar, with a RMS displacement of 0.77 Å.The non-planar saddle conformation obtained from these calculations is also observed in preliminary x-ray structures of NiOETPP and $NiTC_6TPP$.[8]

Visible absorption spectra of the newly prepared porphyrins are also in agreement with the suggestion that increasing the ring size makes the porphyrin less planar. The first visible absorption band for H_2TC_5TPP is obscured by signals from the dication (see note above) but H_2TC_6TPP (678 nm) and H_2TC_7TPP (704 nm) are red-shifted compared to H_2TPP (650 nm). The first visible absorption band of H_2TC_7TPP is in a very similar position to that of H_2OETPP (702 nm). A similar trend is observed for the visible spectra of the dications (Figure 2), from which it is clear that both the first absorption and the Soret band are red-shifted. The visible absorption spectra of the nickel complexes show smaller red-shifts and appear much less sensitive to planarity.


(4) n=1 (4) n=2 (4) n=3 (1)

Figure 1: Energy minimized structures for $NiTC_5TPP$, $NiTC_6TPP$, $NiTC_7TPP$ and NiOETPP.

We have also used Raman techniques to study the nickel complexes of these porphyrins and other planar model compounds. A detailed comparison of the position of structure-sensitive Raman lines with structures obtained from molecular mechanics and X-ray diffraction studies is currently in progress. However, provisional assignments of the Raman spectra appear to show a correlation between the location of high-frequency structural marker lines and non-planarity of the porphyrin macrocycle. For example, v2 for NiOEP, $NiTC_5TPP$, $NiTC_6TPP$, $NiTC_7TPP$ and NiOETPP in CS_2 solution is 1603, 1594 (solid), 1577, 1564 and 1562 cm^{-1}, respectively.

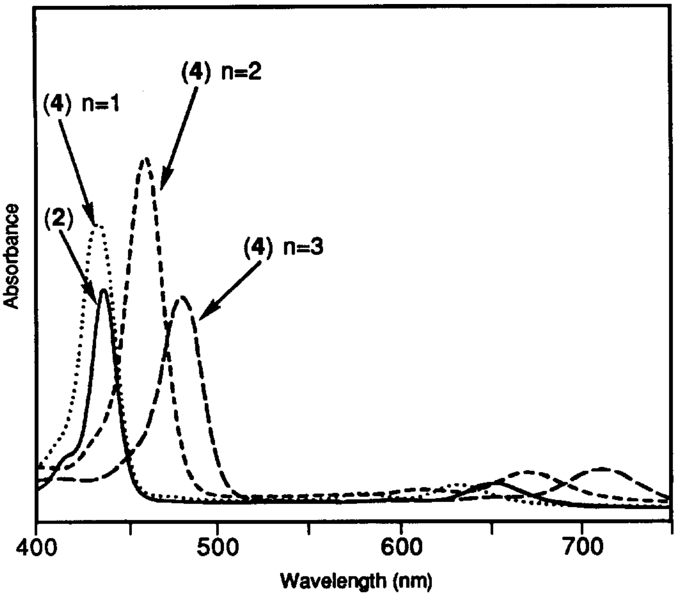


Figure 2: Visible absorption spectra of TC_nTPP dications in CH_2Cl_2.

The very different steric repulsion present in these porphyrins can also be studied by dynamic NMR spectroscopy, as the porphyrin macrocycle undergoes an unusual inversion process. This process is not entirely without precedent. Maruyama and co-workers have observed 'flipping' of 5,15-dialkyl-3,7,13,17-tetraethyl-2,8,12,18-tetramethylporphyrins,[9] which was explained in terms of a syn/anti equilibrium of the 5,15-alkyl groups. We have also reported an inversion process for several OETPP complexes.[10] The dynamic process for OETPP and the tetracycloalkenyl-meso-tetraphenylporphyrins can be explained by reference to the calculated structures of the non-planar porphyrins shown in Figure 1, which show a saddle conformation similar to the crystal structures of several OETPP complexes.[10] A preliminary crystal structure of $NiTC_6TPP$ shows a similar saddle conformation.[8]

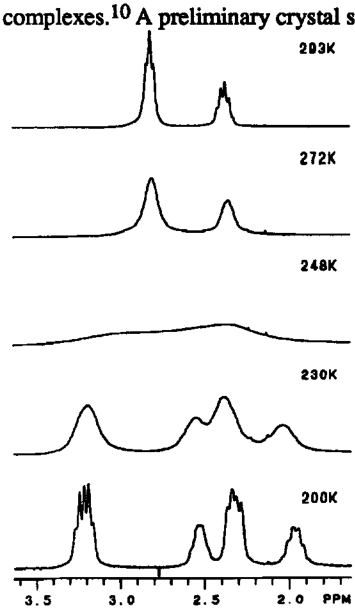


Figure 3: 300 MHz ^1H NMR spectrum of TC_5TPP dication as a function of temp.

We propose that the porphyrin inversion process involves the pyrrole rings flipping to point to the opposite face of the porphyrin, thereby exchanging the chemical shift environments of the methylene protons. When inversion is slow on the NMR time-scale, the NMR spectrum is that expected for a single conformation. When ring inversion is fast the methylene protons yield only average chemical shifts. This is illustrated in Figure 3, which shows the proton NMR spectrum of $H_4TC_5TPP^{2+}$ as a function of temperature. Intriguingly, the dication must be somewhat non-planar to show the methylene protons as being diastereotopic. X-ray structure determinations of the free base and dication are currently in progress and will reveal to what extent protonation alters the porphyrin planarity. The crystal structure of H_4TPP^{2+} shows that protonation causes considerable ruffling of the macrocycle.[11]

This process is likely to be very sensitive to the degree of steric interaction between the peripheral substituents and thereby provide an indirect measurement of the degree of non-planarity, i.e. a more non-planar conformation should be accompanied by an increase in the free energy of activation (ΔG^*) if entropy considerations are neglected. Using a standard equation[12] we have calculated ΔG^* at coalesence. The results (Table 1) show that there is indeed a substantial increase in ΔG^* as the cycloalkenyl ring becomes larger. However, it is interesting to note that steric strain is not the only factor contributing to the free energy of activation. ΔG^* for the porphyrin dications is much larger than for the free-base porphyrins, presumably because of an additional energy requirement to overcome repulsion of the protonated nitrogen atoms. Conversely, the nickel porphyrins have a lower activation barrier than the free-base porphyrins. This difference may arise from a need to overcome repulsion between the NH protons during the inversion process.

Table 1: ΔG* ($kcalmol^{-1}$) for porphyrin inversion.

	TC_5TPP	TC_6TPP	TC_7TPP	OETPP
[Ni-Por]	Poor solubility	<8.5	11.6	13.2
[H_2-Por]	Poor solubility	8.5	16.0	18.1
[H_4-Por]$^{2+}$	11.5	>20	>20	>20

We are currently investigating these novel porphyrins in more detail, including X-ray diffraction, fluorescence and electrochemical studies, and these will be reported in due course.

Acknowledgements.

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