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THE PROTONATION OF CHLORINS (DIHYDROPORPHYRINS)

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Abstract: Octaethylchlorin forms a violet mono-cation and a deep blue di-cation in two discrete stages on spectrophotometric titration with trifluoroacetic acid in chloroform solution, and similar results are obtained with chlorophyll derivatives although the colour changes are much less pronounced.

Both porphyrins and chlorins form di-cationic salts on treatment with strong acids, but the intermediate mono-cationic salts are less well known. Porphyrin mono-cations can only be observed under special conditions[1] (e.g. with glacial acetic acid in acetone, or toluene), and titrations with strong acids afford the di-cation directly. With chlorins, however, the situation is not so clearly defined and the nature of the solvent, as well as the acid and its concentration may determine whether or not the mono-cation and/or di-cation is observed. Thus Delaporte and Leval-Martin[2] reported that phaeophytin-a (1a) forms a mono-cation in acetone/perchloric acid whereas Zanke *et al.*[3] found evidence for formation of both a mono- and a di-cation in aqueous acetone/hydrochloric acid titrations. Katz[4] on the other hand concluded on the basis of visible and n.m.r. spectroscopic titrations that phaeophytin-a (1a) was converted directly to the di-cation with trifluoroacetic acid in carbon tetrachloride. In earlier work, however, Dempsey[5] has described the formation of mono- and di-cationic species of methylphaeophorbide-a (1b) by spectroscopic titrations in aqueous detergent solution.

We find that the much simpler model system, *trans*-octaethylchlorin (2) forms a violet mono-cation in weakly acidic media (e.g. acetic acid) and a deep blue di-cation in strong acids. Spectrophotometric titration of *trans*-octaethylchlorin (2) with trifluoroacetic acid in chloroform affords firstly the mono-cation, and then the di-cation in two discrete stages (Figure). Two isosbestic points (at 390 and 631 nm) are observed in the formation of the mono-cation and the Soret band splits into two peaks, but as the di-cation is formed the Soret band reverts to a single peak and two more isosbestic points are observed (at 398 and 625 nm).

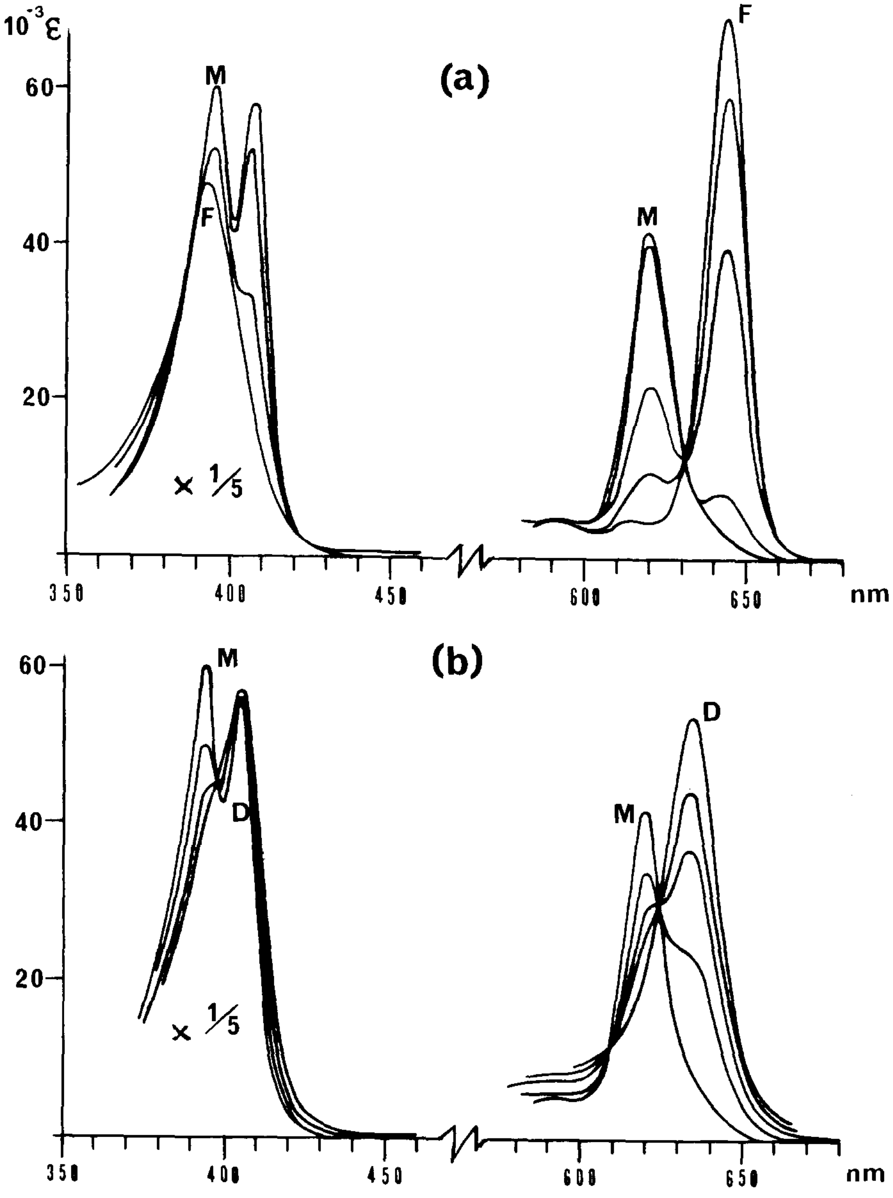
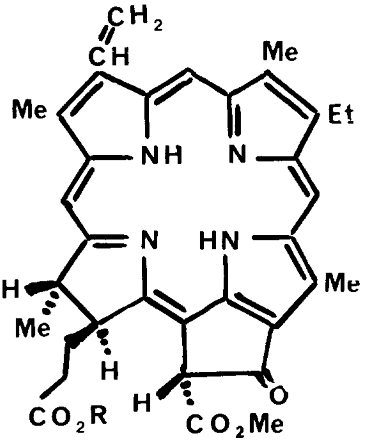


Figure:

Spectrophotometric Titration of trans-Octaethylchlorin (2) in chloroform solution with trifluoroacetic acid

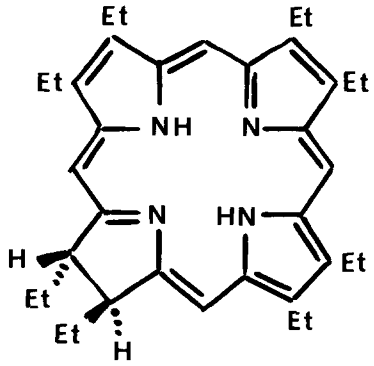
a) Free base (F) to Mono-cation (M)

b) Mono-cation (M) to Di-cation (D)



(1) a) R=Phytyl

b) R=Me



(2)

Similar studies were carried out with methyl phaeophorbide-a (1b) and a number of other chlorins related to chlorophyll, and these also showed stepwise formation of mono- and di-cationic species, although the colour changes observed by eye were much less striking than those with octaethylchlorin. For example, titration of methyl phaeophorbide-a (1b) in chloroform with trifluoroacetic acid afforded firstly a pale green mono-cation and then a deep green di-cation, clear isosbestic points being observed at each stage; the main visible absorption peak shifted from 668 to 652 in the mono-cation and then to 658 in the di-cation, and the positions of these absorptions were very similar to those originally reported by Dempsey[5] for aqueous detergent solutions (673, 656 and 666 nm). The longer wavelength shifts of methyl phaeophorbide-a, compared with octaethylchlorin (646 to 621 in the mono-cation and then to 634 nm in the di-cation), are attributed to the C-ring carbonyl group and the steric effects of the isocyclic ring. It is interesting to note, however, that the violet mono-fluorosulphonate of N-methyloctaethylchlorin has a very similar spectrum[6] ($\lambda_{\text{max.}}$ 399, 415 and 628 nm) to that of the mono-cation of octaethylchlorin ($\lambda_{\text{max.}}$ 396, 408 and 621 nm) although shifted slightly to longer wavelength.

The results obtained with trans-octaethylchlorin (2), and the chlorophyll derivatives were very reminiscent of the behaviour of N-methyloctaethylporphyrin on titration with acid.[7] This led us to the conclusion that like N-methylporphyrins[8] the pKa's of octaethylchlorin are very different from each other, in contrast to N-unsubstituted porphyrins in which the two pKa's are only three units apart (see Table).

TABLE

pKa Values for Porphyrins and Chlorins

	Apparent pKa values determined by TFA titrations in $CHCl_3$		pKa's of N-methyl-Coproporphyrin-I in aqueous solution[8]	pKa's of Coproporphyrin-I in aqueous solution[8]
	Octaethyl chlorin	N-methyl octa-ethylporphyrin		
pK_{a_1}	4.8	6.5	11.7	7.1
pK_{a_2}	2.9	2.6	0.5	4.0

We have estimated apparent pKa values for *trans*-octaethylchlorin and N-methyloctaethylporphyrin by applying the Benesi-Hildebrandt treatment[8] to our spectroscopic titrations with trifluoroacetic acid in chloroform, and these are compared with the data for N-methylcoproporphyrin-I obtained in aqueous solution by Neuberger and Scott.[9] (See Table.) The apparent first pKa of octaethylchlorin is somewhat lower than that of N-methyloctaethyl porphyrin, but the apparent second pKa's of both compounds are closely similar. We thus conclude that *trans*-octaethylchlorin is much more like N-methyloctaethyl porphyrin than octaethyl porphyrin in its behaviour on protonation.

The discrete formation of mono- and di-cationic species has also been observed in n.m.r. spectral titrations, thus confirming the visible spectral results. Work is now in progress on a more detailed study of the chlorins derived from the chlorophylls in order to assess the effects of the isocyclic ring on their spectra and basicity.

Acknowledgements:

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