

Synthesis and Chromophoric Interactions of an 'ortho-Gable-porphyrin.' A Novel Tetraphenylporphyrin Dimer

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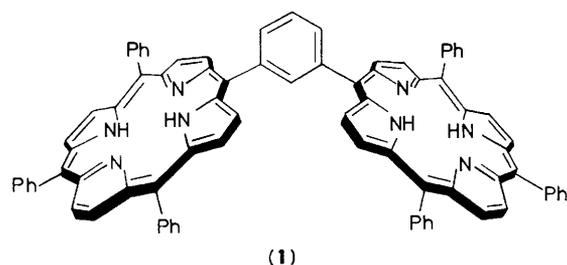
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A newly synthesized 'ortho-gable-porphyrin,' a tetraphenylporphyrin-type dimer with an *ortho*-phenylene bridge, provided a model for closer porphyrin-porphyrin separation.

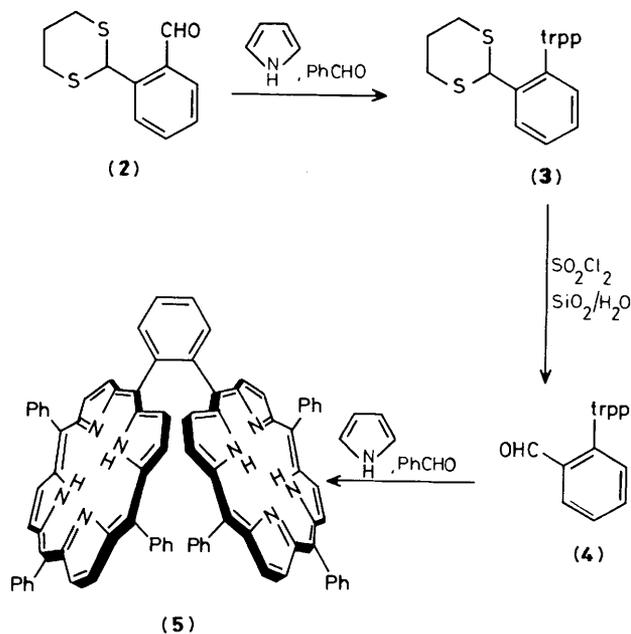
Porphyrin dimers, with their chromophores linked by short chains or rigid spacers to ensure well defined interchromophoric distance and orientation, have been used extensively in biomimetic studies of (light induced) electron transfer and singlet- or triplet-energy transfer.¹ In the recent structural elucidation of the bacterial photosynthetic reaction centre, the critical spacial arrangements of porphyrins have been invoked for with regard to biological functions.² Also, some porphyrin dimers have shown specific activities as catalysts, *e.g.*, for the four-electron reduction of oxygen to water.³

A 'Gable-porphyrin' (1) of a dimeric tetraphenylporphyrin (tpp) type and its metal complexes were introduced first by Tabushi as a local model for the low potential tetra-heme cytochrome *c*₃ and as a model for haemoglobin-type allosterism.⁴ To investigate the effect of closer interchromophoric separation with a smaller dihedral angle between the two chromophores,^{1f,g} we have now synthesised the dimeric porphyrin (5) in which two TPP-units are connected through an *ortho* rather than a *meta* disposition in the central benzene ring. Strong chromophoric interactions, based on the decreased dihedral angle as well as a closer separation between chromophores, have been observed.

The synthesis route is summarized in Scheme 1. Dithianyl-protected *o*-phthalaldehyde (2), obtained from *o*-phthalaldehyde and propane-1,3-dithiol in 57% yield, was cyclised with benzaldehyde and pyrrole following the procedure recently introduced by Lindsey⁵ to give a 16% yield of *o*-dithianyl-tpp (3) via the corresponding porphyrinogen.



Soret band appeared at 423 nm, with *Q* and *R* bands at 516, 550 and 593, 651 nm, respectively; these were almost the same as those of tpp (*cf.* Table 1). An oxidative/hydrolytic cleavage of the dithianyl protecting group⁶ afforded in a 65% yield *o*-formyl-TPP (4), which was subjected again to a second Lindsey-type tpp-ring construction. We assume that, as with other *ortho*-disubstituted tpp derivatives,⁵ the achievement of an equilibrium between open chain precursors and the porphyrinogen, offsets a kinetic effect of steric encumbrance in the attack of pyrrole on aldehyde (4), and is essential for the successful synthesis of (5) (which could be isolated in 11% yield). The biszinc complex, Zn₂-(5), was prepared using the standard procedure in a 70% yield after chromatographic separation.



Scheme 1. trpp = *meso*-triphenylporphyrinyl.

Table 1. Absorption and fluorescence spectra of free and Zn complexes of *ortho*-Gable-, Gable-porphyrins, and tpp.^a

Compound	Absorption, λ /nm			Fluorescence		
	Soret	<i>Q</i>	<i>R</i>	$\lambda_{\max Q}$ (0,0)/nm	$\lambda_{\max Q}$ (0,1)/nm	ϕ_{rel}^d
H ₂ tpp	419	515, 548	592, 647	653	717	0.11
H ₄ -Gable, (1)	416, 428	515, 552	592, 648 ^{b,4d}	654	717	0.13
Zn ₁ -Gable, Zn-(1)	415, 429	515, 551	593, 647 ^{b,4d}	653	716	0.13
H ₄ - <i>o</i> -Gable, (5)	410	524, 556	600, 657	668	728	0.07
Zn(tpp)	425	539, 578		599	647	0.03
Zn ₂ -Gable, Zn ₂ -(1)	416, 431	552, 594 ^{b,4d}		597	648	0.03
Zn ₂ - <i>o</i> -Gable, Zn ₂ -(5)	413	(546)559(570)(605) ^c		615	665	0.015

^a In air-saturated benzene. ^b In CHCl₃. ^c Values in parentheses mean shoulders not clearly separated. ^d Irradiation at 550 nm in solutions with absorbance *ca.* 0.02.

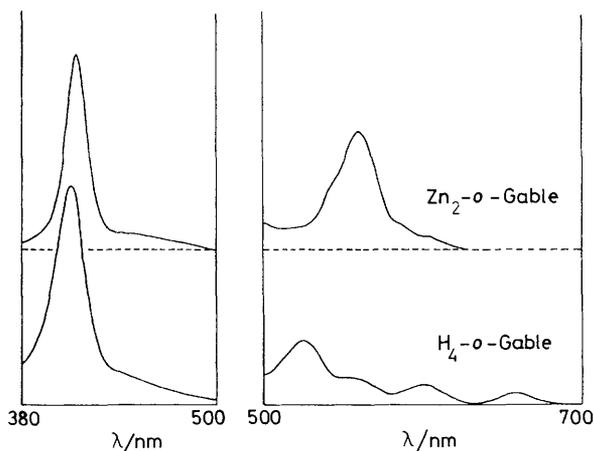


Figure 1. Absorption spectra for (5) and Zn_2 -(5) in benzene.

The Soret-bands in the absorption spectra of (5) and Zn_2 -(5) (Figure 1, Table 1) are significantly blue-shifted by 9 and 12 nm, respectively, compared to those observed for monomeric tpp and Zn(tpp). No splitting was observable for the Soret bands, in sharp contrast to the symmetric splitting pattern observed for (1) and Zn_2 -(1) (dihedral angle of 120°).⁴ The characteristic feature observed here, *i.e.*, a significant blue-shift without an appreciable splitting, is expected for two parallel-interacting chromophores in Kasha's exciton coupling theory⁷ and observed for face-to-face porphyrins linked with two amide bonds,^{3a} or recently reported dimeric porphyrins bridged with a 1,8-anthracene or 1,8-biphenylene bridge,^{1g} both of which have a dihedral angle of 0° . Compared with hitherto known porphyrins with the same dihedral angle of 60° , the magnitude of the blue-shift manifested by (1) was the largest (the centre-to-centre separation of 6.4 Å was estimated from a Corey-Pauling-Koltun model). The magnitude of the shift apparently depends on the centre-to-centre separation, since the biszinc complex of naphthalene-1,7-diyl^{1g} and free base of 1,10-phenanthroline-phenyl bridged^{1f} dimeric porphyrins are blue-shifted by 5 and *ca.* 0 nm at 10 and 13 Å separations, respectively. The visible bands on the other hand are red-shifted by 8–10 nm for (5) compared to tpp. This behaviour has also been noticed in the face-to-face porphyrins.^{3a} The splitting pattern of these visible bands in the case of metal complexes showed an interesting dependence on the nature of the central metal.

The fluorescence spectra of (5) and Zn_2 -(5) show characteristic red-shifts, for all bands, by 11–18 nm. In contrast to

the findings for (1) and Zn_2 -(1), the fluorescence quantum yields for (5) and Zn_2 -(5) appear somewhat quenched. This observation is compatible with the expectation that stronger interaction occurs for dimeric porphyrins with a decreased dihedral angle. Further discussions await measurements of the lifetime of excited species of these fixed geometry, dimeric porphyrins.

All these spectroscopic data for (5) and its biszinc complex, Zn_2 -(5), are indicative of considerable geometry-dependent porphyrin-porphyrin interactions. Comparative studies with free and metal complexes of (5) and other isomeric porphyrin derivatives are expected to provide interesting information on energy and electron transfer, and on the activation of small molecules, *e.g.*, for multi-electron redox reactions.

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