

## Four Orbital Predictions in some Potential Porphin Model Compounds

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**Summary** A comparison is made between the predictions of the four SCF orbital model for porphin and the analogous predictions for a number of conjugated macrocyclic ligands having apparent potential as model compounds for porphin.

THERE is much current activity directed towards the synthesis of conjugated macrocyclic ligands.<sup>1,2,3</sup> The apparent similarity between the electronic spectra of some of these systems and the electronic spectra of  $D_{2h}$  or  $D_{4h}$  porphin has been noted.<sup>1,4</sup>

weak allowed transitions in the visible region and two intense bands in the near u.v.<sup>5,6</sup> All four orbital-orbital transitions are thus electric dipole allowed and the predicted alternating polarisation of the bands has been shown to be correct using MORD<sup>6</sup> and single crystal data.<sup>7</sup>

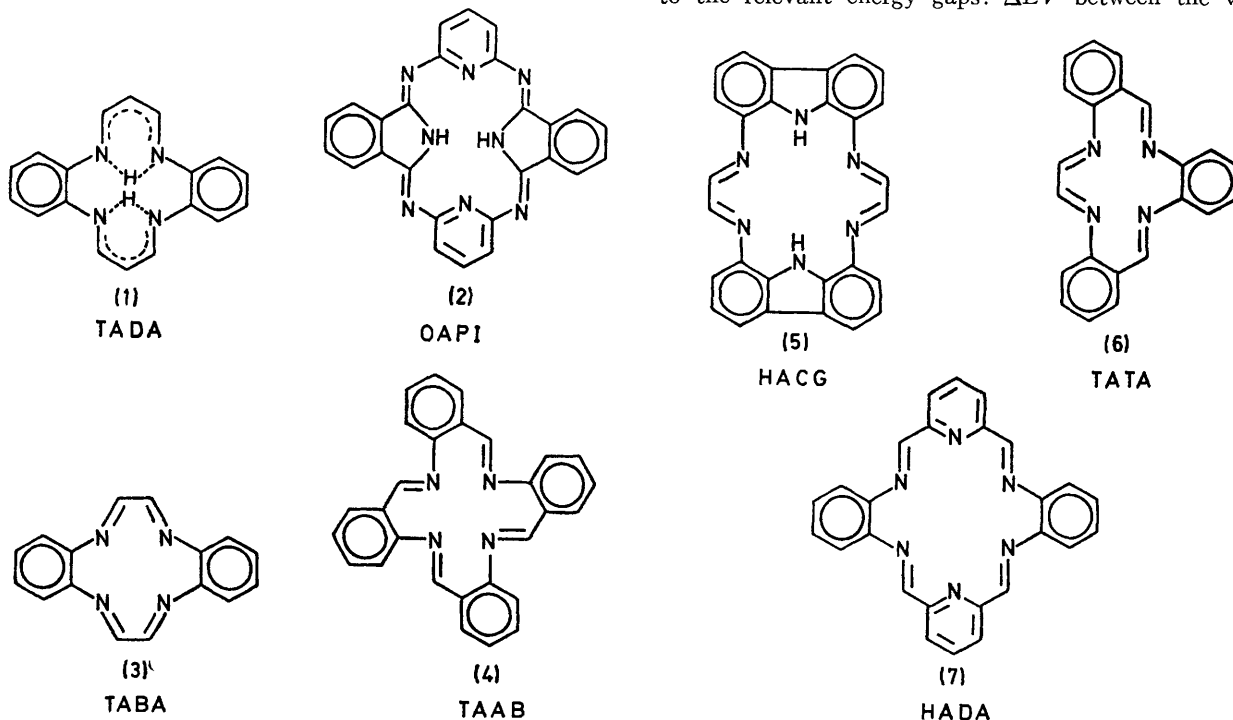
As a preliminary theoretical test of the proposed<sup>1,4</sup> or implied analogy<sup>4,8</sup> between the conjugated ligands shown (1)–(7) and porphin, we have compared the four orbital porphin predictions with those for the macrocycles. In one case, the Busch macrocycle TAAB,<sup>1</sup> we use the  $D_{4h}$  porphin dianion for this comparison. We consider that a

### Four-orbital predictions of SCFMO calculations

Macrocyclic	$\Delta EV$	$\Delta ET$	$\Delta EF$	Transitions allowed	Alternating polarisation
$D_{2h}$ free-base porphin	0.101	4.478	0.584	all four	Yes
OAPI <sup>4</sup>	0.060	4.902	1.019	only two	Yes
TADA <sup>10</sup>	0.720	5.12	1.160	only two	No
HACG <sup>9</sup>	0.063	5.409	0.444	only two	No
TATA	0.660	5.392	0.442	all four	Yes
HADA	0.067	5.853	0.390	only two	No
TABA	0.149	5.267	1.035	only two	No

The four SCF orbital model for free base porphin attempts, with some success, to interpret the electronic spectrum by

successful model will have an orbital energy distribution similar to that of porphin and have therefore paid attention to the relevant energy gaps:  $\Delta EV$  between the virtual



using the lowest ( $b_{3g}$ ) and next lowest ( $b_{2g}$ ) virtual orbitals and the highest ( $b_{1u}$ ) and next highest ( $a_u$ ) filled orbitals.<sup>5</sup> This model is successful to the extent that it predicts two

orbitals,  $\Delta EF$  between the filled orbitals and  $\Delta ET$ , the lowest energy orbital-orbital transition. In addition, the symmetries of the orbitals should afford both four allowed

transitions and alternating polarisation of consecutive bands.<sup>5</sup>

The outcome of this preliminary investigation is summarised in the Table. Only one molecule, TATA, as a result of having  $C_{2v}$  instead of  $D_{2h}$  symmetry meets the 'allowedness' and perpendicular polarisation criteria. However, as TATA does not have replaceable NH protons, a successful chemical analogy with porphin seems unlikely. The "best fit" is given by either the OAPI macrocycle synthesised by Elvidge and Linstead<sup>4</sup> or the interesting  $D_{6h}$  co-ordination hole macrocycle, HACG, currently being investigated by Davis.<sup>9</sup> The latter compound does have two replaceable NH protons, unlike the otherwise similar macrocycle, HADA.

The Busch macrocycle TAAB<sup>1</sup> is unique in this discussion because the next highest filled and the next lowest virtual orbitals are, separately, members of degenerate pairs. The energies, in eV are  $-2.25$ ,  $-2.25$ ,  $-3.122$ ;  $-8.594$ ,  $-9.358$ ,  $-9.358$ . These are to be contrasted with the porphin dianion energies  $+0.133$ ,  $-1.864$ ,  $-3.480$ ,  $-3.480$ ;  $-8.052$ ,  $-8.550$ ,  $-10.516$ ,  $-10.516$ . Transitions between the two non-degenerate orbitals, or between the two sets of doubly

degenerate orbitals are totally forbidden in TAAB. These facts suggest that the detailed nature of the electronic spectrum of TAAB is different from that of porphin, despite the apparent similarity.<sup>1</sup>

An early outcome of more detailed investigations on all these macrocycles is that extension to only a six orbital, nine transition model frequently gives not only improved agreement with experimental band energies, but also alternating polarisation to the intense near u.v.-violet bands which are common to all the calculated and available experimental spectra.<sup>1,4,10</sup> The introduction of extensive singlet single excitation configuration interaction brings about further, but relatively slight improvement.

Full details of the SCF  $\pi$ -electron method may be found elsewhere.<sup>11</sup> Our choice of parameters was based upon those of Nishimoto *et al.*,<sup>12</sup> where appropriate, the average of azomethine and amine values was employed.

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