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A STUDY OF PORPHIN ANALOGUES—I

THE CALCULATED ELECTRONIC SPECTRA OF SOME DERIVATIVES OF [14]ANNULENE

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Abstract The suitability of the 14 atom conjugated perimeter and some of its benzo- and aza-substituted derivatives as potential porphin analogues is assessed by comparing the results of π-electron calculations on the proposed analogue with those on porphin. The calculations are of SCF PPP type, into which very extensive single excitation configuration interaction has been introduced to generate states of π-symmetry.

Attention is drawn to the failure of the "four-orbital-model", and to the comparative success of a ten orbital, twenty five transition model, in correlating with the experimental spectrum of 2,3;9,10-dibenzo-1,4,8,11-tetra-aza[14]annulene (TADA). The calculations predict a buckled carbon framework for TADA.

INTRODUCTION

ANALOGIES have recently been drawn between the electronic spectra of certain macrocyclic ligands and the electronic spectrum of porphin.[1,2] Chemical analogies have been proved in some cases,[3] and hazarded in others.[4]

In these laboratories we are synthesizing a wide range of conjugated macrocycles and their iron, manganese and cobalt complexes. We are investigating the spectroscopy, photochemistry and magnetochemistry of these compounds in order to determine whether one or more of them could serve as a porphin, or metalloporphin analogue. Promising systems will be subjected to stringent enzymatic tests[5] which, if positive, would be of great biochemical significance.

As an aid to the comparison between porphin and the various macrocycles,[2] we have obtained the SCF π-electrons only orbitals and energies. Ideally, the predicted electronic spectrum of a porphin analogue should consist of two well separated weak (allowed) bands in the visible region and two juxtaposed bands, of high intensity, in the violet or near UV region; the four bands should have alternating polarity. Such a spectrum will be termed "porphin-like". We do not demand vibronic splitting, as observed in free-base porphin,[6] as a necessary criterion for a porphin analogue. The question of band polarization can only be determined experimentally by specialized solid-state techniques,[6] and in the light of the correlation of the π-electron SCF results with experiment,[6] we rely on the predictions based on the symmetry of the SCF π-electron eigenvectors.[7]

Fortuitously, the deductions based on the four-orbital predictions for porphin[2] are not proved groundless once configuration interaction between states of the same symmetry is introduced. Usually, little credence can be attached to deductions based on transitions between occupied and virtual orbitals. For this reason, despite the unfavourable four-orbital predictions obtained[2] for a range of conjugated macrocycles, we have examined the effect of introducing very extensive single-excitation configuration interaction. The encouraging outcome for two macrocycles is described below.

The high symmetry of porphin (dianion, D_{4h}; free-base, D_{2h}) leads to degeneracy (D_{4h}) or near degeneracy of the lowest energy pair of virtual orbitals. It thus seems logical to investigate potential porphin analogues by stepwise descent in symmetry from the idealized polygonal perimeter of dimension appropriate to the inner great ring of the macrocycles to be studied.

THEORY AND COMPUTATION

The SCF method of Parr *et al*[7] has been employed in which the molecular orbitals ψ_i are expressed, in terms of atomic 2 p_π orbitals ϕ_μ, as

$$\psi_i = \sum_{\mu} c_{i\mu}\phi_\mu \tag{2.1}$$

the coefficients being the solutions of Roothaan's equations[8]

$$\sum_{v} F_{\mu v}c_{iv} = \varepsilon_i c_{i\mu} \tag{2.2}$$

The elements of the matrix F, which is constructed iteratively during the solution of the set of secular equations

$$|F_{\mu v} - \varepsilon\delta_{\mu v}| = 0 \tag{2.3}$$

are given by

$$F_{\mu\mu} = U_{\mu\mu} + 0{\cdot}5P_{\mu\mu}\gamma_{\mu\mu} + \sum_{v \neq \mu}(P_{vv} - 1)\gamma_{\mu v} \tag{2.4}$$

$$F_{\mu v} = \beta_{\mu v} - 0{\cdot}5P_{\mu v}\gamma_{\mu v}(\mu \neq v) \tag{2.5}$$

where

$$P_{\mu v} = 2\sum_{i}^{\text{occ}} c_{i\mu}c_{iv} \tag{2.6}$$

The ε_1, the energies of the π-electron molecular orbitals, are the roots of the secular equation (2.3). Further details may be found elsewhere.[7]

Our initial choice of parameters, the **H** matrix, diagonalization of which provides the first estimate of the P_{ij}, and the **G** matrix, were based upon those of Nishimoto *et al.*[9]

In addition to the standard method (PPP) we included an option for either or both of two modifications. One of these, the VB method of Nishimoto *et al.*[10] re-estimated the H_{ij} (or β_{ij}) elements for bonded atoms at each iteration using

$$\beta_{ij}^{cc} = -(0{\cdot}51\ P_{ij} + 2{\cdot}04)\ \text{eV} \tag{2.7}$$

and

$$\beta_{ij}^{cn} = -(0{\cdot}53\ P_{ij} + 2{\cdot}24)\ \text{eV} \tag{2.8}$$

Our second modification (VG) re-evaluates the G_{ij} for bonded atoms at each iteration using

$$G_{ij} = 14{\cdot}397/(A_{ij} + R_{ij})\ \text{eV} \tag{2.9}$$

where

$$A_{ij} = 28{\cdot}794/(G_{ii} + G_{jj})\ \text{eV} \tag{2.10}$$

and

$$R_{ij}^{cc} = 1{\cdot}517 - 0{\cdot}18\,P_{ij}(\text{Å}) \qquad (2.11)$$

$$R_{ij}^{cn} = 1{\cdot}451 - 0{\cdot}18\,P_{ij}(\text{Å}) \qquad (2.12)$$

The four SCF methods employed herein are therefore PPP, VB, VG and VB + VG.

The programme, SCFSING, assigns H matrix data from a parameter list, using atomic numbers and number of π-electrons per atom. The G_{ij} matrix elements are similarly assigned and the G_{ij} calculated from these and the atomic co-ordinates using equations (2.9) and (2.10).

The iteration criterion is based on the difference between consecutive estimates of E where $E = 2\sum_{i}^{\text{occ}} \varepsilon_i$. Once this difference drops below 0·00001 eV, iteration ceases. At this point eigenvalues, eigenvectors, charge densities and bond lengths are printed out.

The 3321 matrix elements of the symmetrical 81 × 81 CI matrix,[11] and the transition moments of 81 transitions are then evaluated and read out on to magnetic tape for use by CIPROG which provides state energies, state composition, transition moments and oscillator strengths. SCFSING also automatically performs a 25 × 25 CI (10 orbitals) for both singlet and triplet single excitation states.

THE FOURTEEN ATOM CONJUGATED PERIMETER

The symmetry aspects of the idealized regular polygonal polyenes $C_{4n+2}H_{4n+2}$ have been thoroughly described elsewhere.[12] The highest filled molecular orbital of [14]annulene is of e_{3g} symmetry and the lowest empty virtual orbital is of e_{4u} symmetry within the D_{14h} point group. Promotion of one electron from the former to the latter, a process analogous to one electron excitation within the four orbital model of porphin,[13] will generate singlet (and triplet) states of B_{1u}, B_{2u} and E_{1u} symmetry. The only electric dipole allowed (*xy* polarized) transition is to the last of these, ${}^1A_{1g} \rightarrow {}^1E_{1u}$. Our complete single excitation configuration interaction calculations, using the parameters of Nishimoto *et al.*[9] (recommended by Cizek and Paldus[14] for singlet stable Hartree Fock solutions) and the variable beta procedure,[10] give states at 631 nm (${}^1B_{2u}$), 454 nm (${}^1B_{1u}$) and 290 (${}^1E_{1u}$). The oscillator strength of the transition to the last of these, using the dipole length operator[13] is 3·70. Using rather different repulsion integrals, Heilbronner *et al.*[15] obtained states, using limited configuration interaction, at 571 nm, 464 nm and 369 nm.

If the symmetry is reduced to D_{2h}, then a realistic comparison with experiment can be made, namely, with the electronic spectrum of 15,16-dimethyl-dihydro-pyrene.[15] The data presented in Table 1 indicates that although the general pattern is reproduced theoretically, the calculated oscillator strengths of the two visible bands are particularly unsatisfactory, a situation also encountered in the study of porphin.[13]

In Table 2 we report the results of SCF π-electron calculations on 1,4,8,11-tetraaza[14]annulene (TAA) and two forms (Fig. 1) of the 1,8-dihydro derivative (2H-TAA), using a six orbital, nine transition model with singlet configuration interaction. The introduction of two secondary amine nitrogens is necessary in order to gain chemical similarity with porphin. In so doing, the promising agreement between the calculated spectra of TAA and porphin is considerably reduced. In 2H-TAA we are dealing with a 16 π-electron system, instead of the 14 π-electrons of TAA; the resulting

Table 1. Calculated and experimental bands in the electronic spectrum of the D_{2h} conjugated 14-atom hydrocarbon perimeter

This work	Other workers[15]	Exp[15]
584(0)	634(0)	653(2·5)
445(0·002)	549(·003)	477(3·7)
312(1·732)	297(1·82)	388(4·5)
293(3·287)	261(3·68)	344(4·8)

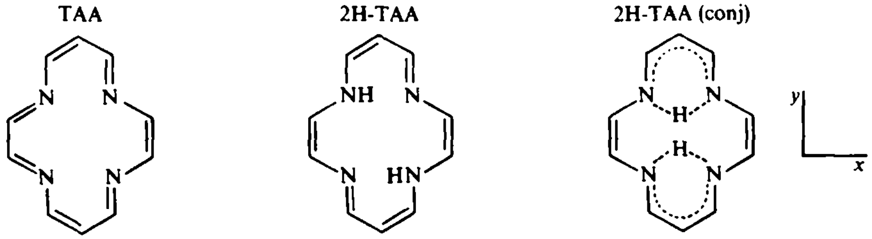

Fig 1. 1,4,8,11-Tetraaza[14]annulene and its 1,8-dihydro derivative.

Table 2. Calculated band energies (nm) and dipole length oscillator strengths of some hypothetical D_{2h} tetraaza[14]annulenes (see fig. 1)

TAA	2H-TAA Non-conjugated	2H-TAA Conjugated
576(0·089)	854(0)	1039(0)
428(0·029)	351(0·266)	361(0·311)
294(1·783)	312(0·374)	315(0·463)
286(3·330)	281(0·938)	299(0·834)
240(0)	257(2·177)	258(2·124)
232(0)	240(0)	242(0)

changes in orbital occupancy and symmetry bring about the contrast between TAA and 2H-TAA.

TETRA-AZA TRIBENZO[14]ANNULENE (TATA)

Derivatives based on the TAA ring system have so far proved inaccessible by the established method of template induced Schiff's base formation.[4, 16] We have, to date, been unsuccessful in preparing the condensation product (TATA) between *o*-amino benzaldehyde, *o*-phenylene diamine and glyoxal in 2 : 1 : 1 molar ratio (Fig. 2)

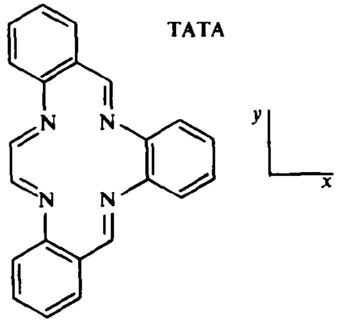
TATA

FIG 2. A tribenzo-tetraaza[14]annulene.

The results of our calculations on this 26 π-electron system are presented in detail in Table 3, together with our porphin calculations (26 π-electrons) employing very extensive single excitation, singlet configuration interaction. Our porphin results are

TABLE 3. EXTENSIVE SINGLET SINGLE EXCITATION CONFIGURATION INTERACTION, USING SCF π-ELECTRON ENERGIES AND ORBITALS. FOR A C_{2v} MACROCYCLE AND D_{2h} FREE-BASE PORPHIN

Tetra-aza-tribenzo[14]annulene					D_{2h} free base porphin			
25 × 25 CI			81 × 81 CI		81 × 81 CI		Hush *et al*[13]	
Energy (nm)	Oscillator strength	Nature of band	Energy (nm)	Osc.	Energy (nm)	Osc.	Energy (nm)	Osc.
419	0·215(Z)	PT(13 → 14)	430	0·179(Z)	690	0·011	735	0·015
409	0·040(Y)	$\text{SUM}^{(12\to14)}_{(13\to15)}$	415	0·029(Y)	575	0·039	587	0·039
325	2·600(Y)	$\text{DIFF}^{(12\to14)}_{(13\to15)}$	328	2·412(Y)	380	0·734	393	0·556
312	1·025(Z)	PT(12 → 15)	322	0·223(Y)	372	0·003		
311	0·130(Y)	MIX	321	0·830(Z)	349	2·459	357	2·840
289	0·133(Z)	MIX	310	0·094(Z)	322	0·013		
273	0·043(Y)	MIX	283	0·116(Y)	321	2·601	333	3·19
267	0·147(Z)	$\text{SUM}^{(9\to15)}_{(13\to16)}$	281	0·208(Z)	318	0·001		

in substantial agreement with those of Hush and Williams[13] who employed an eight orbital, sixteen transition model; the agreement extends to the prediction of a "hidden band" in the region of 390 nm.

Our results for TATA indicate that the third lowest empty, virtual orbital (orbital 15) must be included in a successful limited CI model as two prominent bands include transitions involving this orbital. The predicted spectrum is porphin-like except for the facts of the small separation of the two visible bands and the general relative high energy of all four lowest energy bands.

TETRA AZA DIHYDRO[14]ANNULENE (TADA)

Conformation. We have found that the conformation of the 1,3-di-imine bridge in malondianils[18] changes from *cis–cis* in non-polar solvents to *trans–trans* in polar solvents; the electronic spectrum is a function of this change in conformation. Although the necessary experimental evidence is lacking we consider that because the similarity between malondianil TADA[18, 19] is so great, we are justified in considering other than the *cis–cis* conformation which TADA adopts when combined with a central metal ion. In addition, we note that two crystalline forms of TADA have been isolated, only one of which is isomorphous with the nickel complex.[19] We discuss only the *cis–cis*(CC) and *cis–trans*(CT) conformation (Fig. 3); the *trans–trans–exo* (TTEX) and *trans–trans–endo* (with a heavy atom skeleton allied to pentacene) conformations are discarded due to severe steric hindrance.

The facts that, in $CDCl_3$ solution, the 1-CH and 3-CH units of the di-imine bridge are identical, and the 2-CH unit gives a 1:2:1 triplet of total unit relative intensity show that the CC conformer of TADA exists in this solvent.[19] In malondianil the

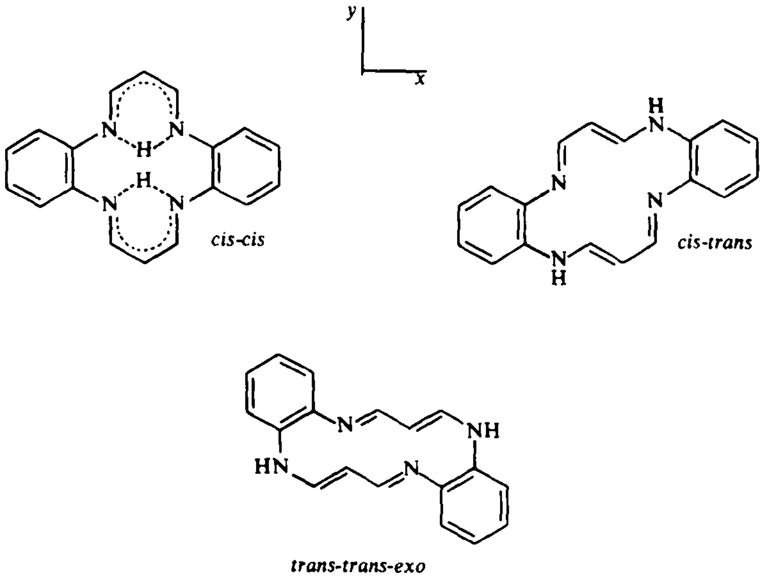

FIG 3. Three possible structures of a dibenzo-tetraaza[14]annulene (TADA).

cis coupling is 6 Hz in chloroform solution[18] (as in TADA[19]) and the *trans* coupling 12 Hz in dimethyl sulphoxide solution, the N—H—N linkages having been broken through the influence of the high dielectric constant of the latter solvent.[18] Thus, if the CT conformer does exist in solution, the signal from the 2-CH proton will consist of four lines of equal intensity, with a spacing of approximately 6 Hz, and the 1-CH and 3-CH chemical shifts and couplings will no longer be identical. We anticipate that this could only occur in highly polar media.

The steric hindrance inside the macrocyclic ring is similar for the CC and CT forms. Although conjugation of the 1,3-di-imine system seems less facile in the latter, we note that the di-imine bridge in 6,7-benzo-1,5 diazepine monohydrochloride[20] is fully conjugated and suggest, therefore, that the di-imine bridge of the CT form of TADA can be treated as a fully delocalized system.

Calculated electronic spectra of planar conformers. Initially, an idealized geometry based on 120° bond angles and a common bond length of 1·4 Å was chosen for both the CC and CT conformers. Using the same initial parameters, the effect of varying the SCF π-electron method (Theoretical section) was investigated. Neither the choice of method nor the choice between equivalent (1·5 π-electrons per atom) or non-equivalent N atoms (D_{2h} symmetry retained) made any significant change in the nature of the calculated electronic spectrum. We thus only report the results of the VB variation of the SCF π-electron method (Table 4).

In order to investigate the effect of in-plane buckling we adapted the co-ordinates of the macrocyclic ring of the CC conformer by using the bond angles based upon the planar projection of [14]-annulene[21] and the bond lengths calculated by the VB method.[10] Little change in the electronic spectrum is predicted.

The above conformers both have features which contrast with the calculated spectrum of porphin. The lowest energy band is totally forbidden, and the two high intensity bands are of the same polarisation. The $10 \rightarrow 13$ transition is predicted to play a more prominent role (lower energy: higher intensity) than the $11 \rightarrow 14$ transition showing that a four orbital model for TADA is unsatisfactory. A possible interpretation of the experimental spectrum[19] is that the centroids at 426 nm and 361 nm correspond to the two calculated $^1B_{3u}$ (x) states near 390 nm and 340 nm, with the lowest energy band unobserved. This will be termed the "planar; double centroid" interpretation.

Calculated electronic spectra of out-of plane buckled TADA. We now confine our attention to the CC conformer of TADA. It is likely that there is some out-of-plane buckling as well as the in-plane buckling already allowed for. Such buckling can be accommodated by appropriate reduction of the initial H_{ij} matrix elements[22] of C—N bonds, for distortions about the N atoms. We have chosen two models for such buckling. The NB model is one in which the carbon skeleton is left unaltered from the in-plane buckled co-ordinates, with the N atoms lifted above or below the molecular plane alternatively, by equal amounts. In the NP model, the N atoms are constrained to be co-planar, and the benzene rings are tilted down by $\theta°$ and the di-imine bridges up by $\theta°$. The NP model relaxes the hindrance between the 1,3-CH protons and the *ortho*-CH protons.[22]

Comparison between the use of the NB or NP models and the experimental spectrum of the free ligand, for a β^{CN} of $-1{\cdot}40$ eV, shows a considerable measurement of agreement in the NP case. This agreement is particularly marked if one takes the centroid of the two observed visible bands and correlates this with the calculated band

TABLE 4. 25 × 25 SINGLET SINGLE EXCITATION CONFIGURATION INTERACTION, USING SCF π-ELECTRON ENERGIES AND ORBITALS, FOR A D_{2h} TETRA-AZA-DIBENZO-DIHYDRO-[14]ANNULENE (TADA)

CT (non-buckled)			CC (non-buckled)			CC (in-plane buckled)		
Energy of State (nm)	Oscillator Strength	Nature of Band	Energy of State (nm)	Oscillator Strength	Nature of Band	Energy of State (nm)	Oscillator Strength	Nature of Band
647 ($^1B_{1g}$)	0·000	PT (12 → 13)	630 ($^1B_{1g}$)	0·000	PT (12 → 13)	652 ($^1B_{1g}$)	0·000	PT (12 → 13)
391 ($^1B_{3u}$)	0·250(*x*)	PT (12 → 14)	386 ($^1B_{3u}$)	1·021(*x*)	PT (12 → 14)	381 ($^1B_{3u}$)	0·481(*x*)	PT (12 → 14)
335 ($^1B_{3u}$)	1·350(*x*)	PT (11 → 13)	342 ($^1B_{3u}$)	0·850(*x*)	PT (11 → 13)	335 ($^1B_{3u}$)	1·257(*x*)	PT (11 → 13)
293 ($^1B_{2u}$)	0·250(*y*)	PT (10 → 13)	298 ($^1B_{2u}$)	0·793(*y*)	PT (10 → 13)	295 (^1A_g)	0·000	SUM 9 → 13 12 → 15
287 (^1A_g)	0·000	MIX	286 (^1A_g)	0·000	MIX	294 ($^1B_{2u}$)	0·442(*y*)	PT (10 → 13)
284 ($^1B_{1g}$)	0·000	PT (11 → 14)	280 ($^1B_{1g}$)	0·000	PT (11 → 14)	280 ($^1B_{1g}$)	0·000(*y*)	PT (11 → 14)
255 ($^1B_{2u}$)	0·193(*y*)	PT (12 → 16)	265 (^1A_g)	0·000	SUM 9 → 13 10 → 14	262 ($^1B_{2u}$)	0·030(*y*)	DIFF 8 → 13 12 → 17
			252 ($^1B_{2u}$)	0·662(*y*)	PT (12 → 16)	256 (^1A_g)	0·000	DIFF 9 → 13 10 → 14

at 426 nm. This implies that the $^1B_{3u}$ (426 nm) state is split and that the transition to the lowest energy $^1B_{1g}$ state is too weak to be observed. An alternative interpretation is to ignore the facts that the calculated intensity and energy of the lowest $^1B_{1g}$ state are so poor. We can then assign the four observed bands to states of symmetry B_{1g}, B_{3u} (x), B_{3u} (x) and B_{2u} (y) involving principally and respectively the 12 → 13, 12 → 14, 11 → 13 and 10 → 13 orbital transitions. We acknowledge that, with the buckled geometry, the symmetry labels are redundant; we retain the nomenclature appropriate to the D_{2h} point group for convenient comparison with the planar systems.

If β^{CN} is reduced to 0·90 eV, using the NP model relevant to the chelate,[19] a similar choice of assignments to those above can be made. We do not assign the 502 nm band to the nickel ion as, in the light of the proven square planar ligand field in the solid,[19] we assume that, in dimethyl formamide solution, we are studying a distorted octahedral complex. The observed extinction coefficient is thus an order of magnitude too high for the 502 nm band to be a d–d band.

However, some care is needed because the energy and intensity of the 502 nm band are almost identical to those observed for d–d bands in some tetrahedral bis-di-iminato Ni(II) complexes[23]. We cannot, therefore, eliminate the possibility of a change from the NP, square planar form in the solid chelate to the NB, squat D_{2d} form in solution. The extension of the NB model to values of β^{CN} less than $-1{\cdot}40$ eV does not lead to agreement with the observed spectrum of the chelate; the state involving principally the 11 → 13 transition proved almost wholly insensitive to buckling in this case.

Eigenvectors of sigma symmetry

The sigma electron system can be investigated by the one-electron Hamiltonian EHMO method,[23] or by the SCF all valence electron CNDO2,[24] method. These methods are described in detail elsewhere,[23, 24] and do not feature herein as the programmes used have been developed and organised by other workers.[25]

TADA, with a basis set of 102 valence orbitals, would involve an unwarranted length of run even if storage difficulties could be overcome.[25] We focus our attention therefore, in this context, upon the fully conjugated dianion of 2H-TAA (Fig 1). This has a basis set of 66 valence orbitals, 36 of which are doubly occupied. In common with the results of Pullman[26] on large heterocyclic natural-product bases, we find that all the σ^* orbitals are higher in energy than the π^* orbitals which strongly suggests that the observed bands in the UV-VIS region do not involve σ-σ^* transitions.

Although the highest-filled bonding orbital in both malondi-imine dianion, and 6,7-benzo-1,5-diazepine monohydrochloride, is of σ-symmetry, in the 2H–TAA dianion, the two highest energy filled orbitals are of π-symmetry. For σ–π^* transition energies, it is appropriate to use the non-virtual empty orbitals of the EHMO method; attention is called to the weaknesses of the EHMO method, as emphatically described by Dewar.[27] Of the seven lowest energy transitions, the first three and last two are of π–π^* type, which suggests that the visible and near UV spectrum will be dominated by π–π^* transitions.

The results on the model 2H-TAA dianion, and the fact that the bands in the near UV/VIS spectrum of TADA all have extinction coefficients of the order of 10^4–10^5 suggest that we are justified in limiting our detailed studies to the π-electron system.

TABLE 5. CALCULATED ELECTRONIC SPECTRA OF BUCKLED FORMS OF TADA USING β^{CN} OF GREATLY REDUCED MAGNITUDES

NB model ($\beta^{CN} = -1·40$)		Free ligand		NP model ($\beta^{CN} = -1·40$)			NP model ($\beta^{CN} = -0·90$)			Chelated ligand	
Energy (nm)	Osc.	Exp. (nm)	$\log_{10}\varepsilon$	Energy (nm)	Osc.	Dominant Transition	Energy (nm)	Osc.	Dominant Transition	Exp. (nm)	$\log_{10}\varepsilon$
493	0·024	436	4·13	577	0·000	(12 → 13)	574	0·000	(12 → 13)	502	3·76
398	0·889	416	4·15	426	0·532	(12 → 14)	466	0·316	(12 → 14)	463	3·78
343	0·248	368	4·71	371	1·586	(11 → 13)	417	0·115	(11 → 14)		
326	0·378	354	4·55	352	0·459	(10 → 13)	414	1·104	(11 → 13)	426	4·74
319	0·017			351	0·000	(11 → 14)	398	0·247	(10 → 13)	399	4·21
311	0·000			327	0·090	(10 → 14)	379	0·083	(10 → 14)		
288	0·000			316	0·082	(9 → 13)	351	0·027	(9 → 13)	355	3·86
				294	0·008	(9 → 14)	340	0·011	(9 → 14)		
				283	0·227	(8 → 13)	319	0·121	(8 → 13)	310	4·00

CONCLUSION

It seems clear that, although the four orbital, four transition model is a satisfactory one for porphin, it is unsatisfactory for a number of similar compounds. Extension to a ten orbital, twenty-five transition model does seem satisfactory; further extension does not appear necessary. The calculated electronic spectrum of TATA affords most of the features demanded of a porphin model. However, the charge distribution on the N atoms in particular (1·20 and 1·17), the absence of secondary NH protons, and the blocking of the bridging C atoms of the 1,3-di-imine units are unfavourable features.

The electronic spectra of chelated *cis–cis* malondianils and free *cis–cis* malondianils are virtually identical,[18,28] because the molecules exist as the dianion in both circumstances. For this reason, and recalling the similarities between TADA and malondianil noted above, we proposed that the substantial change in the electronic spectrum of TADA upon chelation is due to a significant change in shape.

As a result of the dianion-like behaviour mentioned above, we interpret the spectra of the free and chelated ligand in a similar manner. In addition to the favourable fact of the great similarity in the shape of the two spectra (see Ref. 19, Fig 2), we find that we can then successfully predict the observed shifts and intensity changes upon chelation in all but the longest wavelength band. We therefore propose a certain degree of buckling in the free ligand and assign the 354 nm and 368 nm bands to different states, transitions from which are of, predominantly, y and x polarization respectively. This affords the possibility of an analogy with the Soret Band of porphin—an analogy lacking in the planar case. The bands at 399 nm and 426 nm in the chelated ligand are interpreted similarly except for the participation of a second, erstwhile forbidden state in the latter band (Table 5).

We tentatively suggest that, in both spectra, the highest observed band stems from a vibronically allowed (erstwhile $^1B_{1g}$) state, and the next highest observed band stems from an erstwhile $^1B_{3u}$ state, transitions from which are predominantly x polarized. MORD[6] experiments are being planned to clarify the situation.

In the out-of-plane buckled geometry, β^{cn} values of low magnitude need to be chosen. If only the usual interpretation is placed upon these values,[29] then the carbon framework is extremely buckled. We suggest that the low β^{cn} values could also be a measure of bond elongation and torsion.

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