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A STUDY OF PORPHIN ANALOGUES—II
REACTIVITY INDICES AND SPIN DISTRIBUTION IN SOME CONJUGATED POLYAZA MACROCYCLES AND THEIR RADICAL IONS

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Abstract—Some of the calculated ground state properties of the π-electron system of seven conjugated polyaza macrocyclic ligands are reported, and contrasted with the analogous calculated properties of porphin, tetra-aza porphin and their closed shell dianions.

The calculated spin and charge distributions in the anion and cation radicals of the eleven molecules referred to above are also reported in order to assess the perturbation of predicted reactivities by co-ordination to a central paramagnetic metal ion. The similarity between the Elvidge macrocycle (2) and tetra-aza porphin is particularly noteworthy.

1. INTRODUCTION

Amongst the numerous controlling factors of the metabolic roles played by the porphyrins and metalloporphyrins[1] of particular prominence is the necessity for an approximately planar, conjugated macrocycle with N atoms suitably arranged to bind metal ions in a central cavity—the co-ordination hole. The geometry and charge distribution of this co-ordination hole is of considerable importance in determining the nature and strength of the metal ligand bonds.

Guides to the reactivity of a conjugated planar organic molecule are provided by the π-electron charge distribution, the form of the highest occupied and lowest empty π-molecular orbitals (HBO and LAO respectively), and the atom–atom self polarisabilities.[2] Frequently, the reactivity of an organic molecule of the type being discussed can be modified by the influence of the metal–ligand bonds to a paramagnetic centre.[3] Either metal to ligand back donation, or ligand to metal donation can predominate; the appropriate electronic models for the ligand are the radical anion and radical cation respectively.[4]

Allied to our spectroscopic and theoretical studies of the singlet[5] and triplet electronic states of the macrocycles shown in Fig 1, we report here various ground state properties of the relevant neutral and radical ionic species. We intend to compare and contrast the features of the N atom environments, and those of possible substitution sites, in order to assist in our selection of the molecule most suitable to adopt as a porphin analogue.

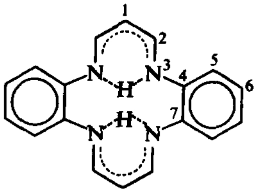
The following macrocyclic ligands will be discussed: 1,5,8,12-tetraaza 5, 12-dihydro 6,7,13,14-dibenzo[14]annulene (1); 7,9,16,18-bis (1,5-pentadienylene) 2,5,11,14-diimino 1,6,10,15-tetraaza 3,4,12,13-dibenzo[18]annulene (2); 1,4,7,10-tetraaza 5,6,11,12-dibenzo[12]annulene (3); 1,5,9,-13-tetraaza 2,3,6,7,10,11,14,15-tetrabenzo[16]-annulene (4); diphenylo[2,3,2′,3′-be] diphenylo [2,-3,2′,3′-kn] 1,4,7,10-tetraaza 4,13-diimino cyclooctadeca 2,5,7,9,11,14,16,18-octaene (5); 1,5,8,12-tetraaza 2,3,6,7,10,11-tribenzo[14]annulene (6); 3,5,12,14-bis(1,5 pentadienylene) 1,4,7,10,13,16-hexaaza 8,9,17,18-dibenzo[18]annulene (7).

2. THEORETICAL

The electron spin density at atom r, ρ_r, may be evaluated either by an iterative self consistent field (SCF) method[6] using a two electron Hamiltonian incorporating electron repulsion terms, or by an extension of the pioneer work of Coulson and Longuet–Higgins[7] on hetero-atom substitution in even-membered conjugated hydrocarbons to perturbations imposed by an odd electron.[8, 9]

The starting point for the SCF method is the assignment of a matrix of attractive terms, H, and of a matrix of repulsion terms G. These matrix elements are assigned from the nature of the heavy atoms (atomic number and number of π-electrons) and the molecular geometry. The matrix H is diagonalised to provide an approximate set of molecular orbitals from which two π-electron density matrices are constructed—one for α-electrons, P^α, and one for β-electrons, P^β. Both P^α and P^β are obtained by summing over the relevant number of occupied orbitals from their respective set of eigenvectors as follows

$$P^\alpha_{ij} = \sum_{k=1}^{n\alpha} c_{ik}c_{jk} \tag{1}$$



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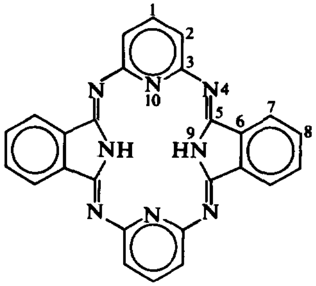

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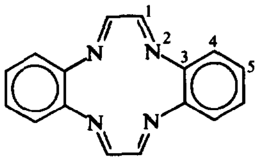

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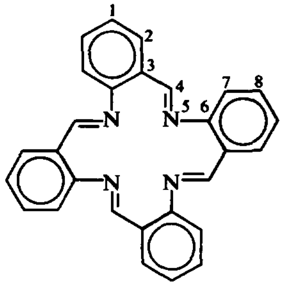
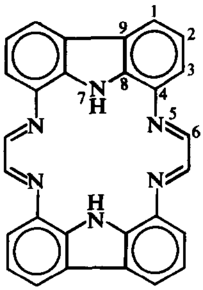
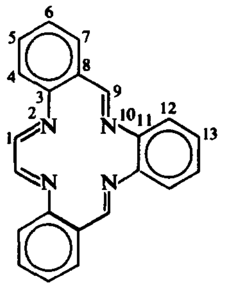


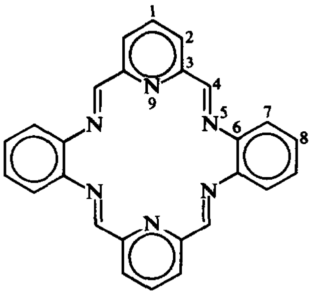
TAAB 4



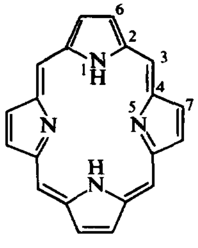
HACG 5



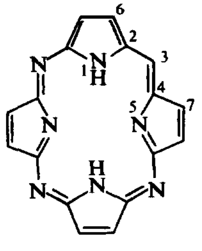
TATA 6



HADA 7



8a,b
Porphin



9a,b
Tetra-aza
Porphin

Fig 1. Labelling and topology of some conjugated macrocycles.

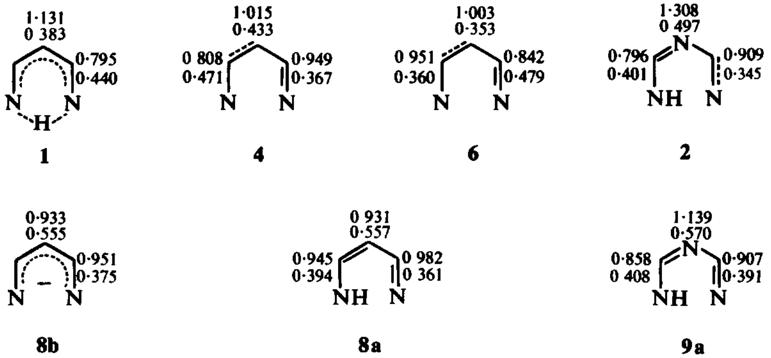


Fig 2. The three-membered conjugated bridges of the inner great rings of some macrocyclic ligands (Top, charge; Bottom, $|\pi_{r,r}|$).

$$P^{\beta}_{ij} = \sum_{k=1}^{n\beta} c'_{ik}c'_{jk} \tag{2}$$

$$P_{ij} = P^{\alpha}_{ij} + P^{\beta}_{ij} \tag{3}$$

where the c_{ik} and c'_{ik} are the i^{th} atomic orbital coefficients in the k^{th} molecular orbital of the sets of α-spin and β-spin eigenvectors respectively, $n\alpha$ and $n\beta$ are the number of α and β electrons and P is the π-electron charge density matrix. New matrices F^{α} and F^{β} may now be defined where

$$F^{\alpha}_{ii} = H_{ii} + \sum_{j\neq i} (P_{ii}-1)\,G_{ij} + P^{\beta}_{ii}G_{ii} \tag{4}$$

$$F^{\beta}_{ii} = H_{ii} + \sum_{j\neq i} (P_{ii}-1)\,G_{ij} + P^{\alpha}_{ii}G_{ii} \tag{5}$$

$$F^{\alpha}_{ij} = H_{ij} - P^{\alpha}_{ij}G_{ij} \tag{6}$$

$$F^{\beta}_{ij} = H_{ij} - P^{\beta}_{ij}G_{ij} \tag{7}$$

Diagonalisation of F^{α} and F^{β} provide two sets of π-molecular orbitals which may then be used to re-evaluate P^{α} and P^{β} respectively. The iterative process thus initiated continues until successive iterations agree to within an acceptable limit.[8] The atomic π-electron spin densities are finally given by

$$\rho_r = P^{\alpha}_{rr} - P^{\beta}_{rr} \tag{8}$$

For systems in which $n\alpha = n\beta + 1$, the ground electronic state should be a doublet spin state with $S = \frac{1}{2}$ and the expectation value $(\langle S^2\rangle)$ of S^2, which is given by

$$\langle S^2\rangle = S(S+1)$$

should be 0·75. However, as Snyder[11] and Amos[6] have explained, the use of different orbitals for different spins produces a molecular wave function which is contaminated by quartet, sextet and higher spin multiplicities. The quartet contamination, which is the principal contamination, can be completely annihilated by the exact formula of Snyder and Amos,[11] or can be extensively but incompletely removed by a more easily used but approximate formula.[6] In this work we use the former, and designate the SCF method used herein by the widely used abbreviation SCFAA.[6,8] The values of $\langle S^2\rangle$ before $(\langle S^2\rangle_{\text{SD}})$ and after $(\langle S^2\rangle_{\text{AA}})$ quartet annihilation are both functions of P^{α} and P^{β}, as, indeed, is the total π-electron binding energy. Except in molecules of perfect polygonal symmetry the form of the molecular orbitals is not determined by symmetry alone; the molecular orbitals are dependent upon the choice of input parameters which in turn influence P^{α} and P^{β} (Eqs 1 and 2). The most satisfactory values of $\langle S^2\rangle_{\text{AA}}$, namely those closest to 0·75, were given, in accord with earlier work,[8] by the use of the charged-sphere repulsion integral G matrix of Pariser and Parr.[12] We do not report the results gained by using the repulsion integrals of Nishimoto and Forster[13] for the pragmatic reason that the values of $\langle S^2\rangle_{\text{SD}}$ so obtained were frequently much in excess of unity.

In the work reported herein the values of $\langle S^2\rangle_{\text{AA}}$ obtained are frequently close to 0·75, showing that the remaining sextet and higher contaminations, which produce a value of $\langle S^2\rangle_{\text{AA}}$ in excess of 0·75, are small. For this reason the *annihilation* of *all* contaminating multiplicities (i.e. doublet *projection*), a formidable task in such large molecules, was not attempted.

The above SCF formalism can be used to gain the form of the perturbation to be inserted into the modified Coulson and Longuet-Higgins method.[7] The original assumption of McLachlan[9] was that, in the first approximation, the β-electrons remain unperturbed during the generation of a monoradical ion. Thus, if Eqs 5 and 7 are respectively subtracted from Eqs 4 and 6 after the first estimates of F^{α} and F^{β} have been made, then the differences, which are the first order perturbations to the H matrix, are given by

$$\begin{aligned} \delta H_{ii} &\equiv \delta\alpha_i = -(P^{\alpha}_{ii} - P^{\beta}_{ii})\,G_{ii} \\ \delta H_{ij} &\equiv \delta\beta_{ij} = -(P^{\alpha}_{ij} - P^{\beta}_{ij})\,G_{ij} \end{aligned} \qquad (9)$$

The only difference between the first estimates of P^{α} and P^{β}, if $n\alpha = n\beta + 1$, is in the orbital occupied by the odd electron, which will be either the highest filled molecular orbital (HBO) or the lowest empty molecular orbital (LAO) of the parent, neutral, diamagnetic molecule. The relevant molecular orbitals are those afforded by diagonalisation of the matrix H where we designate the atomic orbital coefficients of the HBO as c_i^H and those of the LAO as c_i^L. The radical cation perturbations are given by

$$\begin{aligned} \delta\alpha_i &= -(c_i^H)^2 G_{ii} \\ \delta\beta_{ij} &= -(c_i^H c_j^H)\,G_{ij} \end{aligned} \qquad (10)$$

and the radical anion perturbations by

$$\begin{aligned} \delta\alpha_i &= -(c_i^L)^2 G_{ii} \\ \delta\beta_{ij} &= -(c_i^L c_j^L)\,G_{ij} \end{aligned} \qquad (11)$$

Having now obtained an appropriate form for the perturbation imposed by an odd electron, we now return to the perturbation method for diamagnetic species and investigate how this can be modified for the case of perturbations to α-electrons only.

In an even alternant hydrocarbon, the π-electron charge density at atom r, q_r, is unity.[7] For a perturbation $\delta\alpha_h$ to the diagonal matrix element H_{hh}, q_r is given by

$$q_r = 1 + \pi_{r,h}\delta\alpha_h \qquad (12)$$

where $\pi_{r,h}$, an atom–atom mutual polarisability, is expressed as

$$\pi_{r,h} = 4\sum_m\sum_n \frac{c_{mr}c_{nh}c_{mh}c_{nr}}{E_m - E_n} \qquad (13)$$

in which m and n run over occupied and empty molecular orbitals respectively, the c_{kl} are the atomic orbital coefficients, l, in the molecular orbitals, k, and E_k is the energy of the k^{th} molecular orbital.[7] In general, a perturbation will extend over all nuclei and all bonds between them, and in this circumstance, which is of particular relevance in the case of an odd π-electron, the perturbed charge density is given by[7]

$$q_r = 1 + \sum_s \pi_{r,s}\delta\alpha_s + \sum_{tu} \pi_{rr,tu}\delta\beta_{tu} \qquad (14)$$

in which $\delta\beta_{tu}$ is the perturbation to the offdiagonal element H_{tu} and $\pi_{rr,tu}$, an atom-bond polarisability, is defined as

$$\pi_{rr,tu} = 4\sum_m\sum_n \frac{c_{mr}c_{nr}(c_{mt}c_{nu} + c_{mu}c_{nt})}{E_m - E_n} \qquad (15)$$

In non-alternant conjugated molecules the unperturbed charge densities are rarely unity and are obtained from the charge density matrix of the neutral molecule, P^0, where

$$P^0_{ij} = 2\sum_{k=1}^{m} c_{ik}c_{jk} \qquad (16)$$

The final general expression for the charge distribution produced by the perturbation of m electron pairs is therefore

$$q_r = P^0_{rr} + \sum_s \pi_{r,s}\delta\alpha_s + \sum_{tu} \pi_{rr,tu}\delta\beta_{tu} \qquad (17)$$

In any diamagnetic molecule the charge density at an atom r, q_r, is equally divided between the α-electron density (q_r^{α}) and the β-electron density (q_r^{β}) so that $q_r^{\alpha} = q_r^{\beta} = 0{\cdot}5q_r$ and $\rho_r = q_r^{\alpha} - q_r^{\beta} = 0{\cdot}0$. The perturbation imposed on m α-electrons, say, is half that imposed upon m electron pairs.

In both monoradical anions and cations the first order perturbation is imposed upon m α-electrons. In the radical anion the odd electron perturbs the other m α-electrons by exchange[9] but remains unperturbed itself, to first order.[9] In the radical cation the odd electron perturbs the other $m-1$ α-electrons and is itself perturbed by the pair-breaking of ionisation.[8]

We may now obtain an expression for the perturbed values of q_r^{α} and q_r^{β} in both radical ions by substituting Eq 10 or 11 into Eq 17, and imposing half of the perturbation terms in the latter upon the unperturbed α-electron densities. The α-electron and β-electron densities are, respectively, $(c_r^L)^2 + 0{\cdot}5P^0_{rr}$ and $0{\cdot}5P^0_{rr}$ for the radical anion, and $0{\cdot}5P^0_{rr}$ and $0{\cdot}5P^0_{rr} - (c_r^H)^2$ for the radical cation, before any perturbation is imposed. For the radical anion we obtain

$$q_r^{\alpha} = (c_r^L)^2 + 0{\cdot}5P^0_{rr} - 0{\cdot}5\left\{\sum_s \pi_{r,s}G_{ss}(c_s^L)^2 + \sum_{tu} \pi_{rr,tu}G_{tu}c_t^L c_u^L\right\}$$

$$q_r^{\beta} = 0{\cdot}5P^0_{rr}$$

$$\rho_r^A = (c_r^L)^2 - 0{\cdot}5\left\{\sum_s \pi_{r,s}G_{ss}(c_s^L)^2 + \sum_{tu} \pi_{rr,tu}G_{tu}c_t^L c_u^L\right\} \qquad (18)$$

where ρ_r^A is the electron spin density at atom r in the radical anion. Similarly, we may obtain the corresponding radical cation values ρ_r^C where

$$\rho_r^C = (c_r^H)^2 - 0{\cdot}5\left\{\sum_s \pi_{r,s}G_{ss}(c_s^H)^2 + \sum_{tu} \pi_{rr,tu}G_{tu}c_t^H c_u^H\right\} \qquad (19)$$

It is customary[8,9,10] to simplify Eqs 18 and 19 by ignoring the small $\pi_{rr,tu}$ terms and, in addition, by setting all the G_{ss} to a standard value. On the basis of a recent, detailed investigation[8] we adopt the above simplifications herein and use

$$\rho_r^A = (c_r^L)^2 - 0{\cdot}5\bar{\gamma} \sum_s \pi_{r,s}(c_r^L)^2 \qquad (20)$$

$$\rho_r^C = (c_r^H)^2 - 0{\cdot}5\bar{\gamma} \sum_s \pi_{r,s}(c_r^H)^2 \qquad (21)$$

in which $\bar{\gamma}$ is the standard G_{ss} value. If all energy terms (i.e. $\bar{\gamma}$ and the E_k) are expressed in β units[14] ($\beta \doteqdot -4{\cdot}0 \pm 1{\cdot}6$ eV) then the McLachlan parameter,[9] λ, may be introduced

$$\rho_r^A = (c_r^L)^2 + \lambda \sum_s \pi_{r,s}(c_s^L)^2 \qquad (22)$$

$$\rho_r^C = (c_r^H)^2 + \lambda \sum_s \pi_{r,s}(c_s^H)^2 \qquad (23)$$

$$\lambda = \bar{\gamma}/(2|\beta|) \qquad (24)$$

where λ usually has a value between 1·0 and 1·2.[8,9,10] If, in contrast to the practice of Zahradnik,[10] polarisabilities in $|\beta|$ are used (i.e. the $\pi'_{r,s}$ of McLachlan)[9] then the minus sign before the polarisability term must be restored (*cf* Eqs 20 to 24).[8,9]

In this work we have used a Hückel[7] *H* matrix in β units, assigned from the tabulation of Streitwieser,[14] to obtain the polarisabilities for use as either reaction indices ($\pi_{r,r}$),[2,7] or perturbation parameters in conjunction with a value for λ of 1·2. The SCFAA method was applied using the *H* matrix parameters of Nishimoto *et al.*[13] with the charged-sphere *G* matrix elements.[12]

3. RESULTS AND DISCUSSION

3.1 *The co-ordination hole*

Only **1**, **2** and **5** are capable of accommodating a divalent metal ion without the subsequent involvement of charged ligands. In any attempt at a detailed biochemical simulation, one of the above compounds must be selected to the exclusion of the other species listed. We consider that interesting model reactions[15] might be investigated using those other species which proffer a neutral co-ordination hole, and therefore include them in the present discussion.

Compounds **3** and **4** proffer a D_{4h} co-ordination hole, whereas that in **1** and **6** is of D_{2h} symmetry (the dimensions are, approximately 0·24 nm × 0·28 nm). The D_{6h} hole in **5** and **7** is afforded by a hexagon with a face dimension of approximately 0·28 nm; this in turn demands a metal–nitrogen bond length of *ca* 0·28 nm. Considerable distortion from D_{6h} microsymmetry is therefore likely, except for large metal ions. The crystal field expansion and correlation diagrams for d^1 and d^2 metal ions in D_{6h} symmetry will be reported elsewhere. Although the co-ordination hole of the Elvidge macrocycle **2**[16] is apparently rhombohedral, it is a most efficient chelator for a wide range of divalent metal ions, including lead. In common with **1**,[17] the nickel (2) complex of **2** has the magnetic and structural characteristics appropriate for a square planar crystal field.[16,18]

On examination of the reactivity indices of those molecules which have distinguishable —NH— and ═N— chelator units (**2** and **5**), those of **2** are found to be marginally closer to those of free base porphin. A similar examination of those molecules lacking an —NH— unit (**3**, **4**, **6**, **7**) reveals that the reactivity indices of the ═N— units in the Busch[19] macrocycle, **4**, approximate most closely to those of the ═N— units of free base porphin (**8a**).

3.2 *Bridging atoms of the inner great ring*

The Hückel π-electron charges and atom–atom self polarisabilities for the 3-membered conjugated bridges between chelator N atoms are

Table 1. Some π-electron reactivity indices of chelator nitrogen atoms

Type or Label	CHARGE		FRONTIER			Type or Label	CHARGE		FRONTIER		
	HUCK.	SCF	HBO	LAO	$\lvert\pi_{r,r}\rvert$		HUCK.	SCF	HBO	LAO	$\lvert\pi_{r,r}\rvert$
═N—						—NH—					
2	1·291	1·284	0	0·141	0·463	**2**	1·791	1·696	0·047	0	0·140
3	1·174	1·169	0·185	0·197	0·599	**5**	1·807	1·572	0·101	0	0·135
4	1·270	1·219	0·166	0·071	0·475	**8a**	1·791	1·600	0·050	0·057	0·152
5	1·180	1·196	0·123	0·217	0·564	**9a**	1·783	—	0·027	0·037	0·151
6¶	1·205	1·183	0·089	0·225	0·519	$\overset{\cdot\cdot\cdot\cdot\cdot}{-\mathrm{N}-}$					
7 (aza)	1·214	1·178	0·111	0·086	0·489	**1**	1·616	1·521	0·216	0·067	0·306
7 (pyr)	1·189	1·187	0	0·249	0·522	**8b**	1·644	—	0·112	†	0·273
8a	1·433	1·361	0·233	0	0·417	**9b**	1·638	—	0·267	†	0·267
9a	1·429	—	0·363	0	0·414						

(¶ = average) († = double degeneracy)

shown in Fig. 2. The similarity between the free base of tetra-aza porphin and **2** is particularly striking. In contrast, the pronounced differences between **1** and D_{4h} porphin dianion show that the 2-CH units of the 3-membered bridges are certainly not sites of similar reactivity—the frontier orbital densities also support this deduction.

If a particular reaction entails attack at, or interaction with the chelator nitrogens, then the interacting species will encounter forces involving not only the N atoms, but also atoms adjacent to them. Some relevant results are presented in Table 2. Again we find a close equivalent between **2** and **4a**, and there is a less pronounced similarity between either **1** and **8b** or **5** and **8a**. None of the neutral co-ordination hole macrocycles compare favourably with the natural product bases in this context.

3.3 *Reactivity indices of potential sites for side chain substitution*

In this present discussion we are not assessing the reactivity of a particular site with reference to

Table 2. Averaged reactivity indices for sp² carbon units bordering chelator nitrogen

Type or label	SCF π-electron charge	$\lvert\pi_{r,r}\rvert$	Type or label	SCF π-electron charge	$\lvert\pi_{r,r}\rvert$
=N—			—NH		
2	0·878	0·345	**2**	0·870	0·401
3	0·914	0·429	**5**	1·023	0·418
4	0·879	0·419	**8a**	1·041	0·394
5	0·961	0·407	**9a**	0·947	0·408
6†	0·906	0·417	$-\overset{\cdot\cdot\cdot\cdot\cdot}{N}-$		
7 (aza)	0·911	0·431	**1**	0·918	0·407
7 (pyr)	0·921	0·341	**8b**	0·979	0·375
8a	0·989	0·361	**9b**	0·878	0·395
9a	0·846	0·391			

† = the average of two values.

Table 3. Some reactivity indices of =CH— units of the outer great rings of some conjugated macrocyclic ligands.

Name and	Position	CHARGE			FRONTIER		Radical SCFAA charge	
		Hückel	SCF	$\lvert\pi_{r,r}\rvert$	HBO	LAO	CATION	ANION
1	1	1·131	1·179	0·383	0·168	0	1·070	1·179
	2	0·795	0·833	0·440	0·004	0·367	0·834	0·978
	5	1·039	1·034	0·408	0·066	0·023	1·014	1·064
	6	1·025	1·016	0·419	0·031	0·009	0·947	1·067
8b	6	1·011	1·028	0·456	0·040	†	0·990	†
8a	6	0·990	1·031	0·455	0·074	0·053	0·998	1·074
	7	1·040	1·022	0·465	0·002	0·118	0 983	1·088
5	1	0·990	0·983	0·460	0·074	0·045	0·915	1·015
	2	1·023	1·034	0·396	0·033	0·000(2)	0·974	1·074
	3	1·001	0·994	0·458	0·039	0·044	0·964	1·002
	6	0·887	0·873	0·466	0·052	0·140	0·802	0·912
2	1	0·951	0·964	0·395	0	0·019	0·969	1·021
	2	1·035	1·027	0·462	0·208	0	0·903	1·039
	7	0·956	0·963	0·436	0·005	0·032	0·927	0·962
	8	0·975	0·986	0·414	0·014	0·047	0·941	1·037
9a	6	0·968	—	0·467	0·063	0·038	0·967	1·051
	7	1·022	—	0·495	0·010	0·129	0·955	1·069

† = double degeneracy

the facility with which that site might partake in a specified reaction. Rather, we are looking for =CH— sites with a set of reactivity indices similar to those for the outer great ring =CH— sites of porphin and tetra-aza porphin. Our assumption is that identical side chains substituted at each of such a pair of sites would themselves then have an equivalent set of reactivity indices and thereby display a generally similar chemistry. As we are now more closely concerned with biochemical simulation, rather than "model compounds", we will confine our discussion under this heading, to **1**, **2** and **5**. The relevant calculated reactivity indices are presented in Table 3.

Inspection of the data shows that the 3-carbon bridge of **1** continues to be unsatisfactory, and that the 5 and 6 $\overset{\cdots}{-}$CH$\overset{\cdots}{-}$ units of this molecule are more suitable. Position 1 of the Davis[20] macrocycle (**5**) compares favourably with position 6 of **8a**, whereas the comparison between **2** and **9a** is less decisive. However, position 8 of **2** is partially equivalent to position 6 of **9a**.

3.4 *Radical ions and the effects of chelation to a paramagnetic centre*

The McLachlan[8] and SCF AA[11] π-electron spin densities, together with the SCF AA charge densities, are presented in Tables 4 and 5. Because there is such a difference in run time between the McLachlan and SCF AA methods (approximately 15 min compared to 3 hr on a SYSTEMS 4), it would prove convenient to adopt the former; however, we emphasise that although there is a substantial measure of agreement between the two methods in general, there are radical ions for which markedly different answers are obtained (e.g. the radical cation of **5**). It is not possible to predict when such a disparity is likely to arise, and we therefore recommend that the SCF AA method be employed.[8]

If a comparison is made between the SCF π-electron density of the neutral species, and the SCF AA charge of a radical ion, then it is possible to determine which sites are likely to undergo marked changes in reactivity once the radical ionic

Table 4. π-Electron spin density distributions in the radical ions of some conjugated macrocycles affording a doubly charged co-ordination hole

Name and	Label	CATION McL. Spin	CATION SCFAA Spin	ANION McL. Spin	ANION SCFAA Spin
	1	0·114	0·130	−0·070	−0·170
	2	−0·039	−0·075	0·264	0·353
	3	0·136	0·180	0·001	−0·055
1	4	0·056	0·045	0·016	0·038
	5	0·005	0·009	−0·004	−0·013
	6	0·034	0·026	0·007	0·012
$\langle S^2\rangle$SD			1·096		1·025
$\langle S^2\rangle$AA			0·850		0·820
	1	0·024	0·127	0·027	0·119
	2	−0·015	−0·024	0·027	0·021
	3	0·183	0·204	0·087	0·041
	4	−0·036	−0·043	0·047	0·079
8a	5	0·168	0·084	−0·021	−0·015
	6	0·035	0·008	0·022	−0·000
	7	−0·013	−0·001	0·064	0·057
$\langle S^2\rangle$SD			1·045		0·874
$\langle S^2\rangle$AA			0·830		0·762
	1	0·011	−0·026	0·017	0·079
	2	−0·028	0·139	0·003	0·002
	3	0·166	−0·038	0·085	0·024
	4	−0·044	0·126	0·083	0·127
9a	5	0·265	−0·024	−0·026	−0·015
	6	0·030	0·029	0·012	−0·006
	7	−0·011	0·018	0·071	0·072
$\langle S^2\rangle$SD			0·925		0·939
$\langle S^2\rangle$AA			0·776		0·767
	1	−0·040	−0·055	0·007	0·011
	2	0·158	0·190	−0·011	−0·017
	3	0·003	0·004	0·001	−0·007
	4	0·120	0·087	0·060	0·064
2	5	−0·018	−0·039	0·087	0·080
	6	0·011	0·007	0·032	0·052
	7	−0·008	−0·010	0·010	0·006
	8	0·002	−0·001	0·023	0·029
	9	−0·005	0·017	0·097	0·067
	10	0·020	0·077	−0·009	−0·020
$\langle S^2\rangle$SD			1·136		0·833
$\langle S^2\rangle$AA			0·872		0·755
	1	0·046	0·001	0·026	0·040
	2	0·011	0·046	−0·011	−0 027
	3	0·018	−0·020	0·027	0·038
	4	0·036	0·053	−0·013	−0·023
	5	0·075	0·046	0·132	0·080
5	6	0·015	0·008	0·068	0·071
	7	0·055	−0·027	−0·004	0·154
	8	0·029	0·108	0·032	0·023
	9	−0·008	0·020	−0·009	−0·030
$\langle S^2\rangle$SD			0·869		1·054
$\langle S^2\rangle$AA			0·762		0·830
	1	0·068	0·100		
	2	−0·023	−0·034	Double	
8b	3	0·201	0·212		
	6	0·013	0·003	Degeneracy	
$\langle S^2\rangle$SD			1·025		
$\langle S^2\rangle$AA			0·820		

Table 5. π-Electron spin and charge density distributions in the radical ions of some conjugated macrocycles affording a neutral co-ordination hole

Name and Label	CATION			ANION		
	McL. Spin	SCFAA Spin	SCFAA Charge	McL. Spin	SCFAA Spin	SCFAA Charge
1	0·027	0 028	0·770	0·097	0·117	0·945
2	0·113	0·064	1·174	0·110	0·080	1·250
3 3	0·069	0 108	0·897	0·013	0·035	0·943
4	0·001	0·000	0·984	0·015	0·001	1·035
5	0·041	0 050	0·925	0·015	0·017	1·077
$\langle S^2\rangle$SD		0·799			0·789	
$\langle S^2\rangle$AA		0·751			0·751	
1	0·026	0·023	0·793	0·130	0·166	0·952
2	−0·005	−0·007	1·201	0·223	0·174	1·327
3	0·026	0·034	0·925	−0·020	−0·003	0·885
4	−0 003	−0·017	0·992	0·050	0·052	1·037
5	0·056	0·039	0·921	−0·019	−0·021	1·029
6	−0·020	−0·019	0·973	0·049	0·056	1·094
7	0 058	0 042	0·955	−0·021	−0·029	1·022
6 8	−0·001	−0·009	1·042	0·048	0·062	1 050
9	0·110	0·107	0·698	−0·019	−0·019	0·845
10	0 089	0·042	1·241	0·063	0·047	1·227
11	0·108	0 178	0·831	−0·002	−0·001	0·927
12	−0·008	−0·006	1·018	0·013	0·012	1·046
13	0·064	0·092	0·909	0·006	0·004	1·058
$\langle S^2\rangle$SD		0·829			0 831	
$\langle S^2\rangle$AA		0·756			0·756	
1	0·045	0·055	0·957	−0·003	−0·012	1·065
2	0·005	−0·006	0·930	0·038	0·048	1·043
3	0·020	0·034	1 009	−0 011	−0·026	1·012
4	0·026	0·017	0·900	0·044	0 062	0·923
4 5	0·120	0·112	1·213	0·010	−0·001	1·264
6	−0 005	−0·019	0·759	0·140	0·140	0·886
7	0·056	0·084	1·006	0·002	0·005	1·034
8	−0·018	−0·028	0·976	0·030	0·035	1·023
$\langle S^2\rangle$SD		0·897			0·899	
$\langle S^2\rangle$AA		0·772			0·772	
1	−0·024	−0·026	0·943	0·013	0·016	1·022
2	0·092	0·085	0·932	−0·011	−0 001	1·024
3	0·003	−0·008	0·909	0·004	0 008	0·905
4	0·041	0·047	0·780	0·108	0·118	0·918
5	0·053	0·024	1·186	0·030	0·012	1·223
7 6	0·053	0·076	0·906	0 013	0·027	0·950
7	−0·003	−0·003	1·005	−0·000	−0·006	1 026
8	0·030	0·038	0·949	0·008	0·012	1·062
9	−0·012	0·005	1·222	0·196	0·143	1·266
$\langle S^2\rangle$SD		0·840			0·854	
$\langle S^2\rangle$AA		0·757			0·757	

species is generated. The difference between the single determinant values of the SCF π-electron charge density and the values after quartet annihilation are very large (up to 0·5) and it is essential to apply the rigorous quartet annihilation formula.[6,11]

For convenience, the SCF AA charges for potential substitution sites in a limited selection of molecules are presented in Table 3. The deductions made in the previous section will stand, apart from the following qualifications. Molecule **2** continues to agree well with **9a**, with position 1 of the former being more satisfactory than hitherto; position 6 of **1** appears preferable to position 5. If a spin containing metal orbital matches the highest filled ligand molecular orbital in both symmetry and energy, then a degree of radical-cation-like behaviour will be induced in the ligand by back donation of net β-polarised spin from the ligand to the metal. Conversely, if the energy and symmetry matching involves the lowest empty ligand molecular orbital, then the induced behaviour will be that of a radical anion; net α-polarised spin will be delocalised onto the ligand. The deductions made above for the radical ions will also be applicable to the case of co-ordination to a paramagnetic centre. The full details of the effect of co-ordination cannot be assessed until calculations including both the metal, and all valence electrons of the ligand have been performed; the *modus operandi* has been very well reviewed recently.[21] The results for various metalloporphins are available.[22]

The ESR measurements of both paramagnetic complexes and radical ions, and the NMR of the former can provide estimates of the ratios of electron spin densities at the heavy atoms.[4] Such estimates are also afforded theoretically, and the necessary calculated data for π-electrons is provided in Tables 4 and 5. We concede that the all-valence electron INDO[23] method, which includes π–σ exchange, is much more satisfactory than the π-electron SCF AA method. The problems of matrix size, and the time incurred in their diagonalisation, render such a treatment unfeasible.

At present, the ESR spectra of allied ring systems do not afford sufficient resolution, apart from some recent work on phthalocyanins—this latter is still at an early stage.[24] The required rapid electron correlation times, in order to permit the observation of NMR contact shifts, have not yet been encountered in the metal complexes of the conjugated macrocycles **1**, **2**, **5**.

4. CONCLUSION

The degree of suitability as porphin analogues[15] is predicted to be as follows, in decreasing order; **2**, **1**, **5**. Molecule **4** is predicted to be the most satisfactory of the neutral co-ordination hole macrocycles. The search for favourable substituion sites, relevant to the development of porphyrin analogues, has resulted in the conclusion that the decreasing order of suitability of the possible substitution sites is position 8 of **2**, position 1 of **2**, position 6 of **1** and position 1 of **5**.

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