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Ground-State Energies of Mono-, Di-, Tri- and Tetranegative Ions of Porphins and their Metal Complexes

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From a range of porphin and metal porphin molecules, mono-, di-, tri- and tetranegative ions can be formed in solution. The disproportionation energies of these ions, measured by Hush and Clack [6] in dimethylformamide, show similar patterns. For the mononegative and trinegative ions, the disproportion of energies are of comparable magnitudes, but the disproportionation energy of the dinegative ion is 0.3 – 0.4 eV more positive. If it is assumed that the electrons are successively filling the lowest vacant orbital (e_g in D_{4h}) these results can be rationalized. In particular, if it is assumed that the dinegative ion is spin-paired, with ground-state electronic symmetry B_{1g} in D_{4h}, the average difference of 0.3 – 0.4 eV mentioned above should approximate to twice the exchange integral in the antibonding e_g orbital. Calculation of this integral for a number of porphin structures gives good agreement with experiment.

Von einer Reihe von Porphin- und Metallporphinmolekülen können ein-, zwei-, drei- und vierfach negativ geladene Ionen in Lösung hergestellt werden. Die Disproportionierungsenergien dieser Ionen, von Hush und Clack [6] in Dimethylformamid gemessen, zeigen ähnliche Struktur. Für die ein- und dreifach negativ geladenen Ionen ist die Disproportionierungsenergie etwa gleich, dagegen für das zweifach negativ geladene Ion 0,3 – 0,4 eV positiver. Wenn man annimmt, daß die Elektronen nacheinander das tiefste unbesetzte Orbital (e_g in D_{4h}) auffüllen, können diese Ergebnisse erklärt werden. Wenn man insbesondere annimmt, daß das zweifach negativ geladene Ion als Grundzustand einen Singulettzustand der Symmetrie B_{1g} in D_{4h} besitzt, ist die oben erwähnte mittlere Differenz von 0,3 – 0,4 eV angenähert doppelt so groß wie das Austauschintegral im antibindenden e_g-Orbital. Berechnung dieses Integrals für eine Anzahl Porphinstrukturen ergibt gute Übereinstimmung mit dem Experiment.

Une série de porphines et porphines métallés forment des ions mono-, di, tri- et tétranégatifs en solution. Les énergies de disproportionation dans diméthylformamide, présentant de similitudes [6], sont comparables pour les ions mono- et trinégatifs, mais 0,3 – 0,4 eV plus positif pour l'ion dinégatif. Ces résultats sont compréhensibles dans un schéma où les électrons occupent successivement l'orbitale vide la plus basse (e_g en symétrie D_{4h}). En particulier, si l'on adopte l'état fondamental B_{1g} (en D_{4h}) aux spins antiparallèles, pour l'ion dinégatif, les 0,3 – 0,4 eV valent approximativement deux fois l'intégrale d'échange pour l'orbitale e_g antiliante. Le calcul de cette intégrale pour une série de porphines s'accorde bien à l'expérience.

Introduction

Porphins and porphin metal complexes can attach electrons to form negative ions [*3, 4, 6*]. In aprotic solvents such as dimethoxyethane, tetrahydrofuran or dimethylformamide, these ions are relatively stable. Electron addition can be accomplished either by reaction with an alkali metal [*4*], a ketyl [*3*] or by electron uptake from an electrode [*6*]. An interesting feature of these molecules is that the lowest-lying vacant molecular orbital of the porphin ring system is doubly degenerate, or nearly so [*8*]. This orbital can therefore accommodate four electrons.

Experimentally, one can observe successive formation of mono-, di-, tri- and tetranegative ions from a number of porphins and their metal complexes [*4*]. This is unusual. For hydrocarbons it is very difficult to form an ion with more than two electrons added to the neutral molecule (one trinegative hydrocarbon ion has so far been described [*1*]). But in the porphin series it is possible to measure the relative groundstate energies of up to four ions in solution, by determining the successive reduction potentials. These have been obtained for a number of structures, and the pattern of relative stabilities is surprisingly constant. Some typical data are shown in Tab. 1, where successive differences between the first, second, third and fourth reduction potentials are listed.

Table 1. *Differences of reduction potentials (V) for porphin ions in dimethylformamide solution at* 20 °C. ${}^{n}\Delta^{n+1} E^0$ *is* $E^0_{n+1} - E^0_n$*, the difference between the potentials of the* $(n+1)$*th* and n'*th step. The values table are the experimental free energies of disproportionation of the mono-, di- and trinegative ions respectively (data from ref. 6)*

Porphin	$-{}^{1}\Delta^{2}E^0$	$-{}^{2}\Delta^{3}E^0$	$-{}^{3}\Delta^{4}E^0$
Zn tetraphenylporphin	0.40	0.73	0.22
tetraphenylporphin	0.42	0.86	0.15
Aetioporphyrin I	0.44	0.85	*
Zn Aetioporphyrin I	0.38	0.77	*
Cn Aetioporphyrin IV	0.51	0.71	*
Zn tetrabenzporphin	0.37	0.65	0.21
Mg octaphenyl tetraazaporphin	0.44	0.70	0.37

* E^0_4 is too negative to measure for these molecules.

These are equal to the free energies of disproportionation of the ions. Thus, for the ion P^{n-}, the disproportionation process is

$$2\,P^{n-} \rightarrow P^{(n-1)-} + P^{(n+1)-}$$

and the free energy of this reaction is

$$\Delta G = -F\,{}^{n}\Delta^{n+1} E^0 \,,$$

where E^0_n, E^0_{n+1} are the standard n'th and $(n+1)$'th reduction potentials for a particular solvent at a fixed temperature.

These disproportionation energies measure the relative ground-state stabilities of the porphin negative ions. A feature of the results in Tab. 1 is that the mononegative and trinegative ions have comparable disproportionation energies (0.2 — 0.4 eV). This appears to be general. It is found both with porphins and metal porphins and for a variety of substituents. It is therefore interesting to ask whether this reflects general relationships between the ground-state energies of the ions. As will be shown, this does seem to be the case. The results provide support for conclusions about the symmetry of the ground-state eigenfunction of the dinegative ions drawn from an examination of their electronic spectra [*7*].

Theory

The symbol P will be used to denote a molecule with a porphin ring system, and MP for a porphin complex in which the two central hydrogen atoms have been replaced by a divalent metal. The right-hand superscript indicates the zero net charge. Individual porphins will be referred to by suitable abbreviations — e.g., TPP for $\alpha\beta\gamma\delta$ — tetraphenylporphin, TBP for tetrabenzporphin, and TAP for tetraazaporphin.

Similarly, the symbols P^{n-} and MP^{n-} will be used for the ions formed by attaching n electrons to the porphin or its metal complex, respectively.

The choice of orbitals for the π-electron systems of porphins has been discussed in a number of publications. We use here molecular orbitals Φ_i, constructed from atomic functions φ_u,

$$\Phi_i = \sum_u C_{iu}\,\varphi_u \tag{1}$$

the summation being carried over all atoms u of the porphin skeleton.

These orbitals are assumed to satisfy the eigenvalue equation

$$\boldsymbol{F}\Phi = \Phi\,\varepsilon \tag{2}$$

where $\boldsymbol{F}$ is the Hartree-Fock self-consistent field operator and ε is the eigenvalue matrix.

We shall assume here the validity of the Pariser-Parr [*9, 10*] approximation to the self-consistent equations. We suppose also that the orbitals Φ_i are independent of the state of ionization of the porphin system. This assumption, which implies that Koopmans' theorem is identically satisfied, cannot be strictly correct, but it is probably a good approximation. It may be noted, in passing, that these ions provide useful systems for examining the dependence of orbital structure on degree of ionization.

In the ground state of P^0, orbitals $\Phi_1 \ldots\ldots \Phi_n$ are occupied by $2n$ electrons. The single determinant

$$|\Phi_1\overline{\Phi}_1 \ldots\ldots\ldots \Phi_n\overline{\Phi}_n|$$

corresponding to this configuration is taken as the ground state eigenfunction for P^0. Thus:

$$|0, {}^1A_{1g}\rangle = |\Phi_1\overline{\Phi}_1 \ldots\ldots\ldots \Phi_n\overline{\Phi}_n|\,. \tag{3}$$

For any reasonable choice of parameters, the lowest empty orbital in a D_{4h} porphin skeleton has e_g symmetry. In the corresponding porphin, the central protons define a perturbation axis, and the orbital degeneracy of this level is removed. The $b_{2g} - b_{3g}$ splitting can be traced in the visible absorption spectrum of the porphin [*5*]. How far the Jahn-Teller effect will operate to remove the orbital degeneracy of those MP^{n-} ions which have formal E_g ground states is not yet known. In any case, we shall ignore here small splittings of the e_g orbital, and discuss the D_{4h} system.

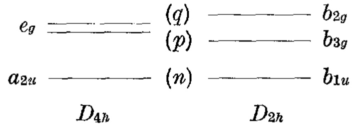

Fig. 1. Highest occupied (n) and lowest unoccupied orbitals (p, q) in metal porphin and porphins with D_{4h} or D_{2h} symmetry (Metal orbitals omitted)

In D_{4h} symmetry (with Φ_p and Φ_q for the components of e_g) the ground-state configurations for the mono-, tri- and tetranegative ions are:

$$\left.\begin{aligned}
|-1, {}^2E_g\rangle &= |\Phi_1\overline{\Phi}_1 \ldots\ldots \Phi_n\overline{\Phi}_n\Phi_p|\,,\ |\Phi_1\overline{\Phi}_1 \ldots\ldots \Phi_n\overline{\Phi}_n\Phi_q| \\
|-3, {}^2E_g\rangle &= |\Phi_1\overline{\Phi}_1 \ldots\ldots \Phi_n\overline{\Phi}_n\Phi_p\overline{\Phi}_p\Phi_q|\,, \\
&\ |\Phi_1\overline{\Phi}_1 \ldots\ldots \Phi_n\overline{\Phi}_n\Phi_q\overline{\Phi}_q\Phi_p|\,. \\
|-4, {}^1A_{1g}\rangle &= |\Phi_1\overline{\Phi}_1 \ldots\ldots \Phi_n\overline{\Phi}_n\Phi_p\overline{\Phi}_p\Phi_q\overline{\Phi}_q|\,.
\end{aligned}\right\} \tag{4}$$

(Throughout, functions are written to satisfy $S_z\,|a\rangle = +\tfrac{1}{2}\hbar\,|a\rangle$).

These functions are straightforward, provided that the basic assumption that the orbital being filled is the lowest e_g level is correct. For the dinegative ion, the choice of ground-state eigenfunction is not so simple. The four configurations arising from $(e_g)^2$ are:

$$|-2, {}^1A_{1g}\rangle = \frac{1}{\sqrt{2}} (|\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_p \bar{\Phi}_p| + |\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_q \bar{\Phi}_q|)$$

$$|-2, {}^1B_{1g}\rangle = \frac{1}{\sqrt{2}} (|\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_p \bar{\Phi}_p| - |\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_q \bar{\Phi}_q|)$$

$$|-2, {}^1B_{2g}\rangle = \frac{1}{\sqrt{2}} (|\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_p \bar{\Phi}_q| + |\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_q \bar{\Phi}_p|)$$

$$|-2, {}^3A_{2g}\rangle = \frac{1}{\sqrt{2}} (|\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_p \bar{\Phi}_q| - |\Phi_1 \bar{\Phi}_1 \ldots . \Phi_n \bar{\Phi}_n \Phi_p \bar{\Phi}_q|) \,. \tag{5}$$

The energies of these configurations, relative to $E\,|\,0, {}^1A_{1g}\rangle$ are as follows:

$$E\,|-2, {}^1A_{1g}\rangle = E_p + E_q + \tfrac{1}{2} (\langle pp \,|\, V \,|\, pp\rangle + \langle qq \,|\, V \,|\, qq\rangle) + \langle pq \,|\, V \,|\, qp\rangle$$

$$E\,|-2, {}^1B_{1g}\rangle = E_p + E_q + \tfrac{1}{2} (\langle pp \,|\, V \,|\, pp\rangle + \langle qq \,|\, V \,|\, qq\rangle) - \langle pq \,|\, V \,|\, qp\rangle$$

$$E\,|-2, {}^1B_{2g}\rangle = E_p + E_q + \langle pq \,|\, V \,|\, pq\rangle + \langle pq \,|\, V \,|\, qp\rangle$$

$$E\,|-2, {}^3A_{2g}\rangle = E_p + E_q + \langle pq \,|\, V \,|\, pq\rangle - \langle pq \,|\, V \,|\, qp\rangle \,. \tag{6}$$

In these equations, the two-electron integrals are of the form:

$$\langle ij \,|\, V \,|\, kl\rangle = \iint \Phi_i^* (1)\, \Phi_j^* (2)\, e^2/r_{12}\, \Phi_k (1)\, \Phi_l (2)\, d\tau_1\, d\tau_2 \,. \tag{7}$$

In D_{4h} symmetry, these equations of course simplify, as $E_q = E_p$ and $\langle pp \,|\, V \,|\, pp\rangle = \langle qq \,|\, V \,|\, qq\rangle$, but it is useful to have them also in their more general form.

From ROOTHAAN's [12] two-electron integral inequalities, it can easily be seen that

$$ {}^1A_{1g} \geq ({}^1B_{1g}, B_{2g}) \geq {}^3A_{2g} \,. \tag{8}$$

Since, in D_{4h}, $\tfrac{1}{2} (\langle pp \,|\, V \,|\, pp\rangle + \langle qq \,|\, V \,|\, qq\rangle) = \langle pp \,|\, V \,|\, pp\rangle$, then

$$\langle pp \,|\, V \,|\, pp\rangle \geq \langle pq \,|\, V \,|\, pq\rangle \,. \tag{9}$$

If we take these integrals as approximately equal (a reasonable assumption) the two lowest configurations are ${}^1B_{1g}$ and ${}^3A_{2g}$, accidentally near-degenerate. The ground state will then be either a spin singlet or a spin triplet, the two configurations lying very close to each other. It can be shown that configuration interaction (which is not explicitly considered here) leads to greater lowering of the singlet than of the triplet state energy. Hence, a singlet ground state is possible. Experimentally, the dinegative ion ZnTPP^{2-} has been shown to be diamagnetic [3], and the electronic spectra of the dinegative ions which have so far been examined [4, 7] (including those of the molecules in Tab. 1) are consistent with the assumption of a spin-paired ground state. We shall assume that this is generally so, and that the dinegative ions have ${}^1B_{1g}$ ground states.

For the four ions of a given porphin, the ground-state energies, relative to E (P) are thus:

$$E\,(\mathrm{P}^-) = E_p$$

$$E\,(\mathrm{P}^{2-}) = 2\,E_p + \langle pp \,|\, V \,|\, pp\rangle - \langle pq \,|\, V \,|\, qp\rangle$$

$$E\,(\mathrm{P}^{3-}) = 3\,E_p + 2\,\langle pq \,|\, V \,|\, pq\rangle + \langle pp \,|\, V \,|\, pp\rangle - \langle pq \,|\, V \,|\, qp\rangle$$

$$E\,(\mathrm{P}^{4-}) = 4\,E_p + 4\,\langle pq \,|\, V \,|\, pq\rangle - 2\,\langle pq \,|\, V \,|\, qp\rangle + 2\,\langle pp \,|\, V \,|\, pp\rangle \,. \tag{10}$$

The four electron affinities $A_1 \ldots\ldots A_4$ of the porphin are given by:

$$\begin{aligned}
-A_1 &= E_p \\
-A_2 &= E_p + \langle pp \mid V \mid pp\rangle - \langle pq \mid V \mid qp\rangle \\
-A_3 &= E_p + 2\,\langle pq \mid V \mid pq\rangle \\
-A_4 &= E_p + \langle pp \mid V \mid pp\rangle + 2\,\langle pq \mid V \mid pq\rangle - \langle pq \mid V \mid qp\rangle\,. \qquad (11)
\end{aligned}$$

As $\langle pp \mid V \mid pp\rangle$ for these systems is of the order of 4 eV, the last three ions are autoionizable, and will exist only in a crystal lattice or in solution. We consider ions in solution. In an ionizing solvent, it is possible to define and measure an oxidation-reduction potential E_n^0 for the process

$$\mathrm{P}_s^{-(n-1)} + e \rightarrow \mathrm{P}_s^{-n}\,, \qquad (12)$$

where the subscript s indicates that the ions are dissolved in the solvent s.

The oxidation-reduction potential can be expressed as

$$-F\,E_n^0 = -A_n + \alpha_{-n} - \alpha_{(n-1)} + C\,, \qquad (13)$$

where α_i is the real free energy of solvation of a species of charge $i\,|\,e_0\,|$, and C is a constant which depends on the particular reference electrode which has been chosen. Absolute values of C are known for some solvents, and could be subtracted from the lefthand side to give $[-C - F\,E_n^0] = -A_n + \alpha_{-n} - \alpha_{-(n-1)}$. Useful information about the solvation terms can be obtained in this way. However, we are interested here only in relative values of E_n^0.

We shall assume that for these ions the dependence of free energy of ion-solvent interaction obeys Born's equation, and is proportional to the square of the ion charge. Then

$$\alpha_{-n} - \alpha_{-(n-1)} = -(1 - 2\,n)\,\alpha_{-1}\,. \qquad (14)$$

The pattern of Fig. 1 shows intervals between successive reduction steps. The potential increments are (writing $F\,(\varepsilon_2^0 - \varepsilon_1^0)$ as $F\,{}^1\Delta^2\,\varepsilon^0$, etc.):

$$\begin{aligned}
-F\,{}^1\Delta^2\,\varepsilon^0 &= A_1 - A_2 + 2\,\alpha_{-1} = \langle pp \mid V \mid pp\rangle - \langle pq \mid V \mid qp\rangle + 2\,\alpha_{-1} \\
-F\,{}^2\Delta^3\,\varepsilon^0 &= A_2 - A_3 + 2\,\alpha_{-1} = 2\,\langle pq \mid V \mid pq\rangle - \langle pp \mid V \mid pp\rangle + \\
&\qquad + \langle pq \mid V \mid qp\rangle + 2\,\alpha_{-1} \\
&\qquad \simeq \langle pp \mid V \mid pp\rangle + \langle pq \mid V \mid qp\rangle + 2\,\alpha_{-1} \\
-F\,{}^3\Delta^4\,\varepsilon^0 &= A_3 - A_4 + 2\,\alpha_{-1} = \langle pp \mid V \mid pp\rangle - \langle pq \mid V \mid qp\rangle + 2\,\alpha_{-1}\,. \qquad (15)
\end{aligned}$$

The approximate form of ${}^2\Delta^3\,\varepsilon^0$ is obtained when the equality sign is used in eq. (9).

Comparison with Experiment

According to these equations, the spacing of oxidation-reduction potentials is:

$$\begin{aligned}
{}^1\Delta^2\,\varepsilon^0 &= {}^3\Delta^4\,\varepsilon^0 \\
{}^2\Delta^3\,\varepsilon^0 &\simeq {}^1\Delta^2\,\varepsilon^0 - \frac{2}{F}\langle pq \mid V \mid qp\rangle\,. \qquad (16)
\end{aligned}$$

For purposes of comparison with the experimental results, we distinguish between species whose prototype molecules are porphin, tetrabenzporphin and tetrazaporphin. The e_g orbitals for these three groups of molecules will naturally be different.

The prediction ${}^1\Delta^2 E^0 \simeq {}^3\Delta^4 E^0$ is well satisfied for Mg octaphenyl TAP (av. ${}^1\Delta^2 E^0$, ${}^3\Delta^4 E^0 - 0.40 \pm 0.04$ V). It is more approximately satisfied for ZnTBP (av. ${}^1\Delta^2 E^0$, ${}^3\Delta^4 E^0 - 0.29 \pm 0.08$ V.) and for the porphins (av. ${}^1\Delta^2 E^0$, ${}^3\Delta^4 E^0 - 0.31 \pm 0.12$), but the magnitudes are certainly comparable and the agreement is probably within the accuracy of the assumptions that have been introduced.

The second prediction is concerned with the difference of disproportionation energies of mononegative and dinegative ions. The relevant data are summarized in Tab. 2. The experimental values of ${}^1\Delta^2 E^0 - {}^2\Delta^3 E^0$ are grouped in the second column. These are of the order of 0.3 eV for the TAP and TBP systems, but the porphin values seem significantly larger. In the third column, theoretical values of $2\,\langle pq \mid V \mid qp\rangle$ are listed for each porphin structure. These have been calculated by Hush and Dodd [7] using interatomic distances derived from Robertson's measurements [11] on phthalocyanine, with the systematic approximations introduced by Pariser and Parr [9]. The orbitals and the values of the heteroparameters used in these calculations have been mentioned briefly in ref. [6]. and will be described in detail elsewhere. The numerical agreement is seen to be quite good. It is stressed, however, that the primary purpose of this paper is to give a general interpretation of the observed relative ion stabilities. Further discussion of these quantities must await more detailed SCF calculations, and also a more detailed consideration of solvation terms*.

Table 2. *Experimental and theoretical values of* ${}^1\Delta^2E^0 - {}^2\Delta^3E^0$ *for porphins. Values of exchange integrals* $\langle pq \mid V \mid qp \rangle$ *are those calculated for the prototype molecules porphin, tetrabenzporphin and tetraazaporphin respectively (see text)*

System	${}^1\Delta^2E^0 - {}^2\Delta^3E^0$ (V)	$2\,\langle pq \mid V \mid qp \rangle$ (eV)
Porphins (averaged)	0.35 ± 0.06	0.54
Zn tetrabenzporphin	0.28	0.22
Mg octaphenyl tetraazaporphin	0.26	0.32

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* Solvation energies of singly-charged radical anions have been recently discussed in ref. [2].

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