Hyperfine Structure in the Electron Spin Resonance Spectra of Reduced Porphins

N. S. Hush[1a] **and J. R. Rowlands**[1b]

Contribution from the Department of Inorganic Chemistry, Bristol University, Bristol, England, and Southwest Research Institute, San Antonio, Texas 78206.
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Abstract: Electron spin resonance spectra with well-resolved hyperfine structure have been obtained by reduction of zinc tetrabenzporphin and zinc etioporphyrin I with sodium in tetrahydrofuran solution. Hyperfine structure has also been observed in the spectrum obtained from etioporphyrin I under the same conditions. The paramagnetic species in each case is considered to be either a trinegative ion of the porphyrin or a phlorin dianion PH^- in which a hydrogen atom is attached to a methine carbon atom of the porphyrin skeleton.

Electron addition to porphin (P) or metal porphin (MP) molecules leads to the formation of a series of negative ions of increasing charge. Closs and Closs[2] studied the reduction of zinc $\alpha,\beta,\gamma,\delta$-tetraphenylporphin in tetrahydrofuran and prepared salts of the mononegative and dinegative ions, corresponding to uptake of one and two electrons, respectively. Dodd and Hush[3] have reported the formation of mono- and dinegative ions of complexes of a variety of substituted porphins, including metal derivatives of etioporphyrin, tetraphenylporphin, tetraazaporphin, tetrabenzporphin, and phthalocyanine. Evidence of two further one-electron steps, corresponding to the formation of trinegative and tetranegative ions, has been obtained by Clack and Hush.[4] Felton and Linschitz[5] have also reported polarographic results on tetraphenylporphin and etioporphyrin complexes which are in agreement with those of ref 3. Recent work on the reduction of metal phthalocyanines[6] shows that salts of negative ions containing from one to four additional electrons can be isolated from solution.

The typical molecular symmetry of divalent metal complexes of porphins is D_{4h}. In some complexes the symmetry is lower, usually because the central metal atom lies slightly out of the plane of the ring. However, perturbations of this type are small and in either case the lowest empty ligand orbital has e symmetry. This means that up to four electrons can be accommodated in this orbital, in agreement with the experiment. An interesting feature of these ions is that the energies of

$$2MP^- \longrightarrow MP + MP^{2-}$$
$$2MP^{2-} \longrightarrow MP^- + MP^{3-}$$
$$2MP^{3-} \longrightarrow MP^{2-} + MP^{4-}$$
$$(MP = \text{metal porphin})$$

the disproportionation reactions are positive and remarkably constant over a range of porphin structures whose M^{II} is a closed-shell ion. An interpretation of this in terms of electron interaction energies has been given by Hush.[7] It should also be mentioned that for some divalent transition metal porphins[5,6] and phthalocyanines[8,9] the first reduction step corresponds to reduction of the metal to the +1 oxidation state; in subsequent steps, this is followed by electron addition to the ring, forming M^IP^{2-} ions, which are the analogs of the $M^{II}P^-$ ions of porphin complex of closed-shell metal ions. These will not be further considered here, as they present special problems of interpretation.

The purpose of this communication is to present some results of measurements of the electron spin resonance spectra of solutions containing reduced porphins.

Closs and Closs[2] established that salts of tetraphenylporphin$^-$ and tetraphenylporphin^{2-} were respectively paramagnetic and diamagnetic in tetrahydrofuran. Similar results have been found in the phthalocyanine series, both for phthalocyanine itself and for closed-shell metal complexes.

The electron spin resonance spectra of a number of mononegative ions of tetraphenylporphin and etioporphyrin derivatives, mostly obtained by electrolytic reduction in dimethyl sulfoxide solution, have been reported by Felton and Linschitz.[5] These exhibit no hyperfine structure and have g values which, although close to the free-spin value, deviate by small but significant amounts in a number of complexes. Similar results have been obtained for metal phthalocyanine negative ions in dimethylformamide solution,[6] also obtained by electrolytic reduction. The lack of hyperfine structure in these spectra has been explained on the basis that the electron is in a doubly degenerate orbital and that the separation of the hyperfine lines in the monoanion in which the spin density is averaged by "fast switching" perturbations (internal or external) to reflect the molecular symmetry is predicted to be smaller than individual line widths.

We have observed similar single-line electron spin resonance spectra of porphin mononegative ions obtained by reduction with sodium metal in tetrahydrofuran solution. The solutions (10^{-3}–10^{-4} M) were prepared by a technique described elsewhere.[9] The electron spin resonance measurements were made at room temperature using a Varian V-4500 X-band spectrometer. Three molecules have so far been studied: zinc tetrabenzporphin, zinc etioporphin I, and etioporphin I (Figure 1). For the latter molecule, the initial reaction with sodium is replacement of the two central ring hy-

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[1] (a) Bristol University, Bristol, England. (b) Southwest Research Institute, San Antonio, Texas.

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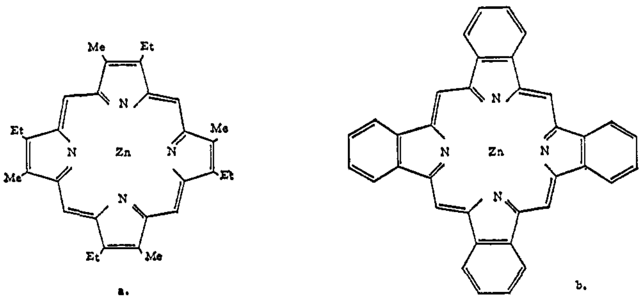

Figure 1. (a) Zinc etioporphyrin I; (b) zinc tetrabenzporphyrin.

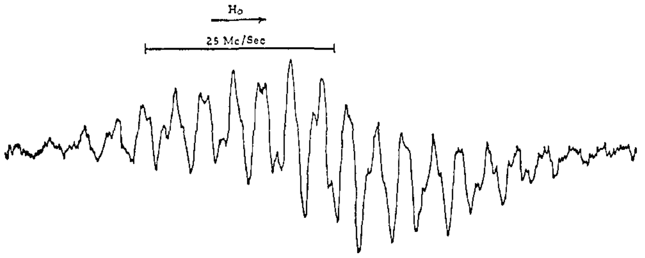

Figure 2. Hyperfine structure of reduced zinc tetrabenzporphyrin.

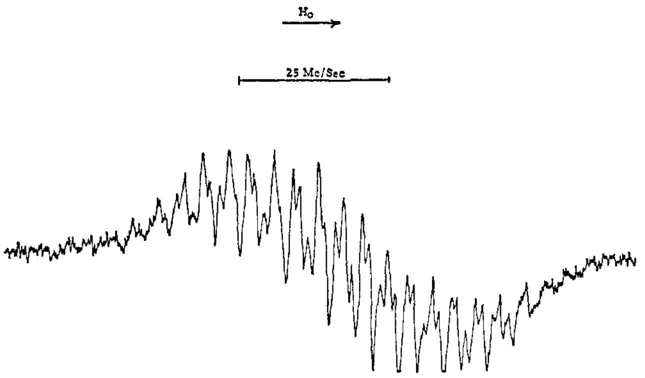

Figure 3. Hyperfine structure of reduced zinc etioporphyrin.

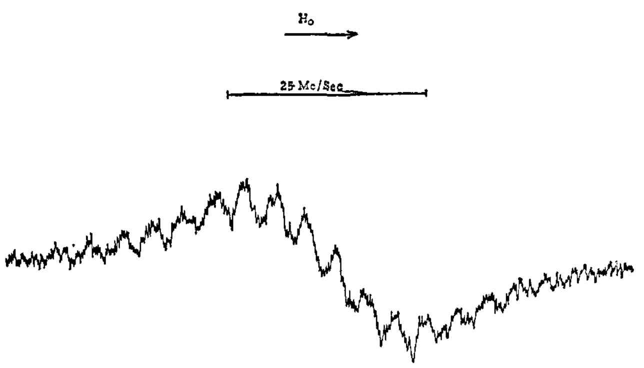

Figure 4. Hyperfine structure of reduced etioporphyrin I.

drogen atoms;[3] reduction of the disodium complex then proceeds in successive one-electron steps.

When the reduction was allowed to proceed past the mononegative ion stage in dilute solution, different results were obtained. In this case, the electron spin resonance spectra of the solution began to exhibit hyperfine structure, which was better resolved as the reduction proceeded.

The course of the reaction was qualitatively followed by observing the characteristic color changes.[3] Thus, for zinc etioporphyrin, hyperfine structure appeared when the green mononegative ion was almost entirely converted to the crimson dinegative ion. The spectra obtained for zinc tetrabenzporphin and zinc etioporphyrin solutions are shown in Figures 2 and 3, respectively. These exhibit similar hyperfine patterns. The spectrum obtained from etioporphyrin solutions (Figure 4) is not so well resolved as the previous two.

The first possibility to consider is that these spectra are those of ions produced by the addition of three electrons to the lowest e_g antibonding orbital. It is not immediately obvious, however, why the trinegative ion MP^{3-} should yield an electron spin resonance spectrum with hyperfine structure whereas both we and other workers[5] have shown that the mononegative ion gives a single-line electron spin resonance spectrum with no observable structure. Furthermore, the observed structure is not compatible with that predicted for a MP^{3-} ion. As in the MP^- ion (as mentioned above) the three electrons in the trinegative ion MP^{3-} are in a doubly degenerate orbital,[3] and the spin density distributions will depend on the type of external or internal perturbation coupling the two components. The average separation of the lines predicted[5] for a system frozen into the e_{gx} (or e_{gy}) configuration for an average configuration $(1/\sqrt{2})(e_{gx} + e_{gy})$, or for "rapid switching" between the two components, is less than line widths usually observed for ions with ^2E ground states. Nevertheless, our observed spectra for zinc tetrabenzporphin and zinc etioporphyrin (Figures 5 and 6, respectively) are at least compatible with the interaction of an unpaired electron with four equivalent nitrogen atoms and four equivalent protons with coupling constants as in Table I, if some allowance is made for some minor inconsistencies in the relative intensity distributions. These discrepancies could well arise from incomplete averaging to zero of both the anisotropic hyperfine interactions and quadrupole interactions. The poor agreement between the computed spin density distribution and the observed could well arise from the fact that no attempt has been made to allow for configuration interaction.

Table I. Observed and Calculated Hyperfine Splittings[a]

	Obsd, gauss	Calcd, gauss	
		$\delta = 0$	$\delta = 1.0$
Zinc tetrabenzporphyrin	A_N 2.59		
	A_H 1.55		
Zinc etioporphyrin I	A_N 2.62	1.36	0.725
	A_H 1.63	2.25	2.58

[a] Calculated values were taken from ref 4.

A second possibility to be considered is that the ion giving rise to the observed structure is the phlorin dinegative ion. It is known from previous work[2,3] that the dinegative ions are relatively easily protonated, and that even in apparently aprotic solvents it is difficult to obtain dilute solutions of the dinegative ions of porphins free from protonated species. Protonation of the dinegative ion of zinc α,β,γ,δ-tetraphenylporphin in tetrahydrofuan leads to the formation of a salt of the phlorin anion $ZnPH^-$, where the hydrogen has added

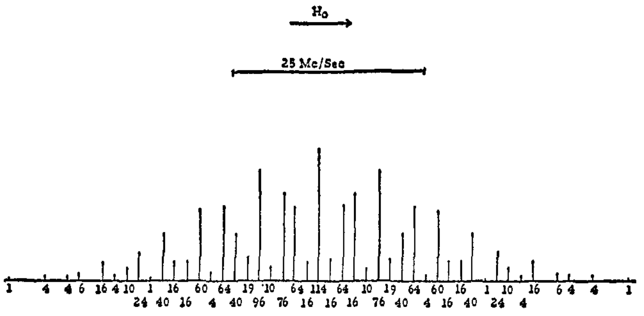

Figure 5. Synthesized spectrum using coupling constants as in Table I.

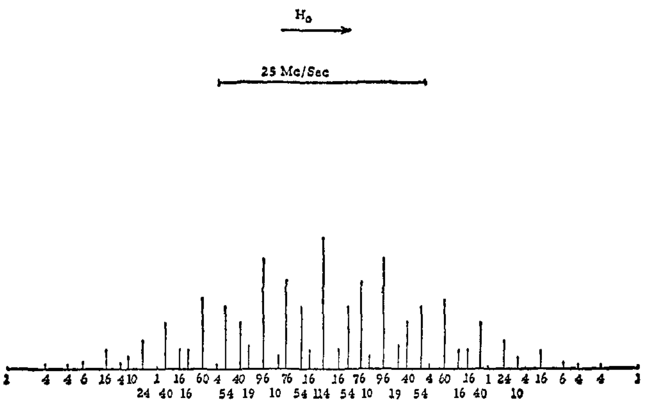

Figure 6. Synthesized spectrum using coupling constants as in Table I.

to a methine carbon atom. The same product is obtained[2] by protonation of the mononegative ion, which disproportionates according to

$$2ZnP^- + H^+ \longrightarrow ZnP + ZnPH^-$$

This is likely to be a general reaction for porphin anions. The phlorin salts and the corresponding dihydroporphin into which the phlorin anion is slowly converted on further protonation are well known. The anion MPH^- or PH^-, which has C_{2v} symmetry, is itself diamagnetic. However, it should reduce relatively easily to the phlorin dianion MPH^{2-} (or PH^{2-}) by uptake of one electron, as simple Hückel calculations show that the lowest empty orbital has binding energy -0.2567β, exactly equal to that of the lowest empty e_g level of porphin itself (see Figure 7 for details of parameters).

It is not accidental that the porphin e_g energy level also occurs in the energy spectrum of the protonated species within the framework of Hückel theory. It is easily shown that doubly degenerate energy levels E_i of an n-center system A will each occur once in the $(n - 1)$-center system A′ derived from A by removal of one of the centers. Furthermore, where the wave functions $|e_i\rangle$ of A, with real components $|e_{1i}\rangle$ and $|e_{2i}\rangle$, are written as linear combination of one-center functions $|\phi_j\rangle$, *i.e.*

$$|e_{1i}\rangle = \sum_{j=1}^{A} C_{1ij}|\phi_j\rangle$$

$$|e_{2i}\rangle = \sum_{j=1}^{A} C_{2ij}|\phi_j\rangle$$

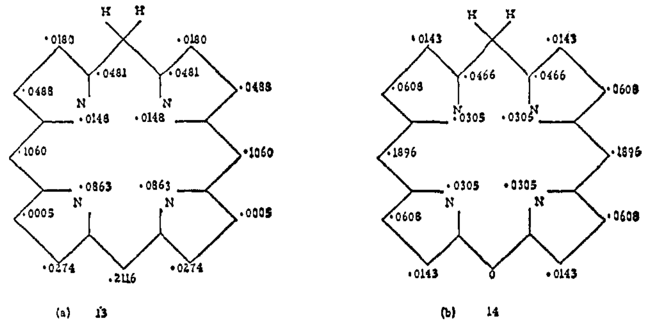

Figure 7. Charge distribution in orbitals 13 (a) and 14 (b) of the porphin phlorin anion values obtained with Hückel parameters $a_N = a_C + 0.66\beta_{CC}$; $\beta_{CN} = \beta_{CC}$.

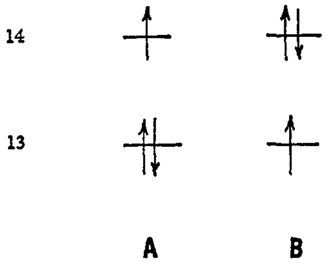

Figure 8. Hückel ground state (A) and excited state (B) for the phlorin dianion (PH^{2-}) (highest two orbitals only).

the orbital $|i(A')\rangle$ of A′ with energy E_i is given by

$$|i(A')\rangle = \frac{1}{\sqrt{1 + \lambda^2}}\{|e_{1i}\rangle + \lambda|e_{2i}\rangle\}$$

where $\lambda = -C_{1ij}|C_{2ij}$.

Explicit calculations show that this is also the lowest empty level of the phlorin anion PH^-. On a one-electron approach, therefore, the half-filled orbital of the phlorin dianion PH^{2-} will be a particular linear combination of the components of the lowest empty porphin e_g level. The charge distribution in this level, *i.e.*, level 14, is shown in Figure 7b for the phlorin with a porphin skeleton.

The distribution in this orbital will give rise to a complex hyperfine pattern, which does not appear to be compatible with any observed. One reason for this may be that configuration interaction has not been taken into account. It is known that the formation of porphin dinegative ions P^{2-} or MP^{2-} from porphin is not satisfactorily described as addition of two electrons to the lowest porphin e_g level. If this were so, the ground state would be a triplet, and the fact that it is, in all cases so far examined, a singlet state shows that configuration interaction with excited states is important in determining the ground-state properties. It is equally likely that the ground state of PH^{2-} is strongly influenced by configuration interaction. It is even possible that the ground state may be the Hückel excited state b in Figure 8 in which an electron has been promoted from the penultimate doubly filled level. The Hückel energy difference between these levels is 0.3131β for the phlorin dianion derived from porphin. However, even this possibility would lead to a calculated hyperfine spectrum which is not compatible with the observed spectra. Taking the values $Q_H = 25$ gauss, $Q_N = 30$ gauss, $Q_{CH_2} = 35$ gauss, the hyperfine constants for the three methine hydrogen atoms (Q_H), the nitrogen atom (Q_N), and the methylene group (Q_{CH_2}) are $A_H = 2[65(2)]$, $5[29(1)]$, $A_N = 2[61(2)]$, and $A_{CH_2} = 6[79(2)]$ gauss, respectively. In computing the methylene coupling we have taken the spin density to be proportional to the square of the sum of the coefficients of the H orbital at each carbon atom, *i.e.*, of the form $Q(C_1 + C_2)^2$ rather than $Q(C_1^2 + C_2^2)$.[8] These couplings would lead to a spectrum with a width of 40 gauss which is far in excess of the experimental spectrum. Furthermore, in order to fit the total number of lines observed, further hyperfine interactions with peripheral methylene groups would have to be invoked, which would make the situation worse.

It is clear on the basis of this discussion that much further experimental work on a range of substituted porphin structures must be carried out before definitive analysis can be attempted. It is also clear that simple Hückel spin density calculations are not sufficiently accurate for meaningful theoretical predictions to be made of the nature of these porphyrin reduction products.

We note in conclusion that Mauzerall and Feher[10] have obtained a transient paramagnetic radical by irradiation of porphin–phlorin mixtures in glycerine solution. This is probably the neutral phlorin radical PH. The identification of intermediates of this type is essential for an understanding of porphin oxidation–reduction reactions, and for an understanding of the electron spin resonance signals observed in photosynthetic materials.[11]

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Photochemical Conversion of 7-Methoxycycloheptatriene to 1-Methoxybicyclo[3.2.0]hepta-3,6-diene[1]

G. W. Borden,[2a] O. L. Chapman, R. Swindell,[2b] and T. Tezuka

Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010.

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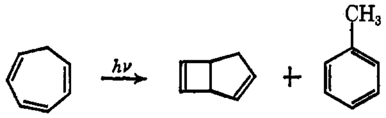
Abstract: The photochemical conversion of 7-methoxycycloheptatriene to 1-methoxybicyclo[3.2.0]hepta-3,6-diene is shown to involve initial photoisomerization to 1-methoxycycloheptatriene followed by photochemical valence isomerization to the bicyclic product. Irradiation of 1-methoxycycloheptatriene gives 7-methoxycycloheptatriene and the bicyclic valence tautomer. The sigmatropic reactions of order [1,7] involved in the interconversion of 7-methoxycycloheptatriene and 1-methoxycycloheptatriene are shown to arise from singlet states. The 1,7-hydrogen shift by which 1-methoxycycloheptatriene is converted to 7-methoxycycloheptatriene is remarkably specific. No 2-methoxycycloheptatriene could be detected. The photochemical valence tautomerization of 1-methoxycycloheptatriene to 1-methoxybicyclo[3.2.0]hepta-3,6-diene is shown to arise from a singlet state of the triene.

Photoisomerization of cycloheptadienes, cycloheptatrienes, and tropolones to unsaturated derivatives of bicyclo[3.2.0]heptane is one of the most generally applicable photochemical reactions.[3] Irradiation of cycloheptatriene gives both toluene and bicyclo[3.2.0]hepta-2,6-diene.[3,4] Toluene is the major product in the vapor phase[4] and the bicyclic valence tautomer in solution.[5] Irradiation of certain substituted cycloheptatrienes gives isomeric cycloheptatrienes by 1,7-hydrogen shifts.[6-8] Thermal isomerization of cycloheptatrienes gives rise to 1,5-hydrogen shifts which lead to isomeric cycloheptatrienes when substituents are present.[9] More complex thermal isomerizations are observed with 7,7-disubstituted cycloheptatrienes.[10]



We now wish to report a photoisomerization reaction which is anomalous both in solution and in the vapor phase with respect to the behavior of cycloheptatriene. Irradiation of 7-methoxycycloheptatriene or 7-ethoxycycloheptatriene in ether solution gives in each case the 1-alkoxybicyclo[3.2.0]hepta-3,6-diene. Yields in excess of 90% have been obtained, and vpc and nmr analysis of the crude reaction mixture shows that the reactions are essentially quantitative.

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