MAGNETIC RESONANCE IN CHEMISTRY, VOL. 35, 566–570 (1997)

EPR and ENDOR on Chlorin Anion and Cation Radicals: Electronic Structure of Models for Photosynthetic Electron Transfer

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Porphyrins are widely used as electron donors in model systems for electron transfer in primary processes of photosynthesis. More recently, chlorins, whose π electron system is more similar to that of chlorophylls, have become available in model compounds. In this study, the electronic structure of 5,10,15,20-tetraphenylchlorinatozinc (ZnTPC) was investigated using electron paramagnetic resonance and electron nuclear double resonance. The orbitals involved in the charge separation and recombination process were studied by performing measurements on the anion and cation radical, respectively. The experimental results were compared with semi-empirical RHF-INDO/SP calculations. On the basis of the results, suggestions for the optimal design of model systems with long-lived charge-separated states are made. The influence of the linking position on the efficiency of charge separation is shown. Ratios of 30:1 are calculated for the efficiencies expected for different linking positions. © 1997 by John Wiley & Sons, Ltd.

Magn. Reson. Chem. 35, 566–570 (1997) No. of Figures: 3 No. of Tables: 2 No. of References: 24

Keywords: EPR; ENDOR; chlorin; anion radical; cation radical; semi-empirical MO calculations; electron transfer

Received 27 January 1997; accepted 6 March 1997

INTRODUCTION

The electronic structure of porphyrins and porphyrin derivatives has attracted scientific interest for several decades. One of the reasons is their biological relevance, be it by transporting oxygen in blood or acting as electron carriers in photosynthesis. The latter aspect is focused on in this paper. In photosynthesis, chlorophylls are primarily involved in photoinduced electron transfer (ET) in the light reactions (primary processes). Biomimetic model compounds to study these events often use porphyrins as light-induced electron donors (D) which are linked to electron acceptors (A). More recently, chlorins, whose π electron system is more similar to that of chlorophylls, have become available in model compounds. In the present study we investigated the electronic structure of chlorins with two main goals: to determine whether the efficiency of the model compound can be improved by making use of the electronic structure, and to elucidate whether the difference in the electronic structures of porphyrins and chlorins can be significant with regard to their respective performances in model compounds.

Optimization refers to high yields and long lifetimes of the charge-separated state (D^+–A^-) of the model compound. This means that the electron transfer rate (k_{ET}) for forward electron transfer (charge separation) (k_{CS}) should be fast, and that the rate for charge recombination to the ground state (k_{CR}) should be slow. According to the Fermi golden rule expression for electron transfer, k_{ET} is given by[1,2]

$$k_{ET} = \frac{2\pi}{\hbar} v_{el}^2 FC \tag{1}$$

where FC is the sum of the Boltzmann weighted Franck–Condon factors and v_{el} is the electronic matrix element. v_{el} depends on distance and orientation of D and A and on their electronic structure. In light-induced electron transfer both frontier orbitals (HOMO and LUMO) of D are involved, the LUMO for charge separation and the HOMO for charge recombination. Consequently, the distribution of these orbitals over D is of interest, and it will have an effect on the efficiency of the model compound. In analogy with the approach used in a related study,[3] we investigated molecular orbitals by measuring the hyperfine (hf) interaction of the unpaired electron with magnetic nuclei by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) methods on the π radicals. The isotropic hf coupling constants (hfcs) determined by EPR and ENDOR on radicals in solution can be related to the MO coefficients. For a given porphyrin or chlorin, HOMO and LUMO are obtained by measuring the cation and anion radicals, respectively. Once both radicals have been characterized, HOMO and LUMO coefficients at individual molecular positions

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* *Correspondence to*: M. Huber.

Contract grant sponsor: Deutsche Forschungsgemeinschaft; *Contract grant number*: SFB 337.
Contract grant sponsor: Fonds der Chemischen Industrie.

CCC 0749–1581/97/090566–05 $17.50

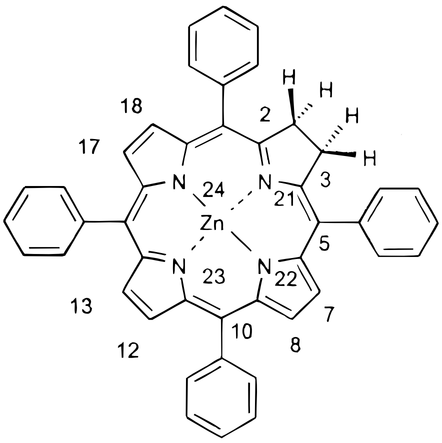

Figure 1. Structure of 5,10,15,20-tetraphenylchlorinatozinc (ZnTPC) and numbering of the positions.

can be determined. This will be the basis for predicting the efficiency of a model compound as a function of the position to which A is linked to D.

In this paper, EPR and ENDOR spectroscopy of cation and anion radicals of 5,10,15,20-tetraphenylchlorinatozinc (ZnTPC; Fig. 1) and the interpretation of the spectra using semi-empirical MO calculations are described. This is followed by a discussion on how these results can be correlated with ET properties and expected efficiencies. A comparison between the electronic structures of chlorins and porphyrins investigated in a related study[3] allows the usefulness of either in model compounds to be evaluated.

EXPERIMENTAL

The synthesis of the 5,10,15,20-tetraphenylchlorinatozinc (ZnTPC) was performed by H. Mößler (AG Kurreck, Free University Berlin).[4] The purity was confirmed by optical spectroscopy.

THF and CH_2Cl_2 were of spectroscopic grade (Merck). THF was dried with sodium–potassium alloy and CH_2Cl_2 with CaH_2.

Chemical reduction of ZnTPC

The samples were reduced chemically with metallic sodium in tetrahydrofuran (THF) in sealed glass vessels under high-vacuum conditions as described previously.[5,6] In the case of the reduction of ZnTPP with sodium, in a side-reaction the central metal ion Zn^{2+} is replaced by two sodium ions.[7] This side-reaction is suppressed by adding a crown ether (18-crown-6). Since for ZnTPC the EPR and ENDOR spectra were identical irrespective of whether the sample was prepared with crown ether (18-crown-6); this replacement reaction does not seem to occur in ZnTPC. Optical spectra taken before reduction and after reoxidation of the reduced sample by air were virtually identical, showing that reduction was reversible. Samples were approximately 5×10^{-4} mol l^{-1} in ZnTPC.

Chemical oxidation of ZnTPC

ZnTPC was oxidized using an eight-fold molar excess of iodine in CH_2Cl_2. Samples were prepared under high-vacuum conditions as described above. Larger amounts of iodine or addition of $AgClO_4$ result in EPR spectra suggestive of the ZnTPP cation radical, indicating that under these conditions the chlorin is oxidized to a porphyrin system. The concentration of ZnTPC was again *ca.* 5×10^{-4} mol l^{-1}.

EPR/ENDOR spectrometer

The ENDOR and TRIPLE spectra were measured on a laboratory-built spectrometer described elsewhere.[8,9] EPR spectra were obtained on a conventional spectrometer (microwave bridge: Varian E102). g Values were calibrated against the known g value of the peri-naphthenyl radical ($g = 2.002\,60 \pm 0.000\,02$).[10]

RESULTS

Anion radical

The EPR spectrum of the anion radical of ZnTPC ($ZnTPC^{-\bullet}$) is shown in Fig. 2(a). It consists of a superposition of individual lines (inhomogeneous broadening), with some residual resolution. Neither the intensity nor the shape of the spectrum changed significantly within the temperature range 180–300 K. The g value of 2.002 00(8) agrees within experimental error with the values reported in the literature.[11] The deviation from a Gaussian lineshape makes it difficult to define a peak-to-peak linewidth as given in the liter-

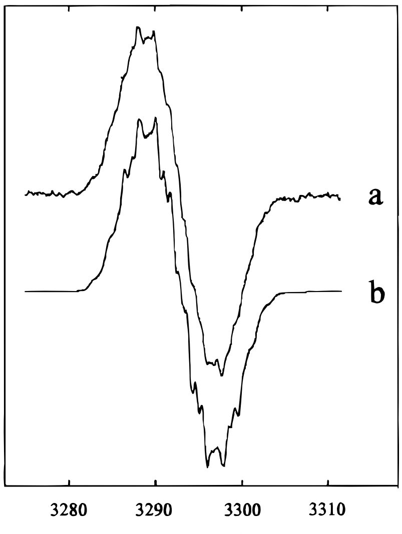

Figure 2. (a) EPR spectrum (first derivative) of $ZnTPC^{-\bullet}$ in THF at room temperature. Microwave power, 2 mW; total measuring time, 80 min. (b) Simulation of the spectrum with hfcs measured using ENDOR. Multiplicities according to the assignments in Table 1. Component linewidth, 0.38 G.

ature, but our value of *ca.* 7 G ($\equiv$0.7 mT) is close to the value of 8.2 G given by Felton and Linschitz.[11] A simulation of the measured spectrum using hyperfine couplings obtained by ENDOR and multiplicities of nuclei obtained from the assignment (see below) is shown in Fig. 2(b). The agreement with the experimental spectrum is very good.

Increased resolution is obtained by ENDOR, where additionally NMR transitions are excited. According to the ENDOR resonance condition:[9,12]

$$\nu_{\mathrm{ENDOR}} = \left| \nu_n \pm \frac{a_{nl}}{2} \right| \tag{2}$$

where ν_n is the Lamor frequency of the free nucleus (for ^{1}H, $\nu_{\mathrm{H}} = 14.00$ MHz, and for ^{14}N, $\nu_{\mathrm{N}} = 1.01$ MHz at 3288 G[12]) and a_{nl} are the hfcs. Each pair of ENDOR lines is displaced symmetrically about ν_n, provided that $\nu_n > a_{nl}/2$.

This is the case for the proton ENDOR spectrum in Fig. 3(b). Six lines corresponding to three hfcs are observed. The corresponding hfcs are given in Table 1.

ENDOR lines associated with the hyperfine interaction of the unpaired electron with nitrogens are expected at lower frequencies. Five ENDOR lines are observed in this spectral region [see Fig. 3(a)]. Lines 4,4′ and 5,5′ are separated by $2\nu_{\mathrm{N}}$. According to the ENDOR resonance condition for $\nu_n < a_{nl}/2$ [Eqn (2)], the corresponding lines are symmetric about $a_{\mathrm{N}}/2$, and thus correspond to the two larger nitrogen hfcs listed in Table 1. Line 6 is the high-frequency line of a small ^{14}N hfc, whose low-frequency counterpart is expected at 90 kHz and therefore cannot be detected for technical reasons. The hfcs are summarized in Table 1.

Table 1. Hyperfine coupling constants (a_{iso}) of ZnTPC anion and cation radicals: experimental values from EPR and ENDOR methods (for details see text)

		a_{iso} (MHz)			
	Numbering	Anion radical		Cation radical	
	of positions[a]	Exp.[b]	Calc.[c]	Exp.[d]	Calc.[c]
^{1}H	8, 17	−5.70	−5.6		−1.1
	7, 18	−4.70	−3.3		−3.9
	2, 3		+1.5[e]	17.1	+19.9[e]
		±0.38			
	12, 13		+0.7		−2.6
^{14}N	21	+7.30	+8.4		+2.0
	23	+5.32	+7.3		+2.8
	22, 24	−2.15	−1.4		+1.6

[a] For numbering see Fig. 1.

[b] From ENDOR in THF, $T = 145$ K. Errors: proton hfcs ±10 kHz, ^{14}N hfcs ±30 kHz.

[c] RHF-INDO/SP method,[18] using mostly standard bond lengths and angles.

[d] From EPR in CH_2Cl_2 at 290 K only the largest hfc is resolved.

[e] Average over all four protons.

In order to aid the assignment of hfcs to individual nuclei, signs of hfcs are useful. The relative signs are obtained by General TRIPLE, an electron–nuclear–nuclear triple resonance method. In the General TRIPLE experiment, the sample is irradiated with a radiofrequency (r.f.) field, whose frequency is resonant with one of the ENDOR transitions of the radical, while the ENDOR spectrum is recorded using the second r.f. frequency.[9,12] The resulting intensity changes reveal the relative signs of the hfcs. For ZnTPC$^{-\bullet}$, the relative signs of all larger hfcs could be determined. Lines 3,3′ do not show significant intensity changes, and therefore are attributed to a superposition of lines having hfcs with opposite signs. The absolute signs of hfcs given in Table 1 are based on a positive sign of the largest ^{14}N hfc, which is chosen for the following reasons.

Spin density is transmitted to the nitrogen via π–σ spin polarization from the spin density in the p_z orbital of the nitrogen atom (ρ_{N}) and from the p_z spin density at neighbouring carbon atoms ($\rho_{\mathrm{C}}, \rho_{\mathrm{C'}}$):[13]

$$a_{\mathrm{N}} = A\rho_{\mathrm{N}} + B(\rho_{\mathrm{C}} + \rho_{\mathrm{C'}}) \tag{3}$$

The exact magnitudes of A and B depend on the type of radical. A can vary from +20 to +30 G and B from −2 to +10 G (1 G $\equiv$ 0.1 mT). This suggests that the largest nitrogen hfc is positive, since a negative hfc

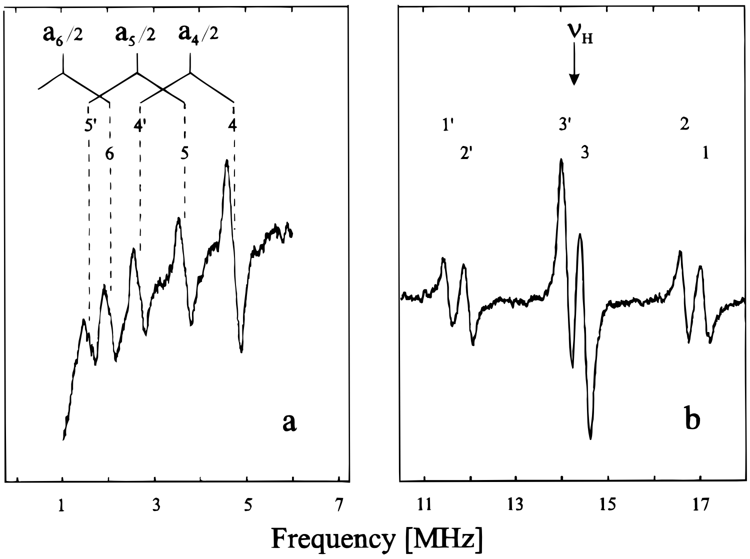

Figure 3. ENDOR spectra (first derivative) of ZnTPC$^{-\bullet}$ in THF at room temperature. (a) ^{14}N ENDOR: microwave power, 13 mW; r.f. power, 130 W; 10 kHz fm (frequency modulation) of the r.f. field with 150 kHz deviation; total measuring time, 40 min. (b) ^{1}H ENDOR: microwave power, 13 mW; r.f. power, 100 W; 10 kHz fm of the r.f. field with 80 kHz deviation; total measuring time, 25 min.

would require unrealistically large positive spin densities (*ca.* 0.8) at neighbouring carbon atoms.

The signs of proton hfcs depend on the sign of the spin density and on the way the proton is linked to the center of π spin density: if a proton is linked directly to a π center (α-proton), a positive spin density results in a negative hfc,[14,15] whereas for a proton separated from the electronic π-system by two bonds (β-proton), the sign must be positive (hyperconjugation).[13,16]

The two largest proton hfcs (hfcs 1 and 2) have a negative sign. Since the corresponding spin density is large it must be positive and, therefore, these hfcs are assigned to α-protons. In ZnTPC α-protons are at positions 7, 8 or 12. The remaining protons (the β-protons at positions 2, 3 and the phenyl protons) are likely to have small hfcs and should contribute to the smallest proton hfc (hfc 3). If all these protons contribute to the ENDOR lines 3,3′, the lack of General TRIPLE response is plausible, since, for example, phenyl protons have hfcs with opposite signs, which can cause cancellation of their General TRIPLE responses.[17]

Semi-empirical MO calculations using the RHF-INDO/SP method[18] were performed to check the assignment. The calculated hfcs are listed in Table 1. The agreement between the calculated and observed hfcs is satisfactory. The multiplicities derived from this assignment yield a good simulation of the EPR spectrum [Fig. 2(b)], whereas other assignments of the nitrogen couplings or some other proton multiplicities could be definitely excluded. The comparison with the hfcs of the structurally similar zincbacteriochlorin anion radical[19] suggests an analogous assignment.

Cation radical

The EPR spectrum of the ZnTPC cation radical is partially resolved into five lines. Its shape and the *g* value of 2.003 01(8) agree well with those published earlier.[20] The intensities of the five-line pattern suggests an interaction of the unpaired electron with four $I = 1/2$ nuclei, i.e. four protons, with an hfc of $a = 6.1$ G. In contrast to the results of Fajer and Davis,[20] the magnitude of this hfc did not change with temperature. The component linewidth of 2.7 G suggests additional small, unresolved hfcs. ENDOR experiments, which would have allowed these hfcs to be resolved, were not feasible, since the EPR transition could not be saturated up to the highest microwave powers available. Non-saturation refers to the signal intensity remaining proportional to the square root of the applied microwave power. This situation persisted even on lowering the temperature and diluting the sample.[13]

The measured hfcs are listed in Table 1. According to MO calculations the largest hfc is assigned to the β protons at positions 2 and 3. The agreement between the calculated and measured values for this hfc is satisfactory, and the assignment agrees with the results of selective deuteration experiments reported by Fajer and Davis.[20] EPR simulation and MO calculations indicate small nitrogen hfcs, suggesting that the HOMO in ZnTPC has an a_{1u} symmetry (although the symmetry of ZnTPC is lower than the D_{4h} symmetry according to which the porphyrin orbitals are classified, we use the labels corresponding to the D_{4h} point group for convenience).[21] Thus, ZnTPC differs from ZnTPP in this respect, since the ZnTPP HOMO has a_{2u} symmetry.

The origin of fast spin–lattice relaxation in ZnTPC$^{+\bullet}$ is unclear. A close energetic proximity of a_{1u} and a_{2u} as discussed by Fajer and Davis[20] can increase the relaxation rate due to the dynamic Jahn–Teller effect,[22] for example.

DISCUSSION

ENDOR experiments on the anion radicals of ZnTPC reveal a detailed picture of the spin density distribution in the LUMO of ZnTPC. The cation radical is less well characterized, but in conjunction with semi-empirical MO calculations a plausible picture of the spin density distribution of the HOMO was obtained. In the anion radical, the degeneracy of the LUMOs expected for porphyrins possessing a fourfold symmetry axis is lifted, and the MO coefficients of the LUMO are given in Table 2. The HOMO has an a_{1u} symmetry, thus differing from the corresponding porphyrin ZnTPP, which has an a_{2u} HOMO.

The close correspondence of the measured and calculated hfcs also provides a test for the quality of the MO calculations in those instances where independent assignments were available. Consequently, HOMO and LUMO wavefunctions are known and can be interpreted in terms of electron transfer properties as discussed in the following. According to electron transfer theory (see Introduction), these MO coefficients enter into the electronic matrix element v_{el} in Eqn (1). Their contribution can be calculated using the molecular orbital overlap approximation introduced by Plato *et al.*[23] for these systems:

$$v_{\mathrm{el}} = K \sum_i \sum_j c_i{}^{\mathrm{D}} c_j{}^{\mathrm{A}} S_{ij}^{\mathrm{DA}} \tag{4}$$

where $c_i{}^{\mathrm{D}}$ and $c_j{}^{\mathrm{A}}$ are the MO coefficients of the relevant orbitals on D and A, respectively, and S_{ij}^{DA} the overlap integrals of the atomic orbitals of atoms of D and A. The latter depend on the distance and orientation of D and A. Thus, in order to calculate absolute

Table 2. MO coefficients of ZnTPC and ratios for different linking positions

Molecular position[a]	Squared p_z orbital coefficients[b] $(c_i^{\mathrm{DLUMO}})^2$	$(c_i^{\mathrm{DHOMO}})^2$	Ratio of squared MO coefficients[c] $(c_i^{\mathrm{DLUMO}}/c_i^{\mathrm{DHOMO}})^2$
8, 17	0.061	0.024	2.5
7, 18	0.046	0.040	1.1
5, 20	0.042	0.018	2.3
2, 3	0.000	0.001	—
10, 15	0.098	0.003	30.3
12, 13	0.011	0.034	0.3

[a] For numbering see Fig. 1.

[b] MO coefficients of singly occupied MO of ZnTPC$^{-\bullet}$ and ZnTPC$^{+\bullet}$ to represent LUMO and HOMO coefficients, respectively, of neutral ZnTPC. Semi-empirical MO method: RHF-INDO; see text.

[c] The squared ratio of MO coefficients $(c_i^{\mathrm{DLUMO}}/c_i^{\mathrm{DHOMO}})^2$ gives the contribution of the electronic structure to $k_{\mathrm{CS}}/k_{\mathrm{CR}}$.

values of v_{el}, summation over pairs of atomic orbitals and wavefunctions would have to be performed. In the present context we are mainly interested in the ratios of rates for CS and CR reactions, i.e. in v_{el}^{CS}/v_{el}^{CR}. Equation (4) can be simplified using the assumptions that conformational changes during electron transfer can be neglected (i.e. S_{ij}^{DA} is constant for CS and CR) and that the MO coefficients of the acceptor orbital remain constant. Under the additional assumption that longer range interactions are negligible, only MO coefficients at the linking position need to be considered. Thus, Eqn (4) reduces to

$$v_{el}^{CS}/v_{el}^{CR} = c_i^{\mathrm{DLUMO}}/c_i^{\mathrm{DHOMO}} \qquad (5)$$

where i refers to the atom at which A is linked to D. Table 2 shows the values obtained for different linking positions. For these calculations, MO coefficients were taken from the results of the RHF-INDO calculations. The fact that ratios $(c_i^{\mathrm{DLUMO}}/c_i^{\mathrm{DHOMO}})^2$ between 1 and 30 are obtained for different linking positions shows that the linking position has some relevance for the efficiency of the model compound. For efficient charge separation the ratio should be large, consequently the acceptor should be attached at the *meso* positions 10 or 15 of the chlorin (see Fig. 1 for the numbering of the positions).

Comparing the expected electron transfer properties of the chlorin with those of the porphyrin donors used more frequently in model compounds the following differences are found. The degeneracy of the LUMO in symmetric porphyrins causes Jahn–Teller distortions, which are absent in the chlorin due to the significantly lower symmetry of the π electron system of the latter. Although we assume that this difference would affect ET properties, the effect of the degeneracy of the LUMOs on electron transfer properties in porphyrins is not understood well enough to be able to draw calculations at this point. With respect to the HOMO, ZnTPP has an a_{2u} orbital, resulting in large overlap integrals for charge recombination at the *meso* positions. The saturated pyrrole ring in the chlorin, on the other hand, favours the a_{1u} orbital in spite of the presence of *meso* phenyl rings, which, in the corresponding porphyrin (ZnTPP), tends to raise energetically the a_{2u} above the a_{1u} orbital.[20,24] Thus, the overlap integrals for charge recombination should be smaller in the chlorin, suggesting a better efficiency for electron transfer in chlorin-based systems.

CONCLUSION

Here and in a related study,[3] an attempt at predicting the ET properties of biomimetic model compounds for the primary processes of photosynthesis has been made. The main goal was to estimate the effect of the electronic matrix element on the efficiency of electron transfer. For the chlorin investigated in the present study a 30-fold increase in the efficiency for specific linking positions is calculated, indicating that the design of model compounds could be aided by the methods proposed. Experimental tests of these predictions are still lacking, however. Nevertheless, chlorin-based model compounds, in which the acceptor is linked to the chlorin *meso* positions via a cyclohexylene bridge, have just been synthesized, and it will be interesting to compare future kinetic data with the predictions made here.

Acknowledgements

We thank H. Kurreck and K. Möbius (Freie Universität Berlin) for providing the support and environment which made this project possible. Help and suggestions by M. Plato (Freie Universität Berlin) concerning MO calculations and theory are gratefully acknowledged. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 337) and the Fonds der Chemischen Industrie (to M.H.).

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