ENDOR Studies of π -Electron Delocalization in Covalently Linked Porphyrin Dimers

Model Systems for the Primary Donor in Photosynthesis?†

Martina Huber‡ and Harry Kurreck

Institute of Organic Chemistry, Free University of Berlin, Takustr. 3, D-1000 Berlin 33, Federal Republic of Germany

Bernd von Maltzan, Martin Plato and Klaus Möbius*

Institute of Molecular Physics, Free University of Berlin, Arnimallee 14, D-1000 Berlin 33, Federal Republic of Germany

The spin density distributions in the cation radicals of various covalently linked tetraphenyl porphyrin dimers and of their monomeric constituents have been studied by liquid-phase EPR, ENDOR and TRIPLE resonance methods to find out whether the dimer systems show intramolecular electron delocalization. Such delocalization is known to occur in the bacteriochlorophyll dimer ('special pair') in photosynthetic reaction centres. The dimers studied in this work are derived from zinc *meso*-tetraphenylporphyrin (ZnTPP) moleties linked either by a phenyl ring at *para* and *meta* positions or by a $-CH_2$ — bridge at *para* positions. ¹H and ¹⁴N hyperfine coupling constants were measured for the dimer and ZnTPP cation radicals. By comparing the hyperfine data it was concluded that in the phenyl-bridged porphyrin dimers the unpaired electron is delocalized over the dimer halves (similar to the 'special pair') whereas in the CH₂-bridged dimer the unpaired electron is localized on one porphyrin unit.

From recent X-ray structure analyses of reaction centres (RCs) of the photosynthetic bacteria Rhodopseudomonas viridis (Rps. viridis)¹ and Rhodobacter sphaeroides (Rb. sphaeroides)² the spatial arrangement of the porphyrin derivatives (e.g. haems and chlorophylls), which act as electrontransfer pigments (cofactors) in the RCs, is known at atomic resolution. A particularly remarkable feature of this arrangement is the existence of a bacteriochlorophyll (BChl) dimer which acts as the primary donor P ('special pair'). In this dimer the BChl molecules are in contact within 3.5 Å and overlap at the pyrrole rings I. An approximate C_2 symmetry, whose axis passes through the dimer, relates the various cofactors (bacterio-chlorophylls and -pheophytins, quinones) in the M and L protein subunits of the RC to each other.^{1,2} From recent ENDOR/TRIPLE and molecular-orbital (MO) studies³ it became clear that the primary donor plays a crucial role in the unidirectionality of the electron transfer along the L branch of the protein.

In order to contribute to a better understanding of the structure-function relationship of the porphyrin-like chromophores in photosynthetic RCs, it is desirable to synthesize covalently linked porphyrin dimers as model compounds for the special pair with well defined distances and orientations. Up to now a large number of porphyrin dimers¶ has been synthesized to serve this purpose.⁴ Common to most of these model compounds is a relatively large separation of the porphyrin macrocycles and conformational flexibility in contrast to the situation in the RCs. Some more rigid model compounds have also been synthesized, *i.e.* porphyrin dimers with short bridges and restricted conformational freedom. Examples are cofacial porphyrin dimers⁵ and dimers in which the porphyrin units are in a fixed pseudo-orthogonal arrangement.⁶ An almost orthogonal arrangement of the various pigments is found along the electron-transfer chain.^{1,2}

In continuation of this work, three novel porphyrin dimers have been synthesized (see scheme 1). While they are based on the same meso-tetraphenylporphyrin (TPP) subunit, distances and orientations of the chromophores differ. For example, two of these dimers (1 and 2) have strong excitonic coupling manifesting itself in a split Soret band in the UV-VIS spectra, whereas the splitting in the third dimer (3) is less pronounced. Since strong excitonic coupling is indicative of the chromophores to be close to each other with a definite orientation,⁷ one can conclude that the conformations of 1 and 2 are almost rigid and thus well defined, while 3 has a larger flexibility and larger centre-to-centre distance. An analysis of the split Soret band in UV-VIS spectra in terms of possible porphyrin dimer conformations with a model of interacting extended dipoles will be given elsewhere.7

EPR and, in particular, ENDOR measurements on the oxidized primary donor P⁺⁺ in bacterial RCs have shown that the unpaired electron is delocalized over both BChl halves of the dimer, indicating strong π - π interaction of the BChl molecules.^{8,9} The same methods have been used to study the spin-density distribution in model dimers, such as the anion radical of phanes in which two aromatic ring systems, *e.g.* benzene, naphthalene, chlorophyll, are connected by bridges of varying length.¹⁰⁻¹² It was found that delocalization occurs only if the interplanar separation is not too large, *e.g.* if the bridge is not longer than three methylene groups.^{10,11} To our knowledge, there exist only two publications so far in which a delocalization of the unpaired electron in doubletstate porphyrin dimers was suspected from the results of EPR measurements.^{13,14} One of the porphyrin dimers investigated was a singly linked chlorophyll dimer,¹³ the other a doubly

[†] In part presented at the 21st Annual ESR Conference of the Royal Society of Chemistry, Cardiff, 1988.

[‡] Present address: University of California, San Diego, Department of Physics B-019, La Jolla, CA 92093, USA.

[¶] Although the term 'dimer' normally implies that the unit has exactly twice the molecular weight of the monomer, it is common use in the literature to apply this term also for π -electron systems linked by a spacer group when the spectroscopic properties of the unit are dominated by the π -electron distribution and interactions in the monomeric halves. Since the covalently linked porphyrins belong to this category, we use the 'dimer' nomenclature throughout this paper.





Scheme 1

linked phane-like porphyrin dimer.¹⁴ In the case of the doubly linked porphyrin,¹⁴ however, it was concluded that dimer aggregates are formed and that delocalization is *inter*-molecular rather than *intra*molecular between the dimer halves.

In the present study we report on the spin-density distribution in the cation radicals of dimers 1-3 obtained by highresolution ENDOR and TRIPLE resonance methods.¹⁵ These results are compared with the spin-density distribution in the cation radical of zinc *meso*-tetraphenylporphyrin (ZnTPP) which represents the monomeric subunit of the dimers 1-3.

Recently, a porphyrin dimer similar to 1 has been synthesized by Heiler *et al.*¹⁶ *via* a different method. Their dimer halves are also linked by a phenyl ring, but the interlinked porphyrins are of the octaethyl type. Steric hindrance of the β -alkyl groups should lead to an orthogonal arrangement of the phenyl ring relative to the porphyrin planes,¹⁶ whereas for dimer 1 steric strain is less pronounced and a nonorthogonal configuration is expected from molecular models.

Monomeric ZnTPP⁺⁺ was investigated earlier by Fajer *et* $al.^{17,18}$ Their EPR study revealed that the cation radical has a ${}^{2}A_{2u}$ ground state in which spin density is mainly localized at the nitrogens and *meso*-carbon atoms. The ${}^{14}N$ hyperfine coupling (hfc) could be determined, but the much smaller proton hfc values were beyond the spectroscopic resolution of EPR. The higher resolution of ENDOR prompted us to reinvestigate also monomeric ZnTPP⁺⁺ in liquid solution. A proton ENDOR spectrum of ZnTPP⁺⁺ in frozen solution was published recently by van Willigen *et al.*¹⁹ In the solid state, however, anisotropic hyperfine contributions broaden the ENDOR lines to the extent that no hyperfine analysis could be given.

Experimental

ZnTPP was synthesized according to ref. (20); the synthesis of 1-3 will be described elsewhere.²¹ All solvents used were of spectroscopic grade. Methylene chloride was dried over calcium hydride, tetrahydrofuran (THF) over Na-K alloy.

The cation radicals of ZnTPP were prepared electrochemically in CH₂Cl₂ with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Alternatively, for ZnTPP and dimers 1–3 chemical oxidation was performed using a 1:1 mixture of AgClO₄ and iodine²² in CH₂Cl₂ or in a CH₂Cl₂-THF 9:1 or 8:2 (vol/vol) solvent mixture. Sample preparation was executed in sealed glass vessels under highvacuum conditions. The solutions were 5×10^{-4} mol dm⁻³ in porphyrin concentration.

In order to control one-electron and formal 'two-electron' oxidation (see Results and Discussion), the amount of oxidizing agent (AgClO₄/I) was varied relative to the dimer concentration in three separate experiments using: (i) a deficit of oxidizing agent ($20 \pm 10\%$ less than equimolar amounts of AgClO₄/I and dimer), (ii) equimolar amounts and (iii) an excess of oxidizing agent (two equivalents of AgClO₄/I per mol dimer). Additional evidence for a distinction between one- and two-electron transfer processes in the porphyrin dimers was obtained from cyclic voltammetry.^{4g} We used cyclic voltammetry to study the redox properties of the dimer 1, as an example (solvent CH₂Cl₂-THF 9 : 1 vol/vol; TBAP as supporting electrolyte; working electrode, platinum; auxiliary electrode, steel; reference electrode, Ag/AgCl).

EPR spectra were recorded on a Bruker (ER 200D) spectrometer, and ENDOR and TRIPLE resonance experiments were performed on a laboratory-built spectrometer described earlier.²³ For cyclic voltammetry commercial instrumentation (Metrohm Polarrecord E 506) was used.

Results and Discussion

Monomer ZnTPP' *

Conclusions about localization vs. delocalization of the unpaired electron in the dimers 1^{++} , 2^{++} and 3^{++} are based on the comparison with the spin density distribution in the monomeric subunit ZnTPP'⁺.

In ZnTPP the four types of symmetry-equivalent protons are eight *ortho*, eight *meta*, four *para* protons of the phenyl substituents and eight pyrrole ring protons (β) [compare fig.



Fig. 1. EPR spectra of ZnTPP'⁺ in CH₂Cl₂, counterion ClO₄⁻, at room temperature (a) and at 200 K (b). Computer simulation of spectrum (a) (dotted curve) involves four equivalent nuclei of I = 1 with hfc a = 1.46 G and a Gaussian single component linewidth of $\Delta B_{pp} = 1.42$ G which contains the unresolved proton hyperfine structure (1 G = 0.1 mT = 2.80 MHz). Computer simulation of spectrum (b) [curve (c)] involves four nuclei of I = 1, a = 1.50 G; eight nuclei of I = 1/2, a = 0.07 G; eight nuclei of I = 1/2, a = 0.28 G; eight nuclei of I = 1/2, a = 0.33 G; four nuclei of I = 1/2, a = 0.41 G; $\Delta B_{pp} = 0.20$ G.

2 (later)]. The EPR spectrum of ZnTPP⁺⁺ is shown in fig. 1. At room temperature [fig. 1(*a*)], it consists of a broad nineline pattern at $g = 2.0027 \pm 0.0001$. At 200 K [fig. 1(*b*)] it shows additional hyperfine structure. In the proton ENDOR spectrum (see fig. 2) six lines can be resolved which are located symmetrically around the Larmor frequency of the free proton, $v_{\rm H}$ ($v_{\rm H} = 14.36$ MHz in our X-band experiment). According to the ENDOR resonance condition¹⁵ for a doublet-state radical,

$v_{\text{ENDOR}}^{\pm} = |v_n \pm a/2|$

where v_n is the nuclear Larmor frequency, each pair of lines is separated by the isotropic hfc, a_i . At 3.1 MHz, the highfrequency ENDOR line of the ¹⁴N nuclei was also detected. The ¹⁴N ENDOR lines are centred around a(N)/2 with a separation of $2v_N$, since $|a(N)/2| > v_N$ (Larmor frequency of the free ¹⁴N nucleus, $v_N = 1.01$ MHz). The corresponding

-1.16

-121



Fig. 2. ENDOR (a) and Special TRIPLE (b) spectra of ZnTPP⁺⁺ in CH₂Cl₂, m.w. power 90 mW; ENDOR (13–16 MHz): temperature (T) 200 K, r.f. power 40 W, 10 kHz f.m. of r.f. field with \pm 30 kHz deviation, total measuring time (t) 30 min; ENDOR (2–4 MHz): T = 254 K, r.f. power 150 W, f.m. deviation \pm 100 kHz, t = 15 min; Special TRIPLE: T = 188 K, r.f. power 40 W each r.f. channel, f.m. deviation \pm 14 kHz, t = 20 min. Owing to the r.f. irradiation scheme applied in Special TRIPLE resonance, the lines appear at frequencies of a/2 separated from the origin of the r.f. frequency axis which corresponds to $v_{\rm H}$ in an ENDOR experiment.^{15c}

low-frequency ENDOR component at *ca.* 1 MHz could not be detected because of intensity problems due to the low hyperfine enhancement of the applied radiofrequency field.²⁴ The ¹⁴N hfc obtained is in good agreement with the value given by Fajer *et al.*¹⁷

Improved resolution of the proton hyperfine structure was obtained by Special TRIPLE, an electron-nuclear-nuclear

0.60^e

1.16

clei ^f	MgTPP' + calculated ^a hfc/MHz	ZnTPP' ⁺ experimental hfc/MHz			1 ^{°+} experimental	2 ^{•+} experimental	3 ^{•+} experimenta
		CH ₂ Cl ₂ ^b	CH ₂ Cl ₂ -THF ^c	nuclei	CH_2Cl_2 -THF ^d	CH_2Cl_2 -THF ^d	CH ₂ Cl ₂ -TH
'N	+ 3.24	+ 4.20	+4.38	¹⁴ N	2.20	2.10	4.17
β	-0.36	-0.20	(-0.10)				
m	+1.47	+ 0.79	+0.80		0.42	0.41	0.75
n	_0.96	_093	0.90	1 H		0.92	

0.61

 Table 1. Experimental and calculated hyperfine couplings (hfcs)

^{*a*} Method: RHF-INDO/SP,²⁶ hfcs calculated from s-spin densities using $a = Q\rho_s$ with Fermi contact parameters $Q_H = 1420$ MHz and $Q_N = 650$ MHz. ^{*b*} ¹H hfcs from Special TRIPLE (T = 193 K), ¹⁴N hfc (T = 254 K) from ENDOR. Accuracy of ¹H hfc: ± 20 kHz, of ¹⁴N hfc: ± 80 kHz. Relative signs from General TRIPLE; absolute signs based on an assumed positive ¹⁴N hfc. ^c Solvent: CH₂Cl₂-THF 9:1 vol/vol. Magnitude of β hfc uncertain due to poor signal-to-noise ratio of corresponding ENDOR signals. Signs in analogy to those of ZnTPP⁺⁺ in CH₂Cl₂. For experimental conditions, see footnote *b*. ^{*d*} Solvent: CH₂Cl₂-THF 8:2 vol/vol. ¹H hfc from Special TRIPLE (T = 210 K), ¹⁴N hfc from ENDOR. For accuracy of hfcs see footnote *b*. Signs of hfcs not determined because of strongly overlapping lines. ^{*e*} For additional hfcs of 0.72 and 1.07 MHz, see text. ^{*f*} Assignment holds for calculated hfcs of MgTPP⁺⁺. For ZnTPP⁺⁺ the assignment of the two ¹H hfcs of largest absolute magnitude could be reversed, since in the simulation of the EPR spectrum [see fig. 1(c)] a somewhat better fit was obtained by using a multiplicity of four nuclei (*para* protons) for |a| = 1.16 MHz instead of assigning eight nuclei (*ortho* protons) to this hfc.

nu

0

-1.00

1089

triple resonance method, where the high- and low-frequency NMR transitions of a particular hfc are irradiated simultaneously.²⁵ The inherently smaller linewidth obtained by this method allowed resolution of the two hfcs which contribute to the outermost proton ENDOR lines (see fig. 2). The ¹H and ¹⁴N hfcs are collected in table 1.

The relative signs of the hfcs were determined by the generalized variant of the electron-nuclear-nuclear triple resonance experiment (General TRIPLE): here one NMR transition is additionally c.w.-irradiated while an ENDOR spectrum is recorded. Characteristic intensity changes in the resulting spectrum reflect the relative signs of the hfcs.²⁷ The absolute signs of the hfcs in table 1 are based on an assumed positive sign for the ¹⁴N hfc (see below). These signs served as the basis of a tentative assignment of the hfcs to molecular positions: it is well established that the ortho and para protons of the phenyl groups have negative hfcs, and the meta protons have a positive hfc, provided the phenyl groups are bound to a carbon atom with positive p_z spin density. This sign prediction holds for all rotational angles of the phenyl ring, although the relative ordering in the absolute magnitude of the hfcs can change. This is predicted by a theoretical phenyl hyperconjugation model which describes π - σ spin delocalization into twisted phenyl rings.²⁸ The only positive proton hfc of ZnTPP⁺ (+0.79 MHz) is therefore assigned to the meta protons of the phenyl substituents. Since all the remaining proton hfcs are negative, the hfc of the pyrrole protons must also be negative, *i.e.* the β carbon atoms adjacent to the pyrrole protons carry a small positive p, spin density. This is in agreement with predictions from earlier MO calculations performed on ZnTPP'+.17

For a more detailed analysis, the proton and nitrogen s-spin densities were calculated using an all-valence-electron MO method of the RHF-INDO/SP type.²⁶ In order to avoid complications in the INDO approximation due to the fully occupied d orbitals of Zn, Mg was used as the central metal in the calculations with d orbitals omitted. This metal replacement is justified on experimental grounds: it does not affect the electron spin density distribution to a great extent, since measured proton hfcs of MgTPP⁺⁺ differ by <20% from those of ZnTPP⁺⁺.²⁹

Standard bond lengths and angles³⁰ were used in the MO calculations except for the geometry in the vicinity of the phenyl rings where steric strain is to be expected. This geometry was determined by energy minimization when varying bond lengths and angles. As a result, a dihedral angle of 50° between the phenyl and porphyrin planes was obtained. Increasing the angle to 60° requires ca. 5 kJ mol⁻¹. which is equivalent to $2 k_{\rm B} T$ at T = 290 K. The bond length between the phenyl rings and the meso-carbon atoms of the porphyrin skeleton is found to be 1.45 Å. The dihedral angle of the phenyl rings compares well with the average of the dihedral angles of 57° obtained by X-ray crystallography of ZnTPP⁺⁺ single crystals.³¹ It should also be mentioned that the bond length between the phenyl rings and the mesocarbon atoms determined by X-ray crystallography varies from 1.48 to 1.51 Å for the individual phenyl rings.³

The calculated hfcs are listed in table 1. There is a reasonable agreement between the calculated ¹⁴N hfc and the experimental value. The hfc of the pyrrole protons (β) is negative and its calculated magnitude agrees well with the measured coupling of -0.20 MHz. The relative ordering of the phenyl proton hfcs, on the other hand, differs from the measured order. However, one has to keep in mind that the absolute differences between the hfcs are so small that their ordering lies within the limits of the accuracy of the MO theory (*ca.* ± 200 kHz). The given assignment of hfcs (see table 1) is further supported by computer simulation of the

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EPR spectrum of ZnTPP⁺⁺ at room temperature [see fig. 1(a)] and at 200 K where it is better resolved [see fig. 1(b) and (c)].²⁹

One-electron vs. Two-electron Oxidation of the Porphyrin Dimers

Since the redox potentials of weakly coupled symmetric dimers are expected to be similar for both dimer halves, it has to be discussed whether one electron or two electrons are abstracted in the oxidation procedure for the sample preparation. The chemical oxidation experiments (i), (ii) and (iii) (see Experimental), and the analysis of the cyclic voltammetry curves led to the following results and conclusions concerning possible one-electron or formal 'two-electron' transfer reactions of the porphyrin dimer 1. When less than equimolar amounts of oxidizing agent are used [case (i)], the EPR and ENDOR spectra of these solutions strongly resemble those measured for the dimer which has been oxidized with equimolar amounts of $AgClO_4/I$ and 1 [case (ii)], except for the weaker signal strength. When, on the other hand, an excess of oxidizing agent is used [case (iii)], the EPR and ENDOR spectra differ considerably from those of cases (i) and (ii), but rather show characteristics very similar to those of monomeric ZnTPP'+, i.e. for this case the EPR and ENDOR spectra point to a different species, where one unpaired electron is confined to one porphyrin unit of 1. Consequently, in order to minimize complications due to the possible presence of two-electron oxidation products, all EPR and ENDOR measurements reported here were performed on dimers oxidized with somewhat less than equimolar amounts of $AgClO_4/I.$

In the cyclic voltammetry recordings of 1 the first oxidation wave has a separation of the anodic and cathodic peak potentials (ΔE) of 175 mV. The peaks are more rounded off than those of ZnTPP ($\Delta E = 125$ mV). Since the first oxidation wave of ZnTPP was shown to correspond to a reversible one-electron transfer step,³² the increase in ΔE for 1 relative to ZnTPP might point to a formal two-electron transfer process: if the separation between the removal of the first and the second electron is between 0 and 100 mV, increased values of ΔE and a flattening of the peaks are expected from theoretical considerations.³³ For quasi-irreversible processes, however, such an analysis becomes ambiguous.³³ Since neither the oxidation experiments nor the cyclic voltammetry measurements unambiguously discriminate between one- and two-electron oxidation of the dimers, the EPR and ENDOR spectra have to be discussed in terms of monoradical or biradical character to clarify this point.

For biradicals in liquid solution three limiting cases have to be considered: (a) the scalar exchange interaction J is much smaller than the isotropic hfc, a, $(|J| \le |a|)$; (b) $|J| \ge |a|$ and (c) $|J| \approx |a|$. A comprehensive review of these cases is given in ref. (34). Here we will focus on the spectral characteristics of symmetric biradicals as, for instance, dimer 1^{2^+} .

(a) If $|J| \le |a|$, the unpaired electrons interchange slowly on the timescale of the smallest hfc, *i.e.* they appear localized on their respective half of the dimer. The system thus behaves spectroscopically as a double doublet. Consequently, the EPR and ENDOR spectra for such a biradical are identical to those of the monoradical, except for a possible line broadening. This is due to additional relaxation effects caused by fluctuations of the electron-electron dipole and exchange interactions.

(b) If $|J| \ge |a|$, the electrons interchange so fast that they appear delocalized over the entire molecule, simultaneously interacting with the nuclei of both halves of the biradical. In

the EPR spectra this is reflected in an increased number of lines relative to the monomer. The spacing between lines belonging to a set of equivalent nuclei in the biradical, *i.e.* the hfc a^{B} , is halved relative to that of the monomer, a^{M} . The ENDOR resonance condition for biradicals with $|J| \ge |a|$ is

$$v_{\text{ENDOR}} = |v_{\text{n}} - M_{\text{s}} a^{\text{B}}|$$

whereas for monoradicals it is15

$$v_{\text{ENDOR}}^{\pm} = |v_{\text{n}} \pm a^{\text{M}}/2|.$$

Since for a biradical $M_s = -1$, 0 and +1, three lines are expected at $v_n + a^B$, v_n and $v_n - a^B$. Owing to the degeneracy of the EPR transitions connecting the $M_s = 0$ level with the $M_s = -1$ and +1 levels, however, the ENDOR line at v_n cannot be observed in isotropic fluid solution (but could be observed in liquid crystals and in solids^{15f}). If one further takes into account that a^{B} is just half of a^{M} , the ENDOR line frequencies of the biradical in fluid solution are identical to those of the corresponding monoradical. Hence, in cases where the biradical consists of two identical subunits, the distinction between mono- and bi-radical by ENDOR line frequencies becomes ambiguous. The presence of two unpaired electrons in the biradical, however, induces fast electron spin relaxation. This causes line broadening and requires considerably higher power levels for saturation than in the case of monoradicals.

(c) In the intermediate case, $|J| \approx |a|$, the EPR spectra are more complex. The relation of the biradical spectrum to the monoradical spectrum is not straightforward and requires the specific properties of the biradical to be taken into account for interpretation. Also in this case, the ENDOR line positions of the biradical are identical to those of the monoradical except for a possible splitting of the line at v_n .³⁵

In the following, the spectroscopic characteristics of biradicals, as outlined above, will be compared with the EPR and ENDOR spectra of dimer 1 oxidized with less than equimolar amounts of $AgClO_4/I$ (these spectra are discussed in detail in the next section).

Case (a): the spectra cannot be due to a biradical with $|J| \le |a|$, since both EPR and ENDOR spectra differ considerably from those of the monomer ZnTPP^{*+} (compare fig. 3 and 4).

Case (b): incidentally, the EPR spectra of biradicals with $|J| \ge |a|$ would be identical to those of a dimer in the monoradical state if the unpaired electron of the monoradical was hopping fast between the dimer halves on the EPR time scale.⁸ Although the EPR spectra of oxidized 1 fit into this category, the ENDOR spectra exclude a biradical species, because in a biradical the ENDOR frequencies would be identical to those in the monoradical. The halving of the hfcs relative to ZnTPP'⁺, which is observed in the ENDOR spectra of oxidized 1 (compare fig. 4), thus contradicts the possibility of the oxidized dimer 1 being a biradical with $|J| \ge |a|$.

Case (c): we cannot a priori exclude the possibility that some combination of J and a exists which would produce an EPR spectrum of a hypothetical biradical similar to that of fig. 3(b). Again, the halving of the hfcs in the ENDOR spectrum of oxidized 1 shows, however, that the observed species is, in fact, not a biradical.

To sum up this discussion, one can state that there is no evidence for biradical contributions to the EPR/ENDOR spectra of oxidized 1. This finding is in accordance with the results of the oxidation experiments described above. We will take this as the basis for the following interpretation of the EPR and ENDOR spectra also for the dimers 2 and 3 as monopositive radicals.



Fig. 3. (a) Superposition of the EPR spectra of dimer 1⁺⁺ (bold line) and ZnTPP⁺⁺ (fine line). (b) EPR spectrum of dimer 1⁺⁺ in CH₂Cl₂-THF (8: 2 vol/vol) at room temperature: computer simulation (dotted curve) involves eight nuclei of I = 1, a = 0.79 G and a Gaussian single component linewidth of $\Delta B_{pp} = 1.1$ G. (c) EPR spectrum of dimer 2⁺⁺ in CH₂Cl₂-THF (8: 2 vol/vol) at room temperature. Best computer simulation (not shown) involves eight nuclei of I = 1, a = 0.75 G and $\Delta B_{pp} = 1.6$ G. (d) EPR spectrum of dimer 3⁺⁺ in CH₂Cl₂-THF (8: 2 vol/vol) at 200 K. Note the similarity in structure and width with the EPR spectrum of ZnTPP⁺⁺ [fig. 1(b)].

Model Dimers 1'+, 2'+ and 3'+

The EPR spectrum of the oxidized dimer 1 [see fig. 3(b)] is an unresolved Gaussian envelope line at $g = 2.0028 \pm 0.0001$. The inhomogeneously broadened EPR lines of 2^{+} and 3^{+} are shown in fig. 3(c) and (d), respectively. Whereas the EPR spectrum of dimer 2^{+} is very similar to that of 1^{+} , both width and structure of the EPR spectrum of dimer 3^{+} are in close analogy to ZnTPP'+. The superposition of the EPR spectra of $ZnTPP^{+}$ and of 1^{+} in fig. 3(a) shows that for the dimer the EPR line is significantly narrower than for ZnTPP'⁺ line. In the ENDOR spectrum of 1'⁺ (see fig. 4), overlapping lines symmetrically arranged around v_H were detected. At temperatures below 190 K the ENDOR intensity decreased distinctly, much more so than for ZnTPP'+. This is to be expected, since the rotational correlation time, which affects the ENDOR enhancement via the relaxation rates, increases with the effective molecular volume; this effect can be compensated by increasing the temperature.²⁶

The line at 2.11 MHz in the ENDOR spectrum of 1^{++} (see fig. 4) is assigned to the high-frequency hyperfine component of the ¹⁴N nuclei. Since the signal-to-noise ratio for this line is rather poor (presumably because of the lower hyperfine enhancement of the r.f. field at such a low frequency²⁴) supporting evidence for a deduced magnitude of 2.20 MHz for the ¹⁴N hfc was desirable. This is offered by the computer simulation of the EPR spectrum, which revealed that the best fit between calculated and experimental EPR spectra is obtained by using this ¹⁴N hfc and a multiplicity of eight

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Fig. 4. Comparison of ENDOR spectra of $ZnTPP^{++}(a)$ and dimer $1^{++}(b)$ in CH_2Cl_2 -THF (8 : 2 vol/vol). Dashed lines indicate that the ¹H hfcs of 1^{++} are halved relative to those of $ZnTPP^{++}$. ENDOR of $ZnTPP^{++}(a)$: experimental conditions as in caption of fig. 2, except for solvent. ENDOR of $1^{++}(b)$: m.w. power 40 mW, (13–16 MHz): T = 237 K, r.f. power 40 W, 10 kHz f.m. with ± 40 kHz deviation, t = 42 min; ENDOR of $1^{++}(1.5-4.0 \text{ MHz})$: T = 254 K, r.f. power 100 W, for other experimental conditions, see caption of fig. 2. (c) ENDOR spectrum of dimer 2^{++} , m.w. power 50 mW, (13–16 MHz): T = 237 K, r.f. power 40 W, f.m. deviation ± 40 kHz, t = 60 min, (1.5–4.0 MHz): T = 270 K, r.f. power 100 W, f.m. deviation ± 100 kHz, t = 20 min. (d) ENDOR spectrum of dimer 3^{++} , m.w. power 60 mW, (13–16 MHz): T = 237 K, r.f. power 40 W, f.m. deviation ± 80 kHz, t = 20 min.

equivalent nuclei with nuclear spin I = 1 [see fig. 3(b)]. The simulations with different ¹⁴N hfcs and different multiplicities are less satisfactory and show that the EPR spectrum is governed by the ¹⁴N hfc.

For comparison, in fig. 4 the ENDOR spectra of the dimers 2^{+} and 3^{++} are also shown, and the extracted hfcs are included in table 1. In the following, the hyperfine structure of the dimers 1^{++} , 2^{++} and 3^{++} will be discussed in relation to that of ZnTPP⁺⁺.

Dimer 1^{•+}

The ¹H and ¹⁴N hfcs measured for 1^{.+} are approximately halved in magnitude relative to those of ZnTPP^{•+} (see fig. 4 and table 1). Furthermore, the simulation of the EPR spectrum suggests that the nuclei of both dimer halves contribute to the hyperfine interaction scheme. Thus the unpaired electron of 1⁺⁺ must be distributed over both halves of the model dimer. Two mechanisms are envisaged for the interaction of the unpaired electron with both halves of the dimer: incoherent hopping of the electron between both dimer halves in a double-minimum potential or coherent π conjugation of the electron over both halves in a single-minimum potential. If the hopping is fast on the EPR timescale, an unresolved, inhomogeneously broadened EPR line is reduced in width by a factor of $1/\sqrt{2}$ relative to that of the monomer when an exact halving of individual hfcs is assumed (symmetric dimer).⁸ The conjugation mechanism requires the formation of a π supermolecule due to a close contact of the monomers with strong π orbital overlap. As a consequence the spindensity distribution in the supermolecule will be rearranged. Compared with the monomeric radical, the individual hfcs will exhibit reduction factors that can deviate considerably from 2.⁹ The small absolute magnitude of the ¹H hfcs in 1^{+} , however, prevents the detection of asymmetries of the electron-spin distribution in the dimer. Consequently, we cannot discriminate between the two mechanisms experimentally. On theoretical grounds, however, a distinction between hopping and conjugation can be attempted.

Such a distinction requires the knowledge of the resonance energy, ε , which is half the energy gap between the symmetrical and antisymmetrical states $(\Psi_A^{+}\Psi_B \pm \Psi_A \Psi_B^{+})/\sqrt{2}$ formed from the wavefunctions of the isolated monomers A and B, and the knowledge of the stabilization energy, ΔV , of an isolated state $\Psi_A^{\star+}\Psi_B$ or $\Psi_A\Psi_B^{\star+}$. A stabilization of the electron on one moiety, described by an unsymmetrical potential, is expected to arise from polarization of the surrounding dielectric medium by the charge of the ion.³⁷ More precisely, ΔV represents half of the difference between the energy of the most favourably solvated localized state and that of the state having the identical arrangement of solvent molecules, but with the electron now localized on the other moiety.³⁸ Hopping will occur if $\Delta V \gg \varepsilon$ and if ΔV is modulated effectively by Brownian fluctuations of solvent molecule configurations to induce transitions between the two localized states.³⁹ In our case, ΔV is estimated to be 1.1 eV using the conventional approach due to Born,40 taking an effective radius r = 6 Å and a relative permittivity D = 9.1 (CH₂Cl₂). The conjugation energy ε , on the other hand, has been calculated by Extended Hückel MO theory to be 0.04 eV. From these theoretical estimates and from the experimentally observed electron delocalization, we therefore conclude that hopping is the prevailing mechanism and that it occurs at a rate which is fast on the EPR timescale.

Dimer 2^{•+}

The EPR and ENDOR experiments on dimer 2^{+} , for which the porphyrin moieties are linked at the *meta* positions of the phenyl bridge, yielded essentially the same results as for the *para* linked dimer 1^{+} , *e.g.* they have identical ¹⁴N hfcs within experimental error. On the other hand, in the proton ENDOR spectrum of 2^{++} three additional pairs of lines were observed which do not exist for 1^{++} . The additional proton hfcs could either be due to an asymmetry in the spin-density distribution over the dimer halves or to the protons of the phenyl ring that links the porphyrin subunits of the dimer. The first interpretation is improbable, however, since no splitting of the ¹⁴N line is observed. Therefore, the additional three proton hfcs are tentatively attributed to the protons in the phenyl bridge which become partly inequivalent by *meta* substitution so that their hfcs could differ from those observed in 1^{++} . Deuteration experiments are planned to make a definite assignment. In conclusion, the experimental results show that also in dimer 2^{++} the unpaired electron is delocalized over both dimer halves.

Dimer 3^{•+}

The EPR and ENDOR experiments on dimer 3^{+} , in which two ZnTPP subunits are linked by a $-CH_2$ bridge, give different results from those of dimers 1^{+} and 2^{+} . The ¹H and ¹⁴N hfcs are the same as for ZnTPP⁺⁺ within experimental error (see fig. 4 and table 1). From these observations we conclude that in 3^{+} the unpaired electron is localized on one porphyrin subunit of the dimer. The electronic interactions between the porphyrin subunits are obviously much smaller in 3^{+} than in 1^{+} and 2^{+} , probably because in 3^{+} methylene bridge connects carbon atoms with low spin density, whereas in 1^{+} and 2^{+} positions of high spin density are bridged by the phenyl group.

Conclusion

The spin-density distributions of ZnTPP'+ and of the porphyrin dimers 1^{+} , 2^{+} and 3^{+} were determined by high-resolution ENDOR and TRIPLE resonance techniques. These methods allowed not only the determination of the ¹⁴N hfcs but also of the proton hfcs which cannot be resolved by EPR. The proton and ¹⁴N hfcs of the dimers 1^{.+} and 2^{.+} are approximately halved relative to those of monomeric ZnTPP'⁺ and a significant narrowing of the inhomogeneously broadened EPR line is observed. These results are consistent with a hyperfine interaction of the unpaired electron with the nuclei of both halves of the model dimer. In this respect the dimers 1^{+} and 2^{+} behave similarly to P^{+} , the 'special pair' donor of bacterial photosynthesis. The porphyrin planes in 1 and 2 are, however, not stacked as in P, which leads to a symmetry in the π - π overlap different from that in P. To our knowledge, this is the first time that an electron delocalization in a porphyrin dimer has been observed consistently by both EPR and ENDOR methods. The cation radical of the dimer 3, on the other hand, did not reveal any reduction of the hfcs or EPR linewidth relative to ZnTPP* and must, therefore, be considered as a 'localized' dimer consisting of two non-interacting monomers on the EPR timescale.

The dimers 1 and 2 may thus serve as a starting point in the endeavour to mimic special features of P in the photoinitiated electron-transfer chain. The efficiency of this chain is governed by π - π overlap and delocalization effects between the cofactors in the photosynthetic reaction centre. An example of such effects was recently discussed in an attempt to rationalize the unidirectionality of the electron transfer along one of the protein branches of bacterial reaction centres.³

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