Time-resolved EPR and ENDOR study of the photoexcited triplet state of free-base tetraphenylchlorin in a crystalline toluene matrix †

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A time-resolved EPR and ENDOR study of the photoexcited triplet state of the free-base tetraphenylchlorin has been made in a polycrystalline toluene matrix at 120 K. Crystallization of the toluene results in a partially aligned sample. The nature of the orientation of the solute molecules is investigated by time-resolved EPR spectroscopy using the anisotropy of the zero-field splitting tensor of the triplet state as the observable parameter. It is determined that 55% of the triplet molecules are oriented in a single crystal-like domain with the triplet z-axes oriented within 15° of the magnetic field. In the ENDOR study selective excitation, of only those molecules which have their triplet z-axes parallel to the magnetic field, has permitted the measurement of the A_{zz} component of the hyperfine coupling tensor of protons, in the reference frame of the zero-field splitting tensor. The sign and magnitude of the matrix couplings are also determined. The use of the partially oriented sample drastically enhanced the signal intensity over that achieved in a randomly oriented sample by increasing the number of molecules with their triplet z-axes parallel to the magnetic field. Additionally, time-resolved ENDOR spectroscopy allowed the hyperfine interactions to be determined at far higher temperatures than usual for the study of triplet states.

Introduction

Chlorins, which are derivatives of porphyrins, are involved in many fundamental biological processes, the most important of which is photosynthesis. Chlorophylls are chlorins containing magnesium, and pheophytin is a free-base form of chlorin. In order to gain a greater understanding of the electronic properties of their excited states many electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) investigations have been performed on the photoexcited triplet state of porphyrins and their derivatives, randomly oriented in solid solution and aligned in host crystals,[1,2] and more recently, in liquid crystals.[3] These studies have mainly been concerned with obtaining information on population dynamics and zero-field splitting (ZFS) tensors.

EPR spectra of triplets randomly oriented in solid solution usually lack resolved hyperfine structure due to the anisotropy of the ZFS and dipolar hyperfine broadening. Due to the anisotropy of the ZFS tensor, however, the EPR resonance condition principally selects, at specific magnetic field values, only a small fraction of the homogeneously oriented molecules, but with specific canonical orientations. Hence, at the canonical orientations, electron nuclear double resonance (ENDOR) spectroscopy is able to extract hyperfine data with a similar orientation selection to that possible for molecules incorporated in diamagnetic host single crystals.[4] In principle, therefore, ENDOR may be used to map the electron spin density in the photoexcited triplet state in much the same way as has been achieved in radicals in single crystals.[5,6]

The disadvantage of using a randomly oriented solid solution is the poor signal size due to the small fraction of molecules selected. n-Alkane host matrices do offer the possibility of single crystal-like orientation,[7–9] but the very low concentration of guest molecules (typically $\leqslant 10^{-5}$ M[10]) and the difficulty of incorporating non-planar porphyrins has limited their use. Liquid crystals have also been used to prepare partially oriented solutions, and have been used in ENDOR studies on radicals in solution,[11] but it has been reported that in frozen liquid crystal solution on photoexcited triplet state molecules ENDOR was not observed.[4]

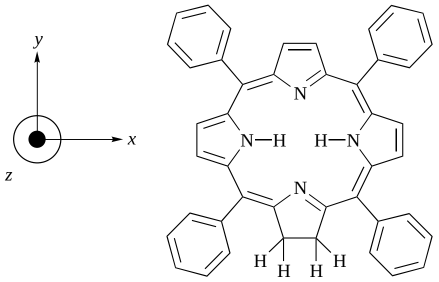

Fig. 1 Molecular structure of free-base tetraphenylchlorin. x and y define the molecular axes system in the plane of the molecule, while the z axis is perpendicular to this plane.

It is well known, although to the best of our knowledge not well documented, that toluene, which has been widely used as a glassy matrix for randomly oriented samples, can crystallize[12,13] and molecules dissolved in it can become partially aligned.[14–17] This effect has been used to obtain anisotropic spectra of biradicals, without the need to prepare mono-crystalline samples.[14] The commensurate increase in signal-to-noise (S/N) has been taken advantage of in a previous time-resolved ENDOR study in this laboratory on the photoexcited triplet state of free-base tetraphenylporphyrin ($^{T}H_2TPP$).[15] The time-resolved EPR experiments reported here demonstrate and attempt to understand the orientation phenomenon of toluene. The photoexcited triplet state of free-base tetraphenylchlorin, $^{T}H_2TPC$ (see Fig. 1) is used as a probe of the crystal structure.

Following light excitation of H_2TPC to the excited singlet state, anisotropic singlet–triplet inter-system-crossing (ISC) occurs to produce $^{T}H_2TPC$. The triplet state is initially spin-polarized, and the spin-polarization then relaxes to Boltzmann equilibrium. The majority of ENDOR studies on photoexcited triplets of porphyrin-type systems[4,18–20] and one on *Rhodobacter sphaeroides* R-26 photosynthetic reaction centers[21] have been performed using steady-state light excitation, radiofrequency modulation and lock-in detection. However, steady-

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† Presented at the 30th International Meeting of the Electron Spin Resonance Group of the RSC, University of Lancaster, 6–10th April 1997.

state ENDOR does not normally permit selection of the initial polarized signal, rather it is averaged over the Boltzmann one, thus reducing the signal intensity. Hence these studies have all been carried out at low temperatures (<40 K) where the spin-lattice relaxation time approaches the triplet lifetime.[4,18–21]

The limitations of steady-state ENDOR for the study of photoexcited triplet states were first recognized by van der Poel *et al.* who used pulsed-ENDOR to study the photoexcited triplet state of free-base porphyrin.[10] An alternative ENDOR strategy, which was demonstrated by Möbius *et al.* for studies of short-lived doublet radicals,[22,23] and recently extended to the study of photoexcited triplets,[15,24,25] is the time-resolved ENDOR technique. This spectroscopy, employing pulsed laser excitation and direct detection (*i.e.* without modulation), allows sole selection of the polarized signal. This results in a drastic enhancement of the ENDOR signal compared with steady-state methods and, additionally, the ENDOR signal of photoexcited triplets can be detected at elevated temperatures.[15]

We have studied $^{T}H_2TPC$ as a model compound for pheophytin with ENDOR spectroscopy in order to derive information on the electronic structure of this excited state where not only the highest occupied molecular orbital (HOMO) but also the lowest unoccupied molecular orbital (LUMO) is involved. The results derived from these experiments shed light on the complex nature of photoexcited states and their interactions with the host matrix.

Experimental

Time-resolved EPR/ENDOR spectra were obtained using a laboratory-built X-band spectrometer which has been described previously.[22] Both microwave (MW) and radio-frequency (RF) fields are applied in the continuous wave (cw) mode, and no field or frequency modulation is used, the EPR and ENDOR signals thus being directly detected. The spectrometer has a response time of approximately 150 ns.

An RF-synthesizer (Hewlett Packard 8660c) in conjunction with a high-power (1 kW) RF-amplifier (ENI A 1000) was used to generate the cw RF-field (2 mT rotating frame) in the TM_{110} ENDOR cavity ($Q \simeq 1500$, 1 turn per mm NMR coil).

An excimer laser (Lambda Physik LPX 100, pulse width 20 ns, 150–200 mJ per pulse, 308 nm, repetition rate 22 Hz) pumping a dye laser (Lambda Physik FL 2002, Rhodamine 6G dye, 581 nm, 15–25 mJ) was used as light source. The transient signals were detected with either a box-car integrator and signal processor (EG&G model 4420/4422 and 4402) or a Tektonix transient recorder (model TDS 520A) interfaced to a PC. The temperature was controlled by a Bruker nitrogen gas flow cryostat ER4111VT.

H_2TPC and D_2TPC were synthesized by H. Mößler (in the group of H. Kurreck, Freie Universität Berlin) according to published procedures.[26] Samples in glass capillaries (internal diameter 3 mm) were prepared at a concentration of 10^{-3} M in toluene (Merck) and perdeuteriated toluene (Aldrich). Oxygen was removed by multiple freeze–pump–thaw cycles under high vacuum conditions. The samples were then sealed.

Randomly oriented solid solutions of $^{T}H_2TPC$ were produced by supercooling the sample rapidly through the melting point of toluene, 178 K, when it forms an optically clear glass. In order to prepare the partially aligned samples, the toluene must be crystallized. This was achieved by cooling the sample through the melting point of toluene into the glass region to below 110 K. Upon warming up to 125–135 K, the toluene undergoes a phase change into its α-crystalline state,[12,13,16] which once formed is stable over all temperatures up to the melting point of toluene. The exact transition temperature depends on the solvent purity.[13] On inspection the sample is found to be in a polycrystalline state. The initial orientation observed showed no dependence on the presence or absence of the magnetic field.[14] Hence, the sample tube, which is perpendicular to the magnetic field, had to be rotated until the required orientation was selected.

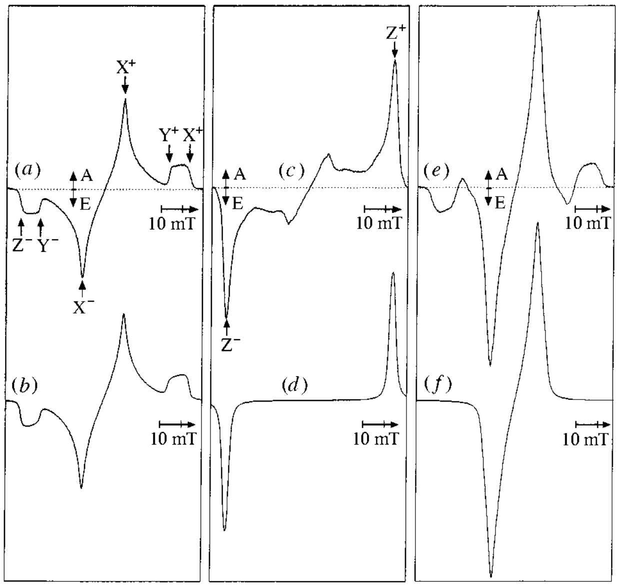

Fig. 2 Time-resolved EPR spectra of $^{T}H_2TPC$ in toluene. (*a*) Randomly oriented and (*b*) simulation; (*c*) partially aligned and (*d*) simulation of the main component; and (*e*) partially aligned after 90° rotation and (*f*) simulation of the main component. Note that the signal amplitudes have not been normalized. $T = 115$ K, integration period = 0–1 μs, $P_{MW} = 20$ mW. A and E stand for absorption and emission, respectively. In (*a*) X^-, Y^-, Z^- and X^+, Y^+, Z^+ are the EPR transitions where the *x*-, *y*-, *z*-axes of the ZFS tensor are parallel to the external magnetic field. In (*c*) the positions Z^- and Z^+ indicate the magnetic field at which the ENDOR spectra in Fig. 5 were recorded.

Results and discussion

EPR spectroscopy

The time-resolved EPR spectrum of $^{T}H_2TPC$ randomly oriented in toluene at 115 K is shown in Fig. 2(*a*). Due to anisotropic ISC, the spectrum is spin-polarized in an EAEAEA fashion (A absorption, E emission). The ZFS parameters ($|D| = 361 \times 10^{-4}$ cm^{-1} and $|E| = 61 \times 10^{-4}$ cm^{-1}) determined by simulation of the spectrum,[27] Fig. 2(*b*), are in good agreement with a previous EPR study.[28] No difference in the ZFS parameters was observed when perdeuteriated toluene was used as solvent, or between $^{T}H_2TPC$ and $^{T}D_2TPC$.

In Fig. 2, the field positions marked Z^- and Z^+ are indicated, they correspond to an orientation of molecules with their molecular *z*-axes parallel to the magnetic field. (− and + stand for low- and high-field, respectively, due to the selection rule $\Delta m_s = \pm 1$, see Fig. 3.) Hence, the high spectral resolution characteristic of ENDOR in triplet state molecules in single crystals can be preserved in disordered solids by restricting the ENDOR experiment to molecules with this specific orientation.[4] The disadvantage is that the EPR signal and by extension the ENDOR signals obtained at these field positions are small. In Fig. 2, the field positions marked Y^-, Y^+ and X^-, X^+ are also shown. These positions indicate transitions due to molecules with their *x* and *y*-axes, respectively, parallel to the magnetic field. However, the orientation selection is not completely pure, as other non-canonical orientations also contribute to the signal intensity at these positions within the EPR linewidths.

The time-resolved EPR spectrum of $^{T}H_2TPC$ in toluene after the toluene matrix has been crystallized is shown in Fig. 2(*c*). It clearly deviates from the 'powder' spectrum observed in Fig. 2(*a*). The signal intensity at the Z^- and Z^+ field positions is substantially increased (typically six times), whilst the orientation selection is preserved: only molecules with their *z*-axes

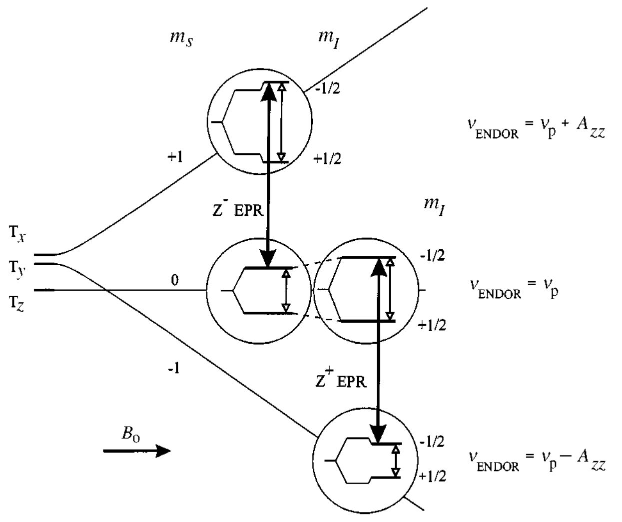

Fig. 3 Spin energy levels in the case of the triplet z-axis parallel to the magnetic field, with $D > 0$ and first-order hyperfine interaction with one proton for $A_{zz} < 0$. The saturated EPR transitions (Z^- and Z^+ EPR) and the ENDOR transitions (ν_p and ν_{ENDOR}) are indicated by arrows.

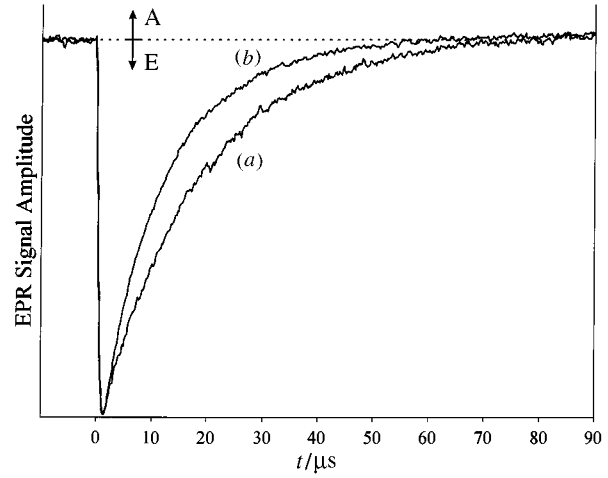

Fig. 4 EPR kinetics of the Z^- component of ^TH_2TPC in (a) glassy and (b) crystalline toluene. $T = 117$ K, $P_{MW} = 0.2$ mW.

parallel to the magnetic field can contribute to signal intensity at these field positions.

In order to understand the partially oriented spectrum in more detail, it is necessary to introduce the parameters θ and φ, which describe the angles that the triplet axes make with the magnetic field.[29] We can define that: when $\theta = 0°$, φ arbitrary, the z-axis is parallel to the magnetic field; when $\theta = 90°$ and $\varphi = 0°$, then the x-axis is parallel to the magnetic field and when $\theta = 90°$ and $\varphi = 90°$, then the y-axis is parallel to the magnetic field.

Using these parameters the main contribution, giving rise to signal intensity at the Z^- and Z^+ field positions, of the partially oriented spectrum has been simulated[27] and is shown in Fig. 2(*d*). It is composed of molecules with $\theta = 0$–$15°$ and $\varphi = 0$–$90°$, *i.e.* the triplet z-axes are aligned within a cone 0–15° around the magnetic field. Nothing can be said about the orientation of the molecular x- and y-axes with respect to the magnetic field, as taking a specific orientation in the molecular xy-plane (*i.e.* a specific value of φ), did not appreciably alter the simulation. The relative proportions of the components contributing to the simulation allowed us to estimate that 55% of the signal intensity is included in the main component. The other components contributing to the spectrum are at different orientations, and do not contribute to the signal intensity at the Z^- and Z^+ positions. It should be noted that in order to simulate the spectrum a slightly larger (2%) value of $|D| = 370 \times 10^{-4}$ cm^{-1} had to be used. This could be a reflection of the effect of the crystal field in the polycrystalline phase of toluene, or some aggregation of the H_2TPC molecules, both of which are well known to affect the ZFS parameters.[30]

In Fig. 2(*e*) is shown the time-resolved EPR spectrum from the same sample in Fig. 2(*c*) after a 90° rotation of the sample tube. The peaks at Z^- and Z^+ have been transformed close to the positions X^- and X^+ in the powder spectrum, Fig. 2(*a*). In Fig. 2(*f*) is shown the simulation of the main spectral component. It was simulated by taking a distribution of molecules with $\theta = 54$–$90°$ and $\varphi = 4.5$–$18°$, *i.e.* the triplet y-axis is oriented almost perpendicular to the magnetic field, while there is a large spread of distributions in the xz-plane.

It can be concluded that the majority of H_2TPC molecules are aligned with their z-axis perpendicular (0–15°), their y-axis almost parallel (4.5–18°) to the cylindrical axis of the sample tube. This implies that the toluene molecules, whose crystalline structure is being probed by the guest molecules, are also oriented parallel to the sample tube. The reason for this is due to the nature of the crystallization process, which can be observed directly by eye and proceeds unidirectionally down the sample tube. Hence, the sample tube is a director. The fact that following a 90° rotation of the sample tube, we observe only the x-orientation and not the y-orientation shows that the molecular planes of the chlorin molecules are not randomly oriented, but that there is also molecular order in this direction. This is not surprising considering that the chlorin molecule is asymmetric (C_{2v} symmetry group), a property that is bound to be reflected in the crystal structure. The relatively flat nature of the chlorin molecule would be expected to be the reason why it can pack in an ordered manner in the toluene host crystal. In a previous study of biradicals,[14] it was another planar molecule that showed such an orientation effect in crystalline toluene. This behaviour is somewhat similar to that of an n-alkane Shpolski-type matrix formed under fast cooling,[31] but has the advantage that it can be formed at much higher temperatures, and with higher concentration of guest molecules.

Fig. 4 shows kinetic traces of the EPR signal taken at the Z^- magnetic field positions in (*a*) glassy [Fig. 2(*a*)] and (*b*) crystalline [Fig. 2(*c*)] toluene, both taken at 0.2 mW microwave power and 117 K. That from the crystallized sample clearly shows a faster decay, *i.e.* the spin-lattice relaxation time, t_1, is shorter. Extrapolation to zero microwave power gives a t_1 of 13 µs for the crystalline compared with 18 µs for the glassy sample. Increased relaxation times in the crystalline phase were also observed in a previous study of the photoexcited triplet state of C_{60} in toluene.[16] The effect may be due to some aggregation of the H_2TPC molecules during the crystallization process, although t_1 did not change if the solution was diluted, and upon aggregation the ZFS parameter D generally shows a decrease,[30] in contrast to what was observed here. Additionally, it is expected that free-base chlorins are less susceptible to aggregation than metallochlorins. The effect may, then, be due to the different environment in the two phases of toluene which is known to have a pronounced effect on relaxation times.

ENDOR

Background. ENDOR experiments performed at the Z^- and Z^+ magnetic field positions in the EPR spectra, see Fig. 2, permit measurement of the hyperfine coupling tensor component, A_{zz}, (including sign relative to that of D) of protons in the reference frame of the ZFS tensor. The triplet spin energy levels for the z orientation, including first-order hyperfine interaction with one proton, for a molecule with $D > 0$ and $A_{zz} < 0$, are shown in Fig. 3. For each EPR transition, there are two ENDOR resonance frequencies [eqns. (1) and (2)] where ν_p is

$$\nu_{ENDOR}(0) = \nu_p \tag{1}$$

$$\nu_{ENDOR}(\pm 1) = \nu_p \mp A_{zz} \tag{2}$$

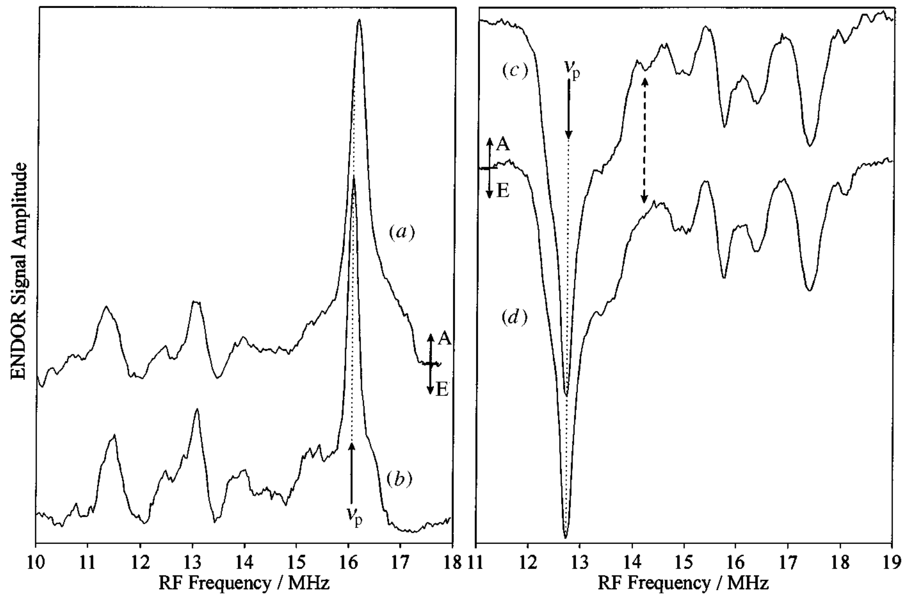

Fig. 5 Time-resolved ENDOR spectra of $^{T}H_2TPC$ in (*a*) protonated and (*b*) perdeuteriated toluene taken at the magnetic field position Z^+ indicated in Fig. 2(*c*). Time-resolved ENDOR spectra of (*c*) in $^{T}H_2TPC$ and (*d*) $^{T}D_2TPC$ in perdeuteriated toluene taken at the magnetic field position Z^- indicated in Fig. 2(*c*). The dashed arrow, (*c*) and (*d*), indicates the ENDOR line that is removed as a result of deuteriation of the central acidic protons. $T = 120$ K, integration period = 3–10 μs, $P_{MW} = 20$ mW, $P_{RF} = 180$ W (2 mT RF field, rotating frame). ν_p indicates the free proton Larmor frequency.

the free proton nuclear Larmor frequency and A_{zz} is the hyperfine coupling tensor component in the direction of the triplet *z*-axis. It can be seen from these equations that the resulting ENDOR spectrum is asymmetric, in contrast to the ENDOR spectra of doublet radicals.[11]

A_{zz} consists of an isotropic (Fermi-contact interaction), A^{iso}, and a dipolar part, A^{dip}_{zz},[32,33] [eqn. (3)], where the index *i* is over

$$A_{zz} = A^{iso} + A^{dip}_{zz} = Q_{CH}\cdot\rho^{2p_z} + \sum_{i=1}^{24} A^{dip}_{zz,i}\cdot\rho_i^{2p_z} \qquad (3)$$

all partial spin densities of carbons and nitrogens in the molecule.

The distribution of spin densities $\rho_i^{2p_z}$ over the molecular frame describes the electronic structure of the triplet state. A^{iso} is proportional to the spin denisty ρ^{2p_z} in the $2p_z$ orbital of the adjacent carbon atom (McConnell relation).[34] A^{dip}_{zz} is the sum of the dipolar interactions of the nuclear spin I_k with every partial spin density $\rho_i^{2p_z}$ in the molecule.[32]

In order to compare A_{zz} and A^{iso} correctly, A^{dip}_{zz} must be known and subtracted from A_{zz}. For doublet radicals A^{iso} can be determined from liquid solution and A^{dip}_{zz} can be measured by incorporating the substance in single crystals. For triplet state molecules it is not possible to determine A^{iso} directly by experiment, and for triplet molecules in disordered matrices it is necessary to resort to calculations to estimate A^{dip}_{zz}, which has been done for several spin density distributions of porphyrins.[1,35,36] It has been estimated that $A^{dip}_{zz} = -1.0$ MHz for α protons and −2.1 MHz for the acidic central protons in the triplet state of porphyrin-type molecules.[19] For both doublet radicals[37] and triplet state molecules[36] the anisotropic hyperfine contribution is typically 50% of A^{iso}. In the case of methyl protons, in doublet radicals, the anisotropic hyperfine contribution is usually much smaller and amounts to about 10% of A^{iso},[12] as the hyperfine tensor has approximately axial symmetry. The β-protons would be expected to have an intermediate anisotropic contribution due to the angle they make with the plane of the molecule.

A comparison of spin densities in the triplet state with that in the cation and anion radicals can be made in the approximation [eqn. (4)] that the triplet π density on the *i*-th carbon atom is the

$$\rho_T(C_i) = [\rho_C(C_i) + \rho_A(C_i)]/2 \qquad (4)$$

average of the π density on the cation (ρ_C) and anion (ρ_A).[38] In the approximation that the same McConnell factors *Q* are valid for the triplet state, the radical cation and the anion,[38] then the isotropic triplet hyperfine couplings are given by eqn. (5), where

$$A^{iso}_T = (A^{iso}_C + A^{iso}_A)/2 \qquad (5)$$

the subscripts T, C and A refer to triplet, cation and anion, respectively.

Results and discussion. The time-resolved ENDOR spectra of $^{T}H_2TPC$ in toluene and perdeuteriated toluene obtained at the magnetic field position Z^+ in Fig. 2(*c*), are shown in Fig. 5(*a*) and (*b*), respectively. Since the Z^+ transition in the EPR spectrum is spin-polarized in absorption, the ENDOR spectra are also spin-polarized in absorption. In Fig. 5 are also shown the ENDOR spectra from (*c*) $^{T}H_2TPC$ and (*d*) $^{T}D_2TPC$ in perdeuteriated toluene, both recorded at the Z^- magnetic field position in Fig. 2(*c*), and accordingly these spectra are spin-polarized in emission.

The dramatic difference in S/N observed between the high-field [Fig. 5(*a*) and (*b*)] and low-field [Fig. 5(*c*) and (*d*)] spectra is due to a hyperfine enhancement of the applied RF field, caused by an increase in the nuclear transition probability within second-order perturbation theory.[39] In the case of only A^{iso}, the effective enhancement of the RF field amplitude for the different m_s levels is given for protons by eqn. (6).[40] In the case

$$\eta(m_s) = (1 - m_s A^{iso})/\nu_p \qquad (6)$$

of radicals this gives rise to a symmetric increase and decrease of the intensity of the ENDOR lines around ν_p proportional to A^{iso}. There are two differences in the application of this equation to the triplet state. Firstly, we are concerned with the $m_s = \pm 1$ levels in the triplet rather than the $m_s = \pm\frac{1}{2}$ levels in a radical and secondly, ν_p is different in the low- and high-field spectra. The overall result is that the S/N in the low-field spectra [Fig. 5(*c*) and (*d*)] is slightly more than double that in the high-field spectra [Fig. 5(*a*) and (*b*)].

The transition at ν_p is composed of two contributions. The main intensity stems from transitions in the $m_s = 0$ manifold. This is common to all protons, thus attaining a high intensity, as can be seen in all spectra in Fig. 5. But there is also a contribution from protons with a weak dipolar interaction with the unpaired electrons, such as protons in the solvent. These give

Table 1 Proton hyperfine coupling components A_{zz} (in MHz) for $^{T}H_2$PTC as derived from the time-resolved ENDOR experiments shown in Fig. 5. The magnitudes were determined by deconvolution of the ENDOR spectra by the program Compass,[43] and the signs as set out in the text. The dipolar 'matrix' couplings are not A_{zz} hyperfine coupling tensor components and so are given the label x in the table (experimental error ±0.1 MHz).

Molecular position	A_{zz}/MHz
α	−1.0 −1.4 −2.1 −2.3 −3.0 −3.3 −3.6 −4.6 −5.3
β	Not observed
Central acidic	−1.6
Phenyl	>+0.7
Matrix	$+1.2 > x > -0.7$

rise to the 'matrix' ENDOR line around ν_p which can be removed by deuteriation of the solvent. Comparison of the spectra obtained with the protonated, Fig. 5(*a*), and perdeuteriated, Fig. 5(*b*), toluene, shows that the line is narrowed and slightly shifted to lower frequency in the latter. An increase in resolution on both sides of ν_p is also observable. We can, therefore, estimate that the dipolar coupling for the matrix protons lies in the range +1.2 MHz to −0.7 MHz. This range of matrix couplings is close to that measured in a previous study of $^{T}H_2$TPP randomly oriented in polystyrol.[19] From experiments on doublet radicals, it has been proposed that these interactions are limited to protons within 6×10^{-10} m.[5,12,41] For a proton 3.5×10^{-10} m away from a 'point' paramagnetic center it has been predicted that, assuming maximum dipolar coupling, a matrix ENDOR line should be observed over the range $\nu_p \pm 1.9$ MHz.[12] The dipolar coupling is, however, reduced in purely aromatic molecules, such as the chlorin, where the unpaired electron(s) are delocalized over a large molecular skeleton.

The ENDOR transitions corresponding to the $\Delta m_s = \pm 1$ EPR transitions in the low-field Z^- [Fig. 5(*a*) and (*b*)] and high-field Z^+ [Fig. 5(*c*) and (*d*)] spectra are reflected on opposite sides of the transition at ν_p. Hence, the transitions can all be assigned to protons. Given that D is positive, as in all large flat molecules,[42] then inspection of the spectra shows that the majority of the A_{zz} proton hyperfine coupling tensor components are negative. Deconvolution of the ENDOR spectra was achieved with the program Compass.[43] The A_{zz} values are collected in Table 1.

The phenyl couplings are expected to be small, positive and unresolved as their hyperfine tensors have no principle axes colinear with those of the ZFS tensor. By comparison with previous work on $^{T}H_2$TPP,[15,19] they can be assigned to the spectral features visible around ν_p, and couplings of less than +0.7 MHz.

The line observed at −1.56 MHz can definitely be assigned to the acidic central protons by the comparison of the ENDOR spectra obtained from $^{T}H_2$TPP and $^{T}D_2$TPP, Fig. 5(*c*) and (*d*), respectively.

Unfortunately no hyperfine data are available for the radical derivatives of H_2TPC, but by analogy to ZnTPC[44,45] and chlorophyll *a*,[46,47] and with reference to theory,[38] it might be expected that the β-protons of H_2TPC should have a large positive A^{iso} contribution to A_{zz}. However, no positive couplings were observed. Additionally, in previous studies in this laboratory on the triplet state of porphycenes,[20] chlorophyll *a* and the primary donor P680 in photosystem II,[25] no lines were observed that could be attributed to β-protons. Studies of doublet radicals in frozen solution have shown that lines of β-protons may be broadened out beyond detection due to inequivalence caused by their immobilization at different dihedral angles.[48] The alternative explanation is that A_{zz}^{dip} is so large and positive that A_{zz} is actually negative: this seems unlikely in view of the previous results for other porphyrinoid systems and we will, therefore, assign all the remaining resolved couplings to the α-protons.

There are at least seven resolved lines in the spectrum and after deconvolution of additional unresolved features, the nine A_{zz} hyperfine coupling components, listed in Table 1, are deduced. In the ground state, however, H_2TPC has C_{2v} symmetry and the ENDOR spectrum should therefore exhibit only three lines due to the three equivalent pairs of α-protons, see Fig. 1. This implies that the symmetry of the molecule is reduced in the triplet state. A reduction from D_{2h} to C_{2h} symmetry was also proposed in a previous ENDOR study of $^{T}H_2$TPP[19] in order to account for the presence of double the expected number of lines attributable to α-protons in the ENDOR spectrum. This is not so unexpected, as theory predicts that there are several triplet states close in energy to the lowest triplet state for chlorins[49,50] so that state mixing with symmetry reduction is likely to occur.

The strikingly variable intensities observed between the different components may support this conclusion, for in time-resolved ENDOR the line intensities are expected mainly to be dependent on the number of nuclei contributing to the line,[51,52] as was indeed observed in previous time-resolved ENDOR studies in this laboratory.[15,22,23] Each of the lines may then be a convolution of contributions from two (or more) different triplet states.

The crystal site could also be responsible for a lowering of the symmetry, an effect that has been observed before in ODMR studies of the triplet state of both porphyrin[53] and chlorin[54] molecules in *n*-octane single crystals, which could be comparable to the toluene matrix used here. On the other hand, in previous studies of $^{T}H_2$TPP equivalent ENDOR spectra were obtained both in randomly oriented polystyrol[19] and in crystallized toluene[15] matrices.

It has also been demonstrated in a previous ODMR study[54] of $^{T}H_2$TPC that photo-induced tautomerization occurs. The tautomer with the N–H H–N axis parallel to the saturated pyrrole bond, see Fig. 1, is the lower energy state and the other, with the N–H H–N axis perpendicular to the saturated pyrrole bond, becomes populated at 4 K after prolonged irradiation at 400 nm.[54] In our EPR experiment, the tautomers cannot be differentiated, as the line widths are much greater than the differences between the ZFS parameters observed in the ODMR experiment.[54] If both tautomers were present it would be expected that additional lines would be observed in the ENDOR experiment with its enhanced resolution. Consider the central acidic protons, in the lower energy state they are equivalent, but in the higher energy state they are not. Hence, if both states were present then three lines should be attributable to them. However, that only one line could be assigned to these protons by deuteriation, Fig. 5(*c*) and (*d*), suggests that only the lower energy tautomer is present in our study.

Conclusions

The nature of the polycrystalline phase of toluene has been investigated by the use of time-resolved EPR on the photoexcited triplet state of free-base tetraphenylchlorin. It has been shown that in this phase approximately 55% of the solute molecules are aligned with respect to both the triplet *z*- and *x*-axes. This ordering has been used to advantage in the following ENDOR study to enhance the S/N by increasing the number of molecules contributing to the signal while maintaining the orientational selectivity. It is expected that this interesting property of toluene can be further investigated and utilized in conjunction with other spectroscopic techniques and with other molecules of interest, especially where single crystals are not available.

The sign and magnitude of the dipolar coupling between the triplet state and the matrix protons have been determined. The sign of the dipolar coupling is a quantity that so far could only be inferred from ENDOR on doublet states in frozen solution. 'Matrix' ENDOR on the triplet state could be usefully employed to probe the immediate environment of the triplet state especially with regard to hydrogen bonding in, for example, metalloporphyrins.

Time-resolved ENDOR has been used to determine the A_{zz} components of the hyperfine coupling tensors of the photoexcited triplet state of free-base tetraphenylchlorin and has shown that a reduction in symmetry, observed in the studies of the photoexcited triplet state of other porphyrinoid molecules, is also present here. Performing ENDOR on the triplet state has allowed some basic assignment to be made as the signs of the hyperfine couplings are immediately deducible from the spectra. Further assignment of the couplings can only be made with the help of extensive deuteriation in conjunction with molecular orbital calculations. Such calculations on the triplet state[1,35] have proved successful for unsubstituted porphyrins where excellent agreement was obtained with experiment.[10,33] In the case of substituted porphyrins, however, the agreement between experiment and theory is much less satisfactory.[19,20,55,56] Further theoretical investigations along these lines using all-valence-electrons self-consistent field molecular orbital calculations are in progress.

Acknowledgements

We are grateful to H. Mößler (in the group of H. Kurreck, Freie Universität Berlin) for the synthesis of the samples. We thank our colleagues at the Freie Universität Berlin: A. A. Dubinskii and M. Plato for helpful discussions; S. N. Batchelor who was involved in the initial experiments; B. Endeward and E. Johnen for computer and technical support; and E. Tränkle for the computer program Compass. This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 337).

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Paper 7/02468A
Received 10*th April* 1997
Accepted 16*th June* 1997