

# Photoionization of TMPD in DMSO solution: mechanism and magnetic field effects

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Photoionization of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in alcoholic solution produces the radical ion pair [TMPD<sup>•+</sup> e<sup>-</sup>]. However, the identity of the negatively charged counter-radical formed by photolysis of TMPD in DMSO (dimethylsulphoxide)/toluene mixtures, for which unusually large effects of weak applied magnetic fields have been observed, is unclear. Modulated MARY (Magnetically Affected Reaction Yield) experiments on solutions containing different isotopomers of TMPD, DMSO and toluene show that the counter-radical is likely to be the solvated electron. This result supports the idea that large effects of weak fields on radical recombination yields can be expected for radical pairs in which the electron–nuclear hyperfine interactions are concentrated in one of the radicals, rather than being distributed more evenly between the two radicals.

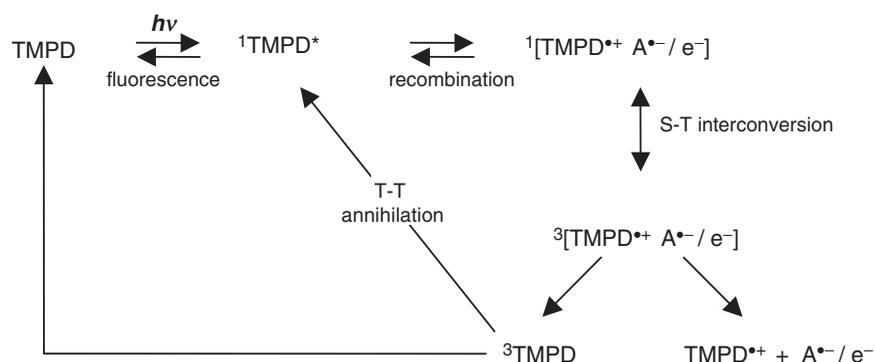
## 1. Introduction

*N,N,N',N'*-tetramethyl-*p*-phenylenediamine, TMPD, readily photoionizes in solution at room temperature to generate free radicals [1]. However, the photophysics of TMPD is quite complex and subtly dependent on experimental conditions. For example, the excited state quenching mechanisms, the spin multiplicity of the radical-generating state and whether the photoionization is mono- or biphotonic are still unclear [2–4]. Techniques employed to investigate the photophysics and photochemistry of TMPD include delayed fluorescence [5], transient absorption [6, 7], photoconductivity [6–9], Raman spectroscopy [10], and time-resolved Electron Paramagnetic Resonance [4, 11]. UV irradiation of TMPD in a variety of solvents (alcohols, alcohol mixtures, dimethylsulphoxide (DMSO)/toluene mixtures) leads to the formation of a spin-correlated radical ion pair. As a consequence, the primary photochemistry can conveniently be studied using the magnetic field-dependence of the radical pair recombination kinetics and/or the reaction product yields [12–14]. Here we use MARY (Magnetically Affected Reaction

Yield) spectroscopy [15] to investigate the photolysis of TMPD in DMSO/toluene solution.

As indicated in scheme 1, continuous illumination of sufficiently low intensity to ensure monophotonic excitation generates a singlet radical ion pair via the singlet excited state, <sup>1</sup>TMPD\* [6, 16]. This radical pair can either (i) recombine to give <sup>1</sup>TMPD\*, (ii) recombine to produce TMPD in the ground state, or (iii) undergo intersystem crossing to produce the triplet radical pair, a process that is strongly magnetic field-dependent [12, 13]. The triplet radical pair has three possible fates: (i) recombination to give the excited triplet state molecule, <sup>3</sup>TMPD, which in turn can undergo triplet–triplet annihilation, <sup>3</sup>TMPD + <sup>3</sup>TMPD → TMPD + <sup>1</sup>TMPD\*; (ii) further singlet–triplet interconversion to regenerate the singlet radical pair; (iii) diffusive separation of the two radical ions. The fluorescent singlet state <sup>1</sup>TMPD\* is therefore populated by two mechanisms: recombination of singlet radical pairs and triplet–triplet annihilation, both of which are in principle magnetic field-dependent [5]. The sensitivity to an applied field arises from the interconversion of states of different spin multiplicity (singlet and triplet states in the case of radical pairs, and singlet, triplet and quintet states in the case of triplet pairs) by intramolecular magnetic interactions (electron–nuclear hyperfine interactions and electron–electron dipolar interactions, respectively).

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Scheme 1. Possible photochemical reactions of TMPD in solution. In alcohol mixtures, the counter radical to  $\text{TMPD}^{\bullet+}$  is the solvated electron ( $e^-$ ) while in DMSO/toluene, it has been suggested that DMSO acts as the electron acceptor [13] producing the radical anion  $\text{DMSO}^{\bullet-}$  ( $A^{\bullet-}$ ).

In both cases, these intersystem crossing processes are modulated by the Zeeman interaction of the electron spins with an applied magnetic field as described, respectively, by the Radical Pair Mechanism (RPM) and the Triplet Pair Mechanism (TPM) [17]. The two mechanisms have distinctive effects on the yield of  $^1\text{TMPD}^*$  and hence on the intensity of its fluorescence. An applied magnetic field of more than a few milliTesla is expected to increase the yield of  $^1\text{TMPD}^*$  formed from the singlet radical pair and to reduce that coming from  $^3\text{TMPD}$  annihilation [5]. Moreover, the dependence of the TMPD fluorescence on the strength of the applied field should reflect the strength of the relevant internal magnetic interactions (hyperfine or dipolar). Previous studies [5, 13, 14] suggest that the RPM contribution is likely to dominate except, perhaps, when high yields of  $^3\text{TMPD}$  result from intense pulsed laser irradiation.

In 1997, Sacher and Grampp reported fluorescence-detected magnetic field effects (MFEs) for TMPD dissolved in a DMSO/toluene mixture using a modulated MARY technique [13]. The authors concluded that the magnetic field-dependence was dominated by the RPM and proposed that the radical pair responsible was  $[\text{TMPD}^{\bullet+} \text{DMSO}^{\bullet-}]$ , formed by photoinduced electron transfer. The suggestion of  $\text{DMSO}^{\bullet-}$  as the counter-radical contrasts with experiments in pure and mixed alcoholic solvents which show that the radical pair consists of the  $\text{TMPD}^{\bullet+}$  and the solvated electron [6]. Here we report the use of isotopically substituted reactants to clarify the identity of the radical pair in DMSO/toluene.

## 2. Experimental

$\text{TMPD-}h_{16}$  and its tetramethyl-deuterated form  $\text{TMPD-}h_4, d_{12}$  were purified using vacuum sublimation. Samples

purchased from Aldrich were found to be contaminated with oxidation products; vacuum sublimation yielded pure white platelets of TMPD that dissolved to produce nearly colourless solutions. The solvents used were of the highest spectroscopic grade supplied by Aldrich. Solutions were purged of oxygen by bubbling with oxygen-free nitrogen prior to the experiments. The concentration of TMPD was  $6 \times 10^{-3} \text{ M}$ , which is low enough that effects of degenerate electron exchange ( $\text{TMPD}^{\bullet+} + \text{TMPD} \rightarrow \text{TMPD} + \text{TMPD}^{\bullet+}$ ) on the MARY linewidth can be neglected ( $k = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in acetonitrile [18]).

The modulated MARY experiment has been described in detail previously [15, 19]. The sample was held in a quartz fluorescence cell mounted at the centre of a set of modulation coils between the poles of an electromagnet. The cell was irradiated continuously with UV light (200–400 nm) from a 100 W xenon lamp. The static field of the electromagnet, which was varied between  $-3 \text{ mT}$  and  $22 \text{ mT}$  (the signs indicating the direction of the field), was complemented by a weak modulation field (amplitude  $0.5 \text{ mT}$ ) oscillating at an audiofrequency of 381 Hz. The sample fluorescence, collected perpendicular to the excitation light using a liquid-filled light guide, was passed through a 400 nm bandpass filter to a photomultiplier tube, the voltage output of which was supplied to a digital phase-sensitive detector. This detection technique produced the first derivative of the modulated fluorescence intensity as a function of the magnetic field strength. The integral of the observed signal is a direct measure of the yield of  $^1\text{TMPD}^*$ .

Quantum chemical calculations were performed on  $\text{DMSO}^{\bullet-}$  *in vacuo* using Gaussian 03 [20]. Equilibrium geometry, saddle point and fragmentation product optimizations were carried out at the DFT B3LYP 6-31+G(2d,p) level of theory with counterpoise correction of basis set superposition error. Hessians were

checked at the end of each optimization, and the intrinsic reaction coordinate was followed from the saddle point in both directions all the way to either reactant or product energy minimum. Hyperfine coupling (HFC) constants were computed using a B3LYP exchange-correlation functional with a mixed basis set (6-311+G(3df) on sulphur and EPR-III on carbon, hydrogen and oxygen) using a B3LYP 6-31+G(2d,p) optimized geometry. The  $^1\text{H}$  HFC reported is a thermal average with respect to methyl group rotation, at 300 K. To compute this average, a series of constrained optimizations was performed with the OSCH dihedral angle incremented from  $0^\circ$  to  $360^\circ$  in  $10^\circ$  steps. HFC constants were computed for the resulting series of geometries and averaged with Boltzmann weights obtained from the corresponding energies.

### 3. Results

#### 3.1. MARY spectra

The solid line in figure 1(a) shows the first-derivative MARY spectrum of a solution of TMPD in a mixture of DMSO and toluene (1:1 by volume). The integrated form of this signal is given by the solid line in figure 1(b). This dependence of the 'singlet yield' (in this case, the yield of  $^1\text{TMPD}^*$ ) on the strength of the applied

static magnetic field is consistent with the RPM for a radical pair created initially in a singlet state [21]. For magnetic fields comparable to or greater than the average hyperfine coupling in the pair, the singlet yield increases with applied static field, levelling off at field strengths much larger than the hyperfine couplings. This behaviour reflects the increased energy gap between the singlet and triplet states arising from the electron Zeeman interaction which hampers singlet-triplet interconversion and so favours recombination from the singlet radical pair. At much lower fields (weaker than the average hyperfine coupling), the efficiency of singlet-triplet interconversion is enhanced by the applied field, leading to a minimum in the singlet yield, known as the Low Field Effect (LFE) [21, 22].

The width of the MARY spectrum can be characterised by the quantity  $B_{1/2}$ , the field strength at which the MFE reaches one-half of its limiting value at high field (figure 1(b)). As discussed below,  $B_{1/2}$  is a function of the magnetic properties (HFC constants and spin quantum numbers) of the nuclear spins in the radical pair. The experimental value of  $B_{1/2}$  for TMPD in DMSO/toluene is  $4.8 \pm 0.2$  mT (solid line in figure 1(b)). This value is identical to that determined by Iwasaki *et al.* [5, 11] for a solution of TMPD in propan-2-ol and appears to be consistent with the measurements of Sacher and Grampp (40:60 DMSO/toluene) [13].

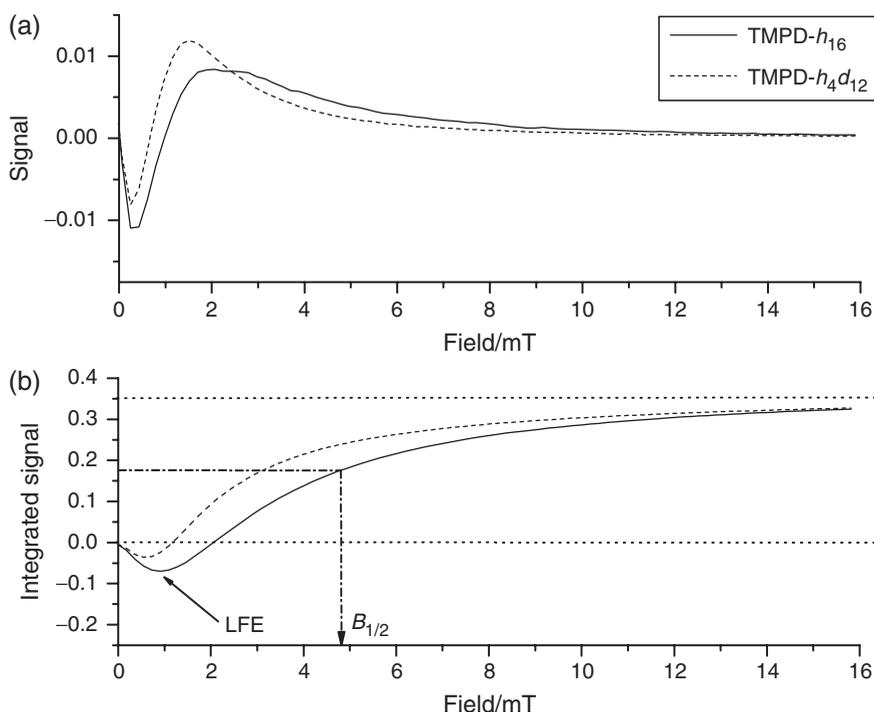


Figure 1. Experimental MARY data obtained for TMPD in DMSO/toluene solution. The static field varies between 0 and 15 mT. Solid line TMPD- $h_{16}$ ; dashed line TMPD- $h_4, d_{12}$ . (a) Experimental first-derivative signal; (b) its integrated form. The signal strength in (a) is given in arbitrary units.

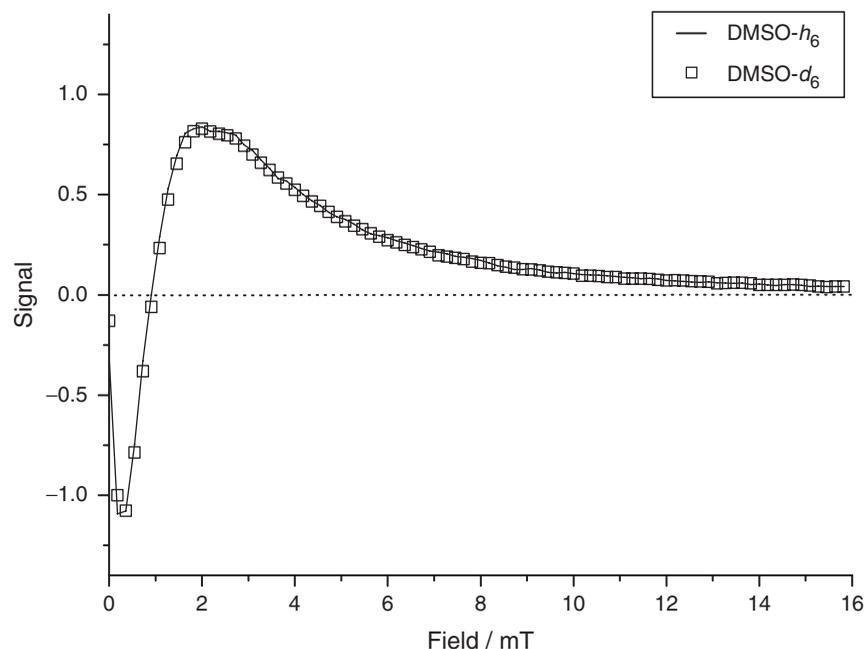


Figure 2. Modulated MARY spectra obtained for TMPD in DMSO/toluene solution. Line: DMSO- $h_6$ ; symbols: DMSO- $d_6$ . The signal strength is given in arbitrary units.

In addition, Iwasaki *et al.* have shown that time-resolved fluorescence detected magnetic resonance spectra of the radical pair can be successfully simulated using the hyperfine couplings of the TMPD cation alone [11].

To investigate further the identity of the magnetic field-sensitive radical pair, modulated MARY experiments were conducted separately in pure toluene and pure DMSO (results not shown). No MFE was found in the former case. However, a much attenuated signal (weaker by a factor of 20) was obtained in pure DMSO. The variation of MFE amplitude in these systems with toluene/DMSO solvent composition has been observed before [13] and indicates a complex dependence of the radical yield on the polarity of the solution. The shapes of the MARY spectra and the  $B_{1/2}$  values for TMPD in pure DMSO and in the DMSO/toluene mixture were identical.

If the counter-radical is derived from DMSO, then substituting the six DMSO protons by deuterons should, in principle, alter the appearance of the MARY spectrum by modifying the HFCs. Figure 2 shows clearly that TMPD dissolved in DMSO- $h_6$ /toluene and in DMSO- $d_6$ /toluene give identical spectra. Additionally, when perdeuterated toluene was used with fully protonated DMSO and TMPD, no change in the shape of the MFE or in the  $B_{1/2}$  value was observed (data not shown).

Table 1.  $B_{1/2}$  values from MARY spectra of TMPD.

Reactant	Solvent	$B_{1/2}/\text{mT}$
TMPD- $h_{16}$	DMSO- $h_6$ /toluene- $h_8$	$4.8 \pm 0.2$
TMPD- $h_{16}$	DMSO- $h_6$	$4.8 \pm 0.2$
TMPD- $h_{16}$	toluene- $h_8$	–
TMPD- $h_{16}$	DMSO- $d_6$	$4.8 \pm 0.2$
TMPD- $h_{16}$	DMSO- $h_6$ /toluene- $d_8$	$4.8 \pm 0.2$
TMPD- $h_4, d_{12}$	DMSO- $h_6$ /toluene- $h_8$	$3.1 \pm 0.1$

Finally, the 12 methyl protons in TMPD were replaced by deuterons (figure 1, dashed lines). The observed value of  $B_{1/2}$  changed from 4.8 mT (for TMPD- $h_{16}$ ) to  $3.1 \pm 0.1$  mT.

Table 1 summarizes the various experimentally determined  $B_{1/2}$  values.

### 3.2. Quantum chemical calculations

*In vacuo*, the ground state of DMSO $^{\bullet-}$  was found to have  ${}^2A_g$  symmetry with a thermally averaged isotropic  ${}^1\text{H}$  HFC constant of  $-0.04$  mT. This radical is unstable, by  $31$  kJ mol $^{-1}$ , with respect to dissociation into the  $\text{CH}_3\text{SO}^-$  anion and a methyl radical  $\text{CH}_3^{\bullet}$ , for which the HFC constant is 2.28 mT [23]. The transition state

for this fragmentation lies  $8.4 \text{ kJ mol}^{-1}$  above the ground state of  $\text{DMSO}^{\bullet-}$ .

#### 4. Discussion

According to Weller *et al.* [24],  $B_{1/2}$  is related to the average HFC constants of the two radicals,  $B_1$  and  $B_2$ , by

$$B_{1/2} = \frac{2(B_1^2 + B_2^2)}{B_1 + B_2}. \quad (1)$$

where

$$B_i = \left( \sum_k I_{ik}(I_{ik} + 1)a_{ik}^2 \right)^{1/2}, \quad i = 1, 2 \quad (2)$$

and  $a_{ik}$  and  $I_{ik}$  are, respectively, the HFC constant and the spin quantum number of nucleus  $k$  in radical  $i$ . Calculated  $B_i$  values for relevant radicals are given in table 2.

From table 2, the average HFC constant for  $\text{TMPD-}h_{16}^{\bullet+}$  (2.50 mT) is very close to half the  $B_{1/2}$  value determined for  $\text{TMPD-}h_{16}$  in DMSO/toluene ( $4.8 \pm 0.2$  mT). Using equation (1), this implies that  $B_2$ , the average HFC of the counter-radical, has two possible values:  $B_2 \approx 0$  or  $B_2 \approx B_1 = 2.5$  mT. Similarly, the calculated  $B_1$  for  $\text{TMPD-}h_4, d_{12}^{\bullet+}$  (1.53 mT) is also about 50% of the observed  $B_{1/2}$  ( $3.1 \pm 0.1$  mT), implying that  $B_2 \approx 0$  or  $B_2 \approx B_1 = 1.5$  mT. Assuming, very reasonably, that the counter-radical is the same for the photolysis of the two TMPD isotopomers, only a counter-radical with a  $B_2$  close to zero is consistent with both observed MFEs.

The conclusion that the counter-radical must have negligible HFC, allows us to speculate on its identity. It is highly unlikely to be any radical derived from toluene, which would almost certainly have substantial HFCs, and which would be inconsistent with the observation of  $B_{1/2} = 4.8$  mT in both pure DMSO and in a mixture of DMSO and perdeuterated toluene.

The DMSO radical anion,  $\text{DMSO}^{\bullet-}$ , with its very small average hyperfine interaction (table 2), at first sight seems a more attractive candidate. However, it is far from clear that, if formed, it would live long enough to give rise to a significant magnetic field effect. The calculations reported above indicate that it is unstable with respect to  $\text{CH}_3\text{SO}^-$  and  $\text{CH}_3^\bullet$ . The wavenumber of the vibration that leads to fragmentation is  $640 \text{ cm}^{-1}$ , which corresponds to a frequency of  $2 \times 10^{13} \text{ Hz}$ .

Table 2. Average HFC constants (equation (2)).

Reactant	$B_i/\text{mT}$
<sup>a</sup> TMPD- $h_{16}^{\bullet+}$	2.50
<sup>d</sup> TMPD- $h_4, d_{12}^{\bullet+}$	1.53
<sup>b</sup> DMSO- $h_6^{\bullet-}$	0.09
<sup>d</sup> DMSO- $d_6^{\bullet-}$	0.02
<sup>c</sup> $\text{CH}_3^\bullet$	3.45
<sup>d</sup> $\text{CD}_3^\bullet$	0.87

<sup>a</sup>Calculated using the HFC constants: 12H, 0.68 mT; 2N, 0.70 mT; 4H, 0.20 mT [4].

<sup>b</sup>Calculated using the HFC constant: 6H, 0.04 mT.

<sup>c</sup>Calculated using the HFC constant: 3H, 2.28 mT [23].

<sup>d</sup>Values for deuterated radicals calculated using  $\gamma_{\text{H}}/\gamma_{\text{D}} = 6.5$  and  $I_{\text{D}} = 1$ .

Because both extremes of the vibration lead to the dissociation, the gas-phase pre-exponential factor would be  $\sim 4 \times 10^{13} \text{ s}^{-1}$ . Together with the activation energy of  $8.4 \text{ kJ mol}^{-1}$ , this leads, at 300 K, to a rate constant for the fragmentation of  $1.4 \times 10^{12} \text{ s}^{-1}$ . In solution this process will be several orders of magnitude slower due to the cage effect, and a reasonable estimate of the rate constant might be  $10^9 \text{ s}^{-1}$ . Pulse radiolysis experiments on pure DMSO have shown that  $\text{DMSO}^{\bullet-}$  rapidly dissociates into  $\text{CH}_3\text{SO}^-$  and  $\text{CH}_3^\bullet$  at room temperature [25]. A lifetime for  $\text{DMSO}^{\bullet-}$  of  $\sim 1$  ns is incompatible with the observation of a strong Low Field Effect, which would require the  $[\text{TMPD}^{\bullet+} \text{ DMSO}^{\bullet-}]$  radical pair to retain its spin correlation for at least 10 ns. If fragmentation of  $\text{DMSO}^{\bullet-}$  takes place on the nanosecond timescale, the magnetic field dependence of the recombination reaction would be dominated by the secondary radical pair,  $[\text{TMPD}^{\bullet+} \text{ CH}_3^\bullet]$  to which spin correlation would be transferred. As a result of the large average HFC of the methyl radical, this species (table 2) is not consistent with the observed values of  $B_{1/2}$  or with the insensitivity of  $B_{1/2}$  to perdeuteration of DMSO. It therefore seems unlikely that the initially formed counter-radical is  $\text{DMSO}^{\bullet-}$ .

If radicals derived from neither toluene nor DMSO can account for the observed MFEs, then the only other candidate radical with negligible HFCs is the solvated electron. This conclusion is entirely compatible with the results of Sacher and Grampp, who seem to have based their proposal of  $\text{DMSO}^{\bullet-}$  on the failure to observe a magnetic field effect in pure toluene solution [13].

A particularly striking feature of figure 1(a), and of the observations by Grampp *et al.* [13, 14], is the unusually large Low Field Effect. It has been suggested that pronounced LFEs are expected, other things being

equal, when one of the radicals has many large hyperfine couplings whilst its partner has hyperfine interactions that are few and small (i.e.  $B_1 \gg B_2$ ) [26]. Studies on four isotopomers of the pyrene/*N,N*-dimethylaniline radical pair in cyclohexanol/acetonitrile solution provide support for this proposition [27]. The LFE predicted in the limiting case of a very long-lived radical pair does not depend strongly on the number or distribution of magnetic nuclei in the two radicals [21]. However, it appears that different behaviour is to be expected for more realistic lifetimes. Thus, the strong LFE provides further support for a magnetically simple counter-radical.

## 5. Conclusions

The results presented here provide strong evidence in favour of  $[\text{TMPD}^{\bullet+} e^-]$  and against  $[\text{TMPD}^{\bullet+} \text{DMSO}^{\bullet-}]$  as the photoinduced radical pair responsible for the observed magnetic field effect on TMPD fluorescence in DMSO/toluene solution. The formation of this radical pair explains very satisfactorily the observed  $B_{1/2}$  values in all systems studied as well as the existence of a large Low Field Effect.

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