
10

SPIN RELAXATION IN Ru-CHROMOPHORE-LINKED AZINE/DIQUAT RADICAL PAIRS

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10.1 INTRODUCTION

Photosynthesis is the inspiration for all efforts to harvest solar energy ranging from solar cells to light-induced water splitting. Historically, synthetic molecular systems that undergo light-induced electron transfer reactions have featured prominently in efforts to functionally mimic photosynthesis.^{1–9} Like the natural system, many of the intermediates and transient products of these light-induced electron transfer reactions are radicals; thus, they are subject to spin-chemical effects.

While artificial photosynthetic mimics come in many manifestations, our efforts have focused predominantly on the class of molecules represented by the structure in Fig. 10.1. These molecules consist of a visible-light-absorbing chromophore in the form of a trisbipyridineruthenium(II) complex (C) linked by flexible polymethylene chains to one or more electron donors (D) and an electron acceptor (A). The electron acceptor is an *N,N'*-dialkylated-2,2'-bipyridine (a so-called “diquat”); and the electron donors are *N*-alkylated phenothiazines. The diquat type acceptor was chosen because

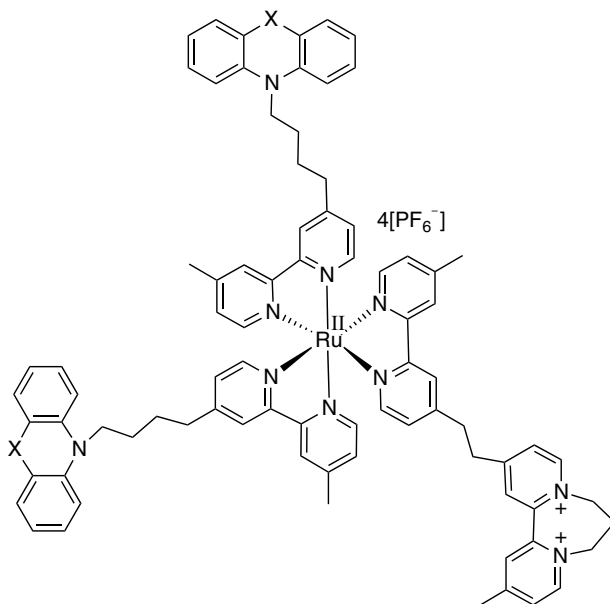


FIGURE 10.1 Donor–Chromophore–acceptor triad. X = a chalcogenide atom: oxygen, sulfur, or selenium.

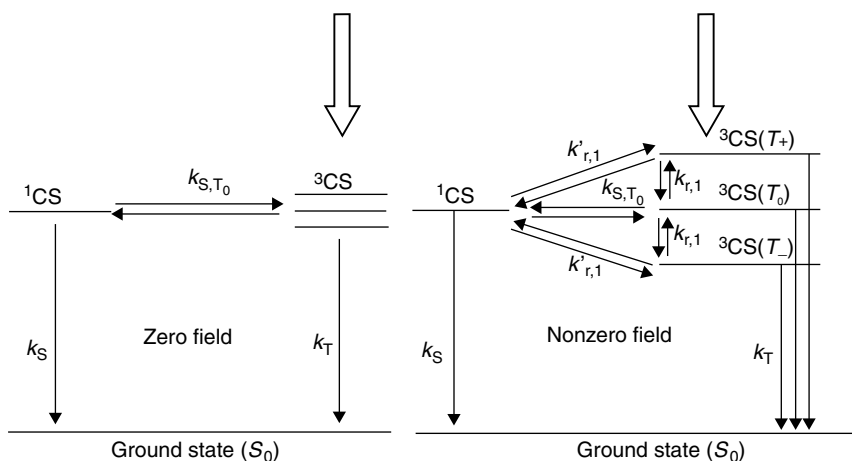
it is possible to tune its redox potential by almost a half a volt by simply altering the length of the alkyl chain connecting to two quaternary nitrogens. Three different but closely related donors are considered in the following discussions: phenothiazine (PTZ), phenoxazine (POZ), and phenoselenazine (PSZ). Finally, the fact that the structure represented in Fig. 10.1 contains two rather than a single donor moiety is a matter of synthetic expediency and is of no functional consequence. Subsequently, we will refer to structures analogous to the one in Fig. 10.1 as DCA triads.

In the ground state, these DCA triads are singlets. Upon irradiation with visible light, a metal-to-ligand charge transfer (MLCT) transition occurs in which an electron from a metal-based d-orbital is transferred to a π^* orbital on one of the bipyridine rings. In less than a picosecond, this state undergoes intersystem crossing to yield a triplet, $^3\text{MLCT}$.¹⁰ It is from this $^3\text{MLCT}$ state that a series of intramolecular electron transfer steps ensues leading ultimately to the charge separated state (CSS). The steps in this electron transfer cascade are first the oxidative quenching of the $^3\text{MLCT}$ state by the diquat acceptor followed by transfer of an electron from one of the donors to the oxidized chromophore; thus, in the resulting CSS the acceptor is reduced, one of the donors is oxidized and the chromophore is returned to the ground state.¹¹ This specific class of DCA triads is quite unusual in that the CSS state is formed with essentially unity quantum efficiency irrespective of the identity of the specific azine donor (i.e., PTZ, POZ, or PSZ) or diquat acceptor.¹¹ Detailed models of the energetics and kinetics of the CSS formation and decay back to the ground state in these specific DCA triad systems have been provided earlier.^{11–21}

Of particular relevance to the present discussion is the observation that the CSS, which is a biradical cation, is formed with essentially pure triplet spin correlation.¹² For energetic reasons, this triplet radical pair cannot recombine to form the ³MLCT state and can only form the singlet ground state. Therefore, direct recombination is spin forbidden. Moreover, because the radical pair which constitute the CSS product can separate only to a limited distance, essentially every CSS recombination event is between the same geminate radical pair—in other words, every reduced acceptor is ultimately oxidized by the donor radical cation that was formed from the same initial photochemical event. The spin behavior of the DCA triad CSS can be effectively explained by application of the relaxation mechanism of Hayashi and Nagakura.²²

Scheme 10.1 shows how this model is applied to the DCA triad CSS under consideration.^{12,23} The reduced diquat acceptor and oxidized azine donor are “normal” organic radicals that can physically separate within CSS to at least 20 Å. Therefore, at zero applied magnetic field, the triplet CSS (³CS) and singlet CSS (¹CS) are nearly degenerate and isotropic hyperfine coupling provides a path to mix these states allowing for CSS decay. In the zero field case, this mixing and transition occur rapidly relative to the singlet decay (k_s). Upon application of a magnetic field, Zeeman splitting of the ³CS occurs yielding three energy states: a magnetic field independent T_0 state and field dependent T_- and T_+ states. The path to the ground state for the T_0 state remains unchanged while at small fields the splitting of the field dependent states exceeds the hyperfine coupling energy, thus diminishing singlet–triplet mixing from those states and retarding their rate of decay to the ground state.¹²

The model in Scheme 10.1 suggests that application of a magnetic field to the CSS should result in biexponential decay kinetics consisting of a field independent (T_0) portion along with a field dependent portion (T_- and T_+). Within the CSS of these DCA triads the oxidized donor and the reduced acceptor each exhibit intense, isolated



SCHEME 10.1

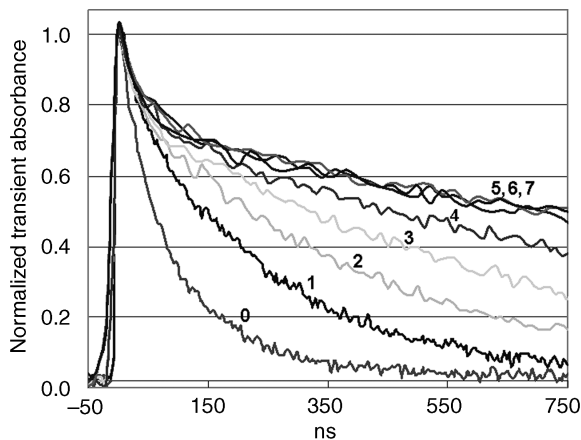


FIGURE 10.2 Field dependent transient absorption for CSS of DCA. (0) 0 mT, (1) 10 mT, (2) 25 mT, (3) 50 mT (4) 100 mT, (5) 300 mT, (6) 600 mT, (7) 1900 mT

features in their respective UV–vis absorption spectra. Thus, it is possible to probe the formation and decay of the CSS by transient absorption spectroscopy at the wavelengths corresponding to either component of the CSS (i.e., the oxidized donor or reduced acceptor). Figure 10.2 is a transient absorption measurement taken for a representative DCA triad at 520 nm that corresponds to the oxidized phenothiazine donor absorption. At time $t = 0$, the excitation laser initiates charge separation leading to CSS formation (subsequently also referred to as the radical pair) and finally to a decay to the ground state. With zero applied magnetic field, the decay of the CSS to the ground state is approximately monoexponential ($\tau = 100$ ns).^{12,23} Upon application of an external magnetic field, the decay becomes distinctly biexponential with a field dependent portion and a field independent portion. This result is a clear demonstration of the applicability of the model in Scheme 10.1 to the DCA system. There are numerous examples in the literature of systems that demonstrate an increase in decay lifetime upon application of a magnetic field. However, no system previously reported has shown such a clear and quantitative demonstration of the predictions of the Nagakura relaxation model: monoexponential decay at zero field with biexponential decay at nonzero field with the predicted weighting (1/3 field independent–2/3 field dependent).

Two magnetic field effect (MFE) studies of CSS formation and decay in these DCA triads have been previously reported.^{12,23} In the first, a series of DCA triads were synthesized with exclusively phenothiazine donors ($X = S$ in Fig. 10.1). The linkages separating the donor and acceptor moieties from the chromophore were altered over the series along with the acceptor redox potential. Results from this study primarily shed light on how the maximum separation distance in the radical pair influenced the spin chemistry. Consideration from this study led to the generation of a second set of DCA species wherein a single optimal DCA structure was chosen (i.e., the one shown in Fig. 10.1) and the identity of donor species was varied (phenoxazine $X = O$, phenothiazine $X = S$, and phenoselenazine $X = Se$). This set of triads was chosen

because they are isostructural, they are qualitatively similar in their CSS formation behavior, the donors have only slightly different (from one another) redox potentials, but vary in the atomic number of the heteroatom and, thus, the expected spin-orbit coupling.

In order to understand the magnetic field dependence of spin relaxation in the CSS, the contributions of various mechanisms need to be considered. These comprise the effects of anisotropic hyperfine coupling, g tensor anisotropy and spin-rotational interaction. All these mechanisms depend on specific magnetic properties of the two radical moieties forming the radical pair in the CSS. In particular, we need the components of the anisotropic hyperfine coupling tensor A_{ii} of the magnetic nuclei and the components g_{ii} of the g tensors of the two radicals. Our approach was to analyze the EPR spectra in liquid solution in as much detail as possible. Since, however, spectra in liquid solution yield only the orientationally averaged isotropic parameters, the measurements were complemented by quantum chemical theoretical calculations yielding all the tensor components, and to use the isotropic information from the spectra to validate the more detailed information from the calculations.

10.2 EPR FOR THE ISOLATED IONS

A detailed discussion of the contribution of various relaxation mechanisms determining the magnetic-field dependence of the decay of the charge separated state in the class of DCA species shown in Fig. 10.1 will follow. However, prior to this discussion it is necessary to establish some properties of the isolated radical species (reduced diquat and the oxidized azine species). The primary information required for these two radical species can be obtained through CW EPR measurements. Unambiguous hyperfine data can be found in the literature for the reduced diquat radical cation.²⁴ Hyperfine coupling constants for the diquat radical are reported as ($n = 2$) ($2 \times a_N = 0.4$ mT, $4 \times a_H = 0.35$ mT, $2 \times a_H = 0.31$ mT, $2 \times a_H = 0.25$ mT, $2 \times a_H = 0.06$ mT, and $2 \times a_H = 0.03$ mT).

The hyperfine information for the series of azine radical donors requires deeper consideration. Gilbert et al. report detailed hyperfine information for unmethylated azine donors.^{25,26} However, the methylated donors provide a better model for application to the DCA species under consideration. Also, the Gilbert studies do not conclusively explain the experimental EPR data, noting a trend of reduced EPR resolution with donor heteroatom size, without conclusive explanation. We therefore have conducted a detailed study of the cw EPR for the oxidized methyl azine radical cation series (MePOZ⁺, MePTZ⁺, and MePSeZ⁺).

Synthesis of the methylated donors can be found in the literature.²⁷ All EPR measurements were recorded with a Bruker EMX 200U spectrometer with a 4102ST resonator and a variable temperature TE102 cavity. Spectra of solid DPPH were collected immediately following each sample run for g value calibration. Solutions of each of the donor radicals were prepared in an N₂ glovebox. Upon mixing of the sample with the oxidant, the sample tube was sealed, removed from the box and frozen in liquid nitrogen prior to the experiment. AlCl₃ oxidant was used in nitromethane

solvent for the MePOZ and MePTZ donors. The MePSZ radical was formed in toluene solvent with thallium acetate and trifluoroacetic acid. The radical species remained stable under the given conditions for approximately 20 min at room temperature. Variables impacting signal broadening (concentration of analyte, microwave power, frequency, temperature, frequency modulation) were arrayed to achieve maximum signal resolution. A concentration of 0.06 mM with room temperature data collection proved optimal for all three species.

Figure 10.3 shows the results for the EPR measurements on the three oxidized donor radical cations. The loss of hyperfine resolution across the series (as noted previously by Gilbert et al.) is obvious within this methylated series.²⁶ The isotropic

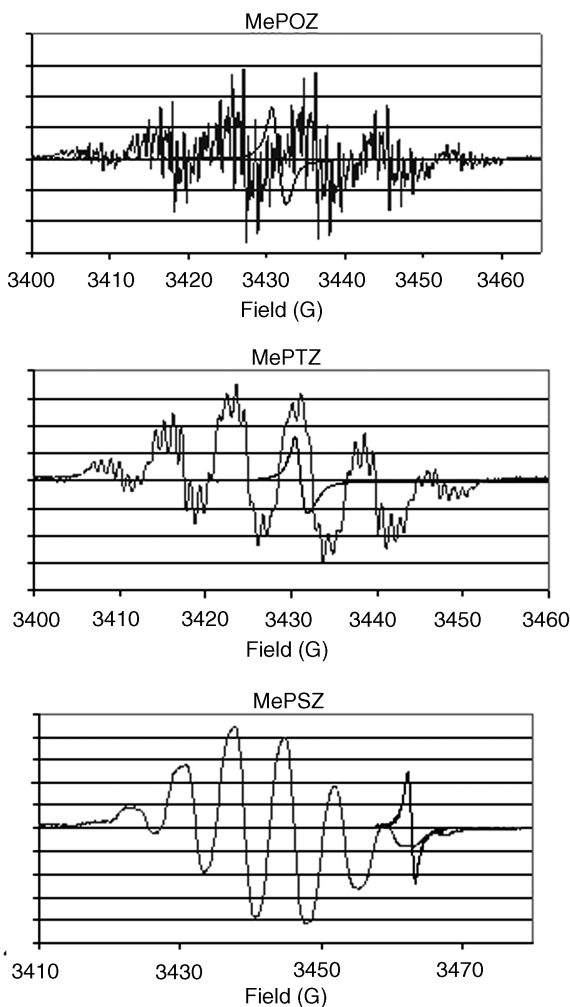


FIGURE 10.3 EPR spectra for the oxidized donor azine series. Each spectrum is overlaid with the relevant DPPH calibration spectrum.

TABLE 10.1 EPR Parameters^a of Me-PXZ Cation Radicals

	MePOZ	MePTZ ^c	MePSZ
a(1N)	9.18	7.56 (7.49)	6.82
a(3H)	9.07	7.22 (7.24)	7.30
a(2H)	2.99	2.17(2.11)	2.13
a(2H)	1.49	0.96 (0.98)	0.92
a(2H)	0.56	0.75 (0.73)	0.77
a(2H)	0.57	0.31 (0.24)	0.43
a(⁷⁷ Se) ^b			23.5 (25) ^d
G	2.0040	2.0052 (2.0052)	2.0153
Linewidth	0.30	0.30	0.55

^aHyperfine couplings and linewidths in Gauss.^bNatural abundance of 7.6%.^cValues from Ref. 25.^dValue for phenoselenazinium cation from Ref. 26.

magnetic parameters and homogeneous linewidth data of the azine radicals are presented in Table 10.1.

The spectral parameters were obtained by fitting the experimental EPR spectra using the WinSim package.²⁸ In order to determine the hyperfine linewidth, the specific modulation amplitude of the CW detection mode had to be taken into account. To this end, the theoretical spectrum with optimized Lorentzian linewidth was used as a starting point. Then the theoretical spectrum with the same hyperfine parameters but a reduced Lorentzian linewidth was calculated and transformed taking into account the broadening due to the CW modulation technique. The reduced Lorentzian linewidth was varied until the best correlation between experimental and modulation-transformed theoretical spectrum was obtained.

In view of the visible differences in resolution of the EPR spectra, it seems astonishing that the linewidth for the MePTZ radical cation is the same as that for MePOZ. However, as is borne out by the simulations, the reason for this deceiving impression is essentially exclusively due to the differences in hyperfine structure that gives more congested lines in the case of MePTZ. For MePSZ there is a noticeable increase in linewidth, but here again the apparent low resolution of the spectrum is largely due to the hyperfine structure. A secondary contribution is the underlying spectrum of 7.6% of the radicals with the magnetic ⁷⁷Se isotope.

The increase in linewidth between MePOZ/MePTZ to MePSZ is due to the spin-orbit coupling effect of Se. (In the case of MePTZ, the increased SOC with respect to MePOZ is not manifest in the linewidth, because other relaxation mechanisms dominate).

10.3 CALCULATION METHODS FOR EPR OF THE ISOLATED IONS

Molecular geometries were optimized using Gaussian03 at a DFT B3LYP/6-31G (2d,2p) level of theory using SCI-PCM solvation model (water). Effective core

potential basis set (CRENBL ECP) was used for selenium. Hyperfine couplings were computed using DFT B3LYP/EPR-II method in SCI-PCM water with a CRENBL ECP basis set for Se. The calculation of g tensors was carried out in ADF2007 using collinear unrestricted ZORA DFT PBE/TZP method.

10.3.1 Calculation of g Tensor Components

Accurate simulation of radical g tensors has only recently become possible, courtesy of accurate solvent models,²⁹ ZORA approximation to Dirac equation,³⁰ and the arrival of an accurate treatment of spin-orbit coupling within the density functional theory.³¹ All these methods are implemented in the ADF 2007 package, which was used for the g tensor calculations reported in Table 10.2.

As these results show, there is very good agreement between the theoretical and the experimental values of the isotropic g factors. Thus, the anisotropic components obtained from the quantum chemical calculations may also be considered as reliable. These components are needed in the following two mechanisms contributing to spin relaxation.

The relaxation mechanism depending on orientational modulation of the Zeeman interaction is determined by the anisotropy of the radicals' g tensors. In an axially symmetric approximation, this anisotropy is given by

$$\Delta g = g_{\parallel} - g_{\perp} \quad (10.1)$$

In Ref. 23, we have assumed that $g_{\parallel}$ equals the value g_e of the free electron,

$$g_{\parallel} = g_e \quad (10.2)$$

Hence,

$$g_{\perp} = \frac{(3g_{\text{iso}} - g_e)}{2} \quad (10.3)$$

TABLE 10.2 Theoretical Components of Radical g Tensors and Derived Quantities

	Phenoxazine	Phenothiazine	Phenoselenazine
g_{xx}	2.00199	2.00189	1.99982
g_{yy}	2.00411	2.00792	2.01654
g_{zz}	2.00433	2.00607	2.02774
g_{iso}	2.0035	2.0053	2.0147
g_{exp}	2.0040	2.0052	2.0153
Δg	-0.00223	-0.00510	-0.02232
$\frac{3}{2}(g_e - g_{\text{iso}})$	-0.00176	-0.00449	-0.01860
δg^2	7.49E-06	4.60E-05	8.56E-04
$\frac{9}{2}(g_e - g_{\text{iso}})^2$	6.23E-06	4.03E-05	6.92E-04

and

$$\Delta g = \frac{3}{2}(g_{\text{iso}} - g_e) \quad (10.4)$$

As the data in the table show, the assumption of axial symmetry is well founded. Comparing the Δg values based on the approximation (10.3) with the quantum chemically derived values according to Equation (10.1) there is also fair agreement.

The spin-rotational interaction is controlled by $\overline{\delta g^2}$, the sum of square deviations between the individual tensor components of g and the free electron value:

$$\overline{\delta g^2} = \sum (g_{ii} - g_e)^2 \quad (10.5)$$

Using, again, approximations (10.2) and (10.3) we obtain

$$\overline{\delta g^2} = \frac{9}{2}(g_{\text{iso}} - g_e)^2 \quad (10.6)$$

As is shown in Table 10.2, the agreement between the results according to the exact Equation (10.5) and the approximation (10.6) is fairly good.

10.3.2 Calculation of Hyperfine Coupling Constants

10.3.2.1 *Ab Initio* Hyperfine Coupling Constants: General Notes The electron-nucleus dipolar interaction that gives rise to hyperfine coupling naturally falls into two categories: the *anisotropic* part corresponding to pure dipolar interaction between electron and nucleus at large separations and the *isotropic* part resulting from a short-range dipolar interaction and stemming from the fact that because of finite size of the nucleus, the spherical average of point-to-point dipolar interaction is not zero. Because this second part results from short-range interactions, it is often referred to as *contact interaction*.³²

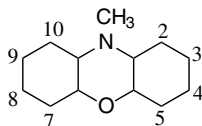
The expression for the anisotropic part of hyperfine coupling involves an integral over the spatial distribution of the unpaired electron, which is relatively easy to compute accurately even at a relatively low level of theory.³³ The contact term, however, includes a delta-function that chips out the wave function amplitude at the nucleus point. The latter is quite difficult to compute both because standard Gaussian basis sets do not reproduce the wavefunction cusp at the nucleus point and because additional flexibility has to be introduced into the core part of the basis to account for the now essential core valence interaction.³⁴

The basis sets and methods adequate for computing contact hyperfine couplings are relatively recent; the best general-purpose methods (DFT B3LYP with EPR-II or EPR-III basis set) were introduced in 1995³⁵ and 1996.³⁶ EPR-II is a double- ζ and EPR-III a triple- ζ basis set augmented by polarization and diffuse functions with core s-type Gaussians uncontracted and a number of tight s-type functions added. Furthermore, contraction coefficients were specifically optimized to reproduce experimental

isotropic hyperfine couplings in a standard set of molecules. Notably, the basis sets have been optimized for computing hyperfine couplings specifically with B3LYP exchange correlation functional, and an attempt to use a different functional, even a fairly good one like B3PW91 or PBE1PBE, usually leads to poorly predicted contact interactions. The anisotropic components, however, are always satisfactory.

The important aspect of *ab initio* hyperfine coupling calculations is the variation of this parameter during molecular vibrations. In the paper that introduces the EPR-II and EPR-III basis sets, Barone and coworkers show that the equilibrium geometry calculation of hyperfine couplings underestimates the large couplings, which are rectified after taking a vibrational average.³⁶ The practical difficulties of performing this averaging even for medium-sized molecules are, however, formidable with a need to compute a Hessian to perform even the simplest vibrational average. Even though the code performing this procedure was available to the authors, the necessary calculations were well out of reach of SGI Altix 4700 supercomputer, with the result that the larger of the computed hyperfine couplings in the tables reported below are noticeably smaller than the experimental values. Annoying as these small deviations might be, the estimates obtained at the equilibrium geometry are still very reliable.³⁷

10.3.2.2 Theoretical Values of Isotropic and Anisotropic Hyperfine Coupling Constants The theoretical values for the various magnetic nuclei in the azine radicals are given in Table 10.3. The correlation of experimental and theoretical values is plotted in Fig. 10.4. The numbering of the protons is given as follows:



As exhibited by Fig. 10.4, the correlation between theoretical and experimental values of the isotropic hyperfine coupling constants is generally very good. However, the

TABLE 10.3 Experimental and Theoretical Values of Isotropic Hyperfine Coupling Constants^a

	Phenoxazine		Phenothiazine		Phenoselenazine	
	Experimental ^b	DFT	Expt ^b	DFT	Experimental ^b	DFT
$a(^{14}\text{N})$	9.18	6.89	7.56	6.12	5.75	8.06
$a(\text{CH}_3)$	9.07	9.50 ^c	7.22	8.11 ^c	7.30	7.83 ^c
$a(\text{H}_{(4)}, \text{H}_{(g)})$	2.99	-2.89	2.17	-2.34	2.13	-2.20
$a(\text{H}_{(2)}, \text{H}_{(10)})$	1.49	-1.34	0.96	-1.06	0.92	-1.07
$a(\text{H}_{(3)}, \text{H}_{(9)})$	0.57	-0.63	0.75	-0.57	0.77	-0.41
$a(\text{H}_{(5)}, \text{H}_{(7)})$	0.56	0.63	0.31	0.50	0.43	0.49

^aValues in Gauss.

^bExperiment is insensitive to HFC sign.

^cAverage for the three protons in the minimal energy conformation of the methyl group.

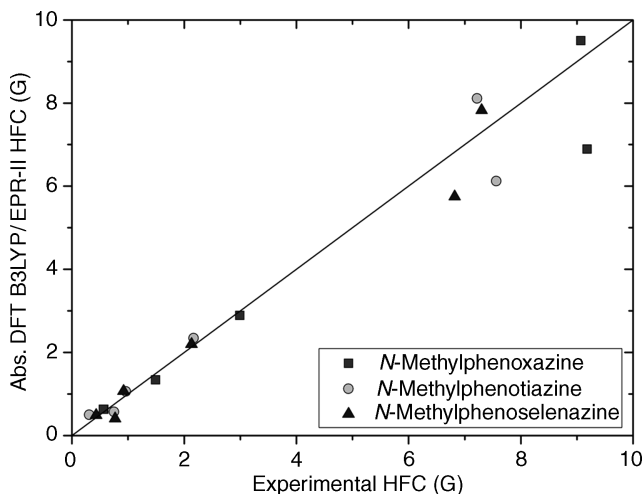


FIGURE 10.4 Experimental versus theoretical hyperfine couplings in phenoxazine, phenothiazine, and phenoselenazine. The three points deviating significantly from the bisector line belong to the ^{14}N nuclei. This deviation is likely caused by the lack of vibrational averaging in the calculation.

nitrogen hyperfine couplings are estimated somewhat too low. As an explanation, one has to consider that in all structures nitrogen is significantly bent out of plane. Thus, some very anharmonic motion is expected to exist along the direction perpendicular to that plane. Vibrational averaging should be taken into account in order to improve the theoretical predictions.

The anisotropic part of the nitrogen hyperfine interaction tensors are given in Table 10.4. As assumed in Ref. 23, these are well described by axial symmetry. The ratio between the axial anisotropy parameter A_N and the isotropic value is fairly constant. However, the value of 2.7–2.8 for this ratio is significantly larger than previously assumed (1.1–1.7²³). The anisotropy parameters for the ^1H -nuclei at the ring positions are in the range of 1–3 Gauss. Thus, neglecting their effect in the

TABLE 10.4 Theoretical Values of the Eigenvalues of the Anisotropic Part of the Nitrogen Hyperfine Interaction Tensors^a

	Phenoxazine	Phenothiazine	Phenoselenazine
$A_{N,xx}$	−6.40	−5.60	−5.30
$A_{N,yy}$	−6.30	−5.50	−5.20
$A_{N,zz}$	12.70	11.10	10.50
ΔA_N	19.05	16.65	15.75
$A_{N,iso}$	6.89	6.12	5.75
$\Delta A_N/A_{N,iso}$	2.8	2.7	2.7

^a Values are given in Gauss; the z-coordinate is perpendicular to the molecular plane, x is parallel to the long axis and y along the short axis of the molecule.

anisotropic hyperfine relaxation mechanism, which is proportional to A^2 , seems well justified. The hyperfine coupling of the methyl group is expected to be near-isotropic due to its rotational motion.

In the diquat radical, the A_N values of the two nitrogens amount to 9.0 G. The anisotropy axes are approximately perpendicular to the rings. Since these rings are, however, significantly rotated against each other due to the strain exhibited by the $(\text{CH}_2)_3$ bridge between the nitrogens, the two anisotropy axes are tilted toward each other by an angle of 53° . Thereby, the combined effect of the two nitrogen couplings in the anisotropic hyperfine relaxation mechanism must be significantly reduced relative to a strictly coaxial situation.

10.4 IMPLICATIONS FOR SPIN-RELAXATION IN LINKED RADICAL PAIRS

It is of interest to see how the information on the magnetic properties of the individual radicals relates to the spin-chemically observed spin relaxation in the Ru-chromophore linked radical pairs. As detailed in Ref. 23, the relaxation rate constant k_r defined in Scheme 10.1 can be extracted from the magnetic field dependence of the radical pair recombination kinetics. The pertinent data points for DCA-POZ and DCA-PSZ are shown in Fig. 10.5 together with the theoretical field dependence of k_r and its various contributions. For DCA-PTZ, no significant deviation from the DCA-POZ case is observed.

Theoretically, T_1 relaxation of individual radicals a and b is related to a k_r contribution in the radical pair by³⁸

$$k_r = \frac{1}{2T_{1,a}} + \frac{1}{2T_{1,b}} \quad (10.7)$$

Our theoretical analysis shall start with the high field behavior of k_r for the DCA-PSZ case. In this radical pair, k_r must be dominated by the short T_1 time of the PSZ radical. From the linewidth, that exceeds those of the radicals POZ and PTZ by 0.25 G, we derive a specific mechanistic contribution to $1/T_2$ of $3.8 \times 10^6 \text{ s}^{-1}$ in this radical.³⁹ It seems natural to assign this to the spin-orbit coupling effect of selenium in this radical, which is also borne out by the values of the g tensor components. This should lead to a large contribution of spin-rotational relaxation for which $1/T_1 = 1/T_2$.⁴⁰ With this interpretation of the excess linewidth and using Equation 10.7, we conclude that for DCA-PSZ k_r should not drop below approximately $2 \times 10^6 \text{ s}^{-1}$. Taking into account various other magnetic field dependent contributions, we found that the magnetic-field independent part for DCA-PSZ amounts to $3.4 \times 10^6 \text{ s}^{-1}$ (cf. Fig. 10.5). This value is close to what is expected ($1.9 \times 10^6 \text{ s}^{-1}$) for the contribution of spin-rotational relaxation from the PSZ radical. Considering the uncertainty of linewidth determined from the CW EPR spectra the agreement seems fair. Adopting $3.4 \times 10^6 \text{ s}^{-1}$ as the spin-rotational contribution to k_r we can estimate a relation between the effective hydrodynamic radius r of the PSZ moiety and the effective viscosity exhibited by it, by

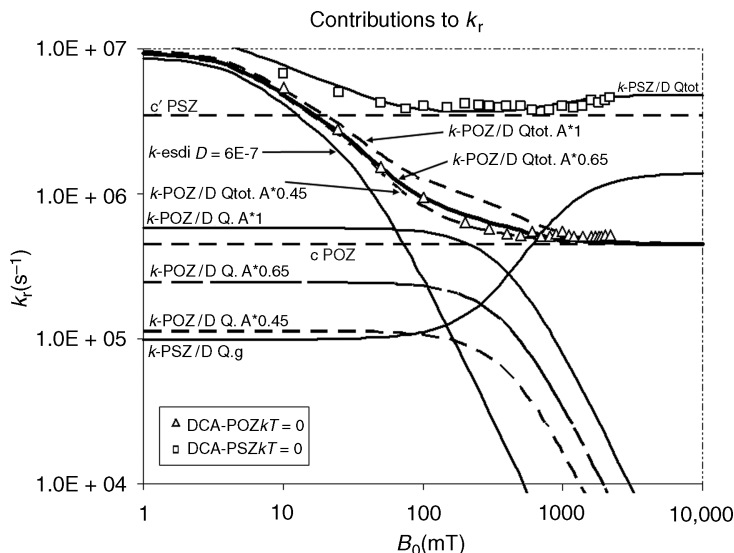


FIGURE 10.5 Contributions to k_r in the theoretical simulation of spin relaxation in the radical pairs from DCA-POZ and DCA-PSZ evaluated under the assumption of $k_T = 0$ (data points). The full simulations are represented by the curves denoted $k\text{-POZ}/DQ_{\text{tot}} \cdot A^*0.45$ and $k\text{-PSZ}/DQ_{\text{tot}}$, respectively. The contribution from the *esdi* mechanism ($k\text{-esdi } D = 6\text{E-}7$) corresponds to an effective translational diffusion constant of $D = 6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The curves indicated as $k\text{-POZ}/DQ \cdot A^*$ represent the contributions of the *ahfi* mechanism, the * indicating the factor by which the theoretical anisotropy parameter A is reduced. The curve indicated by $k\text{-PSZ}/DQ.g$ denotes the contribution due to the g tensor anisotropy in the PSZ radical. The constant values c POZ and c' PSZ represent the field-independent contributions to k_r . For details of the calculation cf. Ref. 23.

using the theoretical relations²³

$$k_{r,\text{sri}} = \frac{1}{2T_{1,\text{sri}}} = \frac{1}{2T_{2,\text{sri}}} = \frac{1}{18} \frac{\overline{\delta g^2}}{\tau_c} \quad (10.8)$$

and

$$\tau_c = \frac{4\pi\eta r^3}{3kT} \quad (10.9)$$

From $k_r = 3.4 \times 10^6 \text{ s}^{-1}$, we obtain $\tau_c = 1.38 \times 10^{-11} \text{ s}$ and $\eta r^3 = 13.8 \text{ cP } \text{\AA}^3$. Assuming an effective radius between 2.5 and 3.0 $\text{\AA}$ that seems geometrically reasonable, the effective viscosity would range between 0.50 and 0.89 cP. For 1,2-dichloroethane, the solvent used in the experiments $\eta = 0.464 \text{ cP}$ at 25 °C. Since, however, the radical is linked to the complex by a tetramethylene chain one might well expect some increase of the effective viscosity for rotational diffusion.

To assess the spin-relaxational contribution $k_{r,ahf}$ of anisotropic hyperfine coupling we only take the contribution from the nitrogen nuclei into account. This approach is justified on the basis of the theoretical DFT calculations showing that the contribution of anisotropic coupling to the ^1H spins is at least by one order of magnitude smaller. Details of the calculations of $k_{r,ahf}$ for the radical pairs are given in Ref. 23. In Fig. 10.5, the curve denoted $k\text{-POZ/DQ.A}^*1$ shows the theoretical field dependence of $k_{r,ahf}$ using the full anisotropic hyperfine couplings as obtained from the DFT calculations. It is apparent that this contribution is quite negligible at low fields and at high fields. So, different mechanisms must contribute in these field regions. At low fields, the main contribution can be assigned to electron spin dipolar interaction (k_{esdi}) between the two radicals which is stochastically modulated by the relative translational diffusion of the two radicals toward each other. This may be parametrized by the distances of closest approach and farthest separation and an effective diffusion constant. For the distance boundaries, limits of 5.5 and 20 Å, respectively, seem reasonable on geometrical grounds. Adopting an effective diffusion constant D of $6 \times 10^{-7} \text{ cm}^2/\text{s}$, the low-field behavior of k_r is well reproduced (for details of the calculations of k_{esdi} Ref. 23). Such an effective value of D is much smaller than to be expected for free diffusion of the radicals in the solvent 1,2 dichloroethane. However, values of such order of magnitude may be expected for pairs of molecules covalently linked by a flexible bridge of the size of the DCA-PXZ systems.^{41,42} A molecular dynamic simulation for our systems should be desirable for a more quantitative modeling of the k_{resdi} contribution.

As is shown in Fig. 10.5, anisotropic hyperfine interaction can only contribute in the intermediate field region. At high fields, even in the case of the DCA-POZ radical pair where the spin-orbit coupling effect on g is too small to cause a significant contribution of spin-rotational relaxation, a field-independent contribution of $k_r \approx 4.5 \times 10^5 \text{ s}^{-1}$ is present. This applies also to the DCA-PTZ radical pair. As for the source of this field-independent contribution, we can only speculate. A vibrational mechanism with very short correlation time has been invoked.²³ Adding the contribution $k_{r,ahfi}$ of the anisotropic hyperfine mechanism to that of the esdi mechanism and the magnetic-field independent contribution obtained from k_r at high fields, the theoretical prediction when using the values of the anisotropic hyperfine constants from the DFT calculations in the intermediate field range lead to k_r values that are clearly higher than observed (cf. the curve denoted $k\text{-POZ/DQ.tot.A}^*1$). In order to become compliant with the experimental field dependence of k_r , we have to reduce the hyperfine anisotropy values by at least a factor of 0.45 (cf. Fig. 10.5). The reason for this discrepancy is not clear at present. Since evaluation of the CW spectra is not sufficient for this purpose, it would be illuminating to access the T_1 times of the free radicals by time-resolved pulsed EPR methods.

Finally, we address the apparent trend of the k_r -values for the DCA-PSZ pair to increase slightly at the high field end. Actually, this trend can be reproduced by the contribution $k_{r,gta}$ of the g tensor anisotropy mechanism, however, using an orientational correlation time τ_c of $8 \times 10^{-12} \text{ s}$ that is only about half the value extracted from a fit of the spin-rotational mechanism, as described above. It is possible that distortional motions of the nonplanar azine ring—which has been invoked to account for the deviation of the isotropic ^{14}N hyperfine constants of the azine radicals

from the theoretical values predicted by DFT—also contributes to the modulation of the g tensor.

In summary, the field dependence of spin relaxation in the Ru-chromophore linked DCA-PXZ radical pairs can be rationalized well in terms of existing spin relaxation mechanisms and the magnetic parameters of the individual radicals taken from CW EPR spectra and DFT calculations. To complete and refine the picture, it would be most rewarding to measure the field-dependent T_1 times of the individual radicals using pulsed FT EPR and to investigate the dynamic motion of the radical moieties in the Ru-chromophore-DCA-PXZ triad by molecular dynamic calculations.

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