A New Mechanism for Chemically Induced Dynamic Nuclear Polarization in the Solid State

Gunnar Jeschke[†]

Contribution from the Institut für Anorganische Chemie, Universität Bonn,
Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

Received October 29, 1997

Abstract: Electron−electron−nuclear three-spin mixing is discussed as a source of a new type of CIDNP effects that is peculiar to the solid state. The build-up of nonequilibrium nuclear spin polarization by this mechanism does not require singlet−triplet branching with different fates of the radicals in the two branches. Rather it is a polarization transfer from the electron−electron zero-quantum transition to the nuclear spins in the vicinity of a 2-fold avoided level crossing. An analytical expression is derived that describes this transfer for short times after the radical generation. Under this condition, the size of the effect is proportional to the static field, to the electron−electron spin coupling, and to the square of the anisotropy of the hyperfine coupling. An estimate of the order of magnitude of the resulting polarization reveals that three-spin mixing could be the source of recently observed solid-state CIDNP effects in bacterial photosynthetic reaction centers. CIDNP effects of this type should occur in a sizeable number of photochemical or thermal reactions in organic solid-state chemistry that involve radical pairs as intermediates.

Introduction

Recently, chemically induced dynamic nuclear polarization (CIDNP) was first detected in the solid state by Zysmilich and McDermott.[1] These observations on quinone-depleted and quinone-reduced bacterial photosynthetic reaction centers were initially rationalized by the radical pair (RP) mechanism of CIDNP that is operative in liquid state.[2] To explain why the polarizations of the singlet and triplet branch do not cancel each other, the additional assumption had to be made that significant ^{15}N and ^{13}C spin−lattice relaxation takes place during the lifetime of 100 μs of the special pair triplet. In a later more detailed investigation, the same authors demonstrated however that part of the CIDNP signals has to be assigned to the bacteriopheophytin that does not pass a triplet state in the reaction cascade.[1c] They concluded that further clarification of the polarization mechanism is necessary.

In a recent theoretical investigation of electron−electron−nuclear three-spin mixing, we found some indication that such mixing can be the source of a new type of CIDNP effects that is peculiar to the solid state.[3] This three-spin mixing (TSM) mechanism does not depend on singlet−triplet branching, so that it may be operative in many solid-state reactions with radical intermediates. Solid-state CIDNP could thus become a promising new tool for studies in the field of solid-state organic photochemistry.[4] After observing nonequilibrium *transverse* nuclear magnetization in an electron paramagnetic resonance (EPR) experiment on bacterial photosynthetic reaction centers and relating it to the three-spin mixing, Kothe et al.[5] suggested that the CIDNP effects observed by Zysmilich and McDermott may also originate from this source.

In this work, we derive for the first time expressions that describe CIDNP generation by the TSM mechanism at the short time scale of the original experiments. These expressions allow one to pinpoint the different preconditions for CIDNP due to the RP and TSM mechanisms and to give an estimate of the order of magnitude expected for the effects. We show that the available information on the molecular and electronic structure of bacterial photosynthetic reaction centers does not yet allow for a precise quantitative prediction of the effects. Nevertheless, the new mechanism can explain the CIDNP effect in the bacteriopheophytin moiety without the assumption of unusually short relaxation times. Finally we discuss features which an ideal model system for the study of TSM mechanism should possess.

Theory

CIDNP effects in solution are mainly due to a spin-sorting process designated as RP mechanism.[2] Radical pairs with a different state of a particular nuclear spin have different probabilities of singlet−triplet conversion, since the conversion frequency depends on the hyperfine coupling. With the help of diffusion, triplet pairs may then predominantly separate, while most of the reactive singlet pairs recombine before they can leave the solvent cage. The escaped radicals from the triplet pairs may then form so-called escape products that are different

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[†] Present address: MPI für Polymerforschung Mainz, Ackermannweg 10, D-55128 Mainz, Germany.

(1) (a) Zysmilich, M. G.; McDermott, A. *J. Am. Chem. Soc.* **1994**, *116*, 8362−3. (b) Zysmilich, M. G.; McDermott, A. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 6857−60. (c) Zysmilich, M. G.; McDermott, A. *J. Am. Chem. Soc.* **1996**, *118*, 5867−73.

(2) (a) Closs, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 4552−4. (b) Kaptein, R.; Osterhoff, J. L. *Chem. Phys. Lett.* **1969**, *4*, 195−7. (c) Kaptein, R. In *Chemically Induced Magnetic Polarization*; Muss, L. T., et al., Eds.; D. Reidel: Dordrecht, The Netherlands, 1977; pp 1−16.

(3) Jeschke, G. *J. Chem. Phys.* **1997**, *106*, 10072−86.

(4) (a) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433−81. (b) Scheffer, J. R.; Garcia-Garibay, M.; Nalamasu, O. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 8; pp 249−347. (c) Ramamurthy, V.; Eaton, D. F. *Chem. Mater.* **1994**, *6*, 1128−36.

(5) Kothe, G.; Bechtold, M.; Link, G.; Ohmes, E., Weidner, J.-U. *Chem. Phys. Lett.* **1998**, *283*, 57−60.

S0002-7863(97)03744-X CCC: $15.00

from the singlet-derived cage products. The spin sorting during the singlet−triplet conversion thus leads to nonequilibrium nuclear spin polarization in the two kinds of products. In solids however, diffusion is usually much too slow to compete with radical pair recombination. Singlet and triplet branch thus lead to the same products and the spin sorting is undone. This mutual cancellation of singlet and triplet pair nuclear polarization will be incomplete if there is differential spin−lattice relaxation in the two branches. In particular, nuclei in triplet pairs are in a paramagnetic environment for a longer time, relax faster during this time, and may thus lose part of their polarization. Exactly the same part of polarization from the singlet pairs would then survive. CIDNP effects from this relaxation-type RP mechanism have been observed indeed in some cases in solutions,[6] but again they are less likely to occur in the solid state where spin−lattice relaxation is generally much slower.

There is however a different possibility for the large initial electron spin polarization to be partially transferred to the nuclear spins. If the eigenstates of the radical pair Hamiltonian are mixtures of electron and nuclear spin states, then evolution under this Hamiltonian may lead to the polarization of the nuclear spins. It has been shown earlier that electron−nuclear two spin mixing in spin-correlated radical pairs is not sufficient for transfer of an observable amount of magnetization to nuclear spins.[7] The significance of electron−electron−nuclear three-spin mixing for transient electron paramagnetic resonance experiments has first been demonstrated by Weber et al.[8] and has been studied in more detail subsequently.[3] In the latter work it has been demonstrated by numerical calculations that three-spin mixing can in principle lead to solid-state CIDNP effects that do not depend on singlet−triplet branching. Instead, CIDNP is caused here by polarization transfer near a *2-fold* avoided level crossing.

To obtain physical insight into this TSM mechanism of CIDNP, we may restrict ourselves to a spin system consisting of two coupled electron spins $S_1 = 1/2$ and $S_2 = 1/2$ and one nuclear spin $I = 1/2$ with an anisotropic hyperfine coupling to the electron spin S_1. The rotating frame high-field[9] Hamiltonian for this system in angular frequencies can be written as

$$\mathcal{H}_0 = \frac{\Delta\Omega}{2}S_{1z} - \frac{\Delta\Omega}{2}S_{2z} + \omega_I I_z + AS_{1z}I_z + BS_{1z}I_x + d'(3S_{1z}S_{2z} - \mathbf{S}_1\mathbf{S}_2) - J\left(2\mathbf{S}_1\mathbf{S}_2 + \frac{1}{2}\right) \quad (1)$$

with

$$\Delta\Omega = \frac{(g_1 - g_2)\beta_e B_0}{\hbar} \quad (2a)$$

$$\omega_I = \frac{g_n\beta_n B_0}{\hbar} \quad (3a)$$

where the parameters J, d', A, and B characterize the isotropic part of the exchange interaction, the electron dipole−dipole interaction, and the secular and pseudosecular part of the hyperfine interaction, respectively. The angular frequency of the rotation of the coordinate frame is given by $\omega_r = (g_1 + g_2)\beta_e B_0/(2\hbar)$. In the course of a chemical reaction, a radical pair is born either in its singlet (S) state or in the T_0 triplet state because of spin conservation. At high fields and in the absence of on-resonant microwave irradiation, further evolution is also restricted to the S-T_0 manifold. A product operator basis for the S-T_0 subspace can now be constructed from operators of the nuclear spin $I = 1/2$ and of a fictitious spin $S' = 1/2$, with the fictitious spin corresponding to the zero-quantum transition of the two electron spins. Correspondence rules between spin operators of the two spins S_1 and S_2 and of the fictitious spin S' have been given previously.[3] The Hamiltonian for the S-T_0 subsystem simplifies to

$$\mathcal{H}_{ST0} = \Delta\Omega S_z' + \omega_I I_z + AS_z'I_z + BS_z'I_x - dS_x' \quad (4)$$

with

$$d = 2J + d' \quad (5)$$

where we have neglected an energy shift $d'/2$ of the whole subspace. It has been shown earlier that the general form of $\mathcal{H}_{ST0}$ remains unchanged for an electron dipole−dipole interaction of general symmetry, an anisotropic exchange interaction, and a coupling of the nuclear spin to both electron spins.[3] The density matrix at the instant of radical pair creation is given by

$$\sigma_0 = \frac{1}{2}E_{S'} \mp S_x' \quad (6)$$

where $E_{S'}$ is the unity operator in the S-T_0 subspace, and where the upper and lower sign correspond to a singlet- and triplet-born pair, respectively.

Several situations of strong spin mixing have been investigated by a truncated Hamiltonian approach before,[3] in the present context it is sufficient to recall that three-spin mixing is at its maximum at the condition

$$2|\Delta\Omega| = 2|\omega_I| = |A| \quad (7)$$

that we call a double matching. The matching of the nuclear Zeeman energy to the first-order energy of the zero-quantum transition does not depend on the external static field, it requires a difference in the g-values of the two radicals of $\Delta g = g_1 - g_2 = 7.651 \times 10^{-4}$ and 3.085×10^{-4} for ^{13}C and ^{15}N, respectively. The matching of the nuclear Zeeman energy to the hyperfine coupling can be achieved by performing the experiments in a suitable static field.

For a discussion of CIDNP effects it is necessary to derive expressions that are valid both in the close vicinity of the double matching and farther off, as both Δg and A depend on the orientation of the radicals with respect to the static field. This is possible at least for very short times by expressing the evolution of the density matrix

$$\sigma(t) = \exp(-i\mathcal{H}_{ST0}t)\sigma_0 \exp(i\mathcal{H}_{ST0}t) \quad (8)$$

by the Baker−Hausdorff formula

$$\sigma(t) = \sigma_0 - it[\mathcal{H}_{ST0},\sigma_0] + \left(\frac{i^2t^2}{2!}\right)[\mathcal{H}_{ST0},[\mathcal{H}_{ST0},\sigma_0]] \mp ... \quad (9)$$

and limiting the expansion to a few terms. The nuclear spin polarization is given by

$$\langle I_z\rangle(t) = \mathrm{Trace}\{I_z\sigma(t)\} \quad (10)$$

Equation 10 has been calculated up to the t^8 term by using

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[6] Hore, P. J.; Kaptein, R. In *NMR Spectroscopy: New Methods and Applications*; Levy, G. C., Ed.; ACS Symposium 191; American Chemical Society: Washington, DC, 1982; pp 285−318.

[7] Jeschke, G.; Schweiger, A. *Mol. Phys.* **1996**, *88*, 355−83.

[8] Weber, S.; Kothe, G.; Norris, J. R. *J. Chem. Phys.* **1997**, *106*, 6248−61.

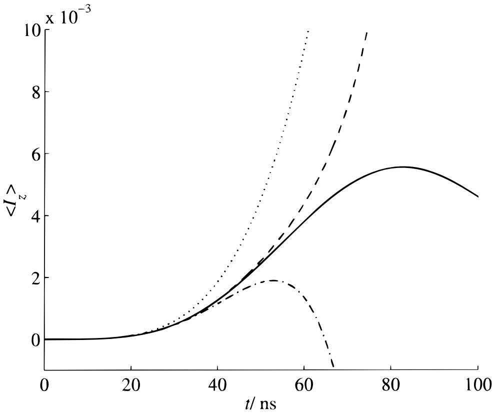

Figure 1. Analytical and numerical calculations of nuclear spin polarization due to the three-spin mixing mechanism for the parameter set $\omega_I/2\pi = 40$, $A/2\pi = 9.7$, $B/2\pi = 6.9$, $d/2\pi = 18.3$, $\Delta\Omega/2\pi = 26.7$ MHz corresponding to pyrrole nitrogens of bacteriopheophytin in photosynthetic reaction centers. Generation of the radical pair in its singlet state at time $t = 0$ was assumed. Solid line: numerical calculation. Dashed line: Baker−Hausdorff expansion up to t^8 term. Dash-dot line: expansion up to t^6 term. Dotted line: expansion up to t^4 term.

Mathematica.[10] The result for a singlet-born pair can be written as

$$\langle I_z\rangle(t) \approx B^2 d\omega_I\left[\frac{t^4}{2\cdot 4!} - C_1\frac{t^6}{4\cdot 6!} + (3C_1^2 + D_1)\frac{t^8}{32\cdot 8!}\right] \tag{11a}$$

with

$$C_1 = A^2 + B^2 + 4d^2 + 9\Delta\Omega^2 + 4\omega_I^2 \tag{11b}$$

$$D_1 = \Delta\Omega^2[14(A^2 + B^2) - 8d^2 - 83\Delta\Omega^2] + 8\omega_I^2(2A^2 + 8d^2 + 7\Delta\Omega^2) \tag{11c}$$

For a triplet-born pair, the effect has the same magnitude but opposite sign.

The expansions up to the fourth, sixth, and eighth power in time t are compared in Figure 1 with a numerical calculation by complete diagonalization of the Hamiltonian. The used parameter set ($\omega_I/2\pi = 40$, $A/2\pi = 9.7$, $B/2\pi = 6.9$, $d/2\pi = 18.3$, $\Delta\Omega/2\pi = 26.7$ MHz) may be typical for the situation in the ^{15}N CIDNP experiments. Numerical calculations throughout this work were performed by implementing density matrix formalism in the MATLAB[11] environment. Obviously, eq 11a−c predicts the CIDNP effect fairly well for times up to about 50 ns for the given parameter set. Since the time constant of the radical pair decay is 20 ns in photosynthetic reaction centers, we may use this equation for a *qualitative* discussion of the ^{15}N CIDNP effect caused by the TSM mechanism. Note however that any *quantitative* predictions should be based on numerical calculations, since the decay of the radical pair is not fast enough for the divergence of the truncated power series to be negligible at later times. Only at low enough static fields or for very fast radical pair decay, it is possible to use truncated Baker−Hausdorff expansion also for quantitative calculations. Experiments at lower fields may thus be advantageous, as this avoids the occurrence of sign anomalies that complicate interpretation of the results (see below).

Similar formulas for CIDNP effects of short-lived radical pairs due to the RP mechanism have been derived by Salikhov et al.[12] by means of an operator formalism and integration of the equations of motion. For comparison, we give their result in a form analogous to eq 11a−c

$$\langle I_z\rangle^{S}(t) \approx \Delta\Omega\cdot A\cdot\frac{t^2}{8} \tag{12}$$

The superscript S indicates that the formula is valid for recombination of the radicals in the singlet state of the spin-correlated pair (in-cage products); products in the triplet branch show exactly opposite polarization, $\langle I_z\rangle^{T}(t) = -\langle I_z\rangle^{S}(t)$

Comparison of eqs 11a and 12 reveals that CIDNP effects due to TSM mechanism evolve more slowly than the ones due to RP mechanism. Interestingly, the TSM mechanism is still operative for two radicals with coinciding g values, and it depends on the magnitude of the pseudosecular term of the hyperfine coupling instead on the magnitude of the secular term. Note that the sign of the CIDNP effect is determined by comparison with Boltzmann polarization which is proportional to $-I_z$ and I_z for positive and negative sign of the magnetogyric ratio, respectively. For the RP mechanism, this leads to a sign inversion of the CIDNP effect for negative magnetogyric ratio. For the TSM mechanism on the other hand, this sign dependence is cancelled by the occurrence of $\omega_I = -\gamma_I B_0$ in the prefactor in eq 11a. Due to the occurrence of ω_I, the enhancement factor is proportional to the static field. The same field dependence is found for the RP mechanism, in this case because of the dependence on $\Delta\Omega$. However, at a given field relative TSM CIDNP effects are proportional to the nuclear Larmor frequency, while relative RP CIDNP effects do not depend on it. As expected, CIDNP effects due to the TSM mechanism vanish if either the coupling between the two electron spins or the pseudosecular coupling between the electron and nuclear spin vanishes. Due to the square dependence on B, they occur predominantly in a cone of orientations near the orientation of maximum pseudosecular hyperfine coupling. For a hyperfine tensor of axial symmetry, this orientation is characterized by an angle of 45° between the unique axis of the hyperfine tensor and the direction of the static magnetic field. The sign of TSM CIDNP effects for short-lived radicals is then expected to be opposite to the sign of d in this orientation. The term short-lived is here defined by the condition

$$T_d^2 C_1 \ll 60 \tag{13}$$

where T_d is the lifetime of the radical pair. At fields as they are used in state-of-the-art NMR spectrometers, even a lifetime as short as 20 ns does not necessarily fulfil this condition. For instance, for a ^{13}C Larmor frequency of 100 MHz, $\Delta g = 0.001$, and $T_d = 20$ ns, condition (13) is strongly violated. Anomalous signs of CIDNP effects for longer-lived radical pairs are also known in the solution case.[12] Finally, TSM CIDNP does not depend critically on the *extent* of three-spin mixing; since at least for short times only the magnitude of the mixing terms in the Hamiltonian is of importance but not the deviation from the double-matching condition (7).

Results and Discussion

Quantitative predictions of solid-state CIDNP effects due to TSM mechanism require numerical calculation of eq 8 and

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(9) Here the term “high-field Hamiltonian” means that the electron Zeeman interaction is much larger than the nuclear hyperfine, exchange, and electron−electron dipolar interactions.

(10) Wolfram Research, Inc., Champaign, IL.

(11) The Math Works, Inc., Natick, MA.

(12) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. In *Spin Polarization and magnetic effects in radical reactions*; Elsevier: Amsterdam, 1984.

integration of the product of $\langle I_z\rangle(t)$ with the fraction of radical pairs that recombine at time t (or react in another way that terminates three-spin mixing). This calculation has to be performed for all orientations of the spin-correlated radical pair with respect to the external field to compute the powder average. Such a computation in turn requires that the g tensors of the two radicals, the electron−electron dipolar coupling tensor, the J coupling of the electron spins, and the hyperfine tensor are all known. Knowledge of a tensor in this sense of the term implies knowledge of the principal values *and* of the directions of the principal axes with respect to the molecular frame. A vast body of information on the electronic and molecular structure of the photosynthetic reaction center of *Rhodobacter sphaeroides* is already available, including a 3.1-Å X-ray structure,[13a] the g tensor of the special pair,[13b] proton spin densities,[13c] and principal values of the nitrogen hyperfine couplings in the special pair radical cation.[13d] Proton spin densities for the bacteriopheophytin radical anion BPheo^- are also known.[14] Reasonable estimates for the nitrogen hyperfine tensor of the BPheo^- can be obtained from recent work on the pheophytin radical anion Pheo^- of photosystem II[16] and from symmetry considerations. Information on the electronic exchange (J) and dipole−dipole coupling in the radical pair has been obtained by time-resolved EPR and reaction-yield detected magnetic resonance (RYDMR).[15] However, to the best of our knowledge the g tensor of BPheo^- and its orientation in the molecular frame are still unknown. MAS observation of the NMR signal at sample spinning speeds that do not completely average out the chemical shift anisotropy further complicates the necessary calculations and opens up cross relaxation pathways between different nuclei. Under these circumstances, precise quantitative predictions for the TSM CIDNP effects cannot be given.

Nevertheless it is possible to derive an estimate for the order of magnitude of the effects. The CIDNP signal in Zysmilich and McDermott's work[1] that is most improbable to arise from the RP mechanism is the one for the pyrrole nitrogens of BPheo^-. The principal values of the ^{15}N hyperfine tensor of the two pyrrole nitrogens of Pheo^- in PS II are given by (2.1, 2.1, 18.5) and (2.9, 2.9, 30.8) MHz.[16] This corresponds to maximum $B/2\pi$ values of 8.2 and 13.9 MHz, respectively. Principal values of the g tensor of the special pair are 2.00329(3), 2.00239(3), and 2.00203(3).[13b] The isotropic g value for BPheo^- is 2.00330(5).[14b] From the values for the exchange and dipolar coupling between the two radicals[15] one can infer that $d/2\pi$ should be in the range between −100 and −20 MHz. At first sight this would suggest a negative nuclear polarization (see eq 3a), hence a positive sign of the ^{15}N TSM CIDNP effect contrary to experimental observations. However, a calculation with $\Delta g = 0.00073$ (difference of the isotropic g values), $A/2\pi = 9.7$, $B/2\pi = 6.9$, $d/2\pi = -60$, $\omega_I/2\pi = 40$ MHz, $T_D = 20$ ns, yields a positive nuclear spin polarization of 2.8×10^{-4}, i.e., a sign anomaly is expected at the field of 9.35 T used in the experiments. The calculated value should be understood as an estimate of the order of magnitude, it corresponds to −80 times the Boltzmann polarization, while estimates for the experimental effect are a factor of −300.[1a,c] Note that the long spin−lattice relaxation time of ^{15}N nuclei in the solid state should allow for the accumulation of polarization from several excitation cycles, so that steady-state effects may well be substantially larger than our estimate for a single cycle.

Numerical calculations also show that the nuclear spin polarization in the singlet and triplet branch due to the RP mechanism is by about a factor of 100 larger than the polarization due to the TSM mechanism. However, the polarizations of the two branches cancel each other exactly unless there is differential relaxation during the lifetime of the special pair triplet of 100 μs. During such a short time, ^{15}N spin−lattice relaxation in a *diamagnetic* reaction center can be safely neglected. For the RP CIDNP to be of at least the same size as the TSM CIDNP, the spin−lattice relaxation time for the bacteriopheophytin nitrogens would have to be as short as 1 ms in the presence of the special pair triplet. With a distance of about 17 Å between the two molecules, this seems to be rather unlikely. The situation is less clear cut for the ^{15}N CIDNP effects in the special pair itself, where the hyperfine anisotropy is smaller[13d] and where it is difficult to give any estimate for the ^{15}N spin−lattice relaxation time in the triplet state. For ^{13}C on the other hand, TSM CIDNP effects would be expected to be substantially larger than for ^{15}N in bacteriopheophytin, as the calculated p_z spin densities on the carbons of the π skeleton[13c] correspond to larger hyperfine anisotropies and ω_I is larger. The explanation of experimentally observed solid-state CIDNP effects at natural abundance of ^{13}C[1b] by the TSM mechanism thus appears to be feasible. In this case, part of the signals tentatively assigned to bacteriochlorophyll[1b] might be due to bacteriopheophytin. If chemical shift differences between the two molecules are similar to the differences between chlorophyll and pheophytin,[17] such an assignment would not be in contradiction to the experimental data. Nevertheless, in the absence of quantitative calculations one cannot be certain if both the RP and TSM mechanism, only the latter, or even a third, hitherto unknown effect have to be invoked for a correct explanation of Zysmilich and McDermott's experimental results. Experiments at lower fields could provide essential new information on that count. By repeating our calculation for a magnetic field of 5.87 T with otherwise unchanged parameters, we find that the sign anomaly should disappear and the CIDNP signal should be about 30 times enhanced with respect to the equilibrium polarization. Such a sign change on going to lower fields would not be expected for the RP mechanism.

Under these circumstances it may furthermore be reasonable to search for CIDNP effects due to the TSM mechanism in simpler model systems. Photochemically generated biradicals in organic crystals may be particularly well suited for this kind of study. If the exchange interaction is strong enough in such a biradical, CIDNP effects due to the RP mechanism are suppressed,[2a] while effects due to the TSM mechanism are expected to be substantial because of the comparatively large value of J and hence d (cf. eq 11a). The anisotropy of the hyperfine coupling and thus its pseudosecular part B is often as large as some 10 MHz for ^{13}C nuclei in organic radicals. Finally, it is much easier to grow single crystals of sufficient

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(13) (a) Chang, C.-H.; El-Kabbani, O.; Tiede, D.; Norris, J.; Schiffer, M. *Biochemistry* **1991**, *30*, 5352−60. (b) Klette, R.; Törring, J. T.; Plato, M.; Möbius, K.; Bönigk, B., Lubitz, W. *J. Phys. Chem.* **1993**, *97*, 2015−20. (c) Lendzian, F.; Huber, M.; Isaacson, R. A.; Endeward, B.; Plato, M.; Bönigk, B.; Möbius, K.; Lubitz, W.; Feher, G. *Biochim. Biophys. Acta* **1993**, *1183*, 139−60. (d) Lendzian, F., Bönigk, B.; Plato, M.; Möbius, K.; Lubitz, W. In *The Photosynthetic Bacterial Reaction Center*; Breton, J., Vermeglio, A., Eds.; Plenum Press: New York, 1992; pp 89−97.

(14) (a) Fajer, J.; Forman, A.; Davis, M. S.; Spaulding, L. D.; Brune, D. C.; Felton, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 4134−40. (b) Lubitz, W.; Lendzian, F.; Möbius, K. *Chem. Phys. Lett.* **1981**, *84*, 33−8.

(15) (a) Hunter, D. A.; Hoff, A. J.; Hore, P. J. *Chem. Phys. Lett.* **1987**, *134*, 6. (b) Proskuryakov, I. I.; Klenina, I. B.; Hore, P. J.; Bosch, M. K.; Gast, P.; Hoff, A. J. *Chem. Phys. Lett.* **1996**, *257*, 333−9.

(16) Deligiannakis, Y.; Rutherford, A. W. *J. Am. Chem. Soc.* **1997**, *119*, 4471−80.

(17) (a) Lötjönen, S.; Hynninen, H. *Org. Magn. Reson.* **1983**, *21*, 757−65. (b) Egorova-Zachernyuk, T. A.; van Rossum, B.; Boender, G.-J.; Franken, E.; Ashurst, J.; Raap, J.; Gast, P.; Hoff, A. J.; Oschkinat, H.; de Groot, H. J. M. *Biochemistry* **1997**, *36*, 7513−19.

size for NMR work from simple organic compounds than from bacterial photosynthetic reaction centers. NMR experiments on single crystals under static conditions would be easier to describe and would open up a more direct way to observe anisotropy of CIDNP effects.

Conclusion

It has been demonstrated by theoretical derivations and numerical simulations that electron−electron-nuclear three-spin mixing can be a source of CIDNP effects that are peculiar to the solid state. This new CIDNP mechanism does not depend on reaction branching. To be operative, it requires a significant coupling between the electron spins in a spin-correlated radical pair and anisotropic hyperfine coupling. These preconditions are fulfilled for many intermediate radical pairs in thermal or photochemical reactions in the solid state. It has been shown that the three-spin mixing mechanism can in principle explain recently observed ^{15}N CIDNP effects in the bacteriopheophytin moiety of photosynthetic reaction centers[1c] that are unlikely to arise from the radical pair mechanism. When properly understood, solid-state CIDNP may become a promising tool for studies in the field of solid-state organic photochemistry.

Acknowledgment. We thank two anonymous referees for pointing out a numerical error and for advising us to ref 15. This work has been supported by a Liebig grant by Stiftung Stipendienfonds of the VCI Deutschland and the German Federal Ministry of Education, Research and Technology.

JA973744U