the reaction occurs in two steps, the singlet–triplet combination can give polarized product as a result of triplet–singlet transitions in the intermediate diradical. In either case, however, the part of the dimerization that leads to polarized product must involve at least one triplet reaction partner.

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[10] Proctor and Gamble Fellow, 1969–1970; IBM Fellow, 1970–1971.

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On the Origin of Nuclear Spin Polarization in Triplet Dimerizations[1]

Sir:

Recently Berson, *et al.*,[2] observed chemically induced dynamic nuclear spin polarization (CIDNP) in the dimers derived from trimethylenemethane derivatives. Since the monomers are known to have triplet ground states,[2,3] it appeared of interest to examine whether the previously proposed radical-pair model of CIDNP[4] can be extended to cover triplet reactions.

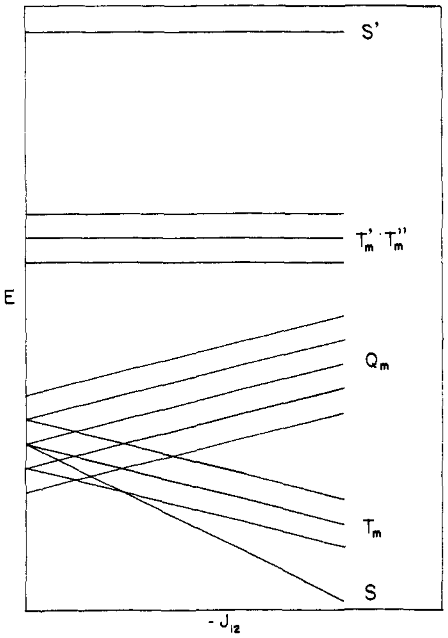

Figure 1. Eigenvalues of $\mathcal{H}_0$ as function of J_{12}. Note: to conserve space, J, given by the separation of T_0' from S' and S at $J_{12} = 0$, has been made unrealistically small compared to the Zeeman splitting.

A four-electron spin system with D_2 symmetry serves as a model for a *weakly* interacting pair of identical triplet molecules. A schematic representation is given in eq 1, where S_1,S_1' and S_2,S_2' represent the electron spins on components 1 and 2 of the triplet pair, respectively.[5] The scalar electron exchange coupling within each triplet molecule is denoted by J, while the intermolecular exchange coupling is given as J_{12}. The nuclei, $i,j, \ldots$ on component 1 with nuclear spins I_i, I_j, ... are coupled only to the electron spins S_1 and S_1' with the isotropic hyperfine coupling constants A_i, A_j, ..., whereas the corresponding coupling on component 2 is denoted with subscripts k, l, ... Neglecting the nuclear Zeeman term and all anisotropic interactions, the spin Hamiltonian describing the stationary system in a strong magnetic field may be formulated as $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{hyp}}$, where the first term describes the isotropic interactions of the electrons with the magnetic field and with themselves and the the second term represents the isotropic hyperfine interactions. For the case of $|J| \gg |J_{12}|$ these terms are given in units of $\hbar$ by

$$\begin{tikzcd}
 & & S_1 & & S_2 & & \\
I_i & A_i \arrow[l] \arrow[r] & J \arrow[u] \arrow[d] & J_{12} \arrow[l] \arrow[r] & J \arrow[u] \arrow[d] & A_k \arrow[l] \arrow[r] & I_k \\
 & & S_1' & & S_2' & &
\end{tikzcd} \qquad (1)$$

$$\mathcal{H}_0 = g\beta H_0 S_z - J(\mathbf{S}_1 \cdot \mathbf{S}_1' + \mathbf{S}_2 \cdot \mathbf{S}_2') - J_{12}(\mathbf{S}_1 + \mathbf{S}_1') \cdot (\mathbf{S}_2 + \mathbf{S}_2') \quad (2)$$

$$\mathcal{H}_{\text{hyp}} = \sum_i A_i I_i(\mathbf{S}_1 + \mathbf{S}_1') + \sum_k A_k I_k(\mathbf{S}_2 + \mathbf{S}_2') \quad (3)$$

where g and S_z are the isotropic g factor and the z component of electron spin of the triplet pair, respectively.

Of the 16 zero-order symmetrized electron spin functions,[6] 9 are derived from the combination of two triplet molecules and can be factored into a quintet, Q_{m}, a triplet, T_{m}, and a singlet, S. Two additional degenerate triplet states, T_{m}' and T_{m}'', originate from the two combinations of one triplet with one singlet molecule and the remaining singlet state S' is obtained from the combination of two singlet molecules. The symmetries and eigenvalues of these states are listed in Table I, and Figure 1 shows the energies as a function

Table I. Eigenstates of $\mathcal{H}_0$ for a Four-Electron System with D_2 Symmetry

$(\rho)_{\text{S,m}}$	Eigenvalue of $\mathcal{H}_0$	m
$(\mathfrak{A})_{2,\text{m}} \equiv Q_{\text{m}}$	$g\beta H_0 m - J/2 - J_{12}$	$2, 1, \ldots, -2$
$(B_1)_{1,\text{m}} \equiv T_{\text{m}}$	$g\beta H_0 m - J/2 + J_{12}$	$1, 0, -1$
$(B_2)_{1,\text{m}} \equiv T_{\text{m}}'$	$g\beta H_0 m + J/2$	$1, 0, -1$
$(B_3)_{1,m} \equiv T_m''$	$g\beta H_0 m + J/2$	$1, 0, -7$
$(\mathfrak{A})_0 \equiv S$	$- J/2 + 2J_{12}$	
$(\mathfrak{A})_0' \equiv S'$	$+ 3J/2$	

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[1] Supported by National Science Foundation Grant No. GP 18719X.

[2] J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971).

[3] P. Dowd, *ibid.*, **88**, 2587 (1966).

[4] (a) G. L. Closs, *ibid.*, **91**, 4552 (1969); (b) R. Kapstein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (c) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (d) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); (e) H. Fischer, *Chem. Phys. Lett.*, **4**, 511 (1970).

[5] Instead of using a basis set of four $S = {}^1/_2$ functions, the problem can also be treated with a basis set of $S = 1$ and $S = 0$ functions.

[6] For a review of the procedure of symmetrization of basis vectors, see P. L. Corio, "Structure of High-Resolution NMR Spectra," Academic Press, New York, N. Y., 1966, Chapter 8.

of J_{12} in the range of very weak interactions ($|J_{12}| < 10^2 A_i$) where J can be considered unchanged. The diagram corresponds to the case of Berson, *et al.*,[2] where the monomers have triplet ground states ($J > 0$) and where the S state correlates with the ground state of the dimer ($J_{12} < 0$).

To include the hyperfine interactions, $\mathcal{H}_{\text{hyp}}$, the electron spin functions are multiplied with the nuclear spin functions, $N_i, N_j \ldots N_k N_l \ldots$, where N_i denotes the spin of the ith nucleus. The product functions thus generated from T_m', T_m'', and S' are eigenfunctions of the total Hamiltonian. This result shows conclusively that no CIDNP can be expected to originate from a weakly interacting singlet–triplet pair or a singlet–singlet pair. In contrast, the functions derived from Q_m, T_m, and S are mixed by $\mathcal{H}_{\text{hyp}}$. For the CIDNP effect, the only off-diagonal elements of interest are those connecting with S, the only state leading directly to dimeric products. It is found that no off-diagonal elements exist between S and any of the Q_m states, but that $\mathcal{H}_{\text{hyp}}$ mixes S with T_m.[7] These elements are conveniently ordered into two groups, 4 and 5, distinguishing between S, T_0 mixing, in which the z component of the nuclear spin functions remain unchanged, and S, $T_{\pm 1}$ mixing accompanied by a change in the z component of both electron and nuclear spins.[8]

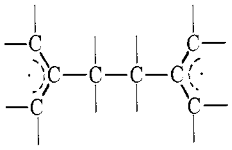
$$\langle T_0, N_i, N_k|\mathcal{H}|S, N_i, N_k\rangle = 2\left(\sum A_i N_i - \sum A_k N_k\right)/\sqrt{6} \quad (4)$$

$$\left.\begin{aligned} \langle T_{\pm 1}, N_i, N_k|\mathcal{H}|S, N_i \pm 1, N_k\rangle &= \pm A_i/\sqrt{3} \\ \langle T_{\pm 1}, N_i, N_k|\mathcal{H}|S, N_i, N_k \pm 1\rangle &= \mp A_k/\sqrt{3} \end{aligned}\right. \quad (5)$$

Because of the small magnitude of the off-diagonal elements, mixing will be important only in regions of near degeneracy which, as shown in Figure 1, exist for very small values of $|J_{12}|$ and for $|J_{12}| \sim {}^1/_2 g\beta H_0$, where S becomes degenerate with T_0 and T_{-1}, respectively. In large magnetic fields, mixing of S with T_{+1} can be neglected over the whole region of J_{12}.

If the time dependence of the Hamiltonian for a reacting system is treated by a step function of J_{12} as previously elaborated,[4] transitions among states will occur with probabilities which are proportional to the squares of the off-diagonal matrix elements connecting the states. In the experiment of Berson, *et al.*,[2] in which the triplet pairs are generated by diffusive encounters of triplet monomers, all states of Q_m, T_m, and S are populated with equal probability. The steady-state population, however, decreases from Q_m to T_m to S because of the difference in exit channels available to the systems in the different states. Diffusive separation is possible for all states; T_m has an additional channel leading to a triplet with intermediate bonding character, while S leads directly to dimer ground state. This population difference can induce a net flow of molecules from either T_0 or T_{-1} to S *via* transitions occurring with probabilities depending on the magnitude of (4) and (5) and, thus, on the nuclear spin states. If T_0, S transitions predominate, the resulting polarization in the dimer will show the "multiplet effect," where each nuclear spin multiplet will have an equal number of enhanced absorption and emission lines.[9] In contrast, if T_{-1}, S transitions are preponderant, all lines in the spectrum should occur in emission. The experimental spectrum is of the latter type, requiring for this mechanism an average value of J_{12} in the triplet pair, closer to ${}^1/_2 g\beta H_0$ than to 0. This is in sharp contrast to most, if not all, radical-pair reactions reported so far where, at large fields, T_0, S mixing accounts for the observations.

A second, and perhaps more likely, possibility for CIDNP to develop reveals itself if one follows the molecules in T_m states to the region of *strong* interactions. In the case at hand, the energy minimum of these states corresponds to structure **1**, where one bond is completed with the remaining two unpaired electrons at maximum separation.[10] If the exchange coupling, J_{12}', in the biradical is small, hyperfine-induced singlet–triplet mixing occurs as previously elaborated for radical pairs.[4] However, with the reasonable assumption that formation of **1** is irreversible, T_0, S mixing cannot yield CIDNP because of the lack of a competitive process, leaving only transition from T_{-1} to S to induce polarization. The corresponding off-diagonal elements of the appropriate two-electron Hamiltonian[4c] take the form of (5) (except that the normalization factor is $1/\sqrt{8}$), predicting emission for all nmr transitions.



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In conclusion it may be stated that triplet dimerizations can give rise to CIDNP signals with the polarizations originating either in the region of weak interactions between the triplet molecules or in transitions of the resulting triplet biradicals if the exchange coupling is small enough. While the former mechanism can give either multiplet or emission spectra, the latter can give rise only to pure emission.

Acknowledgment. I thank Professor Berson for bringing this problem to my attention and for providing me with experimental data before publication.

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[7] There exist off-diagonal elements between Q_m and T_m which, however, do not contribute to the solution of the problem.

[8] If two nonidentical triplets form a pair, (4) contains a term ${}^1/_2 \Delta g\beta H_0$, where Δg is the difference in isotropic g factor of the two components.[4c]

[9] For nonidentical triplets, the Δg term can result in pure emission or absorption, even when T_0, S mixing is the only process.[4c,8]

[10] The same state is formed when T_m' and T_m'' are reaching strong interactions.

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Stabilities of Trivalent Carbon Species. II. Homoaromatic and Antihomoaromatic Species Derived from Protonated Cyclooctatetraene[1]

Sir:

We recently reported results of cyclic voltammetric measurements in concentrated sulfuric acid by means of

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[1] Part I: M. Feldman and W. C. Flythe, *J. Amer. Chem. Soc.*, **91**, 4577 (1969).