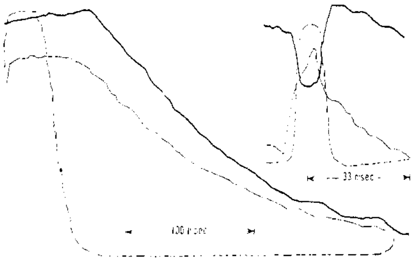

Figure 2. Kinetic curves for anthracene-d_{10} in benzophenone. The dashed curve is the time dependence of the light intensity and the heavy and light curves are the time dependence of a high- and low-field line, respectively.

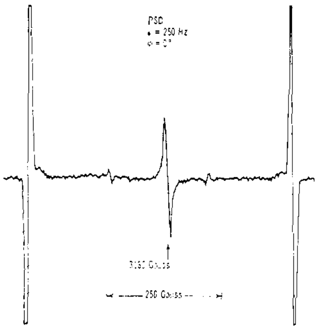

Figure 3. Phase-detected spectrum of phenazine. The central line at $g = 2$ is not identified. A similar light-modulated line appears in many systems.

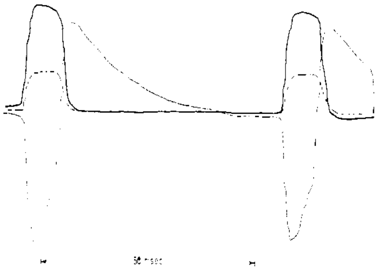

Figure 4. Kinetic curves of esr intensities of phenazine in biphenyl. The dashed curve is the light intensity *vs.* time and the heavy and light ones are the esr intensities of the high- and low-field lines, respectively.

modulation furnishing the reference, yield an almost identical spectrum (Figure 1). More rapid modulation at 250 Hz, again with phase-sensitive detection referenced to the light, yields the bottom spectrum of Figure 1. Some of the lines have disappeared and the surviving ones at low and high fields are inverted relative to each other. Direct observation of the associated kinetic behavior is shown in Figure 2. Under repeated pulses of light of about 10-msec duration, the low-field line is seen to be created with enhanced absorption, the high-field line with decreased absorption.[7]

The phenomena in phenazine in biphenyl host are similar but more pronounced. The spectra observed either under steady illumination or with low modulation are normal. At rapid modulation the phase-detected low- and high-field lines are inverted with respect to each other (Figure 3). The underlying kinetics as observed with pulsed excitation reveal the nature of the inversion. One line is born as an enhanced absorption, the other as an emission (Figure 4). We should note that phenazine in rigid glass does not exhibit the same phenomena. We believe that they exist but occur too rapidly for detection by our present equipment. We shall present detailed kinetic analyses of the phenomena in subsequent publications. We hope that with equipment presently under development the time resolution will be enhanced to permit observation of more rapid transients.

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Haim Levanon, S. I. Weissman*
Washington University
Saint Louis, Missouri 63130

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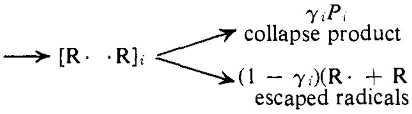
[7] J. Ph. Grivet and J. M. Lhoste, *Chem. Phys. Lett.*, 3, 445 (1969).

Suppression of High-Field (T_0–S) Chemically Induced Nuclear Spin Polarization (CIDNP) by Successive Trapping of Radicals. Persistence of Low-Field (T_1–S) CIDNP

Sir:

Current theory of CIDNP[1] holds the dynamic behavior of associated radical pairs responsible for the preferential formation of products in particular nuclear spin states.[3] Applied to reactions run in high magnetic fields (thousands of gauss), this is a spin selection theory. Each radical pair maintains its original nuclear spin state i as it collapses to products or separates to escaped radicals,[4] but the probability of collapse γ_i varies with i, so that nuclear spin states with larger γ_i are selected for preferential product formation.



$$\longrightarrow [\mathrm{R}\cdot\ \cdot\mathrm{R}]_i \begin{cases} \xrightarrow{} \overset{\gamma_i P_i}{\text{collapse product}} \\ \xrightarrow{} \underset{\text{escaped radicals}}{(1-\gamma_i)(\mathrm{R}\cdot + \mathrm{R}\cdot)_i} \end{cases}$$

According to this theory, there would be no CIDNP if all escaped radicals were somehow converted, with their original nuclear spin states, to P. This would be so even though the behavior of the individual radical pairs would normally give rise to CIDNP.

We report an example of this effect, the reaction of isopropyl chloride with sodium naphthalene. If the propane formed in this reaction resulted only from the *initial engagements* of intermediate alkyl radicals with naphthalene radical anion (:Naph·⁻),[5] it would be

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[1] Accepting popular usage, we adopt the acronym CIDNP for the phenomenon more reasonably termed "chemically induced nuclear spin polarization," in spite of the fact that CIDNP was originally proposed as the name of a *theory* of this phenomenon,[2] not the phenomenon itself, and the fact that this theory no longer seems viable.[3]

[2] J. Bargon and H. Fischer, *Z. Naturforsch. A*, 23, 2109 (1968).

[3] (a) G. L. Closs, *J. Amer. Chem. Soc.*, 91, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, 91, 4554 (1969); 92, 2183, 2186 (1970); G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, 92, 2185 (1970); (b) R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969); (c) F. J. Adrian, *J. Chem. Phys.*, 53, 3374 (1970); (d) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Amer. Chem. Soc.*, 92, 5761 (1970); (e) H. Fischer, *Z. Naturforsch. A*, 25, 1957 (1970).

[4] *Escaped* radicals have been members of an associated radical pair, but they have a vanishing probability of a future mutual collision.

[5] In view of the fact that Noyes' treatment of the diffusion behavior of radical pairs has been made the basis of a promising new formula-

expected to be polarized, but no polarization is observed for reactions carried out in 5000 G. On the other hand, polarization *is* found for reactions carried out in low fields, *e.g.*, 30–100 G, supporting our contention that the reaction mechanism is such that CIDNP might have been expected, on a naive basis, for reactions carried out in *any* field.

These observations are in harmony with the radical pair theory, for which they provide new support. Probably more important, they document a limitation of high-field CIDNP experiments, at the same time underscoring the absence of this limitation for low-field experiments.[7]

Quantitative treatments can be given. Consider the mechanism for formation of propane (RH) in this reaction, as inferred from earlier studies.[8]

$$\begin{tikzcd}
R_iCl \arrow[rr, ":Naph\cdot"] & & R_i\cdot \arrow[rr, shift left, "k_e\ :Naph\cdot"] \arrow[dl, dashed, "k_z"'] \arrow[dr, dashed, "1/(2\tau_R)"] & & {[R_i\cdot\ \ :Naph\cdot^-]} \arrow[ll, shift left] \arrow[r] & {} \\
& Z_i & & R_j\cdot & & \\
& & (j \neq i) & & aR_i:^- \arrow[r, "DME"] & aR_iH
\end{tikzcd}$$

Here k_e is the rate constant for engagements of R· and :Naph·$^-$, k_z is the first-order rate constant of some reaction of R· other than with :Naph·$^-$, τ_R is the nuclear spin relaxation time of R·, and a is the fraction of collapsing radical pairs which produce R:$^-$ (the remainder of the collapsing pairs produce R–Naph:$^-$, which leads ultimately to alkylation products).[8] For secondary radicals, a is about 0.5.

If one ignores the processes represented by dashed arrows, it is clear that no ultimate spin selection could result, since all initially formed R· would be converted to products with their original nuclear spin states intact. Only if the processes represented by dashed arrows drained a significant number of radicals off to products other than P could ultimate spin selection (and CIDNP in RH) be obtained. We must establish whether it is reasonable that these processes are insufficiently rapid for the reaction to lead to high-field (T_0–S)[9] CIDNP.

We treat a one-proton model case, the nuclear spin states being designated 1 and 2. Since the reaction is very fast, complete within the time of mixing, we assume that nuclear spin relaxation of R:$^-$ and RH is negligible during the reaction. Thus, we are interested in the relative total yields of R_1:$^-$ and R_2:$^-$. Replacing the varying concentration of :Naph·$^-$ by a constant mean or effective value $[:Naph\cdot^-]_{eff}$ we solve the kinetics problem represented by the scheme above. The result is that the nmr signal enhancement V of R:$^-$ is

$$V = \frac{\nu}{\nu^0} - 1 = \frac{V^0 + 1}{D + 1} - 1$$

where

$$V^0 = \frac{2(10^5)(\gamma_1 - \gamma_2)}{(\gamma_1 + \gamma_2)} - 1$$

and

$$D = \frac{2k_e[:Naph\cdot^-]_{eff}}{(1/\tau_R) + k_z}\left[\frac{\gamma_1\gamma_2}{\gamma_1 + \gamma_2}\right]$$

These equations rest on the assumption of no spin–lattice relaxation of the product between the time it is formed and the time of the nmr experiment. For the total accumulated R:$^-$ formed in the reaction, ν is the nmr signal intensity; ν^0 is the signal intensity of the identical product after complete spin–lattice relaxation. V^0 is the signal enhancement which would be expected if product resulted only from the set of *initial* engagements of alkyl radicals with naphthalene radical anions. The numerical factors are appropriate to nmr observations with a 60-Mc instrument and a sample at 25°.

Reasonable estimates of the various parameters of these equations are: $k_e \simeq 10^{10}$ sec^{-1};[10] $[:Naph\cdot^-]_{eff} \leq 10^{-2}$ M; $\tau_R \simeq 10^{-4}$–10^{-5} sec;[3a,b] $k_z \leq 10^4$ sec^{-1};[11] γ_1 and $\gamma_2 \geq 10^{-1}$.[14]

Choosing from these ranges so as to minimize D (thereby maximizing V), one obtains

$$V \leq V^0/100$$

Other reasonable choices of parameters ($\tau_R = 10^{-4}$ sec; $[:Naph\cdot^-]_{eff} = 10^{-1}$) lead to attenuation factors as large as 10,000. Thus, it is entirely reasonable that T_0–S CIDNP is not detectable in reactions of alkyl chlorides with sodium naphthalene, even though V^0 may be substantial.

A similar treatment of the T_1–S polarization arising in low-field reactions leads to the expectation that retrapping of escaped radicals does *not* suppress CIDNP.

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tion of the radical pair theory of CIDNP,[3c,6] we believe that his definitions of relevant terms should be adopted. An *encounter* of two radicals begins when, as the result of diffusion, they are brought to "adjacent positions."[6] We suggest that this is signalled by the first *collision* of the two. An encounter ends, perhaps after several collisions, when the radicals diffusively separate. Such a separation need not lead to escaped radicals,[4] since there is a significant probability that radicals which have once encountered will encounter again.[6] Thus, encounters tend to occur in sets. Noyes did not propose a name for such a set of mutual encounters, but one is clearly needed. We use the term *engagement* in this sense. An engagement may be considered to begin with the first collision of two radicals and to end with their last.

(6) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

(7) We previously reported the absence of CIDNP in cyclobutane and ethane formed in high-field reactions of alkyl halides with sodium naphthalene.[3d] Since entropy polarization could not be detected in these products, even if it were present, the previously reported experiments do not speak to the same point as the present ones, for which entropy polarization *could* have been detected, but was found to be absent.

(8) See ref 3d and citations therein.

(9) The mechanism of high-field CIDNP *is* believed to involve mixing of radical pair electronic triplet and singlet states, the triplet involved being the one of $m_s = 0$. Polarization arising through this mechanism is referred to here as T_0–S CIDNP. In low fields, the triplet states of $m_s = \pm 1$ may also mix with singlets effectively. Polarization arising through such mixing is termed T_1–S CIDNP.

(10) E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, pp 7–12, 279–285.

(11) After carefully considering the various alternatives, we concluded that the most likely reaction of R·, other than with :Naph·$^-$, is with naphthalene. We assume that isopropyl radicals are no more reactive toward naphthalene than phenyl radicals. Using the estimate of DeTar (2×10^3 M^{-1} sec^{-1}) for the reaction of phenyl radicals with benzene,[12] the fact that naphthalene is about 20 times as reactive as benzene toward phenyl radicals,[13] and the fact that the maximum concentration of naphthalene in our solutions is 10^{-1} M, we arrive at 10^4 sec^{-1} as the maximum pseudo-first-order rate constant for the reaction of isopropyl radicals with naphthalene.

(12) D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).

(13) D. R. Augood and G. H. Williams, *Chem. Rev.*, **57**, 123 (1957); see Table 8B, p 158.

(14) The rate constant for reaction of 5-hexenyl radicals with sodium naphthalene in DME has been estimated as 2×10^9 M^{-1} sec^{-1} by a competitive kinetic method.[15] Assuming a similar figure for the similar reaction of isopropyl radicals, γ (average for all spin states) $\simeq (2 \times 10^9)/10^{10} \simeq 0.2$. Allowing for a maximal differential among nuclear spin states of 10^{-1} for the average extent of singlet–triplet mixing, 0.1 is an estimate of the minimum value of γ for any nuclear spin state (averaged over the four electronic spin states).

(15) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969).

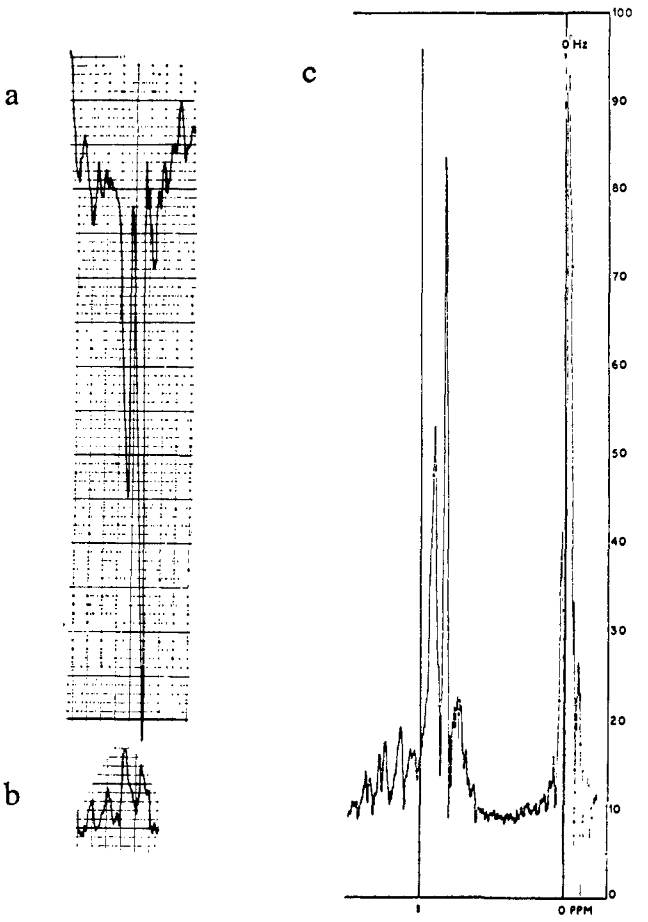

Figure 1. (a) Nmr spectrum of product mixture from a reaction of isopropyl chloride with sodium naphthalene carried out in a field of 60 G. (b) Same, after spin-lattice relaxation. (c) Reference spectrum of authentic propane in DME.

According to the radical-pair theory, T_1–S polarization is not a nuclear spin selection process. Instead, nuclear spin flips accompany T_1–S mixing, so that both the collapsed products and the escaped radicals from the set of *initial* engagements of alkyl radicals with naphthalene radical anions have nuclear spin polarization in the *same* direction. When the escaped radicals reengage naphthalene radical anions (not their former partners), one-fourth of the first collisions can be regarded as electronic singlets. Of these, a certain fraction collapses immediately (or during the first encounters of the reengagements) without undergoing additional nuclear spin flips. Thus, the polarization of the product formed in the set of initial engagements is reinforced, not suppressed.

It should be noted that T_0–S polarization can be effective in any field, so that low-field experiments would ordinarily lead to CIDNP reflecting both T_0–S and T_1–S contributions. In our case, the T_0–S contribution would be pure entropy polarization, while the T_1–S contribution would be pure energy polarization. Only energy polarization is evident (Figure 1). Thus, the T_0–S contribution to CIDNP appears to be suppressed for reactions carried out in low fields as well as in high fields. This extends to reaction fields near zero (earth's field), in which case no polarization is observed.

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John F. Garst,* Franklin E. Barton, II, John I. Morris
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

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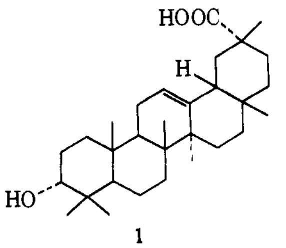
A Highly Twisted Carbon–Carbon Double Bond[1]

Sir:

In recent years compounds containing many types of strained double bonds have been prepared and studied, and particular interest has been given to rotation about a double bond, so called "torsional strain."[2] The high reactivity of such a system resulting from a decrease in the overlap of p electrons usually requires special synthetic methods be employed for their preparation.[3] We wish to report results related to preparation under acidic conditions of an unreactive highly torsionally strained double bond.

King and Morgan[4] reported that the triterpene katonic acid (**1**) underwent normal acetylation with acetic anhydride and pyridine but when treated with acetic anhydride containing a catalytic amount of perchloric acid it yielded a neutral keto acetate for which structure **2** was proposed. They noted that the uv max (EtOH) at 273 nm (ϵ 8900) was well outside the normal limits of 225–252 nm for α,β-unsaturated ketones.[5] This anomalous acetate also was reported to take up 2 mol of hydrogen to yield a product (uv max 217 nm (ϵ 5400, EtOH)) in which the keto group had been replaced by a methylene group. They also prepared, by lithium aluminum hydride reduction, a dihydro product with a uv max at 224 nm (ϵ 5200, EtOH). We have confirmed this latter result and also have obtained an isomeric dihydro alcohol (mp 169–173°) by lithium–ammonia reduction which has a uv max at 229 nm (ϵ 5180, EtOH).[6] These spectral properties, remarkable for compounds containing a lone carbon–carbon double bond, led us to undertake a crystal-structure analysis of this anomalous acetate.



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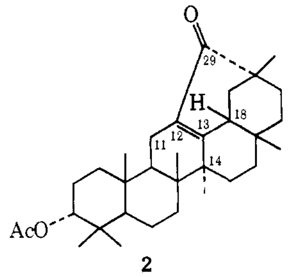

2

Crystals of the acetate, $C_{32}H_{48}O_3$, are monoclinic with the symmetry of space group $P2_1$; the unit cell con-

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[1] The crystal-structure analysis at Oak Ridge National Laboratory was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] For a general review of strained double bonds, see N. S. Zefirov and V. I. Sokolov, *Russ. Chem. Rev.*, **36**, 87 (1967).

[3] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970); J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970), and references cited therein.

[4] F. E. King and J. W. W. Morgan, *J. Chem. Soc.*, 4738 (1960).

[5] For a survey of ultraviolet spectra of unsaturated compounds, see A. I. Scott, "Interpretation of Ultraviolet Spectra of Natural Products," Macmillan, New York, N. Y., 1964.

[6] Both alcohols upon oxidation yielded the same enedione.