Olefin Isomerization *via* Radical-Ion Pairs in Triplet States Studied by Chemically Induced Dynamic Nuclear Polarization (CIDNP)

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Dedicated to the memory of Professor *Hanns Fischer*

Geometric isomerizations of olefins following photoinduced electron transfer (PET) are classified according to the relative energetic positions of the radical-ion pairs and the reactant triplets. Each class exhibits characteristic CIDNP (chemically induced dynamic nuclear polarization) effects, for which typical examples are presented. Time-resolved CIDNP experiments on the system triphenylamine/fumarodinitrile (=(2*E*)-but-2-enedinitrile), where formation of the olefin triplet is impossible, show that there is also no isomerization of the olefin radical anion. With triisopropylamine or fumarodinitrile as the reaction partner for 4,4′-dimethoxystilbene (=1,1′-[(1*E*)-ethane-1,2-diyl]bis[4-methoxybenzene]), both oxidative and reductive quenching give almost mirror-image CIDNP spectra because of the pairing theorem; reverse electron transfer of the triplet radical-ion pairs populates the stilbene triplet only, which then isomerizes. With anethole (=1-methoxy-4-(prop-1-enyl)benzene; M), the competition between electron return of triplet pairs $^3\overline{\mathrm{M}^{\cdot+}\mathrm{X}^{\cdot-}}$ to give either $\mathrm{M}+{}^3\mathrm{X}$ or ${}^3\mathrm{M}+\mathrm{X}$ was studied by using a second isomerizable olefin (diethyl fumarate (=diethyl (2*E*)-but-2-enedioate) or cinnamonitrile (=(2*E*)-3-phenylprop-2-enenitrile)) as the reaction partner X. Classes can be changed by employing PET sensitization. With ACN (anthracene-9-carbonitrile) as the sensitizer, anethole does not produce any directly observable polarizations, but a substitution of $\mathrm{ACN}^{\cdot-}$ by the radical anion of 1,4-benzoquinone (=cyclohexa-2,5-diene-1,4-dione) or fumarodinitrile within the lifetime of the spin-correlated radical-ion pairs leads to very strong CIDNP signals that reflect the effects of both pairs.

Introduction. – When *Hanns Fischer* discovered the CIDNP effect (chemically induced dynamic nuclear polarization) in 1967 [1] together with *Bargon* and *Johnson*, he could not have envisioned that within a few years that seemingly exotic phenomenon would evolve into one of the most powerful tools to study reactions proceeding through radical pairs [2]. The operating principle [3] of CIDNP in high magnetic fields is a sorting of the nuclear spins between the electronic singlet and T_0 states of these pairs, which is caused by nuclear-spin-selective intersystem-crossing rates. The resulting nonequilibrium populations of the nuclear-spin-states, which are created only during the life of the radical pairs, *i.e.*, on a nanosecond to sub-nanosecond timescale, are then passed on to the diamagnetic reaction products, where they typically persist for seconds, thus being observable by NMR and manifesting themselves as anomalous line intensities.

The attractivity of CIDNP for chemists draws on two sources. First, because the effect arises in the paramagnetic intermediates, it allows their detection and characterization in a very similar way as EPR does, but with a time resolution that is still inaccessible to pulsed EPR. In his last years, *Hanns Fischer* exploited that to probe the distance dependence of the exchange integral in rigid biradicals [4], a question that lies right at the heart of quantum mechanics. Second, because the polarizations can be regarded as labels affixed in the paramagnetic world of the intermediates but detected in the diamagnetic world of the reaction products, CIDNP yields unique information about the pathways connecting these two worlds. This makes CIDNP especially attractive for the study of complex reaction mechanism. Examples from *Hanns Fischer*'s own body of work include photoinduced [5a] or thermal [5b–d] transformations of radicals, unstable diamagnetic intermediates [6], and the separation of reverse electron transfer in singlet and triplet pairs [7].

The latter topic is strongly connected to this work on geometric isomerizations of olefins following photoinduced electron transfer (PET), because three conceivable pathways for these processes rely on the triplet exit channel of the intermediate radical-ion pairs. First, if a chemical reaction of the triplet pairs is precluded by thermodynamics, these pairs eventually have to separate to give free radical ions, which might isomerize because of their reduced π-bond order and comparatively long life (typically, tens of microseconds). Second, if electron return is feasible in a triplet state and can populate the olefin triplet, the ensuing decay of that phantom triplet will yield approximately equal amounts of the starting and the isomerized olefin [8], so will cause bidirectional olefin isomerization. Third, a geminate reaction of the radical-ion pair in a triplet state to give a triplet biradical that subsequently undergoes cycloaddition competing with cleavage has been identified as a pathway of unidirectional *cis–trans* isomerization [9–10]. CIDNP Experiments have been essential for unraveling these competing mechanisms [7c][10][11]. In this work, we will focus on the CIDNP effects that are due to the pathways *via* free radical ions and those *via* the olefin triplet; for in-depth investigations of the biradical pathway, see [10][12].

Experimental. – The CIDNP experiments were performed on a 250-MHz NMR spectrometer (*Bruker WM-250*) with a modified probe allowing side-on illumination of the sample. A home-made pulse programmer and data-acquisition system were used. Depending on the excitation wavelength, the light source was an excimer laser (XeCl, 308 nm) or a two-stage dye laser (dye, *RDC-388* from *Radiant Dyes*, 388 nm) pumped by the excimer laser. Each flash delivered 1–2 mJ to the sample. Most photo-CIDNP spectra were obtained with the pseudo-steady-state method described in [13]; for the sequence used for time-resolved measurements, see [14]. Both techniques yield signals undistorted by nuclear-sin relaxation and practically free from the background of unreacted molecules. All chemicals were obtained in the highest possible purity. The solvent, (D_3)acetonitrile was dried over 3-Å molecular sieve, and the reactants were further purified by double distillation *in vacuo* or repeated sublimation at 10^{-6} bar. After preparation, the samples were deoxygenated by bubbling Ar through the solns., and the tubes were then sealed.

Results and Discussion. – *Classification of the Photoredox Systems.* For singlet pairs, reverse electron transfer from the radical anion of the acceptor to the radical cation of the donor is always thermodynamically feasible. As opposed to other types of reactions between two molecules, an electron transfer does not require reactant contact but can also occur over larger distances [15]. Hence, regeneration of the starting materials by that process constitutes the most efficient deactivation channel of singlet ion pairs by far.

In contrast, reverse electron transfer of triplet pairs is only possible if at least one of the reactants possesses a triplet state of lower energy than that of the ion pair [11b][16]. Olefins frequently have low-lying T_1 states, which can be populated by electron return of triplet radical-ion pairs; the factor responsible for the low triplet energy is a perpendicular arrangement of the substituents at the two ends of the former C=C bond, which allows the unpaired electrons to occupy orthogonal orbitals [17]. Radiationless decay of these phantom triplets – which is fast because the potential curves of the ground state and the T_1 state come quite close to each other at that geometry, and might even intersect [17a][18] – will, therefore, result in an approximate 1:1 mixture of the *cis* and *trans* olefin regardless of which configuration of the olefin was employed as the starting material.

The formation of a triplet 1,4-biradical is a completely independent deactivation pathway of a triplet radical-ion pair. The lifetime of the biradical is sufficiently long [19] to allow it to adopt the most favorable conformation around the former olefinic C=C bond. After intersystem crossing, cycloaddition competes with cleavage of the bond connecting the two reactant moieties [20], which will conserve the preferred conformation of the biradical in the regenerated olefin. That biradical pathway of olefin isomerization thus predominantly leads to one of the isomers, normally the *trans* olefin, again regardless of what the geometry of the starting olefin was. In a situation where both biradical formation and electron return are thermodynamically feasible, the latter will prevail if it is sufficiently exergonic, for the reasons given above.

The relative energies of the radical-ion pair and the triplet states of the reactants are thus of fundamental importance for the pathways of PET-induced olefin isomerization, and it seems natural – following ideas originally put forward by *Roth* and *Manion–Schilling* [11a,c] – to systematically classify such photoredox systems on the basis of that criterion, with each class exhibiting a characteristic CIDNP behavior (*Table 1*). We denote the olefin, which can function either as an electron donor or as an electron acceptor, as the *substrate* M, and its reaction partner as X. If the precise function of X is of importance, as for instance in three-component systems with PET sensitization (see below), we specify it in more detail as *sensitizer* S or *quencher* Q. In all our systems, a direct formation of ^{3}M by intersystem crossing of the excited substrate, which would precede or bypass the radical-ion pair, is normally negligible because the competing photophysical and photochemical deactivation processes have much higher efficiencies.

Table 1. *Classification of the Photoredox Systems Consisting of an Olefin M and a Reaction Partner X.* A higher vertical position in the table indicates a higher energy. For further explanations, see the text.

Class I			*Class II*		
(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)
^{3}X	^{3}M				
^{3}M	^{3}X	^{3}M	^{3}X		
$^3\overline{M^{\cdot\pm}X^{\cdot\mp}}$	$^3\overline{M^{\cdot\pm}X^{\cdot\mp}}$	$^3\overline{M^{\cdot\pm}X^{\cdot\mp}}$	$^3\overline{M^{\cdot\pm}X^{\cdot\mp}}$	$^3\overline{M^{\cdot\pm}X^{\cdot\mp}}$	$^3\overline{M^{\cdot\pm}X^{\cdot\mp}}$
		^{3}X	^{3}M	^{3}X	^{3}M
				^{3}M	^{3}X

With systems of *Class I*, the olefin triplet cannot be populated. Potential pathways to isomerization *via* the triplet exit channel of the radical pair either involve a biradical or occur in the radical ion of the olefin. As we will show, time-resolved CIDNP experiments allow a distinction between these two alternatives. For systems of *Class II*, population of the olefin triplet is feasible, and often constitutes the predominant deactivation pathway of the triplet pairs.

A special behavior with respect to CIDNP can be expected for the *Subclasses* (*c*), where ^3X is lowest in energy. In those two cases, ground-state M will be produced by reverse electron transfer not only of singlet pairs but also of triplet pairs: In *Class I* (*c*) no alternative electron-transfer route is open to the latter, and in *Class II* (*c*) that process will completely dominate over the other reverse electron ransfer (*i.e.*, the one producing ^3M and ground-state X) provided that the energy of ^3X is low enough. Because singlet and triplet pairs thus react to give the same product, ground-state M, the spins sorted apart in the radical pairs are collected in the same species, in other words, the sorting is completely undone, and no spin polarizations of M are observable at all, not even in a time-resolved experiment. However, by the addition of a third component as a quencher, polarizations can be made to appear, as we will show below.

The free energy of the radical-ion pair, ΔG°_{et}, can be calculated from the reduction potentials of the respective donor and acceptor $\Phi(D^+/D)$ and Φ (A/A^-), and the relative permittivity ε_r of the solvent by *Eqn. 1*.

When the energy of the excited species is subtracted, this expression turns into the *Weller* equation [21], which yields the free energy of the primary PET. In our solvent MeCN ($\varepsilon_r = 35.94$), the sum of the last two terms of *Eqn. 1* amounts to -5.5 kJ/mol. The pertinent data for the molecules studied in this work are compiled in *Table 2*.

$$\Delta G^\circ_{et} = F[\Phi(D^+/D) - \Phi(A/A^-)] + \frac{251\ \text{kJ/mol}}{\varepsilon_r} - 12.5\ \text{kJ/mol} \tag{1}$$

Electron Return of Triplet Pairs Impossible. A typical example of *Class I* (*a*) is provided by the olefin fumarodinitrile (FN) sensitized by triphenylamine (TPA). Steady-state CIDNP experiments (*i.e.*, with illumination for a time on the order of 0.1 … 1s before acquisition) yield very small polarizations only. However, much stronger signals are observed in time-resolved CIDNP experiments, which are simply nanosecond laser flash photolysis with detection by an NMR pulse (duration, a few microseconds) after a variable delay [24]. As *Fig. 1* shows, the protons of both the sensitizer TPA and the olefin FN are initially polarized, but these polarizations quickly decay to zero or to unobservably small values.

The explanation of that phenomenon, exchange cancellation [25], is well known. The singlet pairs regenerate the starting materials in a geminate reaction, by reverse electron transfer; let a particular proton in them bear a certain amount of nuclear-spin polarization symbolized by $\uparrow$. Triplet pairs cannot react, and will separate to give free radical ions, in which the polarization of the same proton has exactly the same intensity but opposite sign, signified by $\downarrow$. A degenerate electron exchange, as shown in *Eqn. 2* for the olefin radical anion and its parent compound, transfers the polarizations from the free radicals to the starting materials, where they will eventually compensate the existing geminate polarizations (*Eqn. 3*).

Table 2. *Excited-State Energies and Redox Potentials of the Molecules Studied in This Work*

Compound (abbreviation; systematic name)	E_S [kJ/mol]	E_T [kJ/mol]	$\Phi(X^+/X)$ [V *vs.* SCE]	$\Phi(X/X^-)$ [V *vs.* SCE]
cis-Anethole (*c*A; 1-methoxy-4-[(1*Z*)-prop-1-enyl]benzene)	389a)	260b)	1.47c)	
trans-Anethole (*t*A; 1-methoxy-4-[(1*E*)-prop-1-enyl]benzene)	384a)	250b)	1.39c)	
1,4-Benzoquinone (BQ; cyclohexa-2,5-diene-1,4-dione)	247d)	210d)		– 0,51e)
trans-Cinnamonitrile (*t*CN; (2*E*)-3-phenylprop-2-enenitrile)	> 400f)	< 203g)		– 2.39h)
Anthracene-9-carbonitrile (ACN)	299i)	164i)		– 1.37i)
Diethyl fumarate (DEF; diethyl (2*E*)-but-2-enedioate)	> 400f)	277k)		– 1.51l)
trans-4,4′-Dimethoxystilbene (*t*DMS; 1,1′-[(1*E*)-ethane-1,2-diyl]bis[4-methoxybenzene])	341a)	205m)	1.06j)	– 2.44n)
Fumarodinitrile (FN; (2*E*)-but-2-enedinitrile)	> 400f)	260k)		– 1.36o)
Triisopropylamine (TIA)	> 400f)	> 300p)	0.91q)	
Triphenylamine (TPA)	353e)	293e)	0.98e)	

a) Determined from the turning point at the low-wavelength edge of the fluorescence spectrum. b) See [10b], and ref. cit. therein. c) [22a]. d) [22b]. e) [22c]. f) Estimated from the absorption spectrum. g) Value for phenylpropene [11a] as an upper limit. h) [22d]. i) [22e]. j) [23a]. k) Vertical triplet energy [23b]. l) [23c]. m) [11c]. n) [11b]. o) [23d]. p) [23e]. q) [23f].

We stress that there is no such thing as a spin-polarized single molecule. Nevertheless, *Eqns. 2* and *3* are valid if large numbers of molecules are considered.

$$ {}^{\downarrow}\mathrm{M}^{\bullet -} + \mathrm{M}_{(\text{unpolarized})} \rightarrow {}^{\downarrow}\mathrm{M} + \mathrm{M}^{\bullet -}_{(\text{unpolarized})} \qquad (2)$$

$$ {}^{\uparrow}\mathrm{M} + {}^{\downarrow}\mathrm{M} = 2\,\mathrm{M}_{(\text{unpolarized})} \qquad (3)$$

The reason why CIDNP is observable as a transient phenomenon in such systems is that the geminate reaction occurs on a nanosecond timescale but the compensating degenerate electron exchange is much slower. As follows from the described mechanism, the transient polarizations have the signal phases stemming from the singlet pairs. The small polarizations observed in a steady-state experiment or at long delay times (see the tiny residual signal of FN in the top trace of *Fig. 1*) are due to nuclear-spin relaxation in the free radicals, which spoils a perfect cancellation of the polarizations from both exit channels of the radical pairs.

Kapteins's rule for a CIDNP net effect [26] (*Eqn. 4*) establishes a connection between the signal phase Γ_i of an observed proton i ($\Gamma_i = +1$, absorption; $\Gamma_i = -1$, emission), the reaction pathway, specifically the precursor multiplicity μ and the exit channel ε ($\mu = +1$ or -1, radical-pair formation from a triplet or from a singlet precursor, resp.; $\varepsilon = +1$ or -1, product formation from a singlet or from a triplet radical pair, resp.), and the magnetic parameters of the intermediate (sgn Δg, sign of the difference of the g values of the two radicals, with the radical containing proton i taken first; sgn a_i, sign of the hyperfine coupling constant of proton i).

$$\Gamma_i = \mu \cdot \varepsilon \cdot \mathrm{sgn}\;\Delta g \cdot \mathrm{sgn}\; a_i \qquad (4)$$

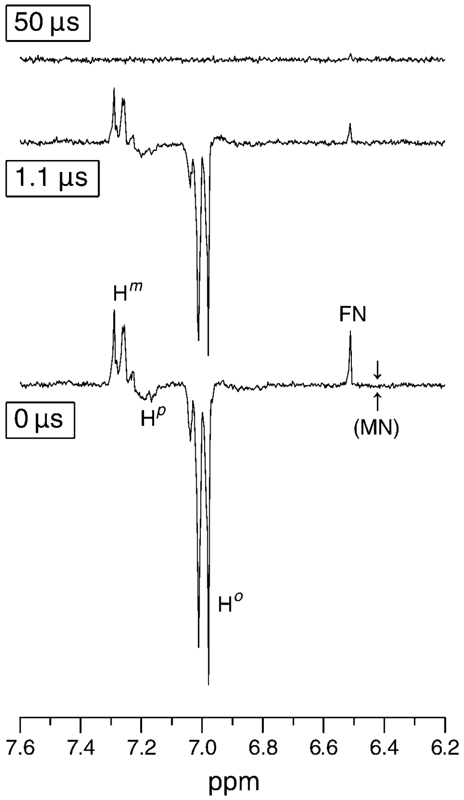

Fig. 1. *Time-resolved photo-CIDNP spectra of the photoredox system triphenylamine/fumarodinitrile* (TPA/FN). Conditions: solvent CD_3CN, T 235 K, excitation at 308 nm, [TPA] = 0.3 mM, [FN] = 1 mM. H^o, H^m, H^p are the signals of the aromatic H-atoms of TPA, and FN denotes the olefinic resonances of FN; the arrows indicate where the resonances of the isomerized olefin maleodinitrile (MN) would occur. The times given at traces are the delays between the laser flash and the start of the probing NMR pulse.

As the following analysis will show, the radical pairs are predominantly formed from triplet precursors ($\mu = +1$): The olefin does not absorb at the excitation wavelength, so the photoreaction necessarily starts with electronically excited TPA. A plot of its relative luminescence quantum yield against the FN concentration in MeCN gave a *Stern–Volmer* constant of $(0.11 \pm 0.01) \cdot 10^3$ M^{-1}. The quantum yield of intersystem crossing of TPA in the unquenched case is 0.88 [27]. Assuming diffusion-controlled quenching ($k_q \approx 2 \cdot 10^{10}$ $\text{M}^{-1}\text{s}^{-1}$), quantum yields of 0.1 and 0.8 are calculated for formation of singlet radical pairs and of ^{3}TPA under the experimental conditions of *Fig. 1*. The unquenched lifetime of ^{3}TPA is 60 ns [28], and diffusion control is also very likely for quenching of ^{3}TPA by FN because of the strong exergonicity (see *Table 2*), so an overall efficiency of 0.44 results for formation of triplet radical pairs. Even though only one-third of the triplet pairs, *i.e.*, only those born in the T_0 state, leads to CIDNP, the triplet precursors are thus seen to outweigh the singlet precursors.

As discussed above, the exit channel for regeneration of the starting olefin is singlet ($\varepsilon = +1$). The proton hyperfine coupling constant in the radical anion $FN^{\bullet -}$ is negative [7a]. The same g value, 2.0028, is reported for the radical cation of the amine [29] and the radical anion of the olefin [7a], but the absorptive signal of the FN protons shows that the g value of $FN^{\bullet -}$ must be the lower of the two.

The time dependence of the polarizations of the FN protons is displayed in *Fig. 2*. Under our experimental conditions (concentration of FN much higher than concentration of free radicals), the second-order reaction between free ions $FN^{\bullet -}$ and $TPA^{\bullet +}$ is negligible compared to the pseudo-first-order degenerate exchange process of *Eqn. 2*, and the time-dependent CIDNP signals $S(\Delta t)$ are well describable by a monoexponential decay [30] (*Eqn. 5*), with the initial and final values given by S_0 and S_∞. When the best-fit result for κ is divided by the concentration of FN, a bimolecular rate constant of $9.8 \cdot 10^8$ $\text{M}^{-1}\,\text{s}^{-1}$ is obtained for the degenerate electron exchange between $FN^{\bullet -}$ and FN at 235 K. That value is quite typical [14][31] for such electron transfers without change of the free energy.

Because the limiting polarization at long times after the flash is quite small (see top trace of *Fig. 1*), this result depends only weakly on the value of S_∞.

$$S(\Delta t) = (S_0 - S_\infty)\ \exp\ (-\kappa\ \Delta t) + S_\infty \qquad (5)$$

In accordance with the described exchange-cancellation mechanism, the much more intense polarizations of TPA (H^o, $a < 0$; H^m; $a > 0$; H^p, $a < 0$; signs from AM1 calculations) all vanish within several microseconds. As *Fig. 1* shows, their decrease is significantly slower than that of the FN signals, in the first place because of the lower concentration of TPA.

Most important for the present work is the observation that no signals of the geometric isomer maleodinitrile (MN) appear in the time-resolved spectra (see *Fig. 1*,

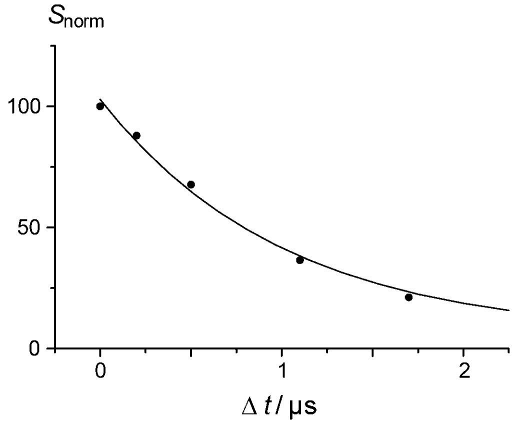

Fig. 2. *Polarization scaled to maximum* (S_{norm}) *of the olefinic H-atoms in fumarodinitrile as a function of the delay* (Δt) *between the laser flash and the NMR detection pulse in time-resolved CIDNP experiments with triphenylamine as sensitizer.* For exper. conditions, see *Fig. 1*. The curve was fitted by *Eqn. 5*, the best fit parameter κ being 0.98 μs^{-1}.

where the position of these missing signals is marked with arrows). An isomerization of free $FN^{\bullet -}$ followed by an electron transfer analogous to *Eqn. 2* would transfer the polarizations existing in the free ions, which are characterized by $\varepsilon = -1$, to MN, whereas an isomerization of $FN^{\bullet -}$ contained in the radical pairs (*i.e.*, an isomerization on a nanosecond timescale or faster) would transfer the polarizations of the singlet exit channel ($\varepsilon = +1$) to MN. Even if exchange cancellation were again operative, these signals would have to show up in time-resolved experiments because of the different timescale of geminate and free-radical processes; their complete absence in *Fig. 1* can only mean that $FN^{\bullet -}$ does not isomerize on a timescale up to at least a few microseconds.

The photoreaction between *trans*- or *cis*-anethole and 1,4-benzoquinone [10a] represents *Class I* (*b*), for which the same behavior as with *Class I* (*a*) – no isomerization *via* the olefin triplet – is expected and found. In that particular case, however, a geminate reaction of the triplet radical pair to give a triplet biradical is feasible, and secondary processes of that intermediate then result in geometric isomerization and cycloaddition. Besides the biradical, some amount of free radical ions is also formed from the triplet pairs, and time-resolved CIDNP measurements [10a] reveal the same exchange cancellation as in *Fig. 1*. Hence, these experiments can be used to separate the reactions involving the free radicals from those occurring *via* the biradicals (or, if applicable, *via* olefin triplets), which are much faster. Because the biradical pathway to isomerization has the same exit channel ($\varepsilon = -1$) as the free radicals, and thus results in similar polarization phases as an isomerization in free ions would, conclusions that are based solely on stationary CIDNP experiments can be prone to misinterpretation¹) in such systems. However, time-resolved CIDNP experiments [10a] have provided unequivocal evidence that both anethole radical cations are configurationally stable.

Electron Return of Triplet Pairs Only Populating the Substrate Triplet. The following two examples of that class, *Class II* (*a*), illustrate yet another facet of nuclear-spin polarizations in these reactions. Depending on the reaction partner, an excited olefin can be quenched reductively or oxidatively. As *Fig. 3* shows, irradiation of a solution of *trans*-4,4′-dimethoxystilbene (*t*DMS) in MeCN yields pronounced CIDNP signals of the starting and the isomerized olefin in the presence of either the electron donor triisopropylamine (TIA) or the previously investigated electron acceptor FN.

The laser light is exclusively absorbed by the olefinic substrate *t*DMS, whose unquenched fluorescence lifetime is assumed to differ only insignificantly from that of *trans*-4,4′-dimethylstilbene (3 ns) [33]. The large exergonicity of electron-transfer quenching in both cases (see *Table 2*) will result in diffusion control; because of the high concentrations of the reaction partners, an efficient formation of the radical pairs $^{1}\overline{t\mathrm{DMS}^{\bullet -}\mathrm{TIA}^{\bullet +}}$ or $^{1}\overline{t\mathrm{DMS}^{\bullet +}\mathrm{FN}^{\bullet -}}$ is thus ensured. After nuclear-spin-selective intersystem crossing to triplet pairs, electron return to give ^{3}tDMS and the respective other reactant X in its ground state is exergonic. Subsequent decay of that phantom triplet will yield approximately equal parts of the starting olefin and its geometric isomer. In contrast, the formation of ground-state *t*DMS and ^{3}X is precluded by thermodynamics in both systems. With the quencher FN, this is borne out by the absence of any signal from its geometric isomer MN, which arises when ^{3}FN is formed (see below, *Fig. 5*).

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¹) For an example, see [32].

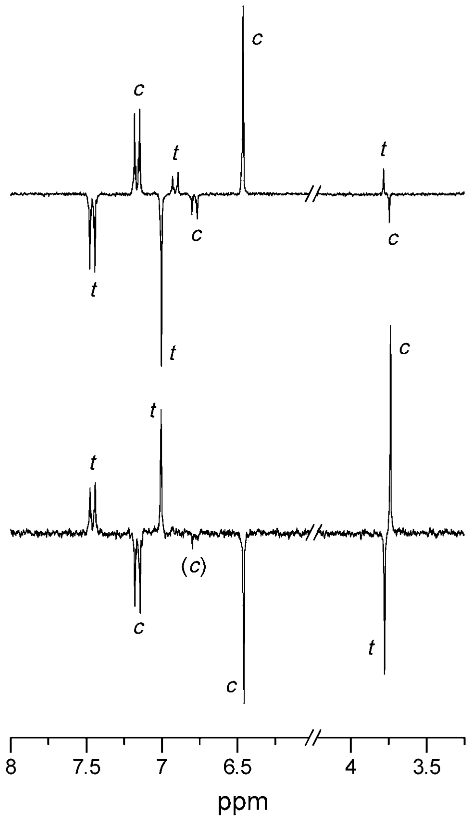


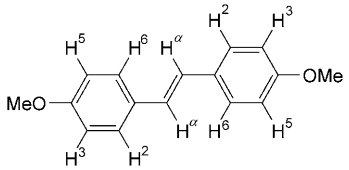
Fig. 3. *Photo-CIDNP effects in two photoredox systems M/Q.* Conditions: olefin (M) *trans*-4,4′-dimethoxystilbene (*t*DMS) 0.3 mM, solvent CD_3CN, *T* 278 K, excitation at 308 nm, quencher (Q) triisopropylamine 50 mM (top trace) or fumarodinitrile 100 mM (bottom trace). The signals labelled *t* and *c* refer to the starting and isomerized olefin, resp. (for assignments, see *Table 3*, below). Both traces were scaled to the same absolute height of H^a in the *cis* isomer (δ(H) 6.46). For further explanations, see the text.

As is evident from *Fig. 3*, the CIDNP subspectra of the *cis* and the *trans* olefin in each experiment are almost exact mirror images of each other. That there must be a phase inversion is obvious from the fact that the starting olefin is regenerated predominantly through the singlet exit channel of the radical pairs and the isomerized olefin exclusively through the triplet exit channel (*i.e.*, ε is opposite for the two isomers). However, the quantitative mirror-image relationship might appear surprising at first, given that the number of isomerized molecules is only about one-third of the number of regenerated starting molecules. It can be understood [11a,c] on the basis of the spin-sorting mechanism of CIDNP: A given proton acquires exactly opposite polarizations in the singlet and triplet pairs, *e.g.*, $+p$ and $-p$. Exclusive transfer of the former to the starting olefin, and partitioning of the latter with probabilities ϕ and $1-\phi$ between the isomerized and the starting olefin will lead to an intensity $-\phi p$ arriving in the isomerized olefin and a partial cancellation of the opposite polarizations $+p$ and $-(1-\phi)p$

reaching the starting olefin that leaves only a remaining intensity of $+\phi p$, *i.e.*, the exact opposite as in the isomer. In contrast to the previous examples, there is no time dependence of the polarization because the reaction through the triplet exit channel is also a geminate reaction, so occurs on the same timescale as the reaction of the singlet pairs.

Within certain limits, the polarization of a particular proton in a product is proportional to its hyperfine coupling constant in the paramagnetic intermediate giving rise to CIDNP [2d]. The so-called polarization pattern – the relative polarization intensities of the different protons in the same product – thus contains similar information as the EPR spectrum of the radicals. The use of the polarization pattern for the identification of the intermediates has been pioneered by *Roth* [34]. *Table 3* lists the hyperfine coupling constants of the radical cation and anion of *t*DMS, which were calculated by AM1. A comparison with *Fig. 3* reveals that they agree well with the relative signs and sizes of the CIDNP signals.

Table 3. *^{1}H-NMR Chemical Shifts in* trans- *and* cis-*4,4′-Dimethoxystilbene* (*t*DMS and *c*DMS, resp.), *and Calculated* (AM1) *Hyperfine Coupling Constants in the Radical Cation* t*DMS*$^{\bullet+}$ *and Anion* t*DMS*$^{\bullet-}$



	δ [ppm]		a_H [mT]	
	*t*DMS	*c*DMS	*t*DMS$^{\bullet-}$	*t*DMS$^{\bullet-}$
H^α	7.00	6.46	−0.381	−0.343
H^2, H^6	7.46	7.16	−0.133	−0.146
H^3, H^5	6.91	6.78	+0.060	+0.024
MeO	3.78	3.74	+0.047	−0.008

A striking effect in the two CIDNP spectra is a second mirror-image relationship, this time not between the *cis* and *trans* olefin within each spectrum, but between the corresponding signals in the two spectra, which holds for all resonances except the extremely weak ones of $H^{3,5}$ and those of the MeO group. The origin of that phenomenon is the pairing theorem [35], which states that the distribution of unpaired spin density in the conjugated π system of an alternant hydrocarbon is basically identical for the radical cation and the radical anion, owing to the symmetry relationship between the HOMO and the LUMO. As is well known [35], the pairing theorem does not extend to connected MeO groups, so the strong discrepancy between the CIDNP intensities of those resonances does not come as a surprise.

In both systems, the precursor multiplicity is singlet ($\mu = -1$) because the stilbene is excited; the isomerization of the substrate occurs *via* the triplet exit channel ($\varepsilon = -1$). With the calculated signs of the hyperfine coupling constants (*Table 3*) and the signal phases observed in *Fig. 3*, *Kaptein*'s rule (*Eqn. 4*) shows that the following relationship between the g values of the radical ions in those systems holds: $g(FN^{\bullet-}) < g(tDMS^{\bullet\pm}) < g(TIA^{\bullet+})$.

Competing Electron Return Pathways of the Triplet Pairs. In *Classes II* (*b*) and *II* (*c*), two routes of reverse electron transfer are accessible to the pairs ${}^3\overline{\mathrm{M}^{\bullet\pm}\mathrm{X}^{\bullet\mp}}$. With the first, ^{3}M and ground-state X are formed, so isomerization of the olefin *via* the triplet pathway occurs and is accompanied by the CIDNP effects discussed in the preceding section. The second route populates ground-state M and ^{3}X. As a direct consequence of the fact that this will not lead to isomerization of M, it will also not produce any nuclear polarizations of the starting olefin M, neither stationary nor time-resolved ones, because the opposite polarizations of the singlet and triplet radical pairs will reach the same species, M, on the same timescale and wipe out each other.

In principle, this opens up the possibility of studying the competition between the two pathways, only one of which leads to CIDNP of the substrate, by measuring the polarization intensity of M in a series of experiments with different X. Apart from the difficulty of reliably measuring absolute CIDNP intensities, which depend on the concentration of the radical pairs, hence on the efficiencies of all preceding photophysical and photochemical steps, an almost unsurmountable problem with that approach is that the exchange of one partner of the radical pair will change the *g*-value difference, to some extent also the diffusional parameters, and thus the absolute polarizations.

The first obstacle can be overcome by evaluating a ratio of polarizations of M and X within the same spectrum, which eliminates all uncertainties associated with the determination of absolute polarizations. As a side effect, this should also largely compensate the effect of Δg: CIDNP of a given proton *i* is approximately proportional to $a_i/\sqrt{\Delta g}$ [2d], so the polarization ratio is basically a ratio of the hyperfine coupling constants. As the diffusional parameters enter the constant of proportionality, their influence is also eliminated when a polarization ratio is formed.

A prerequisite for CIDNP of X, without which there can be no meaningful polarization ratio, is that the singlet and triplet exit channels of the radical pairs lead to different product structures derived from X. Also, both should preferentially be geminate products to avoid problems with complex secondary reactions of free radicals. This suggests to use another isomerizable olefin as the species X. Its CIDNP signals arise in the same way as those of M – in fact, the roles of M and X are interchangeable in such a system of two olefins – but will exhibit the opposite dependence on the pathway of electron return of the triplet pairs as those of M: population of ^{3}X minimizes the polarizations of M and maximizes those of X; population of ^{3}M has the inverse effect.

Two experimental examples are shown in *Fig. 4*. The substrate M common to both is *trans*-anethole (*t*A); as the other olefin X, we chose diethyl fumarate (DEF) and *trans*-cinnamonitrile (*t*CN). The hyperfine coupling constants of the olefinic protons in $\mathrm{DEF}^{\bullet-}$ and $t\mathrm{CN}^{\bullet-}$ should be quite similar, as AM1 calculations indicate. Hence, the heights of their peaks, after taking into account that the signal of *t*CN would be twice as large were it not split into a *d*, directly reflect the amount of isomerization of X, and thus the fraction of triplet radical pairs deactivated by reverse electron transfer to give ^{3}X and ground-state M. As is immediately obvious, there is very little population of ^{3}X in the case of DEF, but a very high amount of it with *t*CN as the second component.

From the data of *Table 2*, it emerges that electron return of ${}^3\overline{t\mathrm{A}^{\bullet+}\mathrm{DEF}^{\bullet-}}$ to give ^{3}DEF and ground-state *t*A is even slightly endergonic, so that system constitutes a borderline case between *Classes II* (*a*) and *II* (*b*). In contrast, population of ${}^3t$CN by reverse

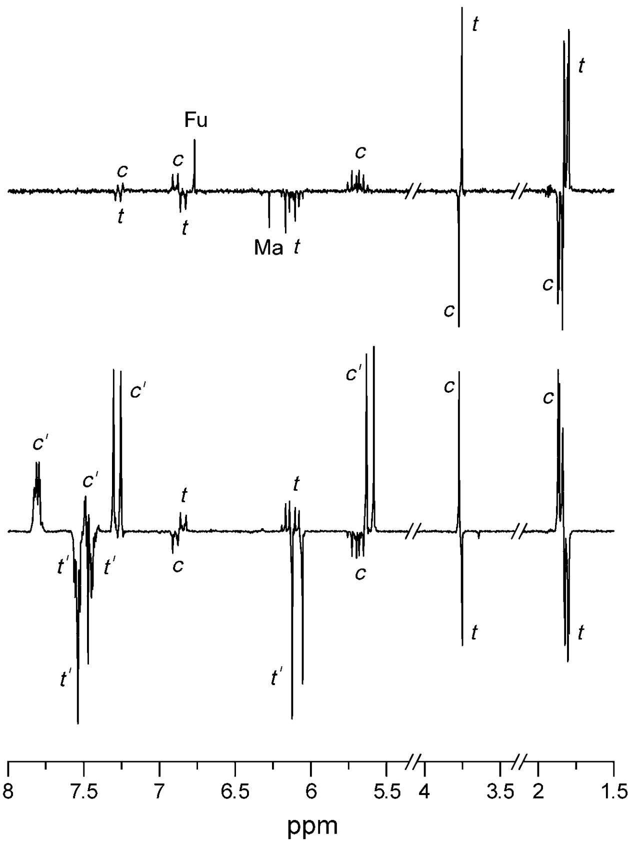


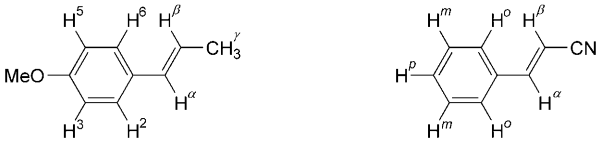
Fig. 4. *Photo-CIDNP spectra of* trans-*anethole* (*t*A; 5 mm) *in the presence of a second olefin* (10 mm). Top: diethyl fumarate; bottom: *trans*-cinnamonitrile. Conditions: in CD_3CN at room temperature, excitation at 308 nm. The terms Fu and Ma denote the olefinic H-atoms of the fumarate and its isomer diethyl maleate. The signals labelled *t* and *c*, and *t*′ and *c*′, resp., pertain to the starting or isomerized anethole and cinnamonitrile (for assignments, see *Table 4*). Both traces were scaled to approximately the same absolute height of the anethole signals. For further explanations, see the text.

electron transfer of $^3\overline{t\mathrm{A}^{\bullet +} t\mathrm{CN}^{\bullet -}}$ is more exergonic by at least 40 kJ/mol than is population of ^3tA, making that system a clear case of *Class II* (*c*). Evaluating the integrals of the olefinic protons H^{β} of *t*A, DEF, and *t*CN (see *Table 4*) shows that the pathway from the radical ion pair to the triplet anethole accounts for *ca.* 75% and 20% of the deactivation of the triplet radical pair in these two systems, reflecting the trend in the thermodynamics.

As the polarization phases indicate, the unknown *g* value of $t\mathrm{A}^{\bullet +}$ must be lower than that of $\mathrm{DEF}^{\bullet -}$ (2.0040) [36] but higher than that of $t\mathrm{CN}^{\bullet -}$, which is expected to be similar to that of $\mathrm{FN}^{\bullet -}$ (2.0028) [7a]. Interestingly, the polarization pattern shows that there is no sign alternation of the hyperfine coupling constants of H^{α}, H^{β} and H^{o} in $t\mathrm{CN}^{\bullet -}$.

CIDNP Appearing Through PET Sensitization. In *Class II* (*c*), formation of ^{3}M can be completely barred by the competing electron transfer to give ^{3}X if the triplet energy

Table 4. *^{1}H-NMR Chemical Shifts in* trans- *and* cis-*Anethole* (*t*A and *c*A, resp.), *and in* trans- *and* cis-*Cinnamonitrile* (*t*CN and *c*CN, resp.). Values in parentheses refer to the corresponding *cis* isomers.



*t*A (*c*A)		*t*CN (*c*CN)	
H_{obs}	δ [ppm]	H_{obs}	δ [ppm]
H^{α}	6.35 (6.35)	H^{α}	7.51 (7.28)
H^{β}	6.12 (5.69)	H^{β}	6.09 (5.61)
H^{γ}	1.81 (1.85)		
H^2, H^6	7.27 (7.26)	H^o	7.54 (7.81)
H^3, H^5	6.84 (6.89)	H^m, H^p	7.47 (7.49)
MeO	3.75 (3.77)		

of X is very low. As emerges from the preceding section, this results in a suppression of all CIDNP signals of M. If, furthermore, X is incapable of undergoing any reaction other than reversible electron transfer, its polarizations will be unobservable as well, because singlet and triplet channels lead to the same species, X. Hence, such a two-component system should not exhibit any CIDNP effects.

The bottom trace of *Fig. 5* shows an example of that class. When the sensitizer anthracene-9-carbonitrile (ACN) is illuminated at 388 nm, a strong luminescence (lifetime 16.9 ns) [23] results, which decreases sharply when *cis*- or *trans*-anethole is added. The reason is electron-transfer quenching of the excited singlet state of the sensitizer by the olefin, which does not absorb at that wavelength. The quenching is sufficiently exergonic (see *Table 2*) to be practically diffusion controlled, and leads to an efficient formation of radical ion pairs [22]. Yet, no CIDNP can be detected because the extremely low triplet energy of that sensitizer makes reverse electron transfer of the triplet pairs to give ^{3}ACN more exergonic by as much as 86 kJ/mol compared to population of the olefin triplet. The almost complete reversibility of that cyclic electron-transfer system is borne out by its extremely high stability: In experiments with several thousand laser flashes, where the absorbed total energy was as high as 5 J, we were not able to detect any isomerization or other chemical change within the sensitivity limit (*ca.* 1%).

As a striking phenomenon, strong polarizations can be made to appear in this system by adding a third component, which produces no CIDNP on its own nor in combination with either of the two other reactants under the experimental conditions; only in the three-component system do CIDNP signals arise. The center and trop traces of *Fig. 5* show this with 1,4-benzoquinone (BQ) or with FN as the third species.

Under the experimental conditions, the added reaction partner neither absorbs noticeably nor can quench the excited sensitizer, so is incapable of influencing the reaction before the stage of the radical-ion pair. The explanation of the CIDNP effects is a PET sensitization [37] as displayed in the *Scheme*. With PET sensitization, a desired

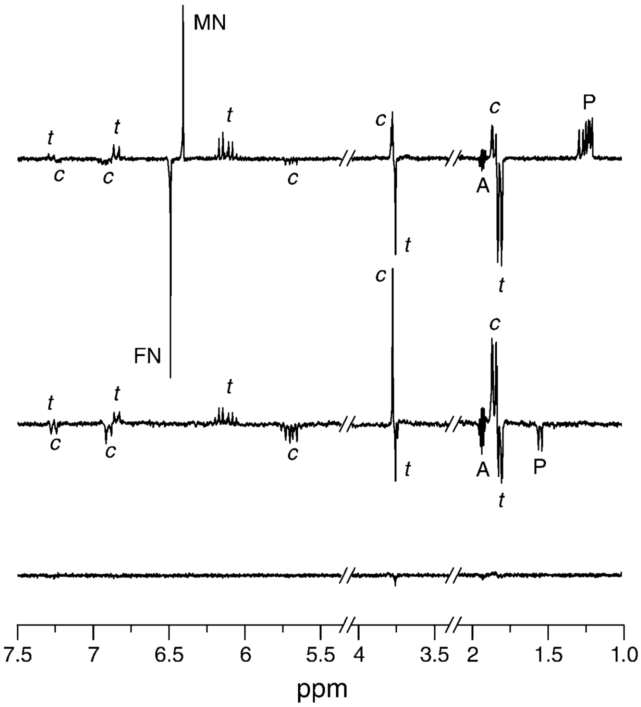
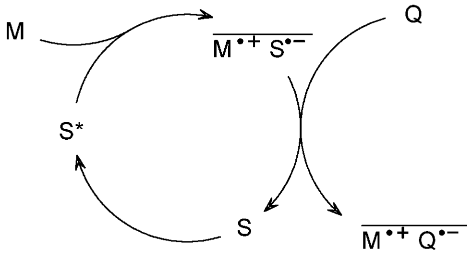


Fig. 5. *Photo-CIDNP experiments with PET sensitization* (see the *Scheme*). Conditions: sensitizer (S) anthracene-9-carbonitrile (1 mM); solvent CD_3CN (at room temperature); excitation at 388 nm. The signals labelled *t* and *c* pertain to *cis*- and *trans*-anethole (for assignments, see *Table 4*); A is an insufficiently suppressed solvent signal, and P denotes a cycloaddition product [10]. For further explanations, see the text. *Top trace*: substrate (M) *trans*-anethole (*t*A; 20 mM); quencher (Q) fumarodinitrile (FN; 90 mM). FN and MN denote the olefinic H-atoms of Q and its isomer maleodinitrile, resp. *Center trace*: substrate (M) *cis*-anethole (*c*A; 25 mM); quencher (Q) 1,4-benzoquinone (13 mM). *Bottom trace*: control experiment; conditions as for *top trace*, but without Q (only S and M present). The very small residual peaks are background-suppression artifacts.

radical pair is obtained in two steps. First, an auxiliary radical pair is produced through PET, and then one of its components is replaced by a thermal electron transfer between a radical ion and a neutral molecule. Not only is this a very useful method to overcome unfavorable absorption properties, but that strategy is also applicable to systems where a direct generation of the second radical pair fails because of side reactions upon excitation of the substrate (for an example, see [38]).

As the reaction scheme indicates, the replacement of $S^{\bullet-}$ by $Q^{\bullet-}$ does not occur in free radicals but in the radical pairs. The system ACN/*t*A/BQ provides very strong evidence for this. When the concentration of the quinone is increased by a factor of *ca.* 100, enough light is absorbed by it to allow carrying out the photoreaction under the same conditions as in *Fig. 5*, but without the sensitizer ACN. The resulting CIDNP spectrum [10a] exhibits exactly the same polarization patterns – with practically the same absolute intensities – as in the center trace of *Fig. 5*; however, all lines are inverted. Because

Scheme. *Photoinduced Electron-Transfer Sensitization for an Electron-Donating Substrate M.* Abbreviations: S: sensitizer, Q: quencher.



of the identical pattern, the radical pair giving rise to the polarizations must be identical in that direct reaction and in the PET-sensitized one, so its decay pathway must also be the same. In other words, Δg, the a_i, and ε cannot differ, and the only explanation of the overall inversion is a change of the precursor multiplicity μ, which is perfectly consistent with ACN being a singlet sensitizer but BQ reacting from its excited triplet state. On the other hand, if the exchange of $ACN^{\bullet-}$ against $BQ^{\bullet-}$ would occur in free radicals and the polarizations be generated in pairs subsequently formed by encounters of two free radicals, no sign change could result because such F-pairs are known to behave qualitatively like triplet-born pairs [2].

As the potentials of *Table 2* show, the oxidation of $ACN^{\bullet-}$ by BQ is sufficiently exergonic to be diffusion controlled, whereas the reaction with FN is only accompanied by a marginal decrease of the free energy. (In [10b], its rate constant was estimated to be $2 \cdot 10^9$ $\text{M}^{-1}\text{s}^{-1}$). It is thus not surprising that significantly higher concentrations of FN are needed to replace $ACN^{\bullet-}$ within the lifetime of the radical-ion pair. Taking into account that the exchange of the sensitizer radical ion against the quencher radical ion will, in general, only be successful if the energy of the radical-ion pair decreases and that the energetic position of the substrate triplet is unaffected by that process, *Table 1* reveals that *Class I* (*c*) can only be converted into *Classes I* (*a*) or *I* (*b*) by it, whereas *Class II* (*c*) can be transformed into all five other classes. Each change of class will lead to a qualitative change of the CIDNP effects, as described in the preceding sections.

From the point of view of CIDNP spectroscopy, PET sensitizations are instances of pair substitution [5b][39], *i.e.*, the transformation of one radical pair into another during the spin-correlated lifetime. Although the polarizations from the first pair are not directly observable because they cancel in the products, the parameters of that pair generally influence the polarizations from the second. One manifestation of that is the described signal inversion in the system ACN/*t*A/BQ, but there also arise characteristic effects on the CIDNP intensities when the rate of pair substitution is changed by varying the quencher concentration. A detailed investigation of such phenomena will be published separately.

Conclusions. – It is seen that a classification of PET-induced olefin isomerization according to the relative energies of the radical-ion pair and the triplet species allows simple predictions of the CIDNP effects. Perhaps the most intriguing aspect is the possibility of changing classes by PET sensitization. As emerges from the discussion of the examples given, CIDNP spectroscopy yields very detailed information about these complex reaction mechanisms and allows an easy separation of the different pathways, because it uses the spin polarizations as labels that are affixed at the stage of the radical-ion pairs. It is a fascinating thought that all this became possible by *Hanns Fischer*'s discovery of what must have looked to him as an instrumental artifact or an error on the part of the operator back in 1967.

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