

Electron-Transfer Photochemistry of *cis*- and *trans*-1,2-Diphenylcyclopropane with Singlet Acceptors: Recombination of Radical Ion Pairs of Singlet and Triplet Multiplicity[†]

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Radical ion pairs generated by photoinduced electron transfer from *cis*- and *trans*-1,2-diphenylcyclopropane to various singlet or triplet acceptors may undergo back electron transfer in pairs of singlet as well as triplet multiplicity. The pair energy relative to the reactant ground states and an accessible triplet state, respectively, determines whether this process is competitive. For the *cis* isomer, *cis*-1•⁺, an additional reaction, *o,o'* coupling, generating 9-methylanthracene, **4**, competes with singlet and triplet back electron transfer. This reaction is not accessible in the chloranil reaction for energetic reasons or from the *trans* isomer on steric grounds.

I. Introduction

The photoinduced geometric or valence isomerization of strained ring compounds is particularly interesting because intermediates of various unusual structure types may be involved. Typically, the rearrangements are studied on suitably substituted derivatives. The substituents serve various purposes: they provide stereochemical labels, reduce the required excitation energy, and move the absorption spectra of the resulting intermediates into an energy range where suitable detectors exist and where the spectra are not obscured by solvents or reagents. The photochemical conversion of 1,2-diphenylcyclopropane (**1**) has been studied extensively by both direct and sensitized irradiation. Different types of intermediates have been invoked for different types of sensitizers.^{1–9}

Hammond and co-workers¹ studied the triplet-sensitized isomerization of *cis*- and *trans*-**1** shortly after this group first encountered cases of energy transfer, termed “nonvertical”, where the resulting triplet states had geometries significantly different from those of the parent ground states.¹⁰ They clearly envisioned a ring-opened triplet state for *cis*- and *trans*-**1**.¹ Shortly thereafter, using an optically active naphthylamine derivative as a sensitizer, Hammond and Cole reported an asymmetric induction of 7%.³ The use of a naphthylamine sensitizer might have raised the question of whether the reaction might proceed via a radical cation intermediate; however, these experiments were carried out at a time when triplet states and exciplexes were the typical reaction intermediates considered and before radical ions would be invoked as reaction intermediates. This work had a major impact on photochemistry because it stimulated renewed interest in asymmetric photochemical induction in solution. The rapid growth of this field can be judged by the number of references (71) in a 1983 review¹¹ compared to 327 references in a review 9 years later.¹²

About 15 years later, Wong and Arnold first postulated the radical cations of *cis*- and *trans*-**1** as intermediates in photo-reactions sensitized by naphthalene, 1-cyanonaphthalene, and 1,4-dicyanonaphthalene (DCN).⁷ Their assignment was based on CIDNP results; they reported an A/E multiplet effect for the benzylic signals of the rearranged donor, *cis*-**1**, when

irradiating DCN in the presence of *trans*-**1**. They interpreted this limited information in terms of three consecutive intermediates, a ring-closed radical cation, a ring-opened radical cation, and a ring-opened triplet state.⁷

More detailed CIDNP results in my laboratory, observed during the photoreaction of chloranil with *cis*- or *trans*-**1**, established unambiguously that the radical cations *cis*- and *trans*-**1**•⁺, have ring-closed structures (i.e., that they have retained their steric integrity⁸). The benzylic proton signals of the reagent showed enhanced absorption whereas the geminate signals showed emission; this polarization pattern supports radical cations with electron spin density on the benzylic carbons. The ring-closed nature of *cis*- and *trans*-**1**•⁺ was derived from the fact that the reaction of *cis*-**1** generated only polarized *cis*-**1** whereas that of *trans*-**1** generated only polarized *trans*-**1** and no rearrangement was observed upon prolonged irradiation.^{8,9}

However, the reaction of *cis*- and *trans*-**1** with excited singlet acceptors, viz., 1,4-dicyanonaphthalene, furnished a seemingly contradictory result. The polarization pattern supported radical cations with the same spin density distribution as that of the ring-closed radical cation discussed above; however, the reactivity appeared to be different because geometric isomerization occurred. The polarization phase indicated that the reagent and rearranged donor were regenerated by different mechanisms. These seemingly incompatible results were reconciled by assuming the consecutive involvement of two consecutive intermediates, the radical cation accounting for the polarization and a triplet state accounting for the rearrangement.⁹

Recently, electron-transfer reactions of *cis*- and *trans*-**1** were reinvestigated with additional sensitizers.¹³ This study confirmed the intermediacy of the previously described triplet state^{8,9} and assigned its free energy ($E_T = 29 \text{ kcal mol}^{-1}$) on the basis of optoacoustic calorimetry.¹³

In this paper, I compare the CIDNP effects obtained with chloranil with those induced in the reactions of two singlet sensitizers with different excited-state energies and reduction potentials. The range of effects observed in these cases indicates a delicate balance between the rates of electron return in singlet pairs, intersystem crossing in the pairs, and the population of a triplet state by electron return in triplet pairs. The divergent effects observed in three different systems with different energetics provide salient insight into the nature of the electron-transfer recombination of radical ion pairs.

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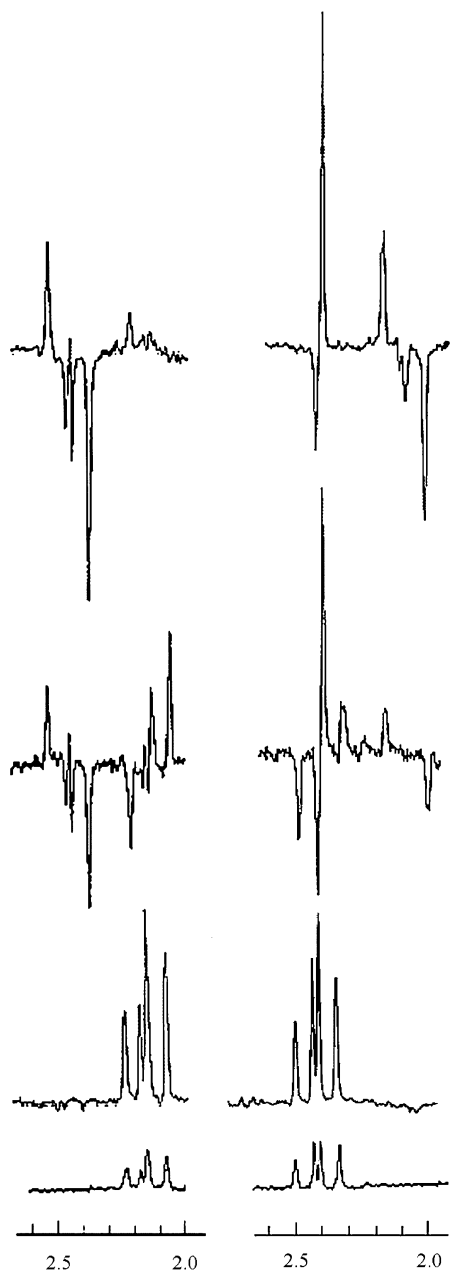


Figure 1. ^1H NMR spectra (90 MHz) observed during the irradiation of chloranil (second from bottom), 1,4-dicyano-naphthalene (second from top), and 9-cyanophenanthrene (top) in acetonitrile- d_3 solutions containing *trans*- (left) or *cis*-1,2-diphenylcyclopropane (right). Dark spectra of *trans*- and *cis*-1 are shown as the bottom trace.

II. Results

The benzylic NMR signals of the *cis* (dd, centered at $\delta = 2.4$ ppm) and *trans* isomers (dd, centered at $\delta = 2.15$ ppm) are distinct and well separated whereas the signals of the geminate cyclopropane protons overlap. Accordingly, the discussion is limited to the benzylic signals. Note, however, that the polarization of the geminate cyclopropane resonances fully supports the conclusions discussed, in cases when it can be observed without being obscured. Figure 1 shows three significantly different polarization patterns obtained with *trans*-1 (left) or *cis*-1 as a reagent (right). Figure 1, bottom left, shows the enhanced signal of *trans*-1 during the photoreaction with chloranil (CA) above the dark signal. The net effect (and the corresponding emission of the geminate resonances, not shown) documents the involvement of a ring-closed radical cation, *trans*-1 \bullet^+ , with significant spin densities on the two benzylic cyclopropane carbons. The

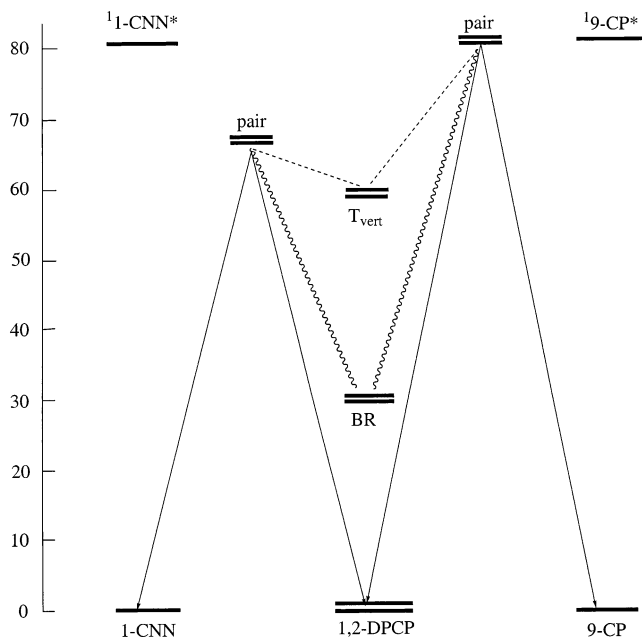


Figure 2. Energy levels of relevant intermediates in the photoreactions of 1-cyanonaphthalene (left) or 9-cyanophenanthrene (right) as sensitizers/acceptors and the 1,2-diphenylcyclopropane isomers as donors; each species or state of the donor is designated by two bars denoting isomers or rotamers. Triplet BET to the vertical or the ring-opened triplet state is designated by dashed or wavy lines, respectively; singlet recombination is denoted by solid arrows.

absence of any polarization for the *cis* isomer shows with special clarity that *trans*-1 \bullet^+ does not rearrange during its lifetime. An equivalent spectrum observed with *cis*-1 as a reagent (bottom right) similarly documents that *cis*-1 \bullet^+ does not rearrange to *trans*-1 \bullet^+ during its lifetime.

In Figure 1, center, I present the CIDNP spectra resulting from the reaction of *trans*- and *cis*-1 with 1,4-dicyanonaphthalene (DCN); they show balanced polarization for *cis*- and *trans*-1. The multiplet patterns for the two isomers have opposite phases, E/A for the reagent donor and A/E for the rearranged isomer. The spectrum observed with *cis*-1 also shows an E/A effect for an additional product ($\delta = 2.4$ ppm), identified as 9-methylphenanthrene.

The third set of spectra (Figure 1 top) were obtained with 9-cyanophenanthrene (CP) as the acceptor/sensitizer. These spectra are unusual because the observed polarization is unbalanced: the spectra show little or no polarization for the reagent donor but strong A/E polarization for the rearranged isomer (i.e., *cis*-1 is polarized when *trans*-1 is the reagent whereas *trans*-1 is polarized when *cis*-1 is the reagent). The reaction of 9-CP with *cis*-1 also generates the strong E/A multiplet effect for 9-methylphenanthrene.

III. Discussion

Two features of the spectra shown in Figure 1 are significant: (1) the gradual transition from a reaction without rearrangement (bottom) to one proceeding with rearrangement and producing balanced polarization (center) to one resulting in preferential polarization of the rearranged donor (top) and (2) the observation of an additional polarized product in two reactions of *cis*-1. We see the key to understanding these effects in the energetic differences between the ion pairs, the reagent ground states, and the potentially accessible donor triplet state. Therefore, I discuss appropriate energetic relationships briefly.

The change in free energy for an electron-transfer reaction (ΔG_{ET}^0) is given by the excited-state energy (E^* , 0,0 transition),

the one-electron oxidation or reduction potentials of donor and acceptor, $E^0_{(D/D^+)}$ and $E^0_{(A^-/A)}$, respectively, and a Coulomb term, $e^2/\epsilon a$, accounting for ion pairing (eq 1):^{14–17}

$$-\Delta G^0_{ET} = E^* + E^0_{(A^-/A)} - E^0_{(D/D^+)} + \frac{e^2}{\epsilon a} \quad (1)$$

The strength or efficiency of an electron acceptor can be gauged by its excited-state reduction potential, $*E^0_{(A^-/A)}$:

$$*E^0_{(A^-/A^*)} = -E^* + E^0_{(A^-/A)} \quad (2)$$

Furthermore, it is useful to consider the pair energy, ΔG^0_{SSRP} (i.e., the free-energy difference between the radical ion pair and the reagent ground states^{15–17}):

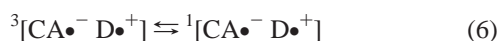
$$-\Delta G^0_{SSRP} = -E^0_{(D/D^+)} + E^0_{(A^-/A)} - \left[\frac{2.6 \text{ eV}}{\epsilon} - 0.13 \text{ eV} \right] \quad (3)$$

Finally, if a donor or acceptor triplet state or biradical is accessible, as is the case in the system discussed here, then it is also useful to consider the pair energy relative to that of the accessible triplet or biradical.

$$-\Delta G^0_{SSRP,T} = -E^0_{(D/D^+)} + E^0_{(A^-/A)} - \left[\frac{2.6 \text{ eV}}{\epsilon} - 0.13 \text{ eV} \right] + E^0_{(T,BR)} \quad (4)$$

The reaction free energy, $-\Delta G_{ET}$, can be tuned by varying the solvent (polarity, viscosity) or one of the reagents (E^* , $E^0_{(A^-/A)}$, $E^0_{(D/D^+)}$). The solvent polarity and viscosity are crucial not only for the electron-transfer step but also for the balance between back electron transfer and potential reaction pathways. For a quencher with an accessible triplet or biradical state, variation of the sensitizer may affect three thermodynamic quantities: the driving force for charge separation, $-\Delta G^0_{ET}$, the pair energy relative to that of the reagent ground states, $-\Delta G^0_{SSRP,G}$, and the pair energy relative to that of the accessible triplet or biradical, $-\Delta G^0_{SSRP,T}$. The balance between $-\Delta G^0_{SSRP,G}$ and $-\Delta G^0_{SSRP,T}$ is of crucial importance because it affects the rates of the competing electron return reactions generating one triplet state versus the reagent ground states. Pertinent data are compiled in Table 1.

The reaction with chloranil was previously explained as proceeding via radical ion pairs—the chloranil radical anion, $CA\bullet^-$, paired with *trans*- or *cis*- $1\bullet^+$ (eq 5).⁸ These pairs undergo hyperfine-induced intersystem crossing on the nanosecond time scale (eq 6). Back electron transfer in singlet pairs regenerates the reagent ground states—CA and *trans*- or *cis*- 1 —the donor molecule being polarized (eq 7). The spin density distribution of *trans*- and *cis*- $1\bullet^+$ accounts for the observed CIDNP effects. The parameters determining the polarization phase are assigned in Table 2.



The polarization generated in the reaction with 1,4-dicyanonaphthalene as the sensitizer/acceptor is compatible with the identical radical cations, *trans*- and *cis*- $1\bullet^+$, this time generated from a singlet precursor, ${}^1DCN^*$, and paired with $DCN\bullet^-$ (eq 8). The change from net to multiplet polarization is due to the lower g factor of $DCN\bullet^-$ compared to that of $CA\bullet^-$. Following

TABLE 1: Thermodynamic Parameters of Acceptor/Sensitizers and Radical Ion Pairs Generated by ET Quenching of Acceptor Excited States by 1,2-Diphenylcyclopropane

sensitizer ^a	^{1,3} E^* (eV)	$E^0_{(A^-/A)}$ (V)	$-\Delta G^0_{ET}$ ^b (eV)	$-\Delta G^0_{SSRP,G}$ (eV)	$-\Delta G^0_{SSRP,T}$ (eV)
chloranil	2.3	+0.02	0.7	1.6	0.35
1,4-DCN	3.45	-1.28	0.5	2.9	1.65
9-CP	3.42	-1.88	-0.1	3.5	2.25
3,3',4,4'-BTDA	2.86	-0.82	0.42	2.44	1.2
TCB	3.83	-0.65	1.56	2.27	1.0

^a CP, cyanophenanthrene; BTDA, benzophenonetetracarboxylic anhydride; DCN, dicyanonaphthalene; TCB, tetracyanobenzene. ^b Calculated with $E^0_{(D/D^+)} = 1.62$ vs SCE;¹³ ${}^3E_{BR} = 29$ kcal mol⁻¹, 1.25 eV;¹³ ${}^3E_1 = 60$ kcal mol⁻¹.⁸

TABLE 2: CIDNP Effects (Γ)^a and Polarization-Determining Parameters for Radical Ion Pairs Generated by ET Quenching of Sensitizer Excited States^b by 1,2-Diphenylcyclopropane

ion pair	product	μ^c	ϵ^d	a_i	a_j	Δg	J_{ij}	σ_{ij}^e	Γ
$CA\bullet^- - t-1\bullet^+$	<i>trans</i> - 1	T (+)	+	benz -	-				A
				gem + benz -					E A
$CA\bullet^- - c-1\bullet^+$	<i>cis</i> - 1	T (+)	+	gem + benz -	+				E E/A
				<i>trans</i> - 1	+				E/A
$DCN\bullet^- - t-1\bullet^+$	<i>cis</i> - 1	S (-)	-	benz -	+		+	+	A/E
				gem + benz -					A/E A/E
				<i>trans</i> - 1					A/E
$DCN\bullet^- - c-1\bullet^+$	<i>cis</i> - 1	S (-)	+	benz -	+		+	+	E/A
				gem + benz -					E/A A/E
$CP\bullet^- - t-1\bullet^+$	<i>cis</i> - 1	S (-)	-	gem + benz -			+	+	A/E A/E
				<i>trans</i> - 1					A/E

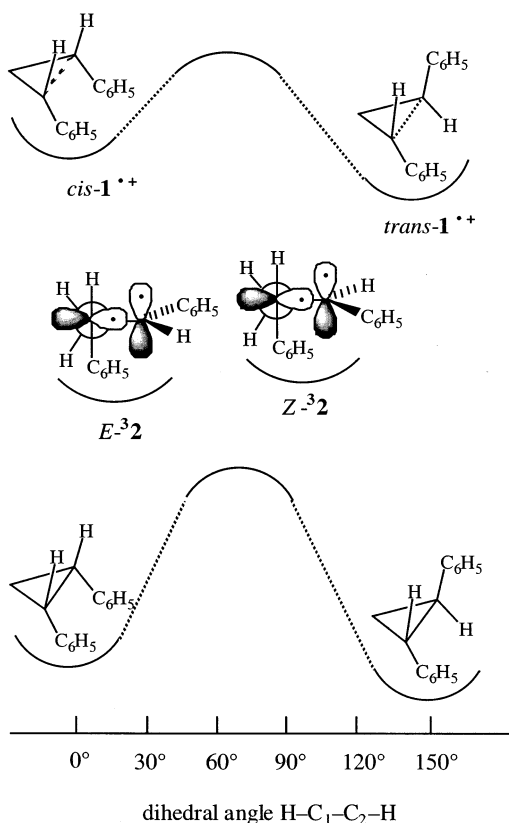
^a CIDNP effects are explained by two sign rules: $\Gamma = \mu\epsilon a_i \Delta g$ or $\Gamma = \mu\epsilon a_i a_j J_{ij} \sigma_{ij}$ from the precursor multiplicity,^c a reaction parameter,^d the signs of the hyperfine coupling constants a_{ij} and J coupling, the relative g factors Δg , and a factor relating the coupled nuclei. ^b CA, chloranil; DCN, dicyanonaphthalene; CP, cyanophenanthrene. ^c Initial (precursor) spin multiplicity singlet, -; initial (precursor) spin multiplicity triplet, +. ^d Singlet recombination, +; triplet recombination, -. ^e Nuclei i and j in the same radical, +; nuclei i and j in different radicals, -.

the evolution of triplet character (eq 9), back electron transfer in singlet pairs regenerates the reagent ground states, DCN and polarized *trans*- or *cis*- 1 (eq 10).



This reaction also generates CIDNP effects for the rearranged donors; the reagent (E/A) and the rearranged donor (A/E) have opposite polarization phases, indicating that the two products

SCHEME 1: Relative Energies and Structural Features of Ring-Closed Radical Cations *cis*- and *trans*-1^{•+} Generating Ring-Opened Triplet-State Rotamers *E*-³2 or *Z*-³2 (in Newman Projections) with Mutually Orthogonal p Orbitals Relative to *cis*- or *trans*-1^a



^a Counterions are omitted for clarity. The barrier for geometric isomerization of the radical cations is likely lower than that for the interconversion of the parent molecules

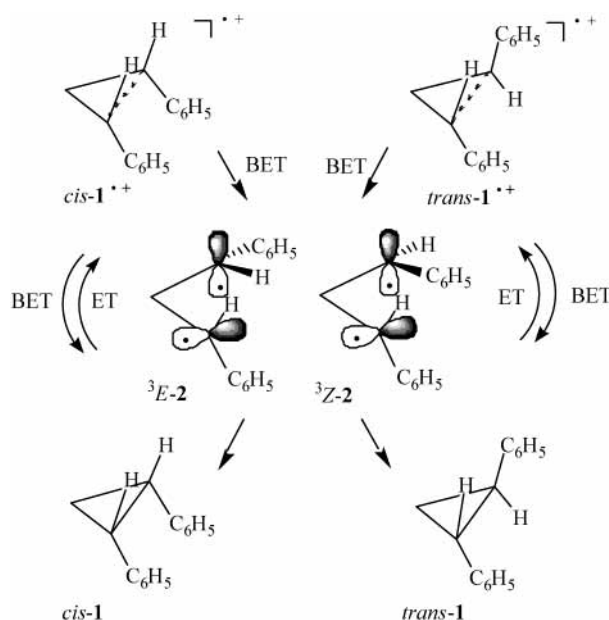
are (re)generated by different pathways. Thus, an additional intermediate that allows for the rearrangement is required; the most plausible candidate is a perpendicular triplet state, *E*-2^{••} and/or *Z*-2^{••}, invoked previously^{8,9} and again recently (eq 11).¹³ These species are likely generated by triplet recombination (i.e., back electron transfer (BET) in triplet ion pairs). Comparable intensities for the reagent and rearranged donors suggest comparable rates for back electron transfer in singlet and triplet pairs (cf. Table 2).

Concerning the nature of the putative triplet states, it is useful to recall their description by earlier authors. Hammond and co-workers wrote, "An obvious mechanism for the reaction involves energy transfer with breaking of the weak carbon-carbon bond connecting the two ring members which bear the phenyl substituents."¹ The current author perceived the necessity of a second intermediate and suggested "the consecutive formation of two different intermediates, the earlier one accounting for the polarization pattern, the second one accounting for the rearrangement."⁹ The second intermediate was described as "a perpendicular triplet state" (i.e., as one in which the spin-bearing p orbitals are orthogonal to each other, *E*-2^{••} and/or *Z*-2^{••} (cf. Scheme 1)⁹).

Triplet recombination of radical ion pairs has been invoked in many systems on the basis of time-resolved optical spectroscopy,^{18–27} magnetic field effects,^{23,24} CIDNP spectra,^{8,9,28–34} optoacoustic calorimetry,^{13,35} or product considerations.^{36–38} The CIDNP method, in general, can unambiguously identify either the spin multiplicity of a radical (ion) pair precursor or the spin

multiplicity of the resulting pair when forming a product.^{39–43} This feature qualifies the CIDNP technique ideally to detect products of triplet recombination; the basic principles underlying the CIDNP method and the features leading to the recognition of triplet-derived products have been reviewed recently.⁴⁴

Two factors play a significant role in the recombination of radical ion pairs of triplet spin multiplicity: the energetics of the corresponding electron transfer and the relationship between the topologies of the potential surfaces of parent molecules, radical ions, and accessible triplet or biradical species. The rate of back electron transfer is determined by the relative energies of the states involved; thus, energetic reasons will determine whether BET can compete with other possible reactions. The topologies of the various states influence the course of the overall reaction. For example, the radical ions (*cis*- or *trans*-1^{•+}) have carbon connectivities related to those of the parent (*cis*- or *trans*-1) whereas the accessible triplet state (biradical) has a different connectivity. Therefore, electron return will populate two rotamers, *E*- and *Z*-2^{••}, of a triplet state with a broken bond; both rotamers should be accessible from both *cis*- and *trans*-1^{•+}.



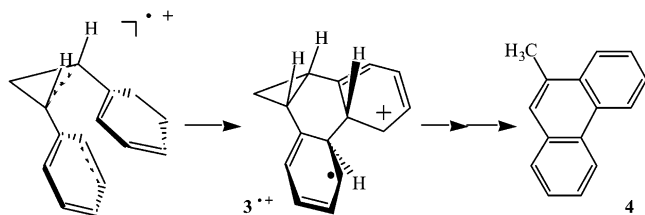
Of course, the triplet species is populated in a vertical fashion, but it will suffer a bond cleavage immediately following the electron-transfer step, most likely without an additional intermediate. As a result, the simple sequence of ET (i.e., eq 8) and BET (i.e., eq 11) may result in a rearrangement.^{8,9,13,34,35,45–47} We agree with the conclusion¹³ that the CIDNP method cannot differentiate between a one-step and a two-step mechanism converting *cis*- or *trans*-1^{•+} to *E*-2^{••} and/or *Z*-2^{••}. Of course, optical spectroscopy cannot rigorously differentiate between these pathways either; it can merely assign an upper limit for the lifetime of the potential additional intermediate.

The CIDNP spectrum observed during the reaction of *cis*-1 with DCN (Figure 1, center right) indicates that a third reaction, one not available to *trans*-1^{•+}, competes with singlet and triplet back electron transfer. The strong multiplet effect at $\delta \approx 2.4$ signifies the formation of 9-methylanthracene, **4**; this conversion can be envisioned via *o,o'* coupling of the phenyl moieties as a reasonable first step. The E/A pattern suggests that the product is generated from singlet pairs (cf. Table 2).

The main difference between the donors, *cis*- and *trans*-1, is the orientation of the phenyl groups. Various systems with two

phenyl groups in proximity to each other undergo *o,o'* coupling; these conversions proceed via excited singlet or triplet states, molecular ions, anions, or free radicals as key intermediates.^{48–52} For example, *cis*-stilbene, *cis*-azobenzene, or diphenylamine form dihydrophenanthrene, dihydrocinnoline, or dihydropyrrole systems, respectively. *o,o'* cyclization of radical cation *cis*-**1**^{•+} would generate dihydrocyclopropaphenanthrene (dihydrodibenzonorcaradiene), **3**^{•+}, whose conversion to 9-methylanthracene, **4**, requires dehydrogenation in the *o,o'* positions and ring-opening with a hydrogen (hydride) shift from one benzylic to the secondary carbon as well as BET.

Because the ET reaction of ¹DCN* with *cis*- or *trans*-**1** results in comparable CIDNP intensities for the isomers (Figure 1, center), singlet and triplet BET must occur at comparable rates. The additional finding of a comparable enhancement for **4** (Figure 1, center right) places the cyclization rate of *cis*-**1**^{•+} into the same time window. The results obtained with 9-cyanophenanthrene (9-CP) provide additional insight.



The PET reaction between 9-cyanophenanthrene and *trans*- and *cis*-**1** (Figure 1, top) can be envisioned to proceed by a mechanism similar to that with DCN: *trans*- and *cis*-**1**^{•+} are generated from ¹CP* and back electron transfer in singlet pairs regenerates polarized *trans*- or *cis*-**1** whereas back electron transfer in triplet pairs generates *E*-**2**^{••} and/or *Z*-**2**^{••}; their decay generates the polarized rearranged donor. The unbalanced polarization (i.e., the fact that the rearranged donor is strongly polarized whereas the reagent donor shows little or no polarization) suggests that the balance between the pathways regenerating the reagent and forming the isomer has shifted relative to the reaction with 1,4-dicyanonaphthalene. This result requires that, with 9-CP^{•-} as the counterion, triplet recombination be faster than the corresponding singlet recombination. The key to understanding this feature lies in the energetics of these systems, particularly in the differences between the free energies of singlet ($-\Delta G^0_{\text{SSRP}}$) and triplet recombination ($-\Delta G^0_{\text{SSRP,T}}$) of the radical ion pairs. The thermodynamic properties of five sensitizers and of the resulting radical ion pairs are summarized in Table 1.

The data show that the ring-opened triplet state, *E*-**2**^{••} and/or *Z*-**2**^{••}, is accessible in all five systems. However, it appears that the energetic requirements for electron return in triplet pairs are somewhat more subtle than the trivial prerequisite that a triplet (or biradical) state of energy E_T exist below the ion-pair energy, ΔG^0_{SSRP} . Electron return can be slow if the free energies are either too large or too small; thus, triplet recombination can be achieved by either increasing or decreasing the energy gap $-\Delta G^0_{\text{SSRP,T}}$. Karki et al. found a triplet yield close to unity for the pair 3,3',4,4'-BTDA^{•-}-*trans*-**1**^{•+} ($-\Delta G^0_{\text{SSRP,T}} = 1.2$ eV);¹³ in this case, triplet recombination must be more than an order of magnitude faster than singlet recombination ($-\Delta G^0_{\text{SSRP}} = 2.3$ eV). Conversely, the low free energy of triplet recombination ($-\Delta G^0_{\text{SSRP,T}} = 0.35$ eV) for the pair CA^{•-}-*trans*-**1**^{•+} causes singlet electron return ($-\Delta G^0_{\text{SSRP}} \approx 1.6$ eV) to be more than an order of magnitude faster. However, the pair 9-CP^{•-}-*trans*-**1**^{•+} has a high value for $-\Delta G^0_{\text{SSRP}}$ (~ 3.2 eV) whereas

$-\Delta G^0_{\text{SSRP,T}}$ (~ 2.25 eV) appears to be more favorable. Likewise, the pair 1,4-DCN^{•-}-*trans*-**1**^{•+} has a high value of $-\Delta G^0_{\text{SSRP}}$ (~ 2.9 eV); again, $-\Delta G^0_{\text{SSRP,T}}$ (~ 1.65 eV) appears to be more favorable. These results suggest an optimal range, 1.0 eV $< -\Delta G^0_{\text{SSRP,T}} < 1.5$ eV, for triplet recombination.

As in the ET reaction with ¹DCN*, the CIDNP spectra obtained in the reactions of *trans*- and *cis*-**1** with ¹CP* follow similar patterns; they also differ in the observation of the E/A multiplet at $\delta \approx 2.4$ due to **4**. The fact that *trans*-**1**^{•+} fails to undergo *o,o'* coupling can be readily ascribed to the steric prerequisites for cyclization. However, the selective formation of **4** in reactions with singlet sensitizers is not intuitively obvious and requires additional comment. We ascribe this observation to the energetic features that also cause triplet BET to be competitive with singlet BET. The free energies of back electron transfer for the pairs CA^{•-}-*cis*-**1**^{•+} ($-\Delta G^0_{\text{SSRP}} \approx 1.6$ eV), 9-CP^{•-}-*cis*-**1**^{•+} ($-\Delta G^0_{\text{SSRP}} = 3.5$ eV), or 1,4-DCN^{•-}-*cis*-**1**^{•+} ($-\Delta G^0_{\text{SSRP}} = 2.9$ eV) are significantly different. The free energy of singlet BET for CA^{•-}-*cis*-**1**^{•+} appears to be more favorable than for either 9-CP^{•-}-*cis*-**1**^{•+} or 1,4-DCN^{•-}-*cis*-**1**^{•+}; therefore, singlet BET for CA^{•-}-*cis*-**1**^{•+} should be much faster than with 9-CP^{•-} or 1,4-DCN^{•-} as the counterion. Singlet BET for CA^{•-}-*cis*-**1**^{•+} also must be faster than *o,o'* coupling of *cis*-**1**^{•+}. However, it is not unreasonable that *o,o'* cyclization competes with the slower triplet BET for pairs 9-CP^{•-}-*cis*-**1**^{•+} ($-\Delta G^0_{\text{SSRP,T}} \approx 2.25$ eV) and 1,4-DCN^{•-}-*cis*-**1**^{•+} ($-\Delta G^0_{\text{SSRP,T}} \approx 1.65$ eV).

Our results and the interpretation offered here suggest an interesting line of investigation. According to Marcus, ET rates are a function of the driving force, ΔG^0 , and a "solvent reorganization energy", λ_s ; ET rates should reach a maximum for $\lambda_s = \Delta G^0$ and decrease at higher driving forces.^{53,54} The existence of an "inverted" region was confirmed by Miller et al. for ET reactions between radical anions and aromatic hydrocarbons in frozen solutions ($0.01 < -\Delta G^0 < 2.75$ eV).⁵⁵ Similarly, intramolecular ET rates in monoradical anions, [A-spacer-B]^{•-}, containing two acceptors linked by a rigid spacer showed a striking deviation from classical Brønsted behavior.^{56,57} The inverted region for charge recombination (BET) was documented by Gould et al.^{58,59} for ET reactions between cyanosubstituted (poly)cyclic aromatic acceptors and methyl-substituted arene donors, including a differentiation between "solvent-separated" and "contact" radical ion pairs.

It would be interesting to probe in an analogous study the BET reactions populating the ring-opened triplet states, *E*-**2**^{••} and/or *Z*-**2**^{••}, or the competing process regenerating the parent molecules. Because the potential surfaces of the parent molecules, *trans*- and *cis*-**1**, the corresponding radical ions, *trans*- and *cis*-**1**^{•+}, and the ring-opened triplet species, *E*-**2**^{••}/*Z*-**2**^{••}, have divergent topologies, singlet and triplet recombination may follow different curves, just as solvent-separated and contact radical ion pairs do.^{58,59} Although BET in singlet pairs may be unexceptional, triplet recombination may have a component that is responsive to "reagent reorganization" in addition to the component describing solvent reorganization. For these reasons, the singlet as well as triplet BET rates for *trans*- and *cis*-**1**^{•+} should make a fascinating research topic.

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References and Notes

- (1) Hammond, G. S.; Wyatt, P.; De Boer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532–2533.
- (2) Griffin, G. W.; Covell, J.; Petterson, R. C.; Dodson, R. M.; Klose, G. *J. Am. Chem. Soc.* **1965**, *87*, 1410.
- (3) Hammond, G. S.; Cole, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 3256–3257.
- (4) Murov, S. L.; Cole, R. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 2957–2958.
- (5) Valyocsik, E. W.; Sigal, P. *J. Org. Chem.* **1971**, *36*, 66.
- (6) Hixson, S. S.; Boyer, J.; Galucci, C. *Chem. Commun.* **1974**, 540.
- (7) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101–2104.
- (8) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956–7958.
- (9) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210–7217.
- (10) Hammond, G. S.; Saltiel, J. *J. Am. Chem. Soc.* **1963**, *85*, 2516–2517.
- (11) Rau, H. *Chem. Rev.* **1983**, *83*, 535–547.
- (12) Inoue, Y. *Chem. Rev.* **1992**, *92*, 741–770.
- (13) Karki, S. B.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Zona, T. A. *J. Am. Chem. Soc.* **1997**, *119*, 431–432.
- (14) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 839–845.
- (15) Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 93.
- (16) Weller, A. *Pure Appl. Chem.* **1968**, *16*, 115.
- (17) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.
- (18) Weller, A.; Zachariasse, K. *J. Chem. Phys.* **1967**, *46*, 4984–4985.
- (19) Grellmann, H.; Watkins, A. R.; Weller, A. *J. Lumin.* **1970**, *1*, 2, 678–692.
- (20) Orbach, N.; Potashnik, R.; Ottolenghi, M. *J. Phys. Chem.* **1972**, *76*, 1133–1139.
- (21) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153–160.
- (22) Orbach, N.; Ottolenghi, M. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; pp 75–111.
- (23) Schulten, K.; Staerk, H.; Weller, A.; Werner, H. J.; Nickel, B. *Z. Phys. Chem. Neue Folge* **1976**, *101*, 371–390.
- (24) Michel-Beyerle, M. E.; Haberkorn, R.; Bube, W.; Steffens, E.; Schröder, H.; Neusser, N. J.; Schlag, E. W.; Seidlitz, H. *Chem. Phys.* **1976**, *17*, 139–145.
- (25) Haberkorn, R.; Michel-Beyerle, M. E. *Z. Naturforsch., A: Phys. Sci.* **1976**, *31*, 599.
- (26) Bube, W.; Haberkorn, R.; Michel-Beyerle, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 5993–5995.
- (27) Michel-Beyerle, M. E.; Krüger, H. W.; Haberkorn, R.; Seidlitz, H. *Chem. Phys.* **1979**, *42*, 441–447.
- (28) Taylor, G. N. Private communication, cited in Roth, H. D. *Mol. Photochem.* **1973**, *5*, 91–126.
- (29) Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6127–6128.
- (30) Bargon, J. *J. Am. Chem. Soc.* **1977**, *99*, 8350–8351.
- (31) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1979**, *101*, 1898–1900.
- (32) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 4303–4310.
- (33) Roth, H. D.; Schilling, M. L. M.; Jones, G., II. *J. Am. Chem. Soc.* **1981**, *103*, 1246–1248.
- (34) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J.; Miyashi, T.; Takahashi, Y.; Konno, A.; Mukai, T. *J. Am. Chem. Soc.* **1988**, *110*, 5130–5136.
- (35) Ikeda, H.; Nakamura, T.; Miyashi, T.; Goodman, J. L.; Akiyama, K.; Tero-Kubota, S.; Houmam, A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1998**, *120*, 5832–5833.
- (36) Climent, M.-J.; Miranda, M. A.; Roth, H. D. *Eur. J. Org. Chem.* **2000**, 1563–1567.
- (37) Roth, H. D.; Weng, H.; Zhou, D.; Lakkaraju, P. S. *Acta Chem. Scand.* **1997**, *51*, 626–635.
- (38) Weng, H.; Scarlata, C.; Roth, H. D. *J. Am. Chem. Soc.* **1995**, *117*, 10954–10962.
- (39) Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157–229.
- (40) Kaptein, R. *Adv. Free-Radical Chem. (London)* **1975**, *5*, 319–380.
- (41) Adrian, F. J. *Rev. Chem. Intermed.* **1979**, *3*, 3–43.
- (42) Freed, J. H.; Pedersen, J. B. *Adv. Magn. Reson.* **1976**, *8*, 2–84.
- (43) Roth, H. D. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds; Wiley: New York, 1996; Vol. 2, 1337–1350.
- (44) Roth, H. D. *J. Photochem. Photobiol., C* **2001**, *2*, 93–116.
- (45) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 716–718.
- (46) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157–6166.
- (47) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 6098–6099.
- (48) Mallory, F. B.; Wood, C. S.; Gordon, J. T. *J. Am. Chem. Soc.* **1964**, *86*, 3094.
- (49) Muszkat, A.; Fischer, E. *J. Chem. Soc. B* **1967**, 662.
- (50) Breslin, D. T.; Fox, M. A. *J. Org. Chem.* **1994**, *59*, 662.
- (51) García, H.; Martí, V.; Casades, I.; Fornés, V.; Roth, H. D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2955–2960.
- (52) Corma, A.; García, H.; Iborra, S.; Martí, V.; Miranda, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 2177–2180.
- (53) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
- (54) Marcus, R. A. *Can. J. Chem.* **1959**, *37*, 155.
- (55) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.
- (56) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
- (57) Closs, G. L.; Miller, J. R. *Science (Washington, D.C.)* **1988**, *240*, 440.
- (58) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.
- (59) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.