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Role of Ion Pairs in the Photochemistry of Electron Donor–Acceptor Complexes. Picosecond Spectroscopic Studies of Arene–Tetracyanoethylene Systems

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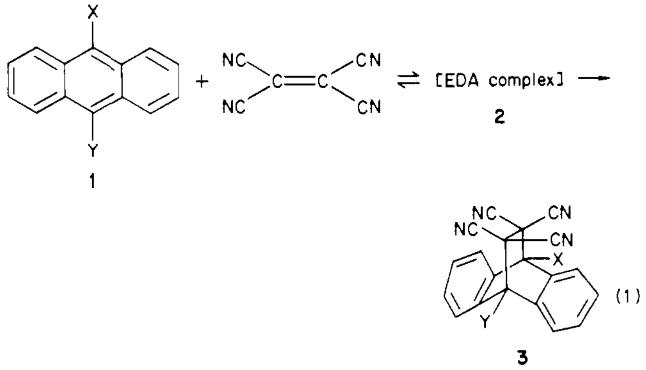
Abstract: Photochemical excitation of the electron donor–acceptor (EDA) complexes of various 9-substituted anthracenes and indene as electron donors (D) with tetracyanoethylene as the common electron acceptor (A) is examined by means of time-resolved picosecond spectroscopy. It is unequivocally established for the first time that specific irradiation of the charge transfer absorption bands of these EDA complexes leads directly to the radical ion pair $[D^{+}\cdot A^{-}\cdot]$ within the time resolution of the laser pulse. The transient absorptions resulting from these geminate radical ions decay in ~60 ps after excitation. In the case of the anthracene–tetracyanoethylene complexes, the photogenerated radical ion pairs simply undergo rapid back electron transfer to afford the original EDA complex. However, the radical ion pair derived from the indene–tetracyanoethylene complex initially reacts to form a fleeting intermediate, and the original EDA complex is regenerated only after ~500 ps.

Charge transfer (CT) interactions provide substantial stabilization of the transition states for cycloaddition reactions, including those which are symmetry allowed.[1] Acceleration of the Diels–Alder reaction, for example, occurs when one partner, usually the diene, bears electron-donating substituents.[2] Lewis acid catalysis of Diels–Alder reactions[3] can be interpreted in terms of complexation of the Lewis acid with heteroatoms on the electron-deficient reactant thereby increasing its demand for electrons. Thermal [2 + 2] cycloadditions also may proceed when the charge transfer stabilization is sufficiently large.[4] Photochemical cycloadditions are facilitated similarly by charge transfer interactions.[5]

Electron donor–acceptor (EDA) complexes have been observed and proposed as intermediates in a number of these reactions.[6] The importance of such complexes in promoting interactiofn and bonding is evident in pericyclic additions, where the entropy of association is negative. The geometric preferences of the complexes may contribute to the regio- and stereoselectivity with which products are formed.[7] Despite evidence for the intermediacy of EDA complexes in photochemical[7] and ground-state[8] cycloadditions, mechanistic studies of thermal reactions largely have generally ignored their involvement along the reaction coordinate.[9]

EDA complexes are formed when two species, one electron rich and the other electron deficient, are mixed.[6a] The mechanism for the development of a strong interaction between the two species consequently is the same as that which encourages bond reorganization. Thus it is known that the interaction of electron-rich olefins or dienes, such as anthracene, with strongly electron-deficient *p*-systems, such as tetracyanoethylene (TCNE), results in the immediate formation of transient colored complexes.[10] According to Mulliken theory,[11] the optical transition responsible for the color involves the promotion of an electron from the highest occupied molecular orbital (HOMO) of the donor component to the lowest unoccupied molecular orbital (LUMO) of the acceptor component in the EDA complex. For a series of donors interacting with a common acceptor, the energies of the charge transfer transitions $h\nu_{CT}$ vary proportionally with the ionization potentials I_D of the donors.[6a,12] In the anthracene–TCNE system, the bleaching of the color due to the EDA complex **2** is associated with the formation of the Diels–Alder product **3** (eq 1).[13]



X = OCH_3, CH_3, C_6H_5, H, CHO, CO_2CH_3, CN, NO_2
Y = OCH_3, Cl, C_6H_5, H

Interestingly, the overall activation free energy for the formation of Diels–Alder products from substituted anthracenes (D) and TCNE corresponds to the energy required to produce the ion pair consisting of $D^{+}\cdot$ and $TCNE^{-}\cdot$ from the EDA complex.[12] The apparent thermodynamic relationship between the transition state for Diels–Alder additions and the ion pair derived from single

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Table I. Charge Transfer Absorptions of Electron Donor-Acceptor Complexes Derived from 9-Substituted Anthracenes and Indene with Tetracyanoethylene[a]

arene	λ_{CT}	A_{max}[b]
9-cyanoanthracene[c]	616	0.125
9-nitroanthracene[c]	610	0.135
10-chloro-9-anthraldehyde[c]	632	0.175
9-anthraldehyde[c]	654	0.260
9-carbomethoxyanthracene[c]	676	0.690
9,10-diphenylanthracene	798	
9,10-dimethoxyanthracene	794	
indene[d]	542, 424	0.45, 0.36

[a] In methylene chloride at 20°C. [b] Absorbance at λ_{CT}(max) in a 10-mm cell immediately after mixing. [c] Anthracene and TCNE concentrations were both 0.020 M. [d] Indene and TCNE concentrations were both 0.015 M.

electron transfer within the EDA complex underscores the prominence of charge transfer contributions in the mechanism of such reactions.

We have initiated a picosecond spectroscopic study of the photochemical behavior of EDA complexes in order to investigate the nature of their excited states. The mechanisms of energy dissipation within the complex will also help to clarify the role that these complexes play in chemical reactions.[14]

Experimental Section

Tetracyanoethylene (Aldrich) was purified by repeated sublimation, first at reduced pressure and then several times at atmospheric pressure. 9-Cyanoanthracene, 9-anthraldehyde, and 10-chloro-9-anthraldehyde (Aldrich) were each purified by three recrystallizations from ethanol. Indene and 9,10-diphenylanthracene (Aldrich, Gold Label) and the solvents dichloromethane, acetonitrile, and methanol (Matheson, Coleman and Bell, Omnisolv, or Aldrich, Gold Label) were used without further purification. 9-Nitroanthracene,[15] 9,10-dimethoxyanthracene,[16] and methyl 9-anthroate[17] were synthesized according to the procedures described in the literature. Other solvents were reagent grade and used as received.

Electronic spectra were obtained on a Hewlett-Packard 8450Å diode-array spectrometer, and the NMR spectra were taken on a Nicolet NT360 (360 MHz) spectrometer. Photochemical irradiations with a focused 500W Xenon lamp, using Corning glass sharp cutoff filters 2-63 (560 nm), 3-71 (460 nm), or 3-74 (400 nm), were performed under argon in 10-mm Pyrex cuvettes containing 2 mL of a solution which was equimolar (0.01-0.1 M) in the arene and TCNE. The concentrations of these solutions were adjusted so that the transmittances were about 10% at the maxima of the CT bands (see λ_{CT} in Table I and Figure 1). In solvents more polar than CH_2Cl_2 (e.g., 1:3 v/v acetonitrile-dichloromethane, acetonitrile, or at -30 °C, 1:3 v/v methanol-dichloromethane), λ_{CT} appeared to be less intense and shifted hypsochromically relative to those observed in CH_2Cl_2 (Table I). Alcoholic solutions of TCNE containing anthracene donors were found to be unstable at temperatures above -30 °C owing to the solvolysis of TCNE.[18] Solutions in chloroform-*d* (Stohler Isotopes) were analyzed by ^{1}H NMR spectroscopy for product formation.

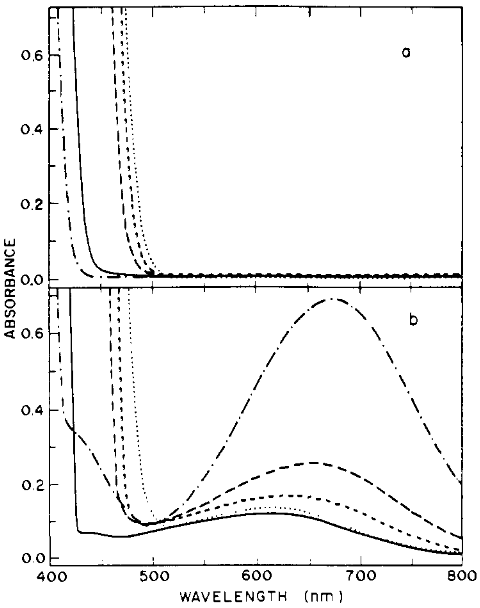

Figure 1. Electronic absorption spectra of (a) various 9-substituted anthracenes (0.02 M) and (b) 0.02 M anthracene with 0.02 M TCNE in methylene chloride at 20 °C: methyl 9-anthroate (-•-), 9-anthraldehyde (--), 10-chloro-9-anthraldehyde (---), 9-cyanoanthracene (—), 9-nitroanthracene (•••).

The absorption spectra of the radical cations of the substituted anthracenes were the result of averaging multiple accumulations of spectra measured through a 0.1-mm gold minigrid electrode maintained at a constant potential with the aid of a Princeton Applied Research Model 173 potentiostat. In each case, the applied potential was set at a value which was sufficiently positive to oxidize the appropriate anthracene rapidly. The details of the electrochemistry of the arenes will be reported elsewhere.[19a] TCNE was similarly reduced at -0.10 V vs. SCE to its monoanion TCNE^{-}·. The methylene chloride solutions contained approximately 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte and either 5.0 × 10^{-3} M anthracene or TCNE. The addition of trifluoroacetic acid [30% by volume for anthracene, 10-chloro-9-anthraldehyde, 9-anthraldehyde, and methyl 9-anthroate and 60% by volume for 9-cyanoanthracene and 9-nitroanthracene] helped to stabilize the radical cations of these species. Its presence caused small (0-5 nm) blue shifts in the absorption spectra relative to those measured in pure methylene chloride.

The picosecond laser system used to obtain the transient absorption data in this study has been previously described in detail.[19b] Briefly, it consisted of a passively mode-locked Nd^{3+}:YAG oscillator which generated a train of 25-ps fwhm, 1064-nm pulses. A single pulse was selected electrooptically from the train and amplified by two Nd^{3+}:YAG amplifiers. The 1064-nm pulse was converted to 532-nm light by means of a second harmonic generating crystal. The 532-nm pulse can then be used directly for sample excitation, passed through a third harmonic generating crystal with the residual 1064-nm laser pulse to produce a 355-nm excitation pulse, or passed through a fourth harmonic generating crystal and doubled to 266-nm light for sample excitation. An interrogating picosecond continuum pulse was produced by passing the sufficiently energetic, residual 1064-nm pulse through a cell containing D_2O/H_2O. The continuum pulse was split into sample and reference pulses before reaching the sample and reference cells. Both continuum pulses were focused on a 0.25-m spectrometer onto a PAR ISIT vidicon interfaced with a PAR 1215 OMA2 and a Data General Eclipse S/130 minicomputer. The laser system was operated in gated-free-run mode at ~1.5 Hz. Difference absorption spectra can be measured over wavelengths ranging from 390 to 840 nm by means of two spectrometer center-wavelength settings which provided a 115-nm overlap of the two spectral windows. Each recorded difference spectrum was the result of at least 120 no-excitation/excitation pairs of laser shots.

Results and Discussion

TCNE forms EDA complexes with anthracene and its derivatives which are ideally suited for our spectroscopic studies. The

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CT bands of some representative EDA complexes **2** are shown in Figure 1b. These absorption bands are sufficiently well-separated from those of the uncomplexed donors **1** (compare parts a and b in Figure 1) and TCNE to ensure that irradiation with the 532-nm 25-ps (fwhm) laser pulse specifically populates only the CT excited state of the EDA complexes. Thus there is no ambiguity about the adventitious excitation of species other than the EDA complexes, so that unrelated and interfering spectroscopic transients cannot arise. In most other systems which have been examined heretofore, the CT bands were not sufficiently well-separated from the absorptions of the uncomplexed components to allow unambiguous and specific excitation of only the EDA complex.[20]

When TCNE and an anthracene **1** are mixed in dichloromethane, the blue or green color of the EDA complex **2** appears immediately (Figure 1). The visible absorptions due to the complex disappear rapidly in the case of anthracene itself or its alkyl derivatives, with the concomitant formation of meso Diels–Alder addition products (eq 1).[13] Subsitution with electron-withdrawing or sterically bulky groups at the meso positions inhibits the cycloaddition. Thus 9-cyano-, 9-nitro-, 9-formyl-10-chloro-, and 9,10-diphenylanthracene form EDA complexes with TCNE which persist indefinitely. Analysis of concentrated solutions of these anthracenes and TCNE by ^{1}H NMR spectroscopy confirms the absence of significant amounts of Diels–Alder adducts. Moreover, both 9-anthraldehyde and methyl 9-anthroate react slowly with TCNE at room temperature to form **3**, but the reactions can be suppressed completely by cooling the mixture to −30 °C.

Selective irradiation through either a Corning 2-63 (560 nm) or 3-ml (460 nm) cutoff filter excites only the EDA complexes (cf. Figure 1). However, irradiation even for extended periods under conditions in which the EDA complexes are thermally stable results in no change in the absorption spectra of the solutions containing the EDA complexes. The Diels–Alder products between anthracenes and TCNE form reversibly and, in many cases, are sufficiently labile to partially revert to educts upon dissolution.[21] However, the failure to isolate photochemical products cannot result from the rapid cycloreversion of Diels–Alder adducts of formyl- and carbomethoxyanthracene because these adducts are stable under the reaction conditions. Since the deactivation of related EDA complexes in their excited singlet states may occur rapidly before products can form,[2e,22] we sought evidence for the formation of transient intermediates using picosecond laser spectroscopy.

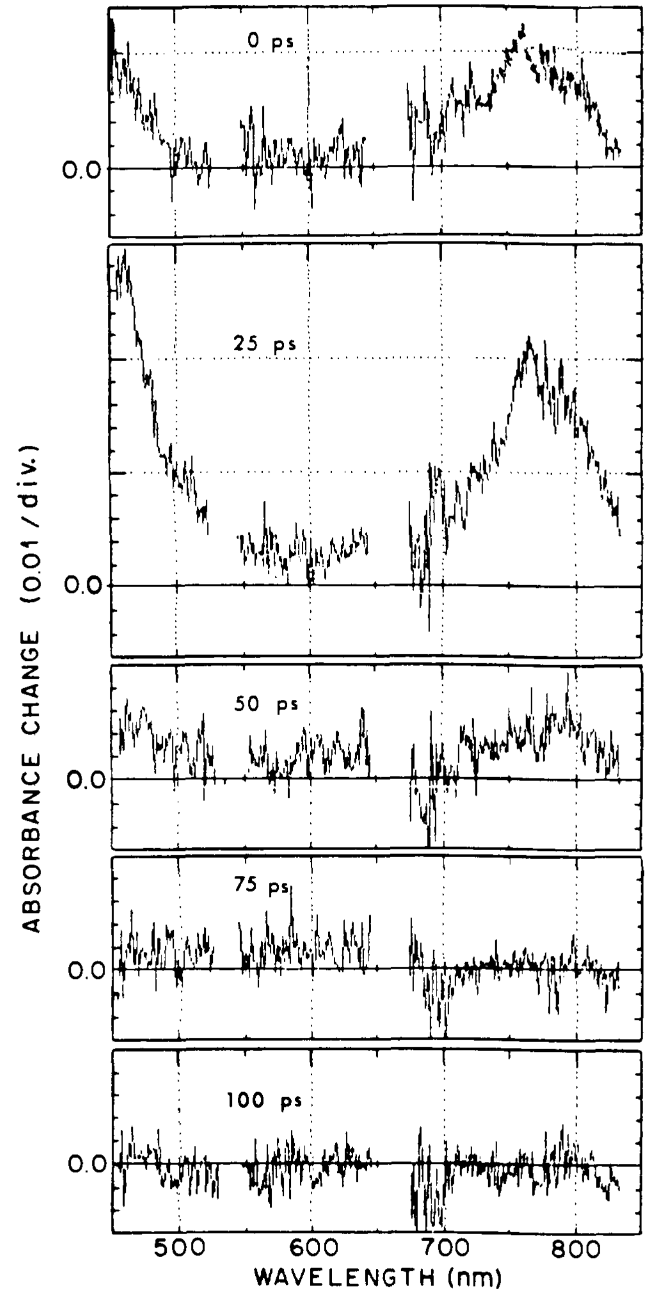

Figure 2. Difference absorption spectra as a function of time after excitation with a 532-nm, 25-ps laser pulse, measured for the 9-cyanoanthracene–tetracyanoethylene (0.08 M each) EDA complex in methylene chloride at 20 °C. The optical path length is 5 mm.

When a 5-mm optical cell containing a solution of TCNE and 9-cyanoanthracene in dichloromethane is irradiated with a 532-nm, 25-ps (fwhm) laser pulse (1–2 mJ), transient absorptions are observed. Difference absorption spectra taken at selected times after excitation reveal the presence of a pair of broad transient absorption bands which are illustrated in Figure 2. One absorption maximum is found near 460 nm, and the other is found near 750 nm. Both bands appear within the period of the 25-ps laser pulse and decay simultaneously within ~60 ps after excitation. The transient absorption spectrum is reproduced by a superposition of the individual absorption spectra of D$^{+\cdot}$ and TCNE$^{-\cdot}$ generated independently by the anodic oxidation of 9-cyanoanthracene and the cathodic reduction of TCNE, respectively, in dichloromethane (Figure 3). The negative absorption arising from depopulation of the EDA complex in the ground state also must be taken into account. Alkali metal salts of TCNE [M^{+} TCNE$^{-\cdot}$][23] exhibit absorption spectra in solution which are

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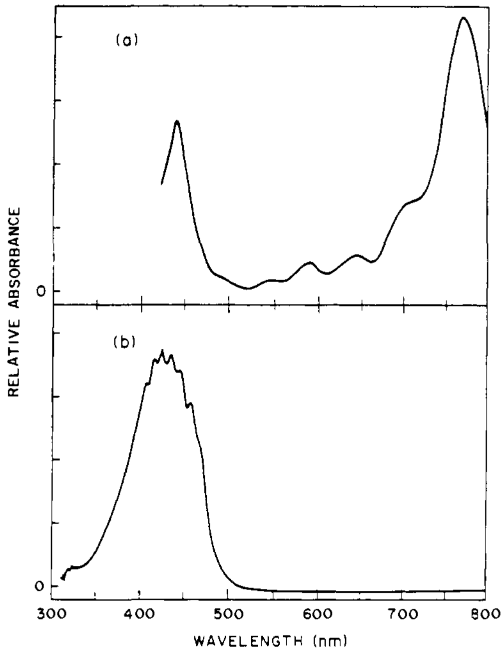

Figure 3. Electronic absorption spectra of (a) the 9-cyanoanthracene radical cation and (b) the TCNE radical anion generated electrochemically in dichloromethane at 20 °C with 0.1 M tetra-*n*-butylammonium perchlorate electrolyte (see Experimental Section for details).

similar to the spectrum of $TCNE^{-}\cdot$ generated electrochemically. We find the maxima in the visible region of the spectra of meso-substituted anthracene radical cations to be similar to, but somewhat red shifted from, those of the anthracene cation radical itself.[24] Since the transient absorptions observed in Figure 2 are essentially a superposition of the absorptions of the individual radical ions of cyanoanthracene and tetracyanoethylene, they must be associated with an ion pair resulting from essentially full electron transfer between the donor and the acceptor.[25]

For the cyanoanthracene–tetracyanoethylene EDA complex, the picosecond absorption data suggest the occurrence of the following processes

$$D + TCNE \rightleftharpoons [D, TCNE] \xrightleftharpoons{h\nu_{CT}} [D^{+}\cdot, TCNE^{-}\cdot] \qquad (2)$$

where [D, TCNE] is the ground-state EDA complex and $[D^{+}\cdot, TCNE^{-}\cdot]$ is the radical ion pair produced by CT excitation. There is no evidence from the picosecond absorption data for either the existence of an excited state of the EDA complex or the formation of any intermediate states or species other than $D^{+}\cdot$ and $TCNE^{-}\cdot$. The electron transfer from the donor to the acceptor in the EDA complex thus effectively occurs with the absorption of a photon. Such a formulation represents in this study a direct confirmation of Mulliken theory,[11] in which excitation into the charge transfer band of an EDA complex consisting of a relatively nonpolar ground state leads to the production of an ion pair.

The species responsible for the 460- and 750-nm transient absorptions have identically short lifetimes. The extremely rapid decay of the radical ion absorptions indicates that the radical ion pair is formed and resides within the singlet manifold during its lifetime. Intersystem crossing would yield an ion pair in the triplet state which is expected to have a lifetime much longer than 60 ps,[26] and which might be expected to decay to form locally excited triplet states of D and TCNE.[27] On the other hand, the time scale of the observed decay is consistent with vibrational and solvent relaxation phenomena.[22] Since the transient absorption bands disappear to regenerate the different absorption to the base line (i.e., ΔA returns to 0) within 60 ps after excitation, the radical ion pair reacts solely via rapid back electron transfer to form the original ground-state EDA complex. Thus, the photochemistry initiated by CT excitation does not give rise to any product formation, but it initiates a series of energy-wasting electron transfer steps ultimately restoring the EDA complex.

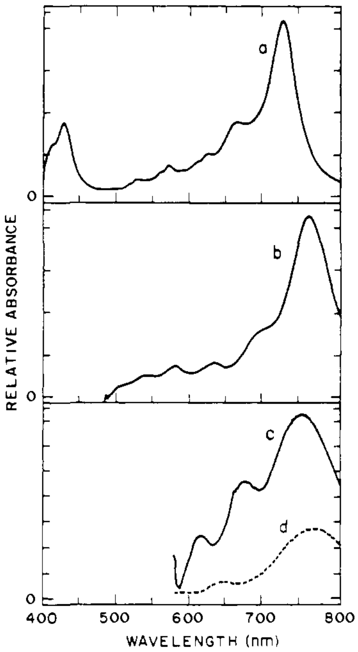

Figure 4. Electronic absorption spectra of the radical cations of (a) anthracene, (b) 9-nitroanthracene, and (c) 10-chloro-9-anthraldehyde (—) and 9-anthraldehyde (---). Expeirmental conditions were the same as those in Figure 3.

Immediately after excitation by the 532-nm pulse, the resulting depopulation of the ground-state EDA complex should result in a broad negative absorption ($\Delta A < 0$) in the 615-nm region where the EDA complex absorbs most intensely. The absence of an observable bleach can be explained by the relatively small value of the extinction coefficient of anthracene–TCNE EDA complexes ($\epsilon_{max} \simeq 250$ M^{-1} cm^{-1} [28]) relative to the absorbace changes arising from the formation of $TCNE^{-}\cdot$ ($\epsilon_{435} \simeq 7100$ M^{-1} cm^{-1} [23c]) and $D^{+}\cdot$ ($\epsilon_{max} \simeq 7700$ M^{-1} cm^{-1} for the anthracene cation radical[29]). Thus we cannot exclude the formation of a short-lived intermediate which does not absorb in the visible region. An intermediate resulting from single-bond formation between $D^{+}\cdot$ and $TCNE^{-}\cdot$ can be ruled out, because similar species have been observed to absorb in the region between 420 and 520 nm.[30] Diels–Alder addition products were not formed (vide supra), so that [4 + 2] cycloaddition also does not occur from this ion pair.

Analogous results were obtained for the other anthracene derivatives. Thus excitation of the EDA complex of 9-nitroanthracene with TCNE at 532 nm immediately afforded the absorptions of $TCNE^{-}\cdot$ and the radical cation of 9-nitroanthracene. This absorption of the latter resembles that of the radical cation generated electrochemically (cf. Figures 4 and 5). The transient absorptions appear within the 25-ps excitation pulse and disappear within about 50 ps. Similarly, the excitation of the EDA complex

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[25] The EDA complex is included as an intermediate in eq 3 by analogy with that in the Diels–Alder reaction in eq 1. Although the EDA complex has been shown to be an intermediate in the [4 + 2] cycloaddition in eq 1,[13] the corresponding experimental evidence is not yet available for the [2 + 2] process in eq 3.

[26] See: (a) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312. (b) Masuhara, H.; Saito, T.; Maeda, Y.; Mataga, N. *J. Mol. Struct.* **1978**, *47*, 243 and references therein. See also ref 20a.

[27] Adams, B. K.; Cherry, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 6904.

[28] Figeys, H. P.; Wilmet-Devos, B. *Bull. Soc. Chim. Belg.* **1970**, *79*, 459.

[29] The value of ϵ has been determined in the spectrum of the anthracene cation radical. See: Torikai, A.; Kato, R. *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 1487. See also ref 12b.

[30] (a) Dallinga, G.; Mackor, E. L.; Stuart, A. A. V. *Mol. Phys.* **1958**, *1*, 123. (b) Chu, T. L.; Weissman, S. I. *J. Chem. Phys.* **1954**, *22*, 21. (c) Similar intermediates have been reported in a 9-cyanoanthracene–olefin system, see: Okada, T.; Kida, K.; Mataga, N. *Chem. Phys. Lett.* **1982**, *88*, 157.

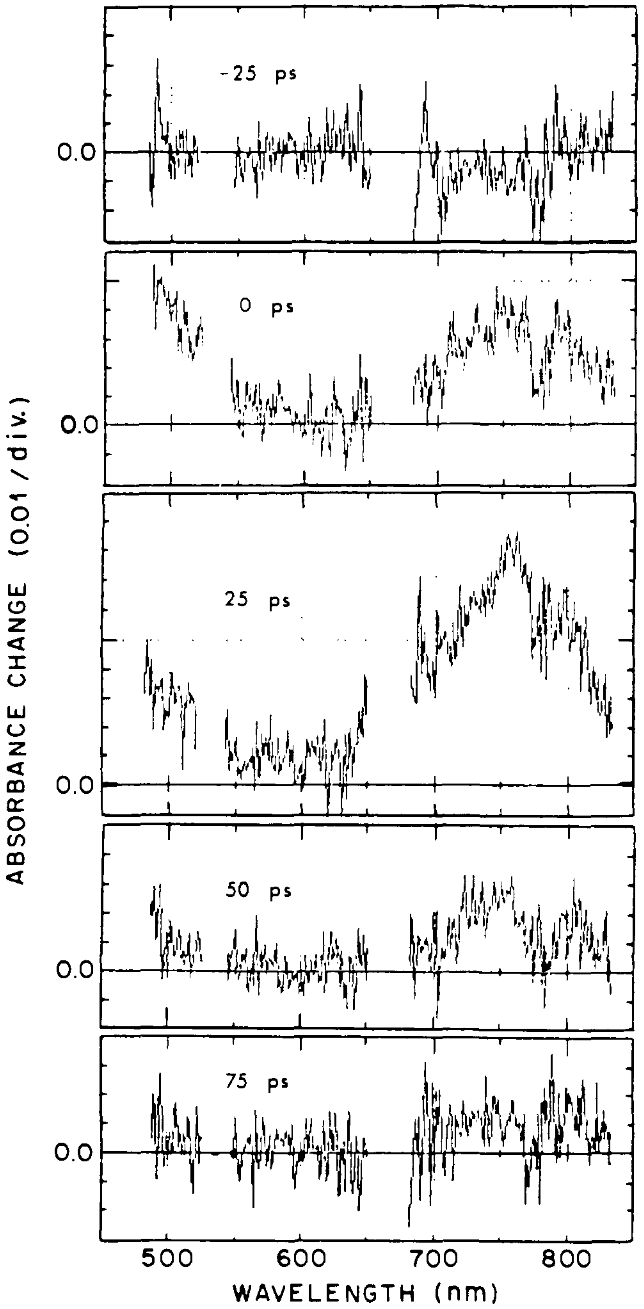


Figure 5. Difference absorption spectra as a function of time relative to excitation with a 532-nm, 25-ps pulse, measured for the 9-nitroanthracene–tetracyanoethylene EDA complex in methylene chloride at 20 °C. The optical path length is 5 mm.

of 9-anthraldehyde with TCNE at room temperature affords the respective radical ions within the duration of the picosecond pulse. Unfortunately, the decay kinetics could not be measured accurately owing to the facile competing reaction of 9-anthraldehyde and tetracyanoethylene to form the thermal Diels–Alder products. However, we could find no evidence for the photochemical formation of any product or of any intermediate states or species other than 9-anthraldehyde cation radical and tetracyanoethylene anion radical which decayed to regenerate the original EDA complex.

All attempts to stabilize or trap the geminate radical ion pair by increasing the polarity and nucleophilicity of the solvent were unsuccessful. The CT absorptions of the EDA complexes are less intense and are shifted hypsochromically in acetonitrile or methanol relative to dichloromethane solvent. In acetonitrile, the radical ion pairs formed following 532-nm CT excitation decayed at similar, or possibly greater, rates. It is known that radical ion pairs may decay more repidly as the ion-pair state becomes lower in energy relative to the ground state.[2e,20g]

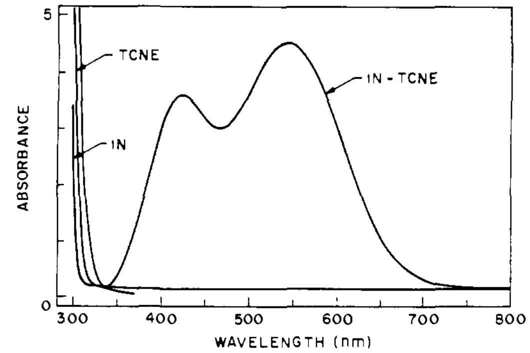
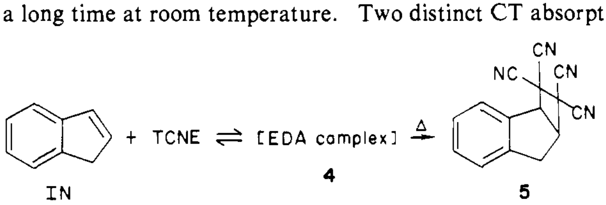


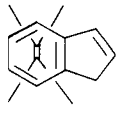
Figure 6. Electronic absorption spectra of 0.015 M indene, 0.015 M tetracyanoethylene, and a mixture of 0.015 M indene and 0.015 M tetracyanoethylene in methylene chloride at 20 °C.

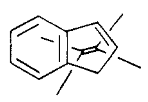
Tetracyanoethylene can undergo [2 + 2] cycloadditions thermally with donor olefins.[4] For example, TCNE reacts slowly with indene in refluxing acetonitrile or ethylene chloride to form a [2 + 2] adduct **5** (eq 3).[4,25] Mixing dichloromethane or acetonitrile solutions of indene and TCNE results in the immediate appearance of the color of the EDA complex **4** (Figure 6), which persists for a long time at room temperature. Two distinct CT absorption bands are visible for this EDA complex. Note in Figure 1 that a second, weaker absorption near 400 nm is also evident for the various anthracene–TCNE EDA complexes. Multiple CT maxima may arise from transitions involving electron promotion from different filled orbitals originating on the donor to the common lowest unoccupied orbital of the acceptor. Good agreement is found between the energy difference of the CT maxima ($\Delta h\nu_{CT}$) and the energy difference of the HOMO and the subjacent molecular orbital (i.e., $IP_1 - IP_2$) of donors in which the HOMO is not degenerate.[6a,19a,31]

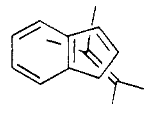


(3)

An X-ray crystallographic investigation has distinguished two different orientations of TCNE relative to hexamethylbenzene in the crystalline EDA complex, however.[32] The broadness of the CT absorptions of EDA complexes in solution suggests that transitions from a continuum of orientations are possible in weakly associated EDA complexes. Monochromatic incident radiation may not afford a uniform excited species,[25] and multiple CT maxima may arise from different EDA complexes or from different preferred geometric orientations of the component species within the EDA complex. Thus, for the indene–tetracyanoethylene EDA complex in solution, an orientation between indene and TCNE with overlap mainly occurring with the benzene ring (as in i) might exhibit an absorption similar to that of the *o*-xylene–tetracyanoethylene EDA complex (λ_{CT} = 438 nm) and could be responsible for the higher energy absorption of the indene–TCNE complex at 424 nm. A stronger interaction between TCNE and the double bond as in ii or iii may be assigned to the lower energy transition.


i


ii


iii

Continuous irradiation of the indene–tetracyanoethylene EDA complex in methylene chloride through either a 2–63 (560 nm)

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(31) Eckhardt, C. J.; Pennelley, R. P. *J. Am. Chem. Soc.* **1976**, *98*, 2034. See also: Pignataro, S.; Aloisi, G. *Z. Naturforsch., A* **1972**, *27*, 1165.

(32) Eckhardt, C. J.; Hood, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 6170.

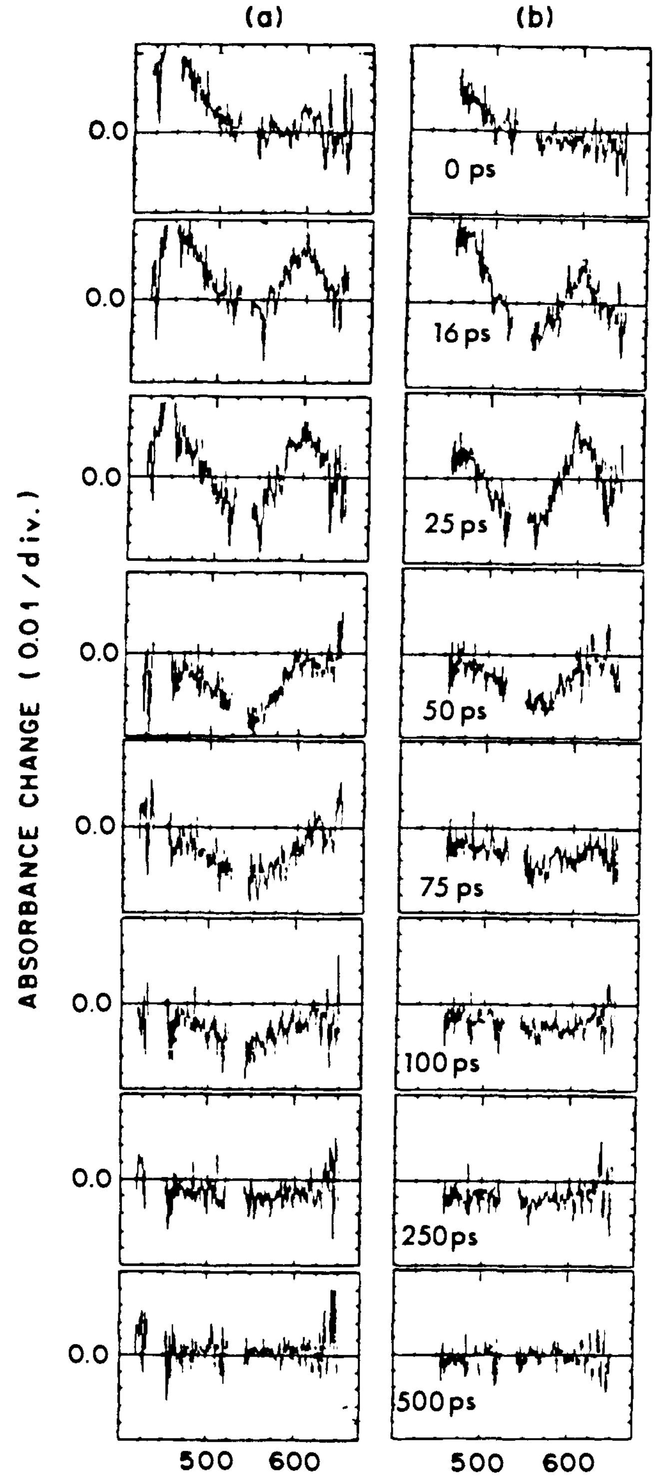
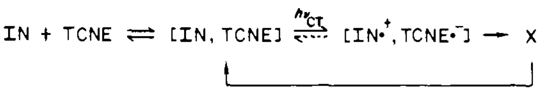


Figure 7. Difference absorption spectra as a function of time relative to excitation with a 532-nm, 25-ps pulse, measured for the indene-tetracyanoethylene (0.02 M each) EDA complex in methylene chloride at (a) 293 K and (b) 262 K. The optical path length is 10 mm.

or a 3–74 (400 nm) Corning glass sharp cutoff filter results in no appreciable change in the absorption of the EDA complex. [However, continuous irradiation of an indene–TCNE solution at wavelengths <320 nm results in the slow consumption of indene.] Excitation into the CT absorption at 532 nm with a 25-ps laser pulse affords two differential absorption bands, one near 460 nm and another near 600 nm (Figure 7). Both transient absorption bands appear within the time duration of the laser pulse. We again assign the 460-nm band to $TCNE^{-}\cdot$. We attribute the 600-nm band to a doublet–doublet absorption of the indene radical cation $IN^{+}\cdot$ on the basis of previous spectroscopic data.[33] The apparent delay between the time when $TCNE^{-}\cdot$ and $IN^{+}\cdot$ absorptions reach their maximum intensities is an artifact caused by temporal dispersion (Chirp) associated with the group velocities of the various probing wavelengths. The rise times of both absorptions are actually the same to within experimental error and are limited by the laser pulse width. No transient absorptions are observed between 640 and 770 nm monitored at times ranging from 0 to 500 ps after excitation.

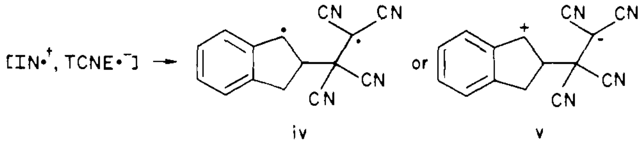
The absorption bands of the radical ions disappear in the same time, i.e., within ~60 ps after the laser pulse. No evidence was found for the existence of intermediate states or species preceding the formation of the radical ions. In particular, there is no evidence for the population of a non-ionic excited state of the indene–tetracyanoethylene EDA complex, because such an excited state would exhibit an absorption which is expected to be bathochromically shifted relative to that of the ground-state complex and should be observable under our experimental conditions.

The rapid decay of the radical ion pair indicates that it is produced and resides in the singlet manifold during its lifetime. However, unlike the anthracene–tetracyanoethylene systems, there is evidence for an intermediate which does not absorb between 420 and 770 nm and which arises from the $[IN^{+}\cdot, TCNE^{-}\cdot]$ radical ion pair. Thus, as the absorption bands of the radical ions disappear, the negative absorption due to the depletion of the ground-state EDA complex persists and becomes quite pronounced in the spectral region between 420 and 650 nm. [Note that λ_{CT} for the indene–tetracyanoethylene EDA complex appears at 424 and 542 nm with a large ϵ_{max} of 2000 M^{-1} cm^{-1} in dichloromethane.[34]] This bleach persists for ~500 ps, but no bleach is observed at longer periods of time (nanoseconds) after excitation. We found no evidence for the existence of any product which was formed irreversibly, and the original EDA complex ultimately is restored to its initial concentration since the base line of the difference absorption returns to $\Delta A = 0$ within 500 ps after excitation. The follwing processes are indicated for the 532-nm excitation of the indene–tetracyanoethylene EDA complex:


$$IN + TCNE \rightleftharpoons [IN, TCNE] \underset{}{\overset{h\nu_{CT}}{\rightleftharpoons}} [IN^{\cdot +}, TCNE^{\cdot -}] \longrightarrow X$$

where [IN, TCNE] is the ground-state EDA complex and $[IN^{+}\cdot, TCNE^{-}\cdot]$ is the radical ion pair produced upon CT excitation.

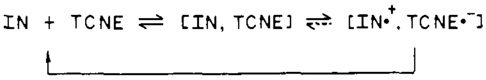
The identity of the transient intermediate is not known, but a possible candidate would be a species X arising from one-bond formation between the radical cations, e.g., iv or v. Such a species



iv v

would be expected to absorb in the region around 200–400 nm but probably would lack strong absorptions above 420 nm.[35] Intermediates of this type have been proposed for thermal [2 + 2] cycloadditions.[4]

Another interesting possibility is that X represents a nonequilibrium geometry of the ground-state EDA complex. The decay of the ion pair may lead to "uncomplexed" indene and tetracyanoethylene rather than (or in competition with) direct regeneration of the EDA complex, i.e.


$$IN + TCNE \rightleftharpoons [IN, TCNE] \rightleftharpoons [IN^{\cdot +}, TCNE^{\cdot -}]$$

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[33] Hilinski, E. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 5193.

[34] Toncheva, V.; Velichkova, R.; Panaiotov, I. M. *Bull, Soc. Chim. Fr., Ser. 5* **1974**, *1033*.

[35] For related benzyl cations and radicals, see: Hanazaki, I.; Nagakura, S. *Tetrahedron* **1965**, *21*, 2441. See also ref 30b.

The rate of formation of EDA complexes from their unassociated components is not known, but presumably it is close to the diffusion-controlled limit.[8-10] Under our conditions, $k_{\mathrm{diff}} \simeq 1.5 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ which is calculated by assuming $k_{\mathrm{diff}} = 8RT/3000\eta$[35a] where $\eta = 0.437$ cP at 298 K.[36] Therefore, with a system consisting of 0.05 M indene and 0.05 M TCNE, the rate of diffusional encounter ($2.6 \times 10^9\ \mathrm{s}^{-1}$) would be of the same magnitude as the rate found for the regeneration of the EDA complex ($>2 \times 10^9\ \mathrm{s}^{-1}$). The latter may exceed somewhat the rate of diffusional encounter, owing to the proximity of indene and TCNE following the decay of the ion pair. This explanation, if valid, would indicate that (a) the formation of the ground-state EDA complex is diffusion limited and (b) the electron transfer in the formation and/or decay of the radial ion pairs may lead to a geometry different from that favored at equilibrium for the ground-state EDA complex. Furthermore, in the case of a diffusion-controlled reaction, there should be a temperature dependence that decreases the rate of regeneration, k_{diff}, to about $1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 262 K because η increases to s0.59 cP.[36b,c] Unfortunately, the resolution of the spectra (Figure 7) does not permit a quantitative experimental differentiation between the regeneration rates of the EDA complexes at 262 and 293 K. The picosecond spectroscopic data indicate regeneration rates of $0.5\text{–}1.0 \times 10^{10}\ \mathrm{s}^{-1}$ which are somewhat greater than those expected for purely diffusional encounter in this temperature range. The resulting IN and TCNE may recombine or undergo reorientation within the solvent cage to reform the EDA complex. We expect that the breaking of the bridging σ bond between indene and TCNE in either iv or v also should represent a process with low activation energy. Thus the temperature dependence of the rate of bond breaking may be small.

Summary and Conclusions

Specific photochemical excitation of electron donor–acceptor complexes involving meso-substituted anthracenes or indene as electron donors and TCNE as the common electron acceptor establishes the direct population of an ion singlet state. The rise times of the transient absorptions of the radical ion pairs are limited by the width of the laser pulse (25 ps). These results represent in these systems a direct confirmation of Mulliken theory, the CT excitation involving essentially complete transfer of an electron from the donor to the acceptor.[11] The radical ion pairs rapidly decay within ~60 ps to ultimately regenerate the original electron donor–acceptor complex. No products are formed irreversibly. However, in the case of indene, an intermediate is formed which does not absorb in the visible region. We are currently infestigating the transient absorption spectra at wavelengths less than 420 nm in an effort to observe and to identify spectroscopically this intermediate. We are also extending out studies to include systems which afford stable photoproducts.[14b]

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Registry No. 1 (X = CN; Y = H)·TCNe, 86885-44-1; **1** (X = NO_2; Y = H)·TCNE, 93350-34-6; **1** (X = CHO; Y = Cl)·TCNE, 93350-35-7; **1** (X = CHO; Y = H)·TCNE, 29844-15-3; **1** (X = MeOC(O); Y = H)·TCNE, 93350-36-8; **1** (X = Y = Ph)·TCNE, 64914-69-8; **1** (X = Y = MeO)·TCNE, 36336-02-4; $\mathbf{1}^{+\cdot}$ (X = Y = H), 34512-28-2; $\mathbf{1}^{+\cdot}$ (X = NO_2; Y = H), 84367-93-1; $\mathbf{1}^{+\cdot}$ (X = CHO; Y = Cl), 93350-37-9; $\mathbf{1}^{+\cdot}$ (X = CHO; Y = H), 91547-89-6; $\mathbf{1}^{+\cdot}$ (X = CN; Y = H), 84985-64-8; IN·TCNE, 7378-72-5; $\mathrm{TCNE}^{-\cdot}$, 34512-48-6.

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[36] (a) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; pp 136–7. (b) Boit, H.-G., Ed. "Beilsteins Handbuch der Organischen Chemie"; Part 1, Springer-Verlag: New York, 1972; Vol. 1, p 36. (c) Griffing, V.; Cargyle, M. A.; Corvese, L.; Eby, D. *J. Phys. Chem.* **1954**, *58*, 1054.

Picosecond Photochemistry of 2,3-Diphenyloxiranes: Reaction from a Vibrationally Unrelaxed Electronic Excited State

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Abstract: Picosecond photochemistry of *trans*-1,2-diphenyloxirane (Ia) and *cis*-1,2-diphenyloxirane (Ib) is studied in cyclohexane and acetonitrile after 266-nm excitation by a 25-ps laser pulse. Carbonyl ylides, IIa and IIb, are formed by disrotatory opening of the singlet electronic excited state of Ia and Ib, respectively. The carbonyl ylides arise in 450 ± 250 ps after excitation in either solvent. After formation, the carbonyl ylides (IIa and IIb) disappear with lifetimes of >250 and 40 ± 20 ns, respectively. Photolysis of Ib in either solvent leads to significant amounts of IIa, the symmetry-forbidden product formed in a conrotatory fashion. It is suggested that the symmetry-forbidden product arises from the vibrationally unrelaxed electronic excited state of Ib.

The photochemistry of diaryloxiranes (I) has received considerable attention.[1] Griffin and co-workers have shown that room-temperature steady-state photolysis of many diaryloxiranes leads to efficient cycloelimination yielding arylcarbenes and carbonyl compounds.[2,3] Low-temperature photolysis of diaryloxiranes at 77 K by Griffin et al.[4-6] and Trozzolo et al.[6,7] has established that carbonyl ylides (II) form along with the carbenes. The opening of diaryloxiranes to carbonyl ylides occurs with conservation of orbital symmetry. Thermally, diaryloxiranes open

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(4) Becker, R. S.; Kolc, J.; Bost, R. O.; Kietrich, H.; Petrellis, P.; Griffin, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 3292.

(5) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302.