the basis that they arise from the vibrational coupling effects described in the previous sections.

The relevant data (including pK_a values of the axial ligands) for all of the complexes studied in this work are given in Table I along with explanatory comments. The dependence of $\nu(^{16}O-^{16}O)$ frequencies on ligand pK_a value for the complexes of a series of substituted pyridines whose basicities span a range of over nine orders of magnitude (pK_a = 0.67-9.70) is demonstrated in Figure 6. With the exception of two points (10 and 11), a linear relationship (correlation coefficient = 0.98) is clearly evident. The low frequency observed for $\nu(^{16}O-^{16}O)$ in the case of 2-BrPy with "unprotected" Co[^{2}H$_8$]TPP (point number 11) can be ascribed to a strong interaction between the bound O$_2$ and excess 2-BrPy, as was described in a previous section.

The anomalous frequency for the 2-BrPy complex with the picket-fence porphyrin (point 10) is not fully understood at this time. It may be pointed out, however, that the pK_a data correspond to measurements in aqueous solution. The value of ν(O-O) for the 2-BrPy complex indicates that the ligand is a stronger base (lower value for ν(O-O)) than is implied by the pK_a value. It may be possible that the inherent basicity is underestimated in aqueous solution as a result of stabilization of the base form by tight association of a molecule of water via formation of hydrogen bonds to the nitrogen and the bromo substituent.

Implications for RR Spectra of Heme Protein-O$_2$ Adducts. Many resonance Raman studies of heme protein complexes with exogenous ligands have been carried out.[3,16-18] Inasmuch as such studies are generally very useful for detecting slight alterations in structure and bonding parameters of these ligands, it is likely that future studies will continue to provide useful information. Therefore, it seems important to consider the implication of the present work for these types of investigations.

The first point to be made is that there are, of course, a number of residues in the heme pocket, notably the imidazole group of the distal histidine, which can associate with the bound exogenous ligand.[16] In addition, the demonstrated coupling with internal modes of bound pyridines in this study, as well as in our previous work,[18] implies that, in the case of heme proteins, internal modes of the proximal imidazole may also couple with the exogenous ligand modes. Inasmuch as there is an apparently critical dependence of energy matching of the interacting modes, this phenomenon is presumably decreased in CO derivatives relative to O$_2$ and NO, which have frequencies closer in energy to internal modes of potentially interacting residues.

In summary, the results presented here show that bands associated with the exogenous ligand (especially O$_2$ and NO) may be perturbed by vibrational coupling as well as by alterations in structure and bonding. Thus, although certain criteria for effective coupling must be met in order for this to be important, it would seem to be essential to give careful consideration to such possibilities if frequency and/or intensity data are to be interpreted in terms of structural and bonding changes.

Cycloreversion Induced by Charge-Transfer Excitation of Electron Donor-Acceptor Complexes. Wavelength-Dependent Photochemistry of Dianthracene

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Abstract: The electron donor-acceptor or EDA complexes of dianthracene (An$_2$ is the σ-dimer of anthracene) and its derivatives with tetracyanoethylene show two unusually well-resolved charge-transfer (CT) bands. Specific irradiation of each of these absorption bands with monochromatic light at five selected wavelengths ranging from 405 to 577 nm leads to the clean cycloreversion of An$_2$ to anthracene. The striking wavelength-dependent quantum efficiency for cycloreversion is analyzed in terms of two different CT ion pairs [An$_2^+$,TCNE$^-$] derived from the photoexcitation of the first and second absorption bands, which correspond to electron promotion from the HOMO and SHOMO (second highest occupied molecular orbital) of the dianthracene donor, respectively. Orbital correlations between dianthracene and anthracene π-dimer reveal that electron promotion from the SHOMO of dianthracene leads to an excited radical ion An$_2^+$ which is more dissociative than that derived from the HOMO transition.

Transient charge-transfer (CT) absorption bands are often observed during the course of many organic and organometallic reactions.[1] These electronic transitions are associated with the presence of metastable electron donor-acceptor or EDA complexes, usually as weakly bound intermediates.[2] According to Mulliken theory,[3] the charge-transfer transitions of EDA complexes involve the electron promotion from the occupied molecular orbitals of the donor (D) to the unoccupied molecular orbitals of the acceptor (A). In those electron donor-acceptor complexes which have relatively nonpolar ground states [D,A], the CT excitation populates an ionic state [D$^+$,A$^-$] consisting of the radical cation of the donor and the radical anion of the acceptor, i.e.,

$$D + A \rightleftharpoons [D,A] \xrightarrow{h\nu_{CT}} [D^+,A^-] \qquad (1)$$
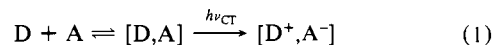
Indeed, we recently observed this CT excited state by time-resolved picosecond spectroscopy of a series of anthracene complexes with

(1) (a) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969. (b) Andrews, L. J.; Keefer, R. Y. "Molecular Complexes in Organic Chemistry"; Holden Day: San Francisco, 1964. (c) Briegleb, G. "Elektronen Donator-Acceptor Komplexe"; Springer Verlag: Berlin, 1961. (d) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(2) (a) Kosower, E. M. *Prog. Phys. Org. Chem.* **1965**, *3*, 81. (b) Colter, A. K.; Dack, M. R. J. *Mol. Complexes* **1973**, *1*, 301. Colter, A. K.; Dack, M. R. J. *Ibid.* **1974**, *2*, 1.

(3) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. Mulliken, R. S.; Person, W. B. "Molecular Complexes: A Lecture and Reprint Volume"; Wiley: New York, 1969.

Table I. Charge-Transfer Transition Energies of the EDA Complexes of Various Arene Donors with Tetracyanoethylene[a]

| arene donor	$h\nu_1{}^d$	$h\nu_2{}^d$	arene donor	$h\nu_1{}^d$	$h\nu_2{}^d$
9,9'-(R,R)-dianthracene			9-R-anthracene[b]		
R = H	52.2	66.5	R = H	39.9	64.3
R = NC	63.6[c]	74.9	R = NC	46.4	
R = CH₃	51.3	66.5	R = CH₃	35.8	
R = OHC	56.1[c]	71.7	R = OHC	43.7	
R = CH₃O	53.0[c]	68.4	R = CH₃O	38.1	
R = CH₃CO₂	57.4[c]	72.0	R = CH₃CO₂	40.4	65.9
triptycene	55.6	71.3	9-R-9,10-dihydroanthracene		
[2.2]paracyclophane	55.0		R = H	66.2	
indane	65.0		R = NC	71.5	
o-xylene	65.3				

[a] In methylene chloride at 25 °C $h\nu_1$ and $h\nu_2$ refer to the first and second CT band (when resolved) measured at λ_{max}.   [b] From ref 16.   [c] Appears as a shoulder.   [d] kcal mol⁻¹.

either tetracyanoethylene (TCNE)[4] or tetranitromethane (TNM)[5] acceptors.

In the TCNE complexes, the efficient chemical evolution of the ion pairs is precluded by rapid back-electron transfer which limits their lifetimes to less than 60 ps,[4] i.e.,

$$[D^+,TCNE^-] \xrightarrow{<60 \text{ ps}} [D,TCNE] \qquad (2)$$
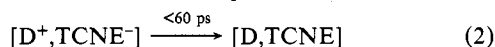
As a result, the quantum yield for the photo-Diels–Alder and related processes is nil ($\Phi \sim 0$). On the other hand, the corresponding TNM complex undergoes efficient photochemistry ($\Phi \sim 1$) owing to the dissociative electron capture by TNM,[5,6]

$$[D^+,TNM^-] \xrightarrow{<10 \text{ ps}} [D^+,C(NO_2)_3^-,NO_2], \text{ etc.} \qquad (3)$$
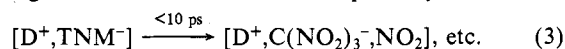
which effectively precludes the back-electron transfer to regenerate the EDA complex as in eq 2.

Charge-transfer excitation has also been reported to be effective in bringing about chemical changes in other systems, where either the radical cation of the donor[7] (D⁺) or the radical anion of the acceptor[8] (A⁻) is unstable. Another characteristic common to these radical–ion intermediates is their involvement in chain mechanisms, e.g., $S_{RN}1$ and related processes,[7,8] An independent CT activation allows for efficient chemistry to occur in such systems even when the propagation sequence is not particularly effective.

Our current interest in the nature of the CT interaction, and its effect on thermal and photochemical reactivity,[4,5,9] has led us

(4) (a) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. (b) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *Ibid.* **1984**, *106*, 8071.

(5) Masnovi, J. M.; Hilinski, E. F.; Kochi, J. K.; Rentzepis, P. M. *Chem. Phys. Lett.* **1984**, *106*, 20.

(6) Chaudhuri, S. A.; Asmus, K. D. *J. Phys. Chem.* **1972**, *76*, 26.

(7) (a) Jones, G., II; Becker, W. G.; Chiang, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 1269. (b) Jones, G., II; Becker, W. G. *Ibid.* **1983**, *105*, 1276. (c) Jones, G., II; Becker, W. G. *Chem. Phys. Lett.* **1982**, *85*, 271. (d) Mukai, T.; Sato, K.; Yamashita, Y. *Ibid.* **1981**, *103*, 670.

(8) For leading references, see: (a) Kornblum, N, "The Chemistry of Functional Groups"; Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives; S. Patai, Ed.; 1982; chapter 10, p 361. (b) Bunnett, J. F.; Singh, P. *J. Org. Chem.* **1981**, *46*, 5022. Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690. (c) Fox, M. A.; Younathan, J.; Fryxell, G. E. *J. Org. Chem.* **1983**, *48*, 3109. (d) Seltzer, S.; Lam, E.; Packer, L. *Ibid.* **1982**, *104*, 6470.

(9) (a) Fukuzumi, S.; Kochi, J. K. *Tetrahedron* **1982**, *38*, 1035. (b) Lau, W.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 5515. (c) Kochi, J. K. *Pure Appl. Chem.* **1980**, *52*, 571.

(10) Dianthracenes are strained, energy-rich cycloadducts which also revert to the anthracene either upon heating[11] or upon exposure to UV irradiation which can be absorbed by its benzenoid chromophores[12] or by triplet[13] and electron-transfer[14] sensitizers.

(11) (a) Chandross, E. A. *J. Phys. Chem.* **1965**, *43*, 4175. Lelande, R.; Calas, R. *Bull. Soc. Chim. Fr.* **1960**, 144. Arecne, F. D. *Ibid.* **1960**, 1356. See also Bouas-Laurent, H. et al. in ref 15 and Stecher, P. G. Ed. "Merck Index", 8th ed.; Merck & Co: Rahway, NJ 1968; p 188. (b) Note that the cycloreversion of dianthracene is a $4\pi_s + 4\pi_s$ process and is thermally forbidden by the Woodward–Hoffman formalism (vide infra).

(12) (a) Yamamoto, S.; Grellman, K. H.; Weller, A. *Chem. Phys. Lett.* **1980**, *70*, 241. Yamamoto, S.; Grellmann, K. H. *Ibid.* **1982**, *85*, 73. (b) Chandross, E. A.; Ferguson, J.; McRae, E. G. *Ibid.* **1965**, *45*, 3546. Chandross, E. A.; Ferguson, J. *Ibid.* **1965**, *45*, 3554. Ferguson, J.; Mau, A. W. H.; Morris, J. M. *Austr. J. Chem.* **1973**, *26*, 91. Ferguson, J.; Mau, A. W. H. *Mol. Phys.* **1974**, *27*, 377. Ferguson, J.; Puza, M. *Chem. Phys. Lett.* **1978**, *53*, 215. Mentor, J.; Forster, Th. *Photochem. Photobiol.* **1972**, *15*, 289.
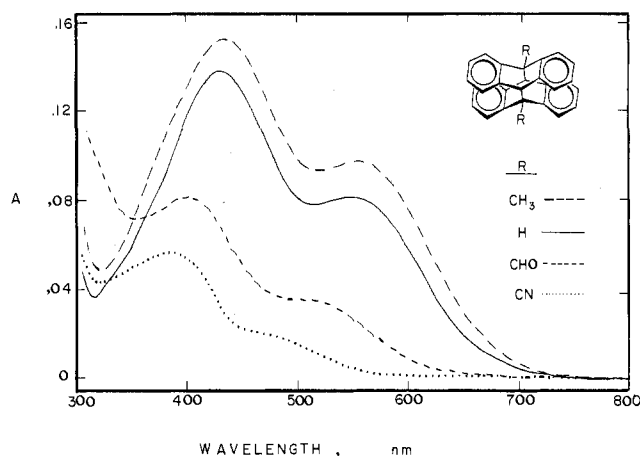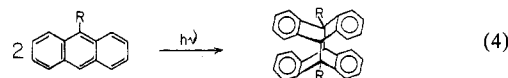

Figure 1. The charge-transfer absorption spectra of the EDA complexes derived from 2.2×10^{-3} M 9,9'-disubstituted dianthracenes and 0.1 M TCNE in methylene chloride at 25 °C.

to focus initially on the fundamental properties of EDA complexes—uncomplicated by chain processes. In this report we examine the cycloreversion of dianthracene induced by the CT excitation of its EDA complex with TCNE. The observation of well-resolved multiple CT bands in this system provides access to the understanding of the wavelength-dependent photochemistry.[10]

Results

The series of head-to-tail dianthracenes (An_2) used in this study were prepared by the photodimerization of 9-substituted anthracenes (An),[15] where R = methoxy, methyl, acetoxy, hydrogen,

$$2 \quad \xrightarrow{h\nu} \quad \qquad (4)$$

formyl, and cyano. All the dianthracenes are optically transparent beyond 300 nm owing to the presence of only benzenoid chromophores.

I. Charge-Transfer Absorption Spectra of Dianthracene–TCNE Complexes. When a colorless solution of TCNE is mixed with that of dianthracene, the brown color of the EDA complex is immediately apparent. This complex persists in methylene chloride solutions for many hours at room temperature if the solutions are carefully shielded from light. The charge-transfer spectrum of the dianthracene–TCNE complex shown in Figure 1 appears with two well-resolved bands at λ_{max} 430 and 550 nm. These CT bands are substantially blue-shifted relative to the absorptions of the

(13) Wang, J.; Ni, J.; Masnovi, J.; Yang, N. C. *Tetrahedron. Lett.* **1982**, *23*, 1231.

(14) Barber, R. A.; de Mayo, P.; Okada, K.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 4995.

(15) Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* **1980**, *52*, 2633.
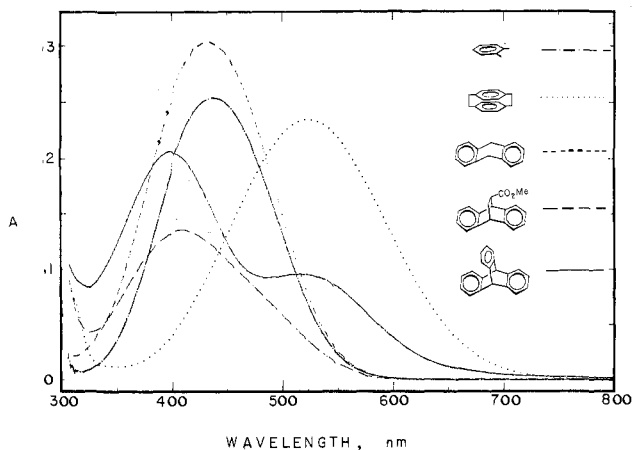
Figure 2. Charge-transfer absorption spectra of various EDA complexes from 4.4×10^{-3} M arene and 0.1 M TCNE in methylene chloride at 25 °C: [2.2]paracyclophane (···), o-xylene (–·–·–), 9,10-dihydroanthracene (- - -), triptycene (—), the Diels–Alder adduct of anthracene and methyl acrylate (– – –).

corresponding anthracene complexes with TCNE (eq 5), as listed in Table I.[16]

$$(5)$$
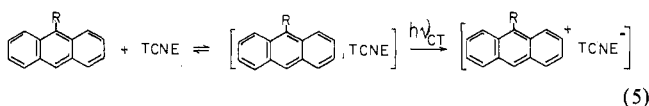
The observation of multiple CT transitions in arene complexes with TCNE is attributed to electron promotion from different high-lying occupied orbitals of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor.[17] Thus the low-energy absorption band at 550 nm corresponds to transitions from the highest occupied molecular orbital (HOMO) of dianthracene;[1a] and we attribute the high-energy band at 430 nm to the transition from the subjacent or second highest occupied molecular orbital (SHOMO).[3] This assignment is supported by the observation of a similar pair of CT absorption bands for the EDA complex of dianthracene with a different acceptor, tetracyanopyrazine,[18] at λ_{max} 380 and 470 nm. The separation of the two bands, $E(CT_1) - E(CT_2)$, corresponds to 14.5 kcal mol^{-1} which is the same as that observed with the dianthracene–TCNE complex (vide supra). Since the separation of the first and second CT bands is independent of the acceptor, we assign the high-energy band CT_2 to the transition from the SHOMO of the donor.[19]

II. Multiple Benzenoid Interactions in the Dianthracene Donor. The (HOMO → LUMO) transition at 550 nm in the dianthracene complex compares with the CT bands in the analogous o-xylene, indan, and dihydroanthracene complexes which are all grouped at 435, 440, and 430 nm, respectively (Figure 2). Such a large shift in λ_{CT} indicates that the HOMO of dianthracene is substantially destabilized relative to that found in an arene donor with a noninteracting benzenoid chromophore, as exemplified by o-xylene, indan, and dihydroanthracene. It is significant that the energy of the first CT transition approaches that observed in Figure 2 for the EDA complex of TCNE with [2.2]paracyclophane in which a pair of benzenoid π-systems is juxtaposed to interact strongly.[20,21] Although the first and second CT transitions appear
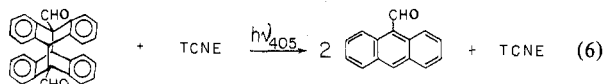
together as a single band in the paracyclophane complex, they are well-resolved in the TCNE complex with triptycene (shown in Figure 2), which bears the closest resemblance to the CT spectra in Figure 1.[24,25]

The bathochromic shift of the CT absorptions (compare the dianthracene complex with the model compounds in Figures 2 and 3 and Table I) suggests that in dianthracene the benzene chromophores interact substantially and the HOMO is delocalized over all four benzene moieties. Such through-space orbital interactions are also shown by the intramolecular CT transitions of triptycene and its derivatives.[24] Furthermore, theoretical calculations suggest that the elongation of the bridging (9,10′ and 9′,10) σ-bonds in dianthracene arises from the substantial through-bond interaction of the benzene π-networks.[26] Another manifestation of the through-space interactions of π-orbitals which depend on distance is shown by the comparison of the CT band of the dihydroanthracene–TCNE complex with that of the Diels–Alder adduct of anthracene and methyl acrylate. In the latter, the presence of the ethano bridge causes a decrease in the dihedral angle between the benzenoid moieties; and a shoulder at lower energy indicative of a new band is discernible in its CT absorption band (see Figure 2).[27] The strongest orbital interaction among three π-systems is found for the tritycene complex in which the CT absorption spectrum shows a well-resolved band at low energy (520 nm)—but not quite at that of the dianthracene complex (550 nm).

Substituent effects on dianthracene also point to a mechanism for electron delocalization involving through-bond interaction via the σ-framework. Thus the substitution of a pair of cyano groups at the bridge-head of dianthracene causes the CT absorption band to shift to higher energy by 11.4 kcal mol^{-1}. Indeed this shift is roughly twice (for two An units) that observed in the anthracene system, i.e., $E_{CT}(H-An/TCNE) - E_{CT}(NC-An/TCNE) = 5.5$ kcal mol^{-1} (see Table I).[28] Such a similarity in the substituent effect induced by a cyano group is consistent with the HOMO of dianthracene involving equal contributions from all four π-systems.

III. Charge-Transfer Photochemistry of Dianthracene–TCNE Complexes. Photolysis of the EDA complex of dianthraldehyde and TCNE was carried out with monochromatic light of wavelength 405 ± 5 nm which corresponds to the maximum of the high-energy CT band. Analysis followed by isolation of the photoproducts anthraldehyde and TCNE indicated the stoichiometry of the photolysis to be cleanly[29]

$$(6)$$

Such a CT-induced cycloreversion of the dianthracene complex

(16) Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. *Can. J. Chem.* **1984**, *62*, 2552.
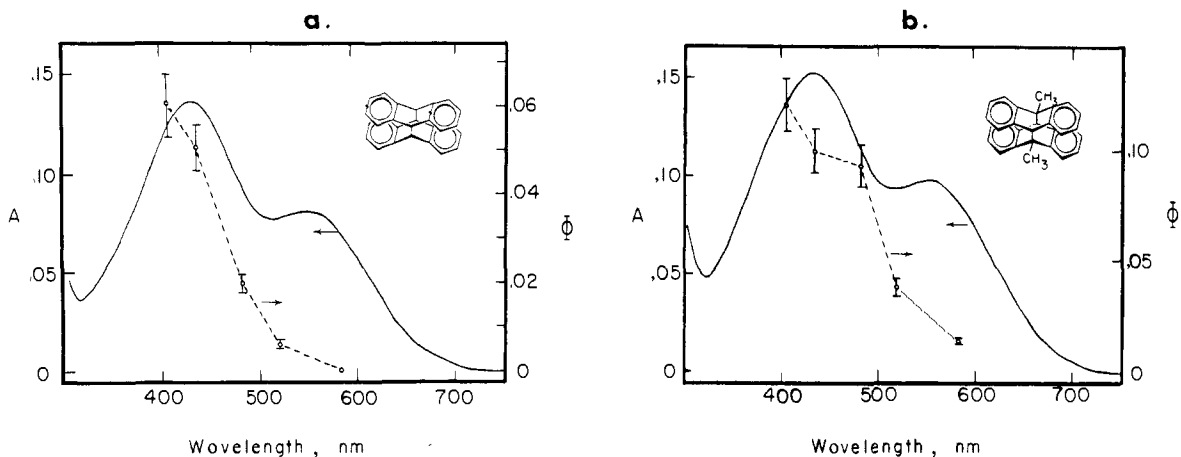
(17) (a) Eckhard, C. J.; Pennelley, R. P. *J. Am. Chem. Soc.* **1976**, *98*, 2034. (b) Pignataro, S.; Aloisi, G. *Z. Naturforsch. A: Phys., Phys. Chem., Kosmophys.* **1972**, *A27*, 1165. (c) See ref 1a. (d) See ref 16.

(18) See: Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116.

(19) See discussion in ref 1a and 17b for the experimental and theoretical basis for this type of assignment.

(20) Kovac, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314. Heilbronner, E.; Yang, Z. *Top. Curr. Chem.* **1983**, *115*, 1.

(21) Note that the CT band of the TCNE complex of the higher homologue [3.3]paracyclophane occurs at 600 nm.[22] In this donor the benzenoid chromophores are further apart, but they are also less distorted.[23]

(22) (a) Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5971. (b) Heilbronner, E.; Yang, Z. *Top. Curr. Chem.* **1983**, *115*, 1. (c) The electronic transitions and PE spectra of cyclophanes (and dianthracenes) are bathochromically shifted relative to that of simple benzenoid models, indicative of interchromophoric interactions. See also ref 11, 12, and 15. The determination of the PES of dianthracene is in progress (with Professor L. Klasinc).

(23) Bernstein, J.; Trueblood, K. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 2078.

(24) (a) Inagaki, S.; Yamamura, K.; Nakasuji, K.; Nakazawa, T.; Murata, I. *J. Am. Chem. Soc.* **1981**, *103*, 2093. Yamamura, K.; Nakasuji, K.; Yamochi, H.; Murata, I.; Inagaki, S. *Chem. Lett.* **1983**, 627. (b) The cation radical of triptycene is delocalized; as indicated by its room-temperature ESR spectrum (septet, $a_H = 2.3$ G): Dessau, R. M. *J. Chem. Phys.* **1971**, *54*, 5430.

(25) It would be desirable to locate the TCNE acceptor in the EDA complexes with triptycene and dianthracene. However, our attempts to grow single crystals for X-ray analysis have not as yet been successful.

(26) Gleiter, R. *Tetrahedron Lett.* **1969**, *51*, 4453. Dougherty, D. A.; Hounshell, W. D.; Schlegel, H. B.; Bell, R. A.; Mislow, K. *Ibid.* **1976**, *39*, 3479. Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* **1978**, *34*, 1441.

(27) The shape of the CT envelope for the TCNE complex of 7-carbomethoxy[2,3],[5,6]dibenzo[2.2.2]bicyclooctane suggests that it actually consists of two partially resolved Gaussians.

(28) Note the 9-cyano substituent shifts the CT band of the 9,10-dihydroanthracene–TCNE complex by 5.3 kcal mol^{-1}.

(29) For the determination of stoichiometry, the photolyses were carried out to low conversions to obviate complications from the CT absorptions of the anthracene–TCNE complexes.[16]

Figure 3. (a) Quantum efficiency for the CT-induced cycloreversion of dianthracene as a function of the excitation wavelength, overlaid on the CT spectrum of the EDA complex with TCNE. (b) Same as (a), except for 9,9'-dimethyldianthracene.

was also observed under similar conditions with the 9-cyano, 9-methoxy, and 9-acetoxy derivatives. The photolysates derived from 9-formylanthracene and 9-acetoxyanthracene upon standing in the dark slowly afforded the corresponding Diels–Alder adducts, i.e.,


(7)

Irradiation of a TCNE solution of the parent dianthracene in methylene chloride at 405 nm caused the bleaching of the brown color of the EDA complex. Analysis and workup of the photolysate indicated that anthracene (trapped as its Diels–Alder adduct) was formed according to the stoichiometry
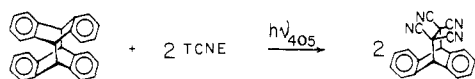

Irradiation of 9,9'-dimethyldianthracene under analogous conditions afforded the same results.

Independent experiments established that the thermal reaction of anthracene and 9-methylanthracene to afford the Diels–Alder adduct with TCNE occurs within the time span required for mixing. By comparison, 9-formyl, 9-methoxy, and 9-acetoxy-anthracenes react with TCNE at substantially slower rates, and they can be, therefore, detected by UV and ^{1}H NMR analysis during the course of photolysis. Finally, 9-cyanoanthracene does not react with TCNE at rates which affect its analysis (cf. eq 6). Such a trend in the reactivities of the various 9-substituted anthracenes toward TCNE suggests that the Diels–Alder adduct in eq 8 results from the separate thermal reaction of anthracene subsequent to the CT-induced cycloreversion described by eq 6, i.e.,

(8)
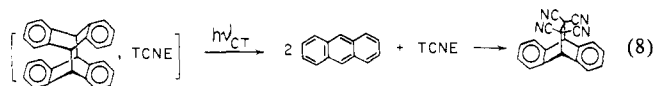
It is important to note that the EDA complexes of either triptycene or [2.2]paracyclophane with TCNE undergoes no net photochemical change upon the irradiation of their CT bands shown in Figure 2.[30] In this regard, their CT behavior is akin to that previously observed in the anthracene–TCNE complexes.[4]

At this juncture we must emphasize that the irradiation of a mixture of dianthracene and TCNE at wavelengths >400 nm specifically excites only the EDA complex. Thus there is no ambiguity about either the adventitious local excitation of the complexed (or uncomplexed) chromophores or the generation of
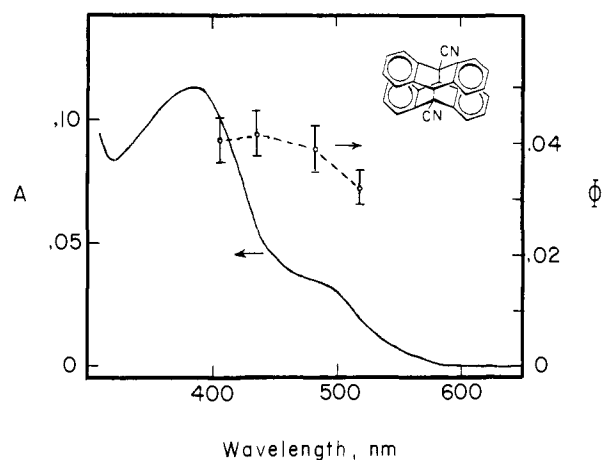
Figure 4. Quantum efficiency for the CT-induced cycloreversion of di-9-cyanoanthracene as a function of the excitation wavelength, overlaid on the CT spectrum of the EDA complex with TCNE.

intermediates which do not arise from the CT excitation of the EDA complex. The photoinduced cycloreversion must, therefore, be a direct consequence of populating the CT excited state.

IV. Wavelength-Dependent Quantum Yields for the Cyclo-reversion of Dianthracene Complexes. The quantum efficiency for the photoinduced cycloreversion of dianthracene was measured at five separate wavelengths encompassing both CT bands of the EDA complex with TCNE (Table I). The variations in the quantum yield over this span are overlaid on the CT spectrum in Figure 3a to emphasize the relationship of the excitation wavelength to the first and second absorption bands. The results clearly show that the excitation into the higher-energy absorption band (CT$_2$) is at least two orders of magnitude more efficient than excitation into the low-energy (HOMO → LUMO) transition.

Substituents on the 9- and 9'-positions of dianthracene provide insight into the wavelength dependence of the quantum yield for cycloreversion. Thus, the substitution of a pair of methyl groups, as in the 9,9'-dimethyldianthracene–TCNE complex, leads to a relatively sharp increase in ϕ_{577} (Figure 3b). However, there is still a factor of 10-fold which favors CT$_2$ insofar as the quantum efficiency for cycloreversion is concerned. Such a difference between CT$_2$ and CT$_1$ is markedly attenuated by two cyano substituents, as in the 9,9'-dicyanodianthracene–TCNE complex. Figure 4 shows the irradiation of the low-energy CT$_1$ band to be almost as efficient as that of CT$_2$. The wavelength-dependent quantum yield for cycloreversion of the formyl derivative is included in Table II. The effects of the substituents on the wavelength-dependent quantum yields for cycloreversion of di-anthracene are compared graphically in Figure 5.

V. CT-Induced Cycloreversion of Olefin Cyclodimers. Following from the efficacy of the charge-transfer and the odd-electron

(30) Note that the photoinduced cycloreversion of paracyclophane to pa-raxylylene can occur at a short wavelength (<260 nm). See: Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 509.

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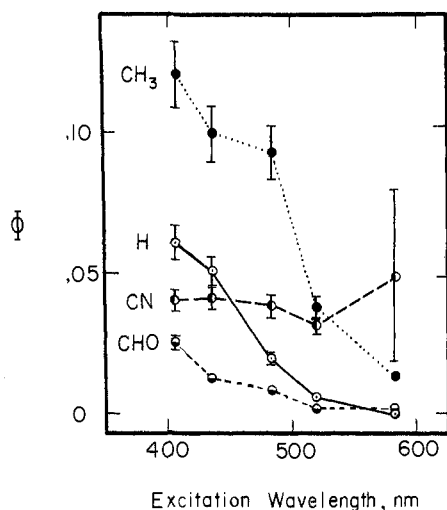**Table II.** Wavelength-Dependent Quantum Efficiencies for the Cycloreversion of Dianthracene with 9,9′-Substituents[a]

dianthracene 9,9′-R,R	excitation wavelength (nm)				
	405	436	480	520	577
unsubstituted	0.061	0.051	0.020	0.0066	0.00052
methyl	0.12	0.10	0.094[b,c]	0.038	0.014
formyl	0.025	0.012	0.0085[c]	0.0020	0.0021
cyano	0.041	0.042	0.039	0.032	(0.05)[d]

[a] In methylene chloride at 22 °C using Reinecke actinometer. [b] Ferrioxalate actinometer. [c] Single determination. [d] Error is ±0.025 due to small absorptivity.

Table III. CT Transition Energies of the EDA Complexes of Various Carbazole Donors with Tetracyanoethylene[a]

donor	$h\nu_1$	$h\nu_2$	$h\nu_3$
N-phenylcarbazole	40.7	49.0	75.7
N-ethylcarbazole	40.1	47.7	73.1
N-vinylcarbazole	41.7	50.0	77.9[b]
vinylcarbazole-[2 + 2]-cyclodimer	40.3	49.1	73.9

[a] Measured in methylene chloride at 25 °C. Each CT band determined at the wavelength of maximum absorbance in kcal mol^{-1}. [b] Appears as a shoulder (see Figure 6).

Figure 5. Effect of 9,9′-(R,R)-substituents on the wavelength-dependent quantum efficiencies for the cycloreversion of dianthracenes: R = CH$_3$ (●), H (⊙), NC (◑), and OHC (◒).

induced cycloreversion of dianthracene, we also examined the corresponding behavior of the [2 + 2]-cycloadducts of olefins. Thus the cyclobutane dimers of olefins are also known to undergo electron-transfer catalyzed cycloreversion, albeit at slower rates.[31] The [2 + 2]-cyclodimer of N-vinylcarbazole (Vc$_2$) rapidly forms an EDA complex with TCNE, the CT spectrum of which displays two major overlapping bands, as shown in Figure 6.[32] [Note that the absorptions of the free carbazole donor cut off at ~360 nm.] The similarity of this CT spectrum with those of N-ethylcarbazole and N-vinylcarbazole (Vc) itself is also included in Figure 6.

The charge-transfer transition energies for the EDA complexes of these carbazoles and tetracyanoethylene are listed in Table III.

The irradiation of the cyclodimer Vc$_2$ was performed in methylene chloride solution with a focused beam from a xenon lamp passed through a glass filter with a sharp cutoff at 440 nm. The latter ensured the specific excitation of only the overlapping CT bands of the EDA complex. No cycloreversion was observed upon prolonged irradiation. The same results were obtained when

(31) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. Beresford, P.; Lambert, M. C.; Ledwith, A. *J. Chem. Soc. C* **1970**, 2508. (b) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265. (c) Mizuno, K.; Murakami, K.; Kamiyama, N.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 462.

(32) The minor CT band at λ_{max} ~390 nm is too close to the absorption tail of the free donor to ensure specific irradiation.
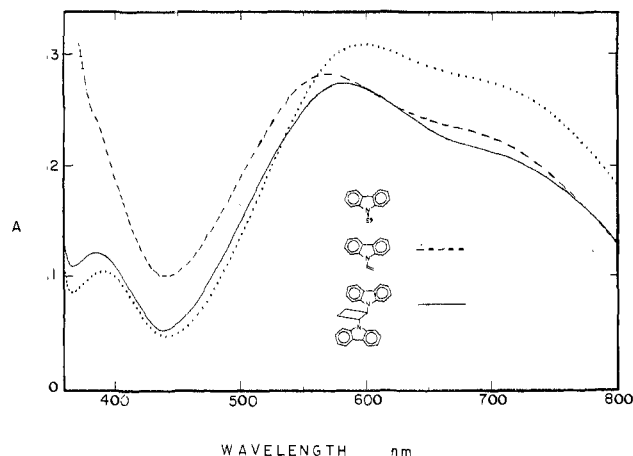
Figure 6. Charge-transfer absorption spectra of the EDA complexes derived from 0.1 M N-ethylcarbazole (···), N-vinylcarbazole (- - -), and the [2 + 2]-cyclodimer of N-vinylcarbazole (—) with 0.1 M TCNE in methylene chloride at 25 °C.

the irradiation was carried out in benzene solution.

Discussion

The cycloreversion of dianthracene An$_2$ attendant upon the CT excitation of the EDA complex with tetracyanoethylene is reminiscent of the photoisomerization of strained hydrocarbons under similar circumstances, as studied particularly by Jones and co-workers.[33] Although both CT systems are qualitatively related by showing wavelength-dependent quantum yields, the intensity of the effects observed differs quantitatively by several orders of magnitude. For example, the quantum yield for the valence isomerization of quadricyclene under nonchain conditions increases several-fold upon increasing the energy of the CT excitation by ~1 eV,[7c] whereas the quantum efficiency for the cycloreversion of dianthracene increases by more than 100-fold under equivalent conditions (see results in Table II). It is important to consider these systems under nonchain conditions since the efficiency of the photochemical process can actually decrease at higher CT-excitation energies, as observed with hexamethyl(Dewar benzene).[7b,34] Doubtlessly those factors previously delineated by Jones and others such as thermally activated processes,[35] ion-pair separations as a function of vibrational energy,[36] etc.,[37] must be taken into account for such wavelength-dependent phenomena.[38] However, the contrasting magnitude of the effect observed in this study argues for some added impetus to drive dianthracene cycloreversion.[39] Accordingly we exploit the well-resolved absorption

(33) See ref 7 for the previous studies of Jones and co-workers pertinent to this study.

(34) We exclude from consideration those results[33] in which a radical–ion chain pertains to the CT-induced photoisomerization. Thus in a chain process, any differences in the initiation (e.g., CT-excitation) step are greatly exaggerated in proportion to the magnitude of the kinetic chain length. An efficient radical–ion chain process is unlikely for dianthracene cycloreversion since the electron-transfer step is endergonic. Thus the irreversible CV of An$_2$ has E_p^a at 1.67 V vs. SCE at 500 mV s^{-1}, compared to the reversible $E° = $ 1.34 V for An.

(35) For example, of the types previously described by Zimmerman and co-workers, see: Zimmerman, H. E. *Pure Appl. Chem.* **1964**, *9*, 493; *Acc. Chem. Res.* **1982**, *15*, 312.

(36) Jones, G., II; Malba, V. *Chem. Phys. Lett.*, in press. We thank Professor Jones for a copy of this preprint prior to publication. (b) See also ref 7a–c.

(37) Environmental effects such as solvent polarity and viscosity, as factors previously identified to affect the efficiency of photochemical electron transfer, are not pertinent to this study. Furthermore, the substituent-dependent behavior of dianthracenes indicate that differences in charge-type and geminate radical pairs are also minor. See: Mataga, N.; Ottolenghi "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979. Masuharu, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312. Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255. Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129. For a review, see: Gordon, M.; Ware, W. R., Eds.; "The Exciplex"; Academic Press: New York, 1975.

(38) Excitation of EDA complexes with slightly differing geometries must also be considered. See ref 4b.

Scheme I[a]

(Filled molecular orbitals)

Anthracene π-Dimer   Dianthracene
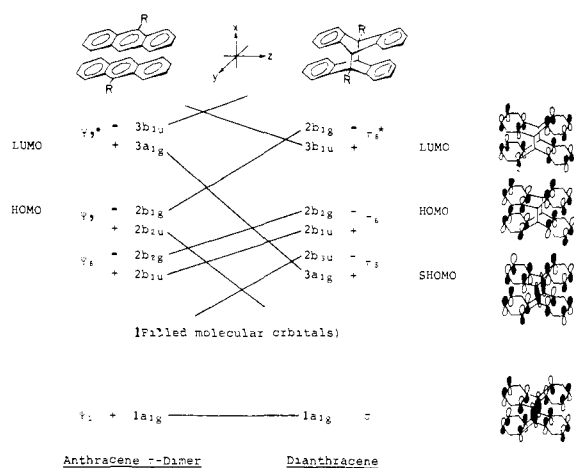
[a] Correlations of the frontier orbitals for the $4\pi_s + 4\pi_s$ cyclo-reversion of dianthracene to anthracene π-dimer in D_{2h} symmetry. The qualitative ordering of the π-orbitals of the anthracene π-dimer follows from those of anthracene in ref 40. The designations + and − refer to the symmetric and antisymmetric combination, respectively, of the anthracene orbitals with respect to σ_{yz}. These orbitals transform into the σ- and π-orbitals of dianthracene indicated. An odd or an even subscript associated with the dianthracene π-orbitals refers to the symmetric or antisymmetric combination, respectively, of the benzenoid orbitals with respect to σ_{xy}. The antibonding orbitals are designated with an asterisk. Mixing of the σ- and π-orbitals of the same symmetry (viz. a_{1g}) will constitute the SHOMO ($3a_{1g}$) of dianthracene[26] illustrated on the right side.
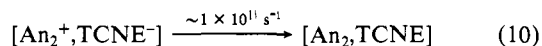
bands CT_1 and CT_2 in Figure 1 to develop additional insight into charge-transfer photochemistry.

I. Orbital Correlation for the CT-Induced Cycloreversion of the Dianthracene Complexes. The origin of the different reactivities arising from the two CT absorption bands of the dianthracene–TCNE complex is revealed by a consideration of the symmetry properties of the molecular orbitals involved in the excitation. The interaction between the π-systems of dianthracene (An_2) will result in the HOMO being of b_{2g} symmetry in the D_{2h} point group, as illustrated in the orbital correlation diagram in Scheme I. Indeed chemically induced dynamic polarization observed in the quenching of chloranil by dianthracene is consistent with their being significant charge density only at the β-positions of the radical cation An_2^+.[14] On the other hand, the second highest occupied molecular orbital (SHOMO) of dianthracene has been calculated to have a_g symmetry;[26] and these orbitals are of mixed σ- and π-character since they derive from the mixing of the $3a_g$ orbital of the π-system with the relatively low-lying σ-orbitals ($1a_g$) of the (9,10′ and 9′,10) bridge.

II. Fragmentation of Dianthracene Cation Radicals. With these orbital correlations in mind, we ascribe the low energy transition (CT_1) to the promotion of an electron from the HOMO of $2b_{2g}$ character (Scheme I) in dianthracene to the LUMO of TCNE in the EDA complex, i.e.,

$$An_2 + TCNE \rightleftharpoons [An_2,TCNE] \xrightarrow{h\nu_{CT}} [An_2^+,TCNE^-] \quad (9)$$

The resulting CT ion pair is expected to decay rapidly back to the original EDA, i.e.,

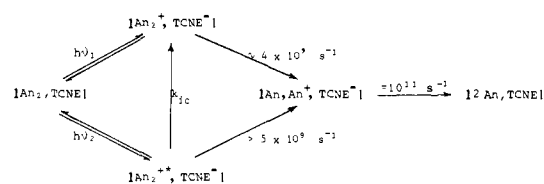$$[An_2^+,TCNE^-] \xrightarrow{\sim 1 \times 10^{11} \, s^{-1}} [An_2,TCNE] \quad (10)$$

Indeed we measured directly the first-order rate constant for the back-electron transfer from the ion pair as in eq 10 to be $\sim 7 \times 10^{10} \, s^{-1}$ by time-resolved picosecond spectroscopy in related systems

Scheme II

(compare eq 2).[41] Accordingly, we predict the cleavage rate of the ground-state An_2^+ to be

$$\left[\frac{\Phi_1}{1 - \Phi_1}\right] 7 \times 10^{10} \, s^{-1} = 4 \times 10^7 \, s^{-1} \quad (11)$$

given the quantum efficiency Φ_1 for cycloreversion from the ion pair derived from CT_1 of $\sim 5 \times 10^{-4}$ (see Table II).

Similarly, we ascribe the high-energy transition CT_2 to the promotion of an electron from the SHOMO of dianthracene to the LUMO of TCNE (vide supra). Since the SHOMO of dianthracene contains a contribution from the bridging (9,10′- and 9′,10-) σ-bonds, the irradiation into the second CT band of the EDA complex will depopulate an orbital which connects the two anthracene moieties. Removal of an electron from such a bonding orbital will result in An_2^+ with weakened bridging bonds and an increased rate of fragmentation, i.e.,

$$An_2^+ \xrightarrow{fast} An^+ + An \quad (12)$$
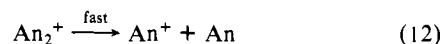
Such an excited radical cation An_2^{+*} is estimated to be ~ 14 kcal mol^{-1} above the ground-state species.[42] The rate of cleavage of An_2^{+*} is predicted to be $>5 \times 10^9 \, s^{-1}$ if the quantum efficiency Φ_2 is taken as 6×10^{-2} (eq 11 and Table II). This value actually represents an upper limit to the lifetime of An^{+*} since the cycloreversion must compete with the internal conversion to the ground state of An_2^+ as well as the back-electron transfer.[43]

III. Wavelength Dependence of Dianthracene Cycloreversion. We conclude from this analysis that the direct dissociation of the dianthracene radical cation from the excited state occurs more rapidly than dissociation from the ground-state An_2^+. The interrelationship among the various competing pathways is illustrated in the general formulation in Scheme II.

According to the formulation in Scheme II, the wavelength dependence of the quantum efficiency for cycloreversion derives from the difference in the rate of fragmentation of the excited dianthracene radical cation relative to that of the ground-state species. Substituents can play at least two roles in this dichotomy. On one hand, an electron-releasing substituent such as the methyl group on dianthracene can lower the energy of the (HOMO → LUMO) CT transition by 0.9 kcal mol^{-1} (Table I). Methyl substitution also increases the efficiency of the cycloreversion from this low-energy transition by a factor of ~ 30 (Table II). The effect may be attributed to destabilizing the steric interactions in the 9,10′- and 10,9′-bonds in An_2^+ and/or the mesomeric stabilization of an one-bond intermediate such as
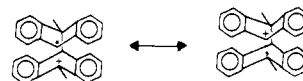
by the 9- and 9′-methyl substituents.[45] On the other hand, substitution of an electron-withdrawing substituent may serve to

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(39) Note that such a driving force has been demonstrated for the EDA complexes of tetranitromethane. See ref 5.

(40) Coulson, C. A.; Streitwieser, A. Jr. "Dictionary of π-Electron Calculations"; W. H. Freeman & Co.: San Francisco, 1965.

(41) Masnovi, J. M.; Hilinski, E. F.; Rentzepis, P. M.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.

(42) Taken to be roughly the difference between CT_2 and CT_1. The overlapping of different CT transitions may also affect this calculation.

(43) Recently two discrete states of the cation radical of hexamethyl (Dewar benzene) separated by ~ 8 kcal mol^{-1} have been identified by CIDNP experiments.[44] The wavelength-dependent photochemistry of the EDA complexes of such donors[7] may also be due in part to state-dependent reactivity of the cation radicals.

(44) Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253.

(45) Increased reactivity may also result from relaxation of the symmetry restrictions upon substitution at the 9 and 9′ positions. (See Scheme I.)

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diminish the difference in the rates of fragmentation of the excited- and ground-state radical cations. For example, the presence of electron-withdrawing groups on dianthracene, particularly at the bridging (9,10'- and 9',10) σ-bonds, will serve to stabilize the σ-system relative to the π-orbitals. This effect will lead to an increase in the energy separation between the σ- and the π-systems and thus decrease the extent of σ-π mixing which is required for the destabilization of An_2^{+*}. Cyano substituents exert a powerful electron-withdrawing influence, and the wavelength dependence of the quantum efficiency for cycloreversion of dianthracene is indeed the lowest with the cyano derivative. The trend in the absolute values of Φ_{405} to vary according to the substituent in the order $CH_3 > H > CN$ (see column 6, Table II) also accords with this notion.[46]

It is interesting to compare the relatively high efficiencies of the CT-induced cycloreversion with the thermal cycloreversion of dianthracene. The latter is considered to be a "forbidden" process according to the Woodward–Hoffman formalism[47] since the SHOMO of dianthracene correlates with the LUMO of the anthracene π-dimer (see Scheme I). Removal of two electrons from the SHOMO would transform the thermal cycloreversion into an "allowed" concerted process.[48] Perhaps the removal of a single electron is sufficient for orbital conservation since there is evidence that the odd-electron (or hole) induced Diels–Alder reaction may be pericyclic.[49,50] A similar argument would explain the wavelength dependence of the cycloreversion of dianthracene upon direct irradiation.[11] The lowest energy excitation of dianthracene is optically forbidden ($3b_{2u} \leftarrow 2b_{2g}$), and irradiation into the weak, long-wavelength absorption at 260–290 nm results in no dissociation from the excited singlet state at 123 K. However, irradiation into the strong absorptions at shorter wavelength (<260 nm) results in efficient cycloreversion even at lower temperatures. Assigning the higher-energy absorption to the allowed (LUMO $\leftarrow$ SHOMO) (or $3b_{2u} \leftarrow 3a_{1g}$) transition would rationalize this behavior. Since the removal of an electron from the SHOMO depopulates an orbital with bonding character in the bridge (vide supra), cycloreversion from this state (though not strictly "allowed" by the orbital correlation in Scheme I) should be more facile than that from the lowest excited state.

The photostability of the TCNE complex of divinylcarbazole Vc_2 stands in strong contrast to the lability of the corresponding An_2 complex. Unlike the dianthracene donor, the similarities in the CT transition energies listed in Table III indicate that the HOMO's in all the carbazole donors are localized predominantly on the aromatic rings. Thus the contrasting behavior in the CT-induced cycloreversion is attributable to the nature of the donor radical cations Vc_2^+ and An_2^+. In particular, the stabilization of Vc_2^+ is achieved by the delocalization of the charge on the carbazole nucleus and not on the cyclobutane moiety. This coupled with a decreased ring strain as a driving force of cycloreversion is apparently sufficient to preclude any effective competition with back-electron transfer as a mechanism for the relaxation of the ion pair $[Vc_2^+,TCNE^-]$.

Summary and Conclusion

The cycloreversion of dianthracene to anthracene is effectively carried out by irradiation with visible light. The technique involves the photoexcitation of the EDA complex with TCNE which shows a pair of well-resolved CT absorption bands at λ_{max} 430 and 550

nm. The wavelength dependence of the quantum efficiency for cycloreversion results from the different rates of reaction from the two excited states of the EDA complex. Thus the specific irradiation of the low-energy band (CT_1) with monochromatic light promotes an electron from the HOMO of dianthracene to the LUMO of tetracyanoethylene to form an ion pair $[An_2^+,-TCNE^-]$ in which the donor radical cation is effectively in the ground state. Cycloreversion of dianthracene from this state is slow compared to charge annihilation by back-electron transfer to restore the EDA complex, i.e., $[An_2^+,TCNE^-] \rightarrow [An_2,TCNE].$[51] Irradiation of the high-energy band (CT_2) promotes an electron from the SHOMO of dianthracene to form an ion pair $[An_2^{+*},TCNE^-]$ in which the donor radical cation is in an excited state, ~14 kcal mol^{-1} higher than the ground state. The faster rate of cycloreversion from the excited radical cation An_2^{+*} derives from the bonding characteristics of the SHOMO. This state-dependent reactivity is revealed by the competitive deactivation to the ground state by rapid back-electron transfer from the ion pair.

We expect time-resolved picosecond spectroscopy similar to our earlier study[4,5] will provide direct evidence for the two kinds of dianthracene radical cations derived from CT_1 and CT_2. Moreover, a CIDNP study of the type recently utilized by Roth and co-workers[44] may provide an alternative confirmation of the existence of two different radical cations resulting from the wavelength-dependent CT photochemistry of EDA complexes.

Experimental Section

Materials. Anthracene, 9-cyanoanthracene, 9-methoxyanthracene, 9-methylanthracene, and 9-anthraldehyde (Aldrich) were recrystallized three times from ethanol prior to use. 9-Anthryl acetate was synthesized by the procedure described in the literature.[53] The corresponding dianthracenes were prepared from saturated solutions of the anthracenes in methylene chloride under argon by irradiation with filtered light (Pyrex) from a 1 kW mercury lamp.[12] The dianthracenes were collected by filtration and were recrystallized repeatedly from either benzene or methylene chloride to ensure the removal and/or conversion of the head-to-head isomer.[54] N-Phenyl-, N-ethyl-, and N-vinylcarbazole (Pfaltz and Bauer) were recrystallized from ethanol. The [2 + 2]-dimer of N-vinylcarbazole was synthesized by the triphenylaminium-catalyzed cyclodimerization of N-vinylcarbazole.[31] Methylene chloride (Aldrich, gold label) was used without further purification.

Photolysis of Dianthracene–TCNE Complexes. Fresh solutions of the dianthracenes were prepared immediately prior to use owing to the thermal lability of some of these photodimers.[54] The photolysis was carried out under argon in 10-mm curvettes containing 1 mL of 2.2 × 10^{-3} M arene and 0.1 M tetracyanoethylene in methylene chloride. Photochemical irradiations were effected with a focused beam from a 500 W xenon lamp passed through an aqueous heat filter and a Edmund interference filter with a full bandwidth at half-maximum at the wavelengths 405, 436, 480, 520, and 577 nm. Changing the concentration of either the arene or TCNE did not affect the appearance of the CT spectra shown in Figure 1 (particularly the relative absorbances of the two bands). The irradiation of the [2 + 2]-cyclodimer N-vinylcarbazole was carried out by a similar procedure, except the filter consisted of a glass filter (Corning no. 3-72) which cutoff sharply below 440 nm.

The photolysis was analyzed by initially concentrating it by the removal of the solvent under argon, followed by the addition of CDCl$_3$. Careful integration of the ^{1}H NMR spectrum of the resulting solution indicated that the disappearance of the dianthracene was directly proportional to the decrease in the intensity of the CT absorbances when the photolysis was carried out to less than 20% conversion. The course of the photolysis of the 9-cyano and 9-formyl derivatives was more conveniently measured by the increase in the absorptions of 9-cyano- and 9-formylanthracene, the longest absorption bands of which appear at 402

(46) Note that this formulation of the wavelength dependence of the quantum yields differs from the usual one involving excitation to higher vibronic states. [For a review, see: Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.] Such an explanation does not readily accord with the substituent effect illustrated in Figure 5.

(47) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395. "The Conservation of Orbital Symmetry"; Academic Press: New York, **1970**.

(48) The catalysis of cycloaddition reactions by Lewis acids may be such an example. Compare Yates and Eaton (Yates, P.; Eaton, P. E. *J. Am. Chem. Soc.* **1960**, *82*, 4436).

(49) (a) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. (b) Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145.

(50) See, however: Groenewold, G. S.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6559, 6575.

(51) Although we took the rate of back electron transfer as 1×10^{11} s^{-1} from ref 41, it may be slower than that measured in other arene–TCNE complexes. Thus the delocalization of the positive "hole" over the π system of An_2^+ would lead to increased charge separation and slower recombination.[52] For example, the observation of CIDNP from An_2^+ allowed its lifetime to be estimated to lie in the range 10^{-6} to 10^{-9} s.[14]

(52) Nishitani, S.; Kurata, K.; Sakata, K.; Misumi, S.; Karen, A.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1983**, *105*, 7771.

(53) Meek, J. S.; Monroe, P. A.; Bouboulis, C. J. *J. Org. Chem.* **1963**, *28*, 2572.

(54) See ref 11.

nm (ϵ 5820) and 401 nm (ϵ 6530), respectively. This technique proved to be sufficiently sensitive to allow very small conversions (typically 0.01%) of dianthracene to be monitored. The absorptions due to the local excitation of the anthracene partially overlapped with those of the EDA complex so that the products competitively absorbed the incident light at 405 nm and (to a very small extent) at 436 nm. For this reason the conversions were kept below 0.1% for the determinations at 405 nm; and under these conditions the products absorbed ≤10% of the incident light. However, agreement within experimental error was obtained with 436-nm excitation (or longer) when the analysis was performed either spectrophotometrically to 0.1% conversion (by monitoring product absorptions) and to <1% conversion (by monitoring the disappearance of the EDA complex) or by ^{1}H NMR analysis to <10% conversion.

The monomers, 9-cyano-, 9-formyl-, 9-methoxy-, and 9-acetoxyanthracene, reacted sufficiently slowly with TCNE for them to be detected by UV or ^{1}H NMR spectrophotometry. Anthracene and 9-methylanthracene reacted with TCNE too rapidly under experimental conditions to detect as such, and only the Diels–Alder adduct was found. In every case the product (either the anthracene or its TCNE adduct) was formed quantitatively (200% yield), based on the conversion of the dianthracene. On standing for longer times, the anthracene monomers derived from the formyl and the acetoxy derivatives slowly reacted with TCNE to form the respective Diels–Alder adducts. The products and stoichiometries of the photochemical reactions were independent of the wavelength of the CT excitation.

The quantum yields for the disappearance of the dianthracenes were determined by Reinecke actinometry.[55] The values of Φ in Table II represent the average of three independent determinations and are reproducible to within ±10%. The quantum efficiencies at 436 and 480 nm were checked with ferrioxalate actinometry.[55] The light intensity from the xenon source was shown to be essentially independent (3.2 ± 0.3 × 10^{-8} einstein) of the monitoring wavelengths used. Owing to the limited solubilities of the dianthracenes, the absorptions arising from the EDA complexes were low. Thus a correction for incomplete light absorption was applied to the quantum yields based upon the transmittance of the solution at each excitation wavelength. This correction varied essentially linearly with the absorbance, but it was appreciable especially at the long wavelengths for the dicyanoanthracene and dianthraldehyde donors. Although greater error limits must be associated with the quantum yields in these cases, standard deviations of ≃10% were still obtained. The high reactivity of the dicyanoanthracene complex at 577 nm was attested to by the observation of substantial reaction after brief (~30 min) irradiation of the solution under conditions in which no reaction was detected for the unsubstituted dianthracene complex under identical conditions despite its much greater absorbance at this wavelength.

The electronic spectra were measured with a Hewlett Packard 8450A diode-array spectrometer capable of 0.1 s time resolution. The NMR spectra were recorded on a Nicolet NT360 (360 MHz) spectrometer.

(55) Rabek, J. F. "Experimental Methods in Photochemistry and Photophysics"; Wiley: New York, 1982; p 944.

Toward a Theory of Chemical Reactivity Based on the Charge Density

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Abstract: This paper presents a theory of chemical reactivity based upon the properties of the electronic charge distribution and the changes in this distribution as induced by vibrational motions. The initial approach of the reactants is determined by aligning local charge concentrations with regions of charge depletion as determined by the Laplacian of their charge distributions, the quantity $\nabla^2\rho$. The energetically most favored nuclear motion of this combined system is the one which induces the largest and most facile relaxation in the charge distribution. This relaxation is approximated by the transition density obtained by mixing in the lowest energy excited state of the combined system. It is found here that the relative approach of the reactants as determined by the properties of their Laplacian distributions leads to the formation of a complex in which the most facile relaxation of the charge density is one that leads to further motion along the reaction coordinate defined by this approach. For example, CO and BH$_3$ may act as donors or acceptors in terms of their Laplacian distributions and in their addition this distribution requires the approach of C to B along the symmetry axis of BH$_3$. The transition densities corresponding to both donor–acceptor possibilities have nearly equal excitation energies and are of the same symmetry: one is π-like and transfers charge to CO and the other is σ-like and transfers charge to BH$_3$. In many cases the regions of space where HOMO and LUMO are most concentrated coincide respectively with the regions of charge concentration and depletion in the Laplacian distribution. Thus the requirements of the frontier orbital model correspond physically to aligning regions of charge concentration with regions of charge depletion. The examples given in this paper demonstrate that the Laplacian distribution provides a bridge between the density and orbital approaches to the understanding of chemical reactivity.

In a chemical reaction there is a continuous change in the distribution of electronic charge from that of the reactants to that of the products. Thus a primary prerequisite for predicting the course of chemical change is a knowledge of how the charge distribution changes for a given displacement of the nuclei. Electronic excitation can also effect a change in the charge distribution, but the ensuing chemistry of the excited or charged state is again governed by the accommodation of this essentially instantaneous change in the charge distribution to the field of the nuclei.

It has been previously shown how second-order perturbation theory can be used to predict the essential features of the change or relaxation in the electronic charge density ρ for a given displacement of the nuclei.[1a,2] This is done by approximating the relaxation in ρ by the transition density obtained by a mixing-in of the lowest energy excited state function of appropriate symmetry, the symmetry being determined by the symmetry of the perturbing nuclear displacement. Assuming that the largest re-

(1) (a) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137. (b) This application is a direct test of the assumption that the vibrational mode that causes a mixing-in of the lowest energy excited state has the lowest force constant within the set of bond stretching constants of a given molecule.
(2) Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164.