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Adiabatic and Charge-Transfer Pathways in the Photocleavage of Dimers and Cycloadducts of Some Aromatic Molecules

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Abstract: The photocycloreversion of the 9-cyanoanthracene (CA) 4 + 4 dimer and of the cycloadducts between CA and anthracene, CA and 2-methylnaphthalene, and anthracene and 2-cyanonaphthalene was investigated at room temperature. This process is essentially adiabatic for the two anthracene–naphthalene cycloadducts and >90% diabatic for anthracene–anthracene cycloadducts. A rationalization is offered on the basis of the correlation diagrams for cycloaddition and is supported by quantum yield and fluorescence studies of both photocycloaddition and cycloreversion. A charge-transfer pathway becomes competitive in polar solvents in both reactions.

Photodimerization of aromatic molecules and cycloreversion of the adducts is a subject of active interest.[1] Since cleavage of the high-energy adducts usually leads to 100% of the starting monomers, such systems can be of interest for energy storage.[2] In several cases chemiluminescence is thermodynamically possible, and experiments have recently borne out this expectation.[3]

Apart from potential application, theoretical treatments and experimental investigations[4-12] have been addressed to the mechanism of photodimerization and cycloreversion, to the intermediate(s) involved (e.g., is there a common intermediate in both photodimerization and photocycloreversion?),[4] or to the role of the adiabatic pathway leading to excited monomer from excited dimer.[11,13] As for the last question, the adiabatic pathway accounts for at most a few percent of the reaction in most reported cases, e.g. for anthracene photodimer (A–A),[5,6] but Yang recently reported that in the case of the benzene–anthracene 4 + 4 adduct photocycloreversion is quantitatively adiabatic.[11]

This prompted us to prepare a series of anthracene–anthracene and anthracene–naphthalene cycloadducts and to measure the steady-state parameters for both photocycloaddition and photocycloreversion with the aim of obtaining some indication about the features of the excited-state surface for cycloaddition through the influence of structure and energy factors on the course of the reaction.

Scheme I

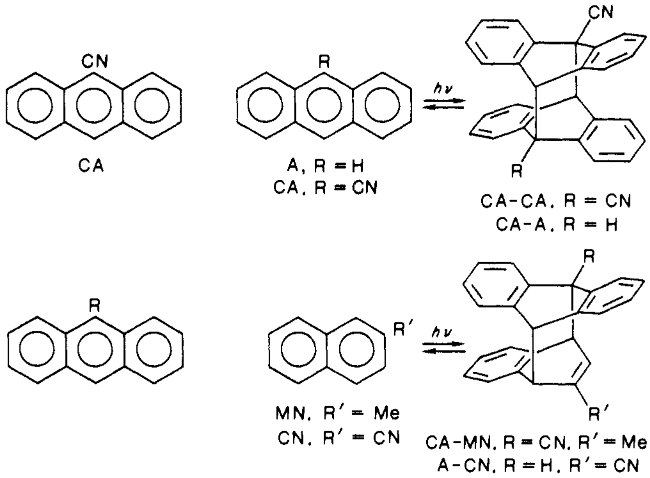

Table I. Cross-Photocycloaddition[a]

excited molecule	quencher	solvent	K_{sv}, M^{-1}	K',[b] M^{-1}	Φ_{lim}[b]
CA	A	cyclohexane	255	220	0.13
		acetonitrile	280	310	0.45
CA	MN	cyclohexane	8	11	0.05
		acetonitrile	15	20	0.1
A	CN	cyclohexane	7	20	0.04
		acetonitrile	8	7	0.1

[a] On irradiation at 405 nm (CA) or 365 nm (A) in degassed solution. [b] Calculated from the double reciprocal plot of Φ (cross-cycloaddition) vs quencher concentration (see the Experimental Section).

Results and Discussion

We previously reported[14] that 9-cyanoanthracene, which is known to efficiently yield the head to tail dimer CA–CA (see Scheme I) on irradiation in solution, in the presence of a 4-fold excess of anthracene (A) gives exclusively the cycloadduct CA–A and in the presence of naphthalene (N) or 2-methylnaphthalene (MN) gives the corresponding cycloadducts CA–N and CA–MN although in these cases CA homodimerization is not eliminated. We explored the photochemistry of unsubstituted anthracene in the presence of naphthalene derivatives and found that a cycloadduct is formed in the case of 2-cyanonaphthalene (A–CN).

Stern–Volmer constants for fluorescence quenching K_{sv} and limiting quantum yields for cycloaddition, obtained from the doubly reciprocal plot Φ^{-1} vs [quencher]$^{-1}$, are reported in Table I. The ratio between the intercept at the origin and the slope in such plots, reported as K' in Table I (see also supplementary

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(12) For a quantitative study of cycloreversion of CA–CA in the crystal state, see: reference 2 and Donati, D.; Sarti-Fantoni, P.; Guarini, G. G. T. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2170. (b) Ebeid, E. Z. M.; Morsi, S. E.; Williams, J. O. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2170.

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Table II. Photocycloreversion

adduct	solvent	Φ_r[a]	$\Phi_{f(M)}$[b]	α_a[c]	$\lambda_{f'}$[d]	$\Phi_{f'}$[d]
CA–CA	cyclohexane	0.45	0.015	0.03	347	0.06
	acetonitrile	0.45	0.035	0.07	338	0.015
CA–A	cyclohexane	0.60	0.01	0.02	350	0.03
	acetonitrile	0.45	0.02	0.05	340	0.012
CA–MN	cyclohexane	0.65	0.4	0.68		
	acetonitrile	0.7	0.4	0.64		
A–CN	cyclohexane	0.8	0.22	0.91		
	acetonitrile	0.7	0.16	0.76		
A–A[e]	MTHF	0.55	0.001	0.006	315	0.002
A–B[f]	methanol	0.86		0.93		

[a] Quantum yield for cycloreversion by irradiation at 280 nm in degassed solution. [b] Yield of the monomer (CA or A) fluorescence. [c] Fraction of the cycloreversion occurring adiabatically. [d] Emission maximum and quantum yield for the fluorescence not attributable to the monomer. Onset of the emission is at ca. 310 nm. [e] From ref 6. [f] From ref 11.

material), is in every case near to K_{sv}, supporting the involvement of the excited singlet in these reactions. No exciplex emission is observed in the CA–A system, nor do concentrated CA solutions show an excimer emission, whereas weakly emitting exciplexes are observed in the CA–MN and A–CN systems. Purification of the dimers is possible through chromatography and low-temperature recrystallization. All of the dimers decompose rather than melting, yielding solely the starting monomers.[12] The anthracene–anthracene adducts CA–CA and CA–A decompose at a significant rate in solution at ca. 80 °C, and for the anthracene–naphthalene adducts decomposition is noticeable slightly above room temperature. No chemiluminescence could be visually detected when refluxing saturated solutions of these dimers in *n*-heptane.

Thermal stability is at any rate sufficient to allow the study of photochemical decomposition at room temperature. Similar to previously reported 9,10-anthracene dimers,[5-9] the present compounds show in the UV spectrum a low-intensity band tailing until ca. 290 nm, which well corresponds to the *o*-xylene chromophore present in these compounds. Irradiation into this band causes clean cycloreversion to the starting monomers in both degassed and air-saturated solution. Quantum yields for decomposition determined at 20 °C in degassed solution are reported in Table I. The extent to which these photoreactions occur adiabatically to yield excited monomers was determined by measuring the monomer fluorescence emission under the same condition. In the case of the anthracene–anthracene adducts, two weak emissions, one centered at 340 nm and one corresponding to the monomer emission, were observed, their ratio being reversed in polar vs apolar solvents. In the case of the anthracene–naphthalene adducts, only a strong anthracene emission was observed (Table I). When the presence of the anthracene absorption at ca. 255 nm and the correspondence of the excitation spectrum with the adduct absorption were checked, it could be determined whether part of the emission observed was due to monomer present as an impurity in the adduct. Quantitative determination was possible with measurement of the fluorescence on irradiation at 360 nm, where the adducts do not absorb. In this way, it was determined that the samples of CA–CA and CA–A used contained no detectable monomer impurity, whereas the samples of CA–MN and A–CN contained a small amount of monomers, and correction for its contribution to the observed fluorescence was possible. Since every run caused a noticeable increase in the fluorescence, although there was a minimal change in the absorption spectrum, every sample was run only once.

From the yield of monomer fluorescence by irradiating the adduct and literature values of fluorescence quantum yield for CA and A, the fraction of excited dimers reaching the singlet excited state of the monomer was calculated (α_a in Table II).

The present results in connection with results from other laboratories[4,11] suggest some considerations about the general features of singlet-state aromatic photodimerization as well as observations concerning the role of charge-transfer pathways specific for these cyanated derivatives.

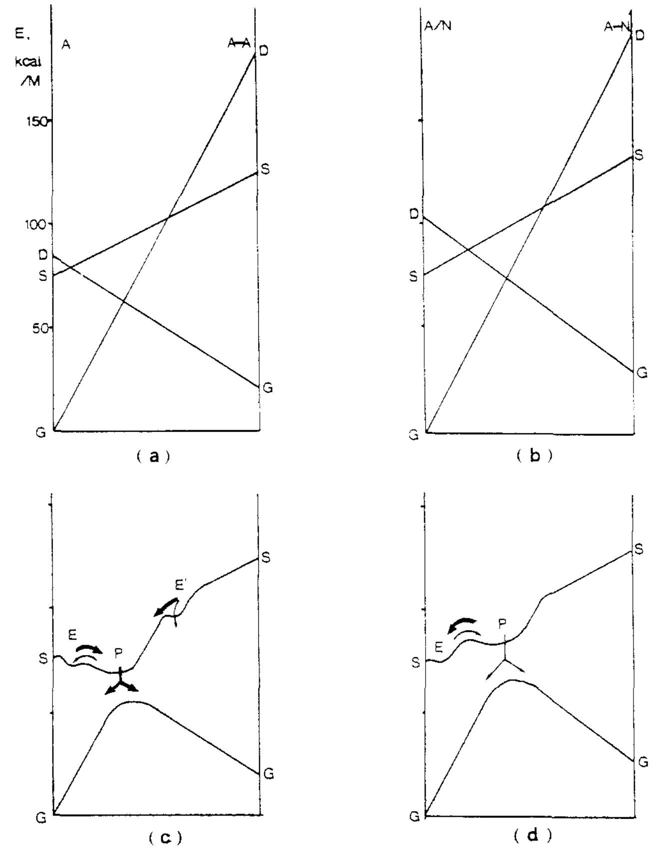

Figure 1. (a,b) State correlation diagram for anthracene (A) dimerization and anthracene–naphthalene (A–N) cross-dimerization. Notice that in the latter case the singly excited surface (S) rises more steeply and crossing between ground-state (G) and double-excited (D) surfaces occurs later. The energy of dimer A–A is put equal to that of the CA–CA dimer;[2] that of adduct A–N is obtained by adding a contribution (13 kcal M^{-1}) for the different loss of aromaticity. Energy of S states corresponds to that of first excited singlets and that of D states to the sum of the triplets. (c,d) Same diagrams when taking into account avoided crossing and secondary minima as hypothetized from the photochemistry of these systems. Favored pathways are indicated by thick arrows. Irradiation of A (Figure 1c) leads to efficient complexation. The exciplex E is nonemitting primarily because of easy crossing to the pericyclic minimum P, from which partitioning to ground-state monomer and dimer takes place. Starting from the excited dimer, cycloreversion is essentially diabatic, though encountering a weakly emitting "tight exciplex" E′. Upon irradiation of A in the presence of N (Figure 1d), weak exciplex emission and inefficient cycloaddition are observed; irradiation of A–N adduct causes essentially adiabatic cycloreversion.

$4\pi_s + 4\pi_s$ photocycloaddition and reversion are usually discussed on the basis of correlation diagrams such as those depicted in Figure 1.[15] Caldwell[16] has predicted the feasibility of such reactions through the evaluation of the slope of the surface connecting the doubly excited state (D) of the reagents (the energy of the D state in most cases corresponds to the sum of the triplet energies of the two molecules involved) and the ground state (G) of the products. Assuming only HOMO–HOMO and LUMO–LUMO interaction, he obtains the interaction energy $\Delta E_p(r)$ of the two triplets as

$$\Delta E_p(r) = c^2\gamma(r)$$

where c^2 is calculated on the basis of MO coefficients at the reacting centers and $\gamma(r)$ is the resonance integral for end-on interaction of carbon 2p orbitals at distance *r*. With some assumptions the "earlyness" of the crossing of the surface connecting

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[15] For the state correlation diagram for allowed photocycloaddition, see: Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970. (b) Gerhartz, W.; Poshusta, L. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *98*, 6427.

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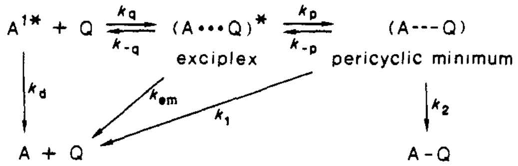
Scheme II[a]



[a] A, aromatic; Q, quencher.

the singly excited (S) states with the D → Q, surface, i.e. the condition for high reactivity, can be evaluated in terms of the quantity $\gamma(r_c)$, where r_c is the distance of the molecules at the crossing of the surfaces.

$$\gamma(r_c) = (E_TA + E_TB - E_SA)/c^2$$

By using tabulated Hückel coefficients[17] and excited-state energies[18] one obtains $\gamma(r_c) = 5.0$ kcal M^{-1}, corresponding to a facile reaction for anthracene dimerization, 17.8 kcal M^{-1}, corresponding to moderate reactivity for anthracene–naphthalene 4 + 4 cycloaddition, and 24.6 kcal M^{-1}, corresponding to no reaction for anthracene–benzene cycloaddition.

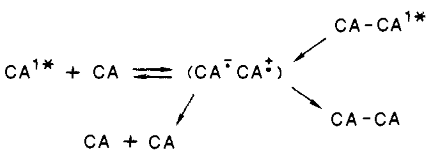
When the role of exciplexes is taken into consideration, one can expect an adverse effect, since formation of a stable exciplex lowers the singly excited surface and thus delays crossing with the doubly excited surface, as it has been shown to be the case for pyrene.[16]

In the case of CA–CA dimerization and CA–A cycloaddition *both* K_{sv} and Φ_{lim} are high and excimer emission is absent (Table I). Thus, (i) the excimer is short-lived, and (ii) there is no substantial barrier between the exciplex minimum and the pericyclic minimum leading to reaction (Figure 1a,c). With reference to Scheme II, at the concentration used quenching of singlet excited A takes place at a diffusion-controlled rate, and $k_q[Q] \gg k_{-q}$ and k_d, and $k_p \gg k_{-q}$, k_{em}, and k_{-p}. Thus, $k_p \geq 10^8$ s^{-1}, since k_{em} is expected to be greater or equal to 2×10^7 s^{-1}. Complexation of singlet excited monomer is efficient, and the favored process from the exciplex is crossing to the pericyclic minimum, since no barrier is encountered in this direction. This is most economically rationalized by admitting that exciplex and pericyclic minima have the same geometric arrangement and differ only as far as the distance between the monomers is concerned.

It is immediately seen from Figure 1c that this explains that cycloreversion proceeding along the singly excited state surface occurs essentially diabatically, since access from the pericyclic minimum to the exciplex minimum and hence to excited monomer is difficult. The pathway for cycloaddition and the pathway for cycloreversion go through a common (pericyclic) minimum and the chemical yield reflects partitioning from this minimum. Thus, the sum of the limiting quantum yield for dimerization [$\simeq k_2/(k_1 + k_2)$] and the quantum yield for cycloreversion approach 1 (0.73 in cyclohexane, 0.9 in acetonitrile for the CA–A system), the difference being in part attributed to the small part of cycloreversion proceeding adiabatically.

These general features are probably common to the dimerization of other anthracenes, and indeed photodimerization is usually efficient and dimer photocleavage diabatic.[1,5,6] Substituents, however, can have an important effect on the reaction; as an example, steric repulsion may lower reaction quantum yield while conserving an efficient monomer quenching, as is the case with 9,10-dimethylanthracene, since in this case the otherwise fast collapse of E to P (see Figure 1c) is prevented. On the other hand, when the correlation diagram for anthracene–naphthalene dimers (and, still more clearly, anthracene–benzene dimers) is considered, the main difference is that the doubly excited state of the monomer is higher in energy, and thus the pericyclic crossing is late; furthermore, the singly excited surface rises more sharply toward the higher lying S state of the dimer.[19] Thus, the situation is unfavorable *both* to formation of the excited complex *and* to reaction. In Scheme II, $k_q[Q]$ is now lower than k_{-q} (see Table I; K_{sv} is 20–40 times lower than in the anthracene–anthracene case). This is probably due to a decrease in k_q rather than on increase in k_{-q}, since also k_{em} becomes competitive in this case (see below). Furthermore, k_p is now lower than k_{-p}; that is, there is a sizable barrier to the access of the pericyclic minimum (Figure 1d). Thus, from both the pericyclic and the exciplex minimum, the favored pathway is toward the excited monomer rather than toward the adduct. Indeed, both K_{sv} and Φ_{lim} are low in the antracene–naphthalene case and negligible in the anthracene–benzene case. A weak exciplex emission is observed with the naphthalenes as quenchers, indicating that in this case there is a shallow exciplex minimum (limited red shift from the monomer emission) not apparent in the anthracene–anthracene case due to a too large value of k_p.

Scheme III[a]



[a] CA, 9-cyanoanthracene.

Conversely, when we start from the excited dimer, the singly excited surface does not encounter a convenient minimum allowing crossing to the ground state, and thus the reaction proceeds essentially adiabatically to the excited monomer (see the high α_a in Table II).

The 340-nm emission for CA–CA and CA–A and the effect of polar solvents remains to be discussed. As for the first question, a very weak emission at 313 nm has been previously reported for anthracene and 9-methylanthracene dimers.[6] In that case, fluorescence is reasonably attributed to the excited intact dimer and corresponds in shape and position to that expected from the *o*-xylene chromophore. This does not hold in the present case since emission is much more red-shifted and intense. We were unable until now to trace this unusual emission to an impurity or to a photoisomer (cycloreversion is quantitative; see the Experimental Section). If the emission arises indeed from excitation of the dimer, it might be due to a different exciplex encountered before the pericyclic minimum (left side of Figure 1c). This exciplex is very tight and thus is higher in energy than the monomer but could still enjoy some stabilization, partially accounting for the less than unitary efficiency of the dimer photocleavage.

As for the medium effect, it can be noticed that quantum yield both for cycloaddition and for adiabatic cycloreversion of the dimer increases in acetonitrile vs cyclohexane or benzene (while the 340-nm emission from the dimer decreases). This suggests that in polar solvents a substantial part of the reaction occurs through a different mechanism involving a radical-ion pair, e.g. (CA$^{\bullet-}$–CA$^{\bullet+}$) or (CA$^{\bullet-}$–A$^{\bullet+}$), that is reached by charge transfer both between the excited- and ground-state monomer and during the cleavage of the excited dimer (Scheme III). Some precedent could be indicated in the finding by Manring et al. that the photocleavage of linked anthracene dimers involves a complex in apolar and the radical-ion pair in polar solvents[4a] and in the observation of a ionic pathway in other pericyclic photoreactions, e.g. Dewar benzene isomerization.[20,21]

In conclusion, the present data suggest that the same minima (exciplex and pericyclic) are involved in photochemical cycloaddition and cycloreversion of aromatics, and the relative efficiency of the different pathways from these minima determines the overall quantum yield of both processes. Thus, efficient dimerization corresponds to poor adiabatic contribution in the cycloreversion

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[17] Streitwieser, A. *Dictionary of π-Electron Calculation*; Pergamon: Oxford, 1965.

[18] Murov, S. *Handbook of Photochemistry*; Dekker: New York, 1973.

[19] For previous observations of the effect of the reagent excitation energy on the adiabatic yield, see Jones's work on hexamethyl Dewar benzene photosensitized cycloreversion.[20]

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[21] Jones, G.; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1276. Jones, G.; Chiang, S. H. *Ibid.* **1979**, *105*, 7421.

and vice versa. The excited surface may include a further minimum between the dimer and the pericyclic minimum. Furthermore, there is a concurrent charge-transfer pathway that becomes important in polar solvents.

Experimental Section

The UV spectra were recorded on a Cary 19 spectrophotometer, the IR spectra on a Perkin-Elmer 257 spectrophotometer, the NMR spectra on a Brucker 200 instrument, the mass spectra on a Du Pont 492-B instrument, and the fluorescence spectra on an Aminco-Bowman MPF or a Perkin-Elmer 3000 spectrofluorimeter.

Spectroscopic grade solvents were used as received. 9,11-Dicyano-9,10,11,16-tetrahydro-9,10[9′,10′]-anthracenoanthracene (CA–CA), 9-cyano-9,10,11,16-tetrahydro-9,10[9′-10′]-anthracenoanthracene (CA–A), and 9-cyano-12-methyl-9,10,11,14-tetrahydro-9,10[1′,4′]-naphthalenoanthracene (CA–MN) were prepared as previously reported[14] and purified by column chromatography and low-temperature recrystallization.

12-Cyano-9,10,11,14-tetrahydro-9,10[1′,4′]-naphthalenoanthracene (A–CN) was analogously obtained in 20% yield from the irradiation of a deaerated acetonitrile solution containing 1×10^{-2} M CN and 2.5×10^{-3} M A and was purified as above. This compound showed the following: mp 169–170 °C; IR 2220 cm^{-1}; NMR (C_6D_6) δ 3.32 (14 H), 3.7 (11 H), 3.88 (9 H), 3.98 (10 H), 6.27 (13 H), $J_{13-14} = 7.6$ Hz, $J_{9-10} = 11$, $J_{11-13} = 1$, $J_{10-11} = 10.8$.

Measurements. Measurements were carried out in dilute solution in 1-cm optical path cuvettes. Degassing was effected by four freeze–degass–thaw cycles to 10^{-5} Torr.

Fluorescence quenching was measured in the presence of 10^{-3}–10^{-1} M quencher, and linear Stern–Volmer plots were obtained (see supplementary material).

Quantum yields for dimerization were measured at 365 (for anthracene) or at 405 nm (for CA) on an optical bench fitted with a high-pressure mercury (Osram HBO 200 W) arc and interference filters ($\Delta\lambda_{1/2}$ 5 nm) by using potassium ferrioxalate as an actinometer. Solutions of CA (2×10^{-4} M) (quantum yield for dimerization is 0.009 in MeCN and 0.006 in cyclohexane) and solutions of A (5×10^{-4} M) ($\Phi = 0.02$ in MeCN and 0.008 in cyclohexane) were used in the presence of increasing amounts of the other monomer. The formation of CA–A was directly monitored by HPLC, but since measurement of the formation of CA–MN and A–CN was less reliable, the yield of the cross dimer was obtained in these cases by substracting the yield of homodimer from the total consumption of CA or A, respectively (all determined by HPLC; see supplementary material).

Quantum yield for cycloreversion was determined by using the 150-W high-pressure xenon lamp and the monochromator of the Aminco-Bowman spectrofluorimeter centered at 280 nm with a 5-mm entrance slit and by monitoring monomer formation by UV spectroscopy.

Evolution of the absorption spectrum under irradiation in a typical case is reported as supplementary material along with representative examples of the emission observed under this condition. While, in the case of A–CN and CA–MN, this corresponds to the fluorescence of the corresponding anthracene derivatives, with CA–CA and CA–A, an additional short wavelength emission is observed. The excitation spectrum for the two emissions (in the region 250–290 nm) is virtually superimposable and corresponds to the absorption spectrum of the dimers. This is not a really satisfactory criterium with such featureless spectra. Repeated purification did not change the ratio between the two emissions. However, the short-wavelength emission is much more quenched by oxygen. Luminescence quantum yields, from which the yield for the adiabatic pathway was calculated, were obtained from the corrected fluorescence spectra by comparison with 2-methylnaphthalene ($\Phi_F = 0.24$), anthracene ($\Phi_F = 0.30$), and 9-cyanoanthracene ($\Phi_F = 0.9$) in cyclohexane as standards.[22] Each sample was run only once in order to avoid interference from monomers formed during the running of the spectrum. The presence of monomers in the samples considered was determined by examining the UV spectrum and by monitoring the monomer fluorescence on excitation at 360 nm where the dimer does not absorb. In this way, when the absorbance of monomers and dimers at the exciting wavelength (280 nm) is taken into account, it was possible to substract from the observed monomer fluorescence observed the part due to preformed monomer. This was ≤2% for CA–CA and CA–A dimers and up to 15–20% for CA–MN and A–CN dimers.

Acknowledgment. We thank the Consiglio Nazionale delle Ricerche, Rome, for supporting this research.

Registry No. CA, 1210-12-4; A, 120-12-7; MN, 91-57-6; CN, 613-46-7; CA-A, 105597-99-7; CA-MN, 105597-98-6; A-CN, 113236-48-9; CA-CA, 33998-38-8; N, 91-20-3; A-A, 1627-06-1; A-N, 116724-66-4.

Supplementary Material Available: Figures of Stern–Volmer quenching, double reciprocal plots, time evolution, and absorption and emission spectra (6 pages). Ordering information is given on any current masthead page.

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[22] (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970. (b) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.