

in all solvents which decays back to the 11-cis Schiff base (quantum yield varying from 0.03 to 0.09 and lifetime varying from ms to 120 s).

On the basis of photoisomerization results previously known for 11-cis-retinal and 13-demethylretinal as well as our data for the 13-demethyl-11-cis Schiff base, single bond conformer distribution cannot account in any significant manner for the variation of the efficiency of isomerization of the 11-cis SB as a function of the polarity of the solvent.

(2) For the 11-cis Schiff base, the increase in the efficiency of isomerization as a function of principally the polarity of the solvent is assigned to be the result of increased mixing of a "Bu" state into a lowest "Ag" state with a concomitant decrease in the energy of activation of isomerization. The mixed electronic state from which isomerization begins cannot be clearly assigned as Franck-Condon or equilibrium in nature. If the lifetime for isomerization is very fast, that is ~ 5 ps, then the originating state nature is Franck-Condon.

On the basis of the results given in item 1, it is clear that there is nothing special about the "Ag" state regarding its photochemical lability. In fact, the lowest excited state becomes less photoisomerization labile as the "Ag" character becomes more pure.

(3) The protonated 11-cis Schiff base exhibits only minor variation in the quantum yield of isomerization (0.19 ± 0.03) as a function of the nature of the solvent in marked contrast to the Schiff base. Moreover, the isomerization efficiency of the Schiff base in polar solvents is as high as, or even higher than, that of the protonated Schiff base in any solvent.

Protonation of the Schiff base results in (a) increased state

mixing of "Bu" into "Ag" relative to that in the Schiff base (or "Bu" somewhat lowest), (b) lowering of the energy of activation to a nominally minimal value to permit significant isomerization which is relatively insensitive to the nature of the solvent, and (c) elimination of a side reaction transient present in the Schiff base.

(4) The mixing given above, "Bu" into "Ag", is the opposite of that proposed by theory to account for efficient isomerization of the protonated Schiff base. Moreover, twisting in the excited state as previously proposed is not a requirement for mixing.

(5) Previously reported large variations in the quantum yields of isomerization of the protonated 11-cis Schiff base with exciting wavelength in methanol were not found in this study for five solvents (including methanol).

(6) A proposal is made for the mechanism of the primary photoreaction of the vision process based on our earlier results and results reported herein.

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Registry No. 11-cis-Retinal butylamine Schiff base, 52647-48-0; 13-demethyl-11-cis-retinal butylamine Schiff base, 94801-26-0; retinal butylamine Schiff base, 36076-04-7; 13-demethylretinal butylamine Schiff base, 73432-31-2.

Observation of a Common Intermediate in the Photocycloaddition and Photocycloreversion of Linked Anthracenes

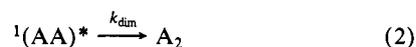
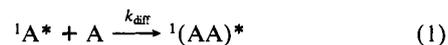
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Abstract: Picosecond dynamics of intramolecular photocyclization (**1** \rightarrow **2**) for a series of anthracenes linked at the 9 position (**1**) have been measured after 355-nm excitation by a 25-ps laser pulse. Picosecond dynamics for the corresponding photocycloreversion (**2** \rightarrow **1**) have also been measured after 266-nm excitation of **2** by a 25-ps laser pulse. It is shown that electronic excitation of either **1** or **2** creates a common intermediate (CI). The electronic structure of the CI is different in polar vs. nonpolar solvents and leads to differing absorption spectra for the CI in various solvents. The absorption spectrum of the CI in acetonitrile is consistent with a structure where electron transfer has occurred from one anthracene ring to the other. The absorption spectrum of CI in diethyl ether is less definitive. The rate of CI formation from the lowest excited singlet of **1**, S_1^* (**1**), is dependent on solvent and is consistent with charge transfer occurring in the transition state from S_1^* (**1**) to CI. Consideration is given to the coincidence of excimer and ion-pair structures for linked arenes in polar media.

Anthracene photodimerizations were first reported by Fritzsche¹ and have since been the subject of intensive investigations.² The generally accepted mechanism involves interaction of singlet excited anthracene ($^1A^*$) with ground-state anthracene (A) to form an excimer ($^1AA^*$) which disproportionates between dimerization (k_{dim} , to give products linked at the 9 and 10 positions) and internal conversion (k_{ic} , to give two ground-state anthracenes), Scheme I.

Scheme I



Recently, investigations have been carried out with linked systems in which intramolecular interactions (including dimerization) can occur between two anthracene moieties which are connected by an alkyl chain.³⁻¹⁵ An advantage of using linked

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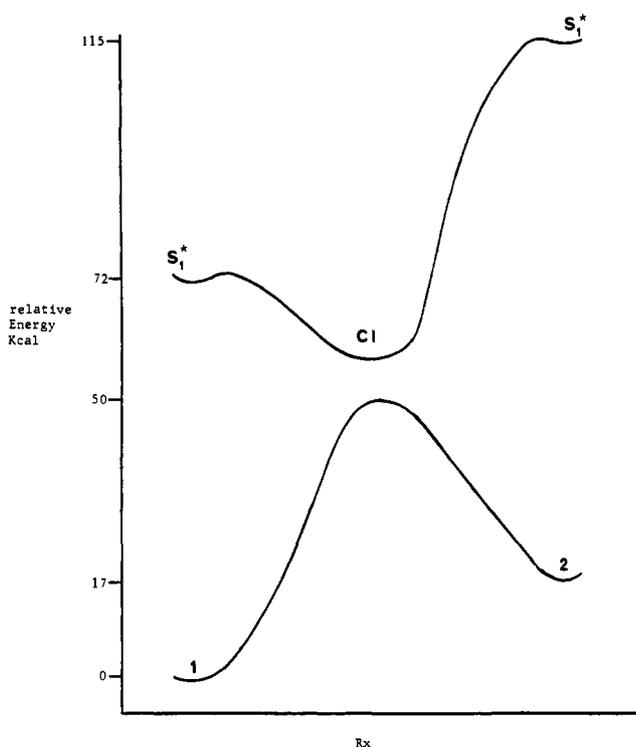
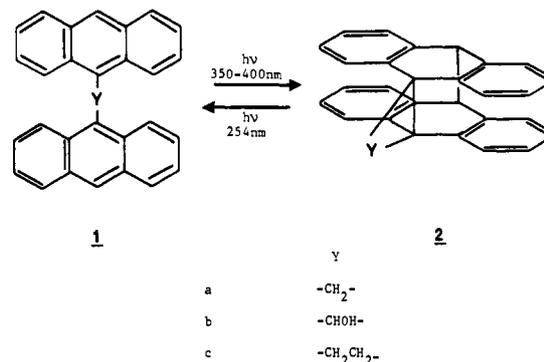


Figure 1. Energy surface relationship for $1 \rightleftharpoons 2$ (from ref 3).

anthracenes is to avoid the diffusion-limited step of excimer formation (k_{diff} , Scheme I).

In the case of 9,9'-dianthryl (Bian) it has been proposed that in the excited state intramolecular charge transfer occurs between anthracene moieties.^{5,6} In polar solvents, the $S_n^* \leftarrow S_1^*$ spectra for Bian are comparable to the superposition of the anthracene radical anion and radical cation spectra.¹⁰ No intramolecular cyclization is observed with Bian, due to steric constraints.

It has been shown by two of the present authors³ that bis(9-anthryl)methanes photodimerize efficiently.¹⁵ For the parent compound, bis(9-anthryl)methane (**1a**), the quantum yield for internal dimerization (ϕ_{12}) is 0.15 and the quantum yield for cleavage of **2a** (ϕ_{21}) is 0.76 in benzene.³ Similarly, ϕ_{12} for bis(9-anthryl)methanol (**1b**) is 0.29 and ϕ_{21} for **2b** is 0.81.³ In both cases (**1a** \rightleftharpoons **2a**, **1b** \rightleftharpoons **2b**) the sum of the quantum yields for the two processes is 1.0 (within experimental error), suggesting a common intermediate (CI) is formed quantitatively in the photodimerization and photocycloreversion reactions. These observations, along with calorimetric determination of the relative energy of **1a** and **2a**, led to the proposed potential energy surface



for photoisomerization shown in Figure 1.³

In Figure 1, the common intermediate is expected to assume the structure of the reaction midpoint, excited-state geometry known variously as a "pericyclic minimum",¹⁶ a "bifunnel",¹⁷ a "biradical",¹⁸ or a "hole",¹⁹ features generally proposed for pericyclic processes which are ground-state forbidden and excited-state electronically allowed. A distinction has been made^{3,4} between a permissible intermediate, the classical excimer, whose structure depends on π overlap, and the pericyclic minimum biradicaloid, the intermediate for anthracene addition which allows an efficient jump between proximal S_1 and S_0 surfaces.

The intervention of common intermediates in cycloadditions and cycloreversions has been proposed for a variety of reactions^{20,21} including cis-trans isomerizations of olefins²² and electrocyclic interconversions of butadiene and cyclobutene derivatives.²³ However, to our knowledge spectroscopic observation of a CI in pericyclic reactions has not been reported.

In this paper we report on the use of picosecond laser absorption spectroscopy to study the photocycloaddition of **1** (a and b) and the photocycloreversion of **2** (a and b). We observe common intermediates for the reactions $1 \rightarrow 2$ and $2 \rightarrow 1$, in particular charge-transfer intermediates, which appear exclusively on flash excitations in a polar solvent.

Experimental Section

Materials. Acetonitrile (Mallinckrodt) was distilled from P_2O_5 and stored over 3 Å molecular sieves. Diethyl ether (Mallinckrodt AS), ethanol (U.S. Industrial Chemicals), cyclohexane (Eastman, Spectra ACS), methylene chloride (Fisher), and benzene (Mallinckrodt) were used as received. Bis(9-anthryl)methane (**1a**), bis(9-anthryl)carbinol (**1b**), 1,2-bis(9-anthryl)ethane (**1c**), and the corresponding dimers of **1a** and **1b**, **2a** and **2b** were prepared and purified by methods described previously.³

Picosecond Laser Experiments. The laser apparatus has been described in detail previously.²⁴ Briefly, the picosecond absorption spectrometer consists of a 10-Hz Nd³⁺-YAG laser (Quantel International, YG-400) with a pulse width of 25 ps. The detector is a OMAII Vidicon (PAR-1215-1216-1217) interfaced to a 200-mm spectrograph (JY-UFS-200). The 355-nm pulse used to irradiate **1a**, **1b**, and **1c** was ~ 0.2 mJ focused to an area of ~ 5 mm². The 266-nm pulse used to irradiate **2a** and **2b** was ~ 0.1 mJ focused to an area of ~ 3 mm². Each spectrum is the average of at least 200 laser pulses. Solutions of **1b** and **2b** in all solvents employed were 1.8×10^{-3} M. The **3a** solution in methylene chloride was 1×10^{-3} M. Low conversion of **1** to **2** (<5% in all cases) during 355-nm excitations of **1** will have no effect on the results as the product **2** does not absorb at 355 nm. However, 266-nm irradiation of **2** creates a product (**1**) with a larger extinction coefficient (ϵ) at 266 nm than the starting material (for **2b**, $\epsilon_{266} = 5000$ cm⁻¹ M⁻¹; for **1b**, $\epsilon_{266} = 24,000$ cm⁻¹ M⁻¹). Because of the possibility of irradiating **1** at 266 nm,

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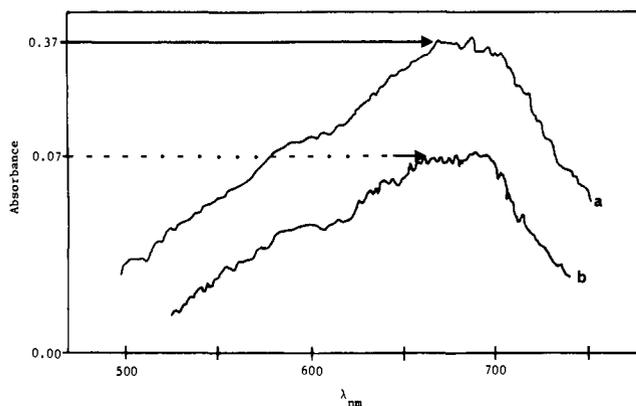


Figure 2. Spectra observed after 60-ps (a) 355-nm excitation of **1a** in CH_3CN (upper spectrum) and (b) 266-nm excitation of **2a** in CH_3CN (lower spectrum).

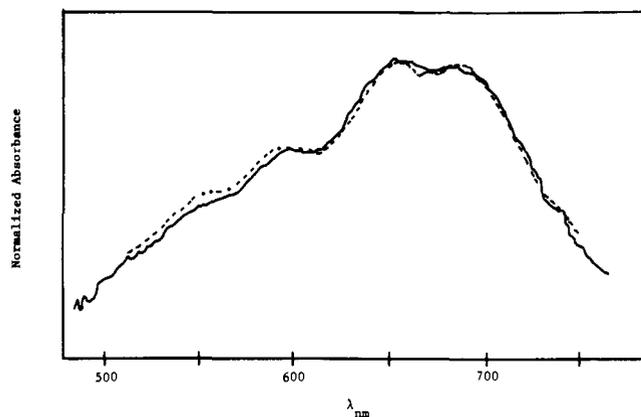


Figure 3. Spectra observed after 60-ps (a) 355-nm excitation of **1b** in CH_3CN (—) and (b) 266-nm excitation of **2b** in CH_3CN (---).

solutions were stirred during irradiation and were not irradiated past 2% conversion. Furthermore, the same results were obtained for **2b** in acetonitrile when the solution was passed through a flow cell as when the solution was stirred. Laser excitation of **1c** was done in methylene chloride rather than acetonitrile due to its insolubility in acetonitrile.

Results

Laser Excitation of 1a, 1b, and 1c at 355 nm. Laser excitation (355 nm, 0.2 mJ) of either **1a** or **1b** in acetonitrile (saturated and 1.8×10^{-3} M, respectively) produced similar transient spectra within 60 ps of the laser flash (Figures 2 and 3). For **1a**, Figure 2a, the transient produced has a λ_{max} of ~ 690 nm, with an absorbance of 0.37 OD, and the indication of a shoulder at 595 nm. The lifetime of this transient is 1.0 ± 0.1 ns. Under the same conditions, benzophenone, which is utilized as a calibration compound, has a triplet-triplet absorbance at 525 nm of 0.85 OD when probed 60 ps after excitation. The transient formed from **1b** in acetonitrile, Figure 3a, has two λ_{max} of similar intensities at ~ 655 and ~ 690 nm and a distinct shoulder at 595 nm and decays with a lifetime of 1.1 ± 0.1 ns. The shape of the transient spectra from **1a** and **1b** in acetonitrile does not vary with time. Similar excitation of **1b** in ethanol (1.8×10^{-3} M) produced the transient shown in Figure 4a (λ_{max} 655 nm, shoulder at 595 nm) 60 ps after the laser flash. The peak at 655 nm decayed with a lifetime of 1.3 ± 0.1 ns. It is apparent that the peak at 595 nm decays prior to the peak at 655 nm; however, the relationship between the two decay rates cannot be determined from the present data. Irradiation of **1b** in diethyl ether (1.8×10^{-3} M) produced a transient 30 ps after excitation with a λ_{max} at 595 nm (Figure 5a) which decayed to a nondescript spectrum by 360 ps (Figure 5b). Irradiation of 1,2-bis(9-anthryl)ethane (**1c**) in methylene chloride (1×10^{-3} M) produced the spectra shown in Figure 6. With **1c** it is apparent that the peak at 595 nm decays prior to the peak at 690 nm. Laser excitation of **1a** in benzene (5×10^{-4} M) produced a transient (λ_{max} at 595 nm) which decayed with a

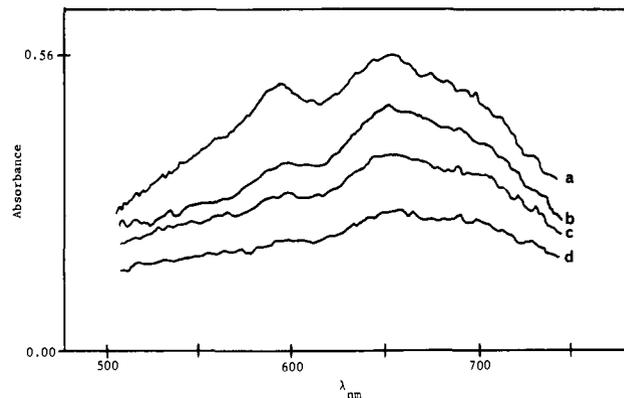


Figure 4. Spectra observed after 355-nm excitation of **1b** in $\text{CH}_3\text{CH}_2\text{OH}$: (a) 60 ps, (b) 360 ps, (c) 600 ps, (d) 1.0 ns.

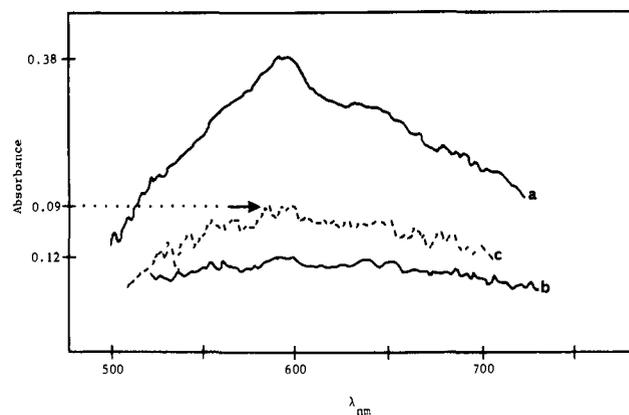


Figure 5. Spectra observed after 355-nm excitation of **1b** and 266-nm excitation of **2b** in $(\text{CH}_3\text{CH}_2)_2\text{O}$: (a) **1b**, 30 ps (—); (b) **1b**, 360 ps (—); (c) **2b**, 50 ps (---).

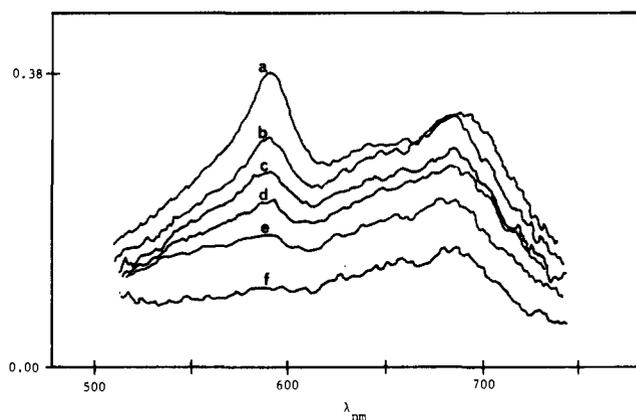


Figure 6. Spectra observed after 355-nm excitation of **1c** in CH_2Cl_2 : (a) 60 ps, (b) 310 ps, (c) 560 ps, (d) 1.0 ns, (e) 1.9 ns, (f) 4.2 ns.

lifetime of 1.3 ± 0.2 ns. At 4.5 ns a broad and structureless spectrum remained, similar to that observed with **1b** in diethyl ether at 360 ps.

Laser Excitation of 2a and 2b at 266 nm. Laser excitation (266 nm, 0.1 mJ) of **2a** in acetonitrile (saturated) produced the transient shown in Figure 2b with a λ_{max} at 690 nm. The transient from **2a** decayed with a lifetime of 1.0 ± 0.3 ns. Irradiation of **2b** in acetonitrile (1.8×10^{-3} M) produces a transient, whose spectrum is shown in Figure 3b, that decays with a lifetime of 1.2 ± 0.1 ns. The transient spectra produced by 266-nm excitation of **2b** (Figure 3b) and by 355-nm excitation of **1b** (Figure 3a) have identical spectral profiles and lifetimes. The amount of transient observed 60 ps after 266-nm excitation of **2b** was 39% that observed after 355-nm excitation of **1b**. Furthermore, the amount of triplet benzophenone observed 60 ps after 266-nm excitation

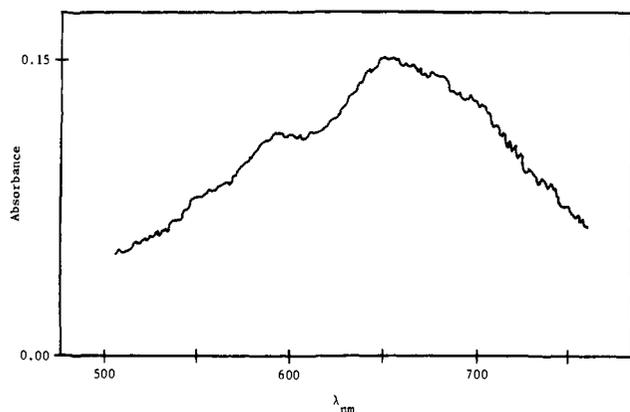


Figure 7. Spectrum observed after 266-nm excitation of **2b** in $\text{CH}_3\text{C}-\text{H}_2\text{OH}$, 50 ps after laser.

of benzophenone was 39% that observed after 355-nm excitation of benzophenone. If it is assumed that the quantum yield for triplet benzophenone formation is wavelength independent, then 266-nm irradiation of **2b** and 355-nm irradiation of **1b** create the transient, Figure 3, with approximately the same quantum yield. Laser excitation of **2b** in ethanol (1.8×10^{-3} M) produced a transient within 60 ps, Figure 7, which decayed with a lifetime of 1.3 ± 0.1 ns. The transient spectra from **2b** and **1b** at 350 ps in ethanol are similar; however, contrary to the transient from **1b**, the transient from **2b** does not show an enhanced peak at 595 nm immediately following excitation. Excitation of **2b** in diethyl ether (1.8×10^{-3} M) produced a transient with a nondescript spectrum shown in Figure 5a within 50 ps of the laser pulse which decayed with a lifetime of 0.6 ± 0.1 ns. The broad spectrum from **2b** and **1b** in diethyl ether are similar at 360 ps (Figure 5, b and c); however, they differ at 30 ps where **2b** does not show the sharp peak at 595 nm that **1b** shows. The intensity of the broad spectrum from **2b** (266-nm excitation) in diethyl ether was 35% of the intensity of the broad spectrum from **1b** (355-nm excitation) which again indicates (vide supra) that the transient from 355-nm irradiation of **1b** is formed with the same quantum yield as the transient from 266-nm excitation of **2b**, assuming the same transient is formed from **1b** and **2b**.

Discussion

The spectra in Figure 2 indicate that a common intermediate (CI) is formed in acetonitrile when **1a** is irradiated at 355 nm and **2a** is irradiated at 266 nm, based on spectral profile and decay lifetimes. Similarly, a CI is formed in acetonitrile when **1b** is excited at 355 nm and **2b** is excited at 266 nm. In Figure 3, the two spectra have been normalized to emphasize their spectral identity. In acetonitrile, excitation of **1** creates an excited singlet state which decays to the CI within 30 ps. Similarly, excitation of **2** creates an excited singlet state which decays to the CI within 30 ps. The similarity between the spectra in Figures 2 and 3 and that seen with 355-nm excitation of **Bian** in acetonitrile (which has λ_{max} at 690 and 645 nm and a shoulder at 595 nm)¹⁰ suggests that the electronic structure for the common intermediate corresponds to the full separation of charge producing a radical anion and radical cation (i.e., an ion pair like intermediate) with the probable contribution of a state with local excitation on an anthracene moiety. The CI is formed with the same quantum yield from either direction. An estimate for the quantum yield of zwitterionic intermediate formation may be obtained from the picosecond absorption data for **1a**. The extinction coefficient for the zwitterionic intermediate for **1a** at 690 nm should be similar to that for the zwitterionic intermediate for **Bian**, which is approximately $3000 \text{ M}^{-1} \text{ cm}^{-1}$ at 690 nm.¹⁰ Assuming a quantum yield of 1.0 for the production of the zwitterionic intermediate from **1a**, the ratio of absorbances for the λ_{max} of **1a** zwitterion to the benzophenone triplet, $\epsilon = 7630 \text{ M}^{-1} \text{ cm}^{-1}$ at 525 nm^{24b}, should be 0.39 ($3000 \text{ M}^{-1} \text{ cm}^{-1} / 7630 \text{ M}^{-1} \text{ cm}^{-1}$). From the absorption spectra at 60 ps for **1a** and benzophenone, the observed ratio is 0.43 (0.37 OD/0.85 OD). If the zwitterionic intermediate

were to represent a minor mode of decay, then the observed ratio of absorptions would be much less than 0.39, contrary to observation. Therefore, the zwitterion intervenes along the reaction coordinate for both photocycloaddition and photocycloreversion in acetonitrile.²⁵

The time evolution of the transient spectrum from **1b** in ethanol is shown in Figure 4a-d. There is an initial decay of the shoulder at 595 nm prior to the decay of the 655-nm peak. This initial decay corresponds to the decay of the first excited singlet state of **1b** to the CI. The assignment of the 595-nm peak to the $S_1^* \leftarrow S_1^*$ is based on its similarity to anthracene's $S_1^* \leftarrow S_1^*$ transition at 605 nm.¹⁰ Furthermore, when **1a** is irradiated at 355 nm in benzene, a transient spectrum is produced with λ_{max} at 595 nm which decays with a 1.3 ± 0.2 ns lifetime. The fluorescence lifetime of **1a** is 1.1 ns in benzene.³

The results from **1c** in methylene chloride are also consistent with initial formation of S_1^* (**1c**) which has a λ_{max} at 595 nm. S_1^* (**1c**) subsequently decays to a species with λ_{max} at 690 nm, the CI, in 2 ns. The slower rate of S_1^* (**1c**) decay relative to S_1^* (**1b**) most likely is due the CI formation being dependent on proximity of the two anthracene rings which for **1c** requires prior rotation about the ethane linkage.

On the basis that S_1^* provides a residual transient absorption (595 nm) for **1a** in acetonitrile (note discussion of fluorescence below), one concludes that equilibrium between the locally excited state and the zwitterion state must be established within 30 ps, a not unexpected result for closely spaced (ca. 0.3 nm) anthracene moieties. This equilibrium, which favors the zwitterion, is apparently established more slowly for **1b** in ethanol (Figure 4) and for **1c** in CH_2Cl_2 (Figure 6).

The amount of S_1^* (peak at 595 nm) observed at 60 ps from **1a** and **1b** is thus dependent on solvent polarity. In acetonitrile ($\epsilon = 36.2$), the spectrum observed immediately after 355-nm excitation of **1b** is the same shape as that observed at later times, indicating little S_1^* (locally excited **1b**) is present even 30 ps after laser excitation. In ethanol ($\epsilon = 24.3$), the spectrum observed 60 ps after 355-nm excitation of **1b** has enhanced absorbance at 595 nm which is gone by 360 ps. The 595-nm peak dominates the spectrum observed in diethyl ether ($\epsilon = 4.3$) at 30 ps and is gone by 360 ps. With **1a** in benzene ($\epsilon = 2.3$), S_1^* (**1a**) has a lifetime of >1 ns. The amount of S_1^* of **1a** observed falls off in the order benzene $>$ diethyl ether $>$ ethanol $>$ acetonitrile. This result is consistent with charge transfer occurring in the transition state leading from S_1^* to the CI.

The spectrum observed 30 ps after 355-nm excitation of **1b** in diethyl ether is dominated by the 595-nm peak due to S_1^* (**1b**), Figure 5a. Within 350 ps, S_1^* (**1b**) decays to a species with a broad structureless spectrum. This latter species is similar to that observed after 266-nm excitation of **2b**, Figure 5, b and c, and are presumably the same species. These results would indicate that the CI formed in diethyl ether when either **1b** or **2b** are irradiated is not the same CI formed when the irradiation is performed in acetonitrile. Unfortunately, it is difficult to assign the structure responsible for these spectra due to their nondescript nature.

One possible candidate for CI in nonpolar solvents is an excimer. Excimer fluorescence has been detected for 9-methylanthracene²⁶ and the parent unlinked anthracene²⁷ in fluid solution. An excimer emission has also been reported for **1c** in nonpolar solvents (hexane or benzene)³ and in various low-temperature matrices.^{11b} Even in the case of **1a**, chromophore interaction through excitation resonance ($M^*M \leftrightarrow MM^*$) appears possible, although not geometrically favored, since **1a**, prepared by reverse photoisomerization of **2a** in a crystal of **2a** at 10 K, has been shown to display

(25) Bergmark, W. R., unpublished results. The quantum yield for isomerization **1a** \rightarrow **2a** in acetonitrile is not substantially different (0.077) from the value observed for benzene solvent (0.15).

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long-wavelength dimer-like ground-state absorption ($\lambda_{\text{max}} = \text{ca. } 500 \text{ nm}$).^{11c} On the other hand, the rather featureless excited-state absorption observed in our study of excitation of **1a** in benzene or **1b** in diethyl ether is not readily matched with the transient absorption assigned to the anthracene excimer ($\lambda_{\text{max}} = 345, 373, \text{ and } 850 \text{ nm}$) obtained on laser excitation of anthracene (the "broken dimer" of photodissociated dianthracene) prepared in a 2-methyltetrahydrofuran matrix at 77 K.²⁸ The assignment of transient structure for the experiments in nonpolar solvents remains uncertain, since the observed species is also not readily associated with a biradicaloid structure, assuming a classical structure similar to diphenylmethyl ($\lambda_{\text{max}} = 535 \text{ nm}$).²⁹

Concerning the transient assignment for **1a-c** for polar media, one issue requires clarification. Should the zwitterion state be considered an excimer, stabilized predominantly by charge resonance, with an attendant emission spectroscopy and potential photoreactivity? The contribution of charge resonance ($M^+M^- \leftrightarrow M^-M^+$) to stabilization of an excimer has been understood for some time.³⁰ In calculations on the hydrogen excimer (H_4^*), Gerhartz, Poshusta, and Michl³¹ considered the approach of two ions (H_2^- and H_2^+) to an interaction distance and noted the indistinguishability of exciton and charge-transfer states for the excited dimer geometry at short distances. Notably, charge resonance is expected to be isotropic (no sandwich geometry required) in contrast to the stabilizing influence of excitation resonance, a strongly polarized dipole-dipole interaction.^{30a} The effect of polar solvents on excimer structure has been noted and discussed for linked arenes, including anthracenes.^{10,32} Red-shifted, unstructured, excimer-like emission has been reported for bi-

anthryl,^{10,32} linked pyrenes, and **1c** in acetonitrile.³³ The emission of **1a** in acetonitrile is similarly altered with some broadening of the normal anthracene vibronic progression, some tailing toward the red and an overall reduction in fluorescence yield.³⁴ The spectrum is consistent with a small contribution of fluorescence from locally excited **1a** (S_1^*) with an overlap of the nearly isoenergetic but weakly fluorescent excimer. One can estimate from the spectral data an S_1^* energy of 3.1 eV and, analogous to the data from deconvoluted spectra of bianthryl in acetonitrile, an excimer energy of ca. 2.9 eV. The ion pair energy for two anthracene moieties is 2.9 eV, neglecting Coulombic stabilization.³⁵ Thus the excimer, in acetonitrile, should be considered as having an electronic structure corresponding to full charge separation.

In summary, electronic excitation of either **1** or **2** leads to a common intermediate on the excited state potential energy surface. The electronic structure of this intermediate is dependent upon the solvent. The absorption spectrum of the CI in acetonitrile is characteristic of species where there is full separation of charge producing an intramolecular radical anion-radical cation. The nature of the common intermediate observed in diethyl ether cannot be defined.

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Optimized Intermolecular Potential Functions for Amides and Peptides. Hydration of Amides

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Abstract: Recently reported optimized intermolecular potential functions have been tested in Monte Carlo statistical mechanics simulations of dilute aqueous solutions of formamide, *N*-methylacetamide (NMA), and dimethylformamide (DMF). The computed heats of solution at 25 °C and 1 atm are all near -20 kcal/mol, which is in reasonable accord with experimental data. Extensive structural results are reported for the aqueous amides. Each amide forms two hydrogen bonds at the carbonyl oxygen with water molecules. The hydrogen on nitrogen in NMA participates in an additional hydrogen bond, and the NH_2 group in formamide has 1-2 water molecules attached as hydrogen bond acceptors. Caging occurs around the hydrophobic methyl groups in NMA and DMF; the water molecules in these regions show little net interaction with the solutes. The intermolecular potential functions are also shown to describe isolated amide-water complexes well in comparison to results of ab initio molecular orbital calculations.

The structure and function of proteins are strongly influenced by the interactions between the biomolecules and their aqueous environment. Consequently, it is important to obtain a molecular level understanding of the hydration of proteins and their constituents.¹ One promising means for obtaining such information

is through molecular dynamics and Monte Carlo statistical mechanics simulations. Though substantial activity exists in this

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