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PHOTOISOMERIZATION OF BIS(9-ANTHRYL)METHANE AND OTHER LINKED AN--ETC(U)
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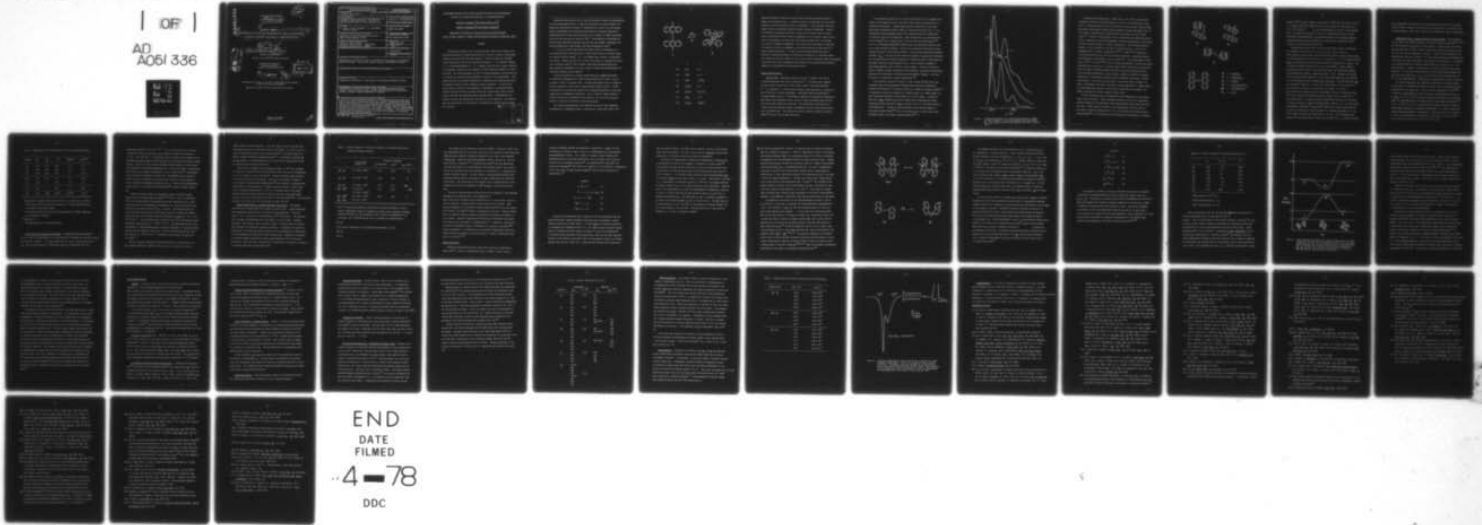
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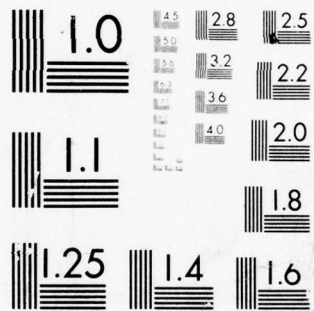
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PHOTOISOMERIZATION OF BIS(9-ANTHRYL)METHANE AND OTHER LINKED ANTHRACENES.

THE ROLE OF EXCIMERS AND BIRADICALS IN PHOTODIMERIZATION.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of linked anthracenes capable of storing photon energy through endo- ergic valence photo-isomerization have been studied. Photophysical and photo- chemical characteristics of the systems have been completely characterized by measurement of fluorescence quantum yields and lifetimes, and efficiencies for forward and reverse isomerization. The release of energy stored in photoisomers has been measured using kinetic and calorimetric techniques. From emission and lifetime data the respective roles of excimers and biradicals in anthracene photodimerization have been defined.		

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PHOTOISOMERIZATION OF BIS(9-ANTHRYL)METHANE AND OTHER LINKED ANTHRACENES.

THE ROLE OF EXCIMERS AND BIRADICALS IN PHOTODIMERIZATION.¹

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ABSTRACT

Fluorescence characteristics including quantum yields and lifetimes, and quantum efficiencies for photoisomerization ($1 \rightarrow 2$) for a series of anthracenes linked at the 9-position have been measured. Emission yields and lifetimes (nsec) decrease for the series, dianthrylcarbonate ($\tau_f = 5$), dianthryl ethanes, ($\tau_f \sim 2$), dianthrylmethanes ($\tau_f \leq 1$). Quantum yields are not so much a function of chromophore linkage but are responsive to the substitution pattern at 10,10' positions. For dianthrylethanes but not for dianthrylmethanes, excimer emission is observed for sandwich dimers generated in glasses at low temperatures. High photoreactivity for proximal anthracenes is identified with intersecting plane as opposed to parallel plane (sandwich excimer) geometries. In accord with recent theory, biradicals are proposed as intermediates in photodimerization. Formation and partitioning of these species ($1,4$) respectively control excited singlet lifetimes and photodimerization quantum yields. Thermochemical and kinetics data for the thermal back reaction ($2 \rightarrow 1$) are reported. The measurement and significance of latent heats of isomerization (photon energy storage) are discussed.

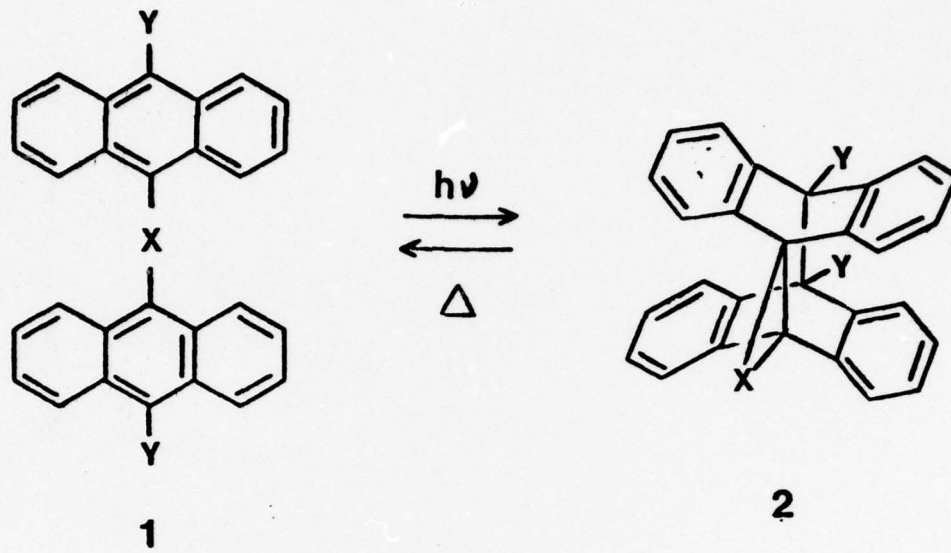
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Anthracene dimerizations have a long and important history in photochemistry. Solid state photodimerization is generally observed and routine photolysis of moderately concentrated solutions of anthracene and a host of its derivatives leads to photodimers with relatively high chemical and quantum efficiency.³ Photodimerization of the parent system was first reported in 1866⁴ and quantum yield data were available as early as 1925.⁵ The mechanism of photodimerization has been examined extensively over the last two decades, including an impressive gathering of spectroscopic and other photophysical data.⁶

It is not so widely appreciated that dimerization of anthracenes is a photoreaction which reversibly stores a significant fraction of photon energy as chemical potential energy⁷ (i.e., the thermal back reaction is exothermic; vide infra). Weigert was the first to note this feature of storage and conversion of radiant energy.⁸ More recently, anthracene photodimerization has been considered prototypical of cyclic organic systems with some potential for reversible storage of solar energy.⁹

We were attracted by an energy storage feature of linked anthracenes, intramolecular photoaddition of which requires formation of a small ring ($\lambda + \lambda$, where λ = one- or two-atom link). Increased bond angle strain in photoisomers was expected to significantly amplify photon energy fixation. Linked chromophores also provide the possibility of enhanced absorption at long wavelengths due to chromophore interaction. Thus, a study of linked systems in principle provides an assessment of the potential for driving increasingly endoergic reactions with photons of decreasing energy.

The linked anthracenes were also expected to provide a test regarding intermediates in photodimerization. According to a widely held view of the



	<u>X</u>	<u>Y</u>
(a)	-CH ₂ -	H, H
(b)	-CHOH-	H, H
(c)	-CHOH-	H, OCH ₃
(d)	-CH ₂ CH ₂ -	H, H
(e)	-CH ₂ CH ₂ -	CH ₃ , CH ₃
(f)	-OCO ₂ -	H, H
(g)	-CH ₂ CH ₂ -	-CH ₂ CH ₂ -

mechanism,⁶ excited singlet and ground state anthracene molecules diffuse together in an attractive way. A sandwich excimer is formed when the interaction reaches a critical distance (3.5 Å for anthracene). Closer approach from this stage results in sigma bond formation finally leading to photodimer. Clearly, the binding of anthracene moieties at rather short distances and at various angles prescribed by overall molecular geometry (as in 1) places severe restrictions on the degree of excimer-like stabilization (known to be at a maximum in a parallel sandwich arrangement). Less obvious are the effects of reducing the number of possible arrangements of anthracene moieties on the rate of internal photocycloaddition. In order to more precisely define the role of excimers in photodimerization our efforts were directed to (1) obtaining physical evidence for excimer states for the closely linked anthracenes under environmental conditions which favor chromophore interaction and (2) correlating any observed tendency for excimerization with photoreactivity.

Results and Discussion

Spectral Data. Absorption spectra for 1 are, in general, the same as unlinked anthracenes with similar substitution.¹⁰ Of special note, however, are the relative intensities of the vibronic bands of the long wavelength ${}^1A \rightarrow {}^1L_a$ absorption. In each case the vibronic bands decreased in intensity on going from long to shorter wavelength. (Absorption data are summarized in the Experimental Section.) The absorption spectrum of tetrabenzo(2.2)paracyclophane (1g) is quite different with a series of broad overlapping bands tailing into the visible range (out to 550 nm). This absorption is the result of a strong interaction between aromatic chromophores (exciton splitting and anthracene ring distortion). The spectrum has been considered in detail by several authors¹² and will not be dealt with here.

The fluorescence spectra of λ in fluid solution at 25° are in general the normal, mirror-image emissions (with small Stokes-shifts) characteristic of substituted anthracenes. Compound λ_d and λ_e are exceptional in that they have broad, overlapping vibronic bands as illustrated for λ_d in Fig. 1. The tetrabenzo(2.2)paracyclophane λ_g does not fluoresce within our capabilities of detection even at low temperature. These observations are consistent with those of Kaupp¹³ and of Mataga *et al.*¹⁴ but not those of Shizuka *et al.*^{12c} At 77 K in 2-methyltetrahydrofuran (2MTHF) glass we observed an emission similar to that reported by Shizuka. We have not assigned this emission as fluorescence from λ_g for the following reasons. The excitation spectrum was markedly different ($\lambda_{\text{max}} = 410 \text{ nm}$) from the absorption spectrum of λ_g ; emission intensity was not diminished but somewhat enhanced on irradiation until a point where the absorption spectrum of λ_g disappeared (*i.e.*, it was entirely converted to photoisomer λ_q which does not absorb in this region). Finally, solutions of λ_g were slightly unstable presumably forming polymeric (potentially fluorescent) material with alternating 1,2-ethylene and 9,10-anthryl linkages. This polymerization is pronounced at higher temperatures.^{12a}

A more rigorous search for excimer or other unusual emission from λ was conducted using the low temperature photocleavage technique introduced by Chandross and Ferguson¹⁵ and applied recently to a number of relevant systems.¹⁶ The approach involves the synthesis of "sandwich dimers" or "broken dimers" by short wavelength photolysis of photodimers at 77 K (or lower). Irradiation (254 nm) of λ_{a-c} in 2MTHF glasses gave samples which displayed only normal fluorescence (that observed for λ_{a-c} in glasses at 77 K or in fluid solution at room temperature). Unusual or long wavelength excimer emission common to anthracene sandwich dimers^{16a,b} was not observed, even on using a more rigid hydrocarbon glass (3:2 methyl cyclohexane/decalin^{16a}).

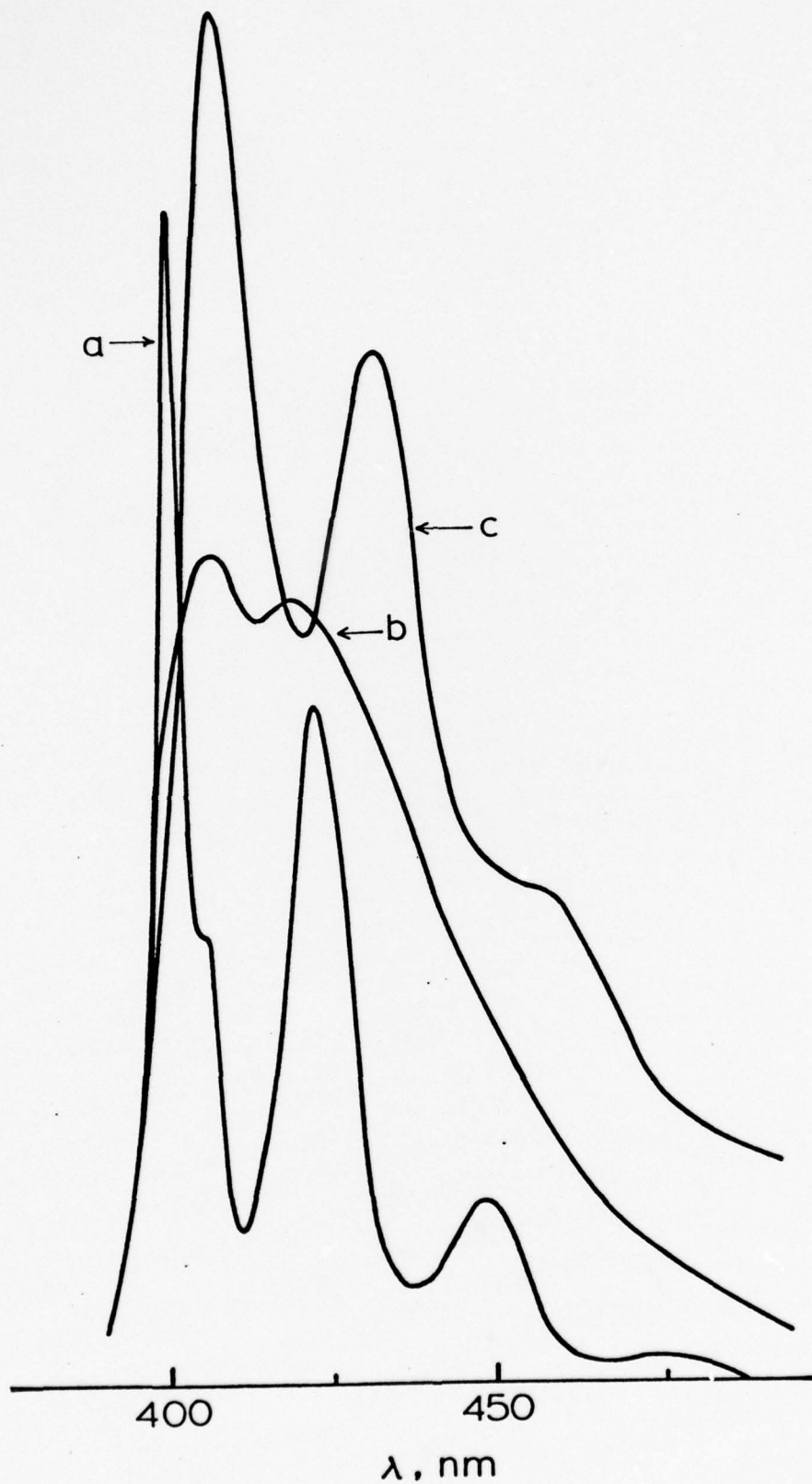
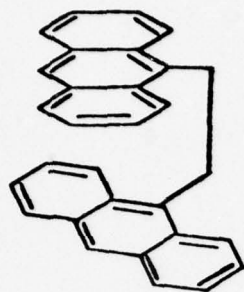


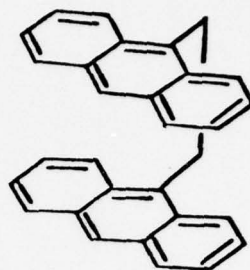
Figure 1. Fluorescence spectra of 1,2-bis(9-anthryl)ethane in 2MTHF: a) 77°K, b) 300°K, c) 77°K from photolysis of photoisomer $2d$. When sample is melted and refrozen, emission c) reverts to a).

Cleavage of photoisomer $2d$ in a 2MTHF glass at 77 K gave a sample which displayed an emission spectrum deceptively similar to the fluorescence of $1d$ at 77 K. Notable however was an 8 nm red shift in the principal vibronic bands and a weak structureless emission which extended to longer wavelengths (Fig. 1). The spectral characteristics of $1d$ have been the subject of several recent reports.¹⁴ Emission from $1d$ appears to be a complicated and subtle function of medium, temperature, excitation wavelength, and mode of generation of the linked anthracene (photocleavage vs. ordinary dissolution). The consistent pattern, however, is the appearance of two types of emitting species. The first is responsible for a slightly red-shifted ("P"^{17a} or "Type I"^{17b}) fluorescence (< 500 nm) which may or may not have structure and which is observable even at room temperature (prominently in polar solvents^{17c}). The second family of emissions ("Q"^{17a} or "Type II"^{17b}) occurs at longer wavelengths (> 500 nm) only after photocleavage in glasses or in crystals where lattice constraints are important. These two types of emitting species have been associated with partially and fully eclipsed conformations of $1d$ (3 and 4), rotamers or families of rotamers representing, respectively, minimal and more pronounced interaction of anthracene moieties. We identify the principal 77 K emission shown in Figure 1 as Type I fluorescence (the Type II emission is barely detectable in a 2MTHF glass). The room temperature spectrum is most likely a combination of "monomer" (extended conformer 5) and Type I emission (vide infra).

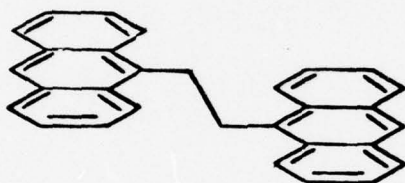
Excimer fluorescence was not observed for the carbonate $1f$ at room temperature in fluid solution. Short wavelength photolysis of $2f$ in low temperature glasses appeared to be complicated; clean photocleavage to the broken dimer did not occur. Other reports of emission from dianthracenes linked by three or more atoms include the observations of (1) no fluorescence for 6 (after matrix photocleavage)¹⁸, (2) fluorescent and non-fluorescent conformations of similarly



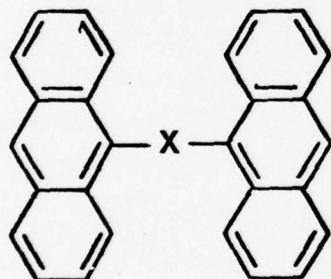
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6 X = $-\text{CH}_2\text{CH}_2\text{CH}_2-$

7 X = $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$

8 X = $-\text{CH}_2\text{OCH}_2-$

9 X = $-\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2-$

10 X = $-\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}_2\text{C}-$

11 X = $-\text{COOCO}-$

prepared λ ¹⁸ (3) normal "monomer" fluorescence for λ ¹⁹ (4) dual (Type I and Type II) emission from λ ¹⁹ and λ ²⁰ and (5) a 520 nm (Type II) fluorescence ($\phi_f = 3.5 \times 10^{-3}$) for λ ²¹. The latter measurements were made at room temperature. The report by Ferguson¹⁸ is part of a comprehensive study of linked anthracenes (anthracenophanes and dianthrylalkanes) in which emission and absorption spectra have been recorded for a wide range of temperatures and a variety of species have been identified.

Principal conclusions drawn from the spectral data involve the relationship between linked anthracene structure and the tendency toward excimerization or excited state delocalization (the extent to which excited states are stabilized due to the interaction of chromophores). (1) The dianthrylmethanes (λ _{a-c}) are negligibly stabilized through overlap of anthracene pi systems. The distance and angular dependence of exciton splitting^{6b} is severe enough to preclude any benefit from a slight distortion away from the presumed (ground state) equilibrium geometry (interplanar angle = 110°). Moreover, the system resists any detectable compression of the rings which might have been enforced in a low temperature matrix (photocleavage technique). Excited states for λ _{a-c} are essentially localized. (2) For the dianthrylethanes, excimer geometries are achievable, depending on dianthracene environment. Distortion away from the near sandwich ground state geometry (for λ ₄, an interplanar angle of 38° and an average interplanar distance of about 3.5 Å) is beneficial in the excited state. A secondary minimum representing limited pi-pi interaction is readily achieved for unrestricted λ _{d,e} (Type I species, e.g., λ ₃ or some other "intermediate" geometry),²² whereas more significant relative stabilization of the excited state results from enforcement of a compressed geometry in a rigid matrix (Type II species for broken dimers, e.g., λ ₄). (3) The appearance of excimers for the systems having larger than two-atom links is a complex function

of the population of conformations with overlapping anthracenes and the competition of modes of decay for these geometries (particularly, the relative rate of reactive decay - vide infra - which is more important at higher temperatures).

Photoisomerization. Quantum yield and Lifetime Studies. Photoisomerization of each of the linked anthracenes J has been previously reported^{12-14,17,23} with the exception of J_c which is a new compound. Quantum yields for forward and back reaction are shown in Table 1 along with fluorescence yields and lifetimes for the linked anthracenes in benzene. Trends in the photochemical and photophysical data are as follows. (1) Isomerization quantum yields depend less on the type of linkage X and more on the nature of substituents Y. (2) Fluorescence quantum yields and lifetimes depend primarily on X and not on Y. The series methanes < ethanes < carbonate J_f is followed for emission yields and lifetimes. (3) The sum of quantum yields for photoisomerization (forward and back) and fluorescence ($\phi_{12} + \phi_{21} + \phi_f$) are nearly unity (estimated error of 10% for each determination). Fluorescence for photoisomers J_g was not observed.

The linked anthracenes show important similarities to unlinked systems. A large number of anthracene derivatives have been shown to photodimerize with efficiencies in the range 0.05 - 0.25 at the high concentration limit.^{3b,24} In addition, phenomenological rate constants for photoisomerization (ϕ_{12}/τ_f ; for J_{a-c} , $0.1-1.0 \times 10^9 \text{ sec}^{-1}$) compare favorably with pseudo first-order constants for photodimerization of anthracene and 9-substituted derivatives,^{3c,d} $0.4-1.0 \times 10^9 \text{ sec}^{-1}$ at 1 M, a concentration well above the level of complete concentration quenching of anthracene fluorescence (i.e., where virtually all excited state deactivation is bimolecular). These data point to a similarity of inter- and intramolecular cycloadditions with regard to processes which limit lifetime and which lead to reaction inefficiency.

Table 1. Photochemical and Photophysical Data for Linked Anthracenes λ .

System	ϕ_{12}^a	ϕ_{21}^a	ϕ_f^b	$\tau_f^b(\text{nsec})$	$k_q\tau(M^{-1})^c$
(a)	0.15	0.76	0.06	1.1	11.1
(b)	0.29	0.81	0.02	0.3	5.3
(c)	0.05	(0.70)	0.02	0.3	<0.03
(d)	0.26	0.55	0.16	1.7	15.6
(e)	0.04	--	0.14	2.0	2.7
(f)	0.02	--	0.30	4.0	72.2
(g)	0.36	0.60 ^d	<0.001 ^e	(\sim 0.03) ^f	0.33

^aIsomerization quantum yield, benzene, 25°; $\lambda \rightarrow \lambda'$, 366 nm, $\lambda' \rightarrow \lambda$, 285 nm.

^bFluorescence yield and lifetime in benzene, 25° (single photon counting measurements except where noted).

^cStern-Volmer quenching constant for N,N-dimethylaniline (DMA) quenching of fluorescence in benzene.

^{d,e}Note Ref. 21.

^fFrom DMA quenching of photoisomerization.

Sensitization and Quenching Experiments. Although anthracene photodimerization is now well established as a singlet reaction,²⁵ we wished to exclude an important role for triplets in linked anthracenes for reactive (and unreactive) decay. Known rate constants for intersystem crossing in anthracenes fall in a

narrow range around $5 \times 10^7 \text{ sec}^{-1}$.^{6f,9} The sum of depletion rates (from the lifetimes) for one- and two-atom linked anthracene singlets corresponds to $k = 0.5 - 3.3 \times 10^9 \text{ sec}^{-1}$. A significant role for triplet states appears to be excluded, barring an unusual rate enhancement for intersystem crossing in linked systems. Support for this view was obtained through attempts at sensitization by acetophenone or *m*-methoxyacetophenone ($E_T = 74$ and 72 kcal/mol , respectively) both of which are capable of populating T_1 and T_2 states of λ .²⁶ Photoisomerization could not be effected in either case. Acetophenone sensitization resulted in small non-thermally reversible (*vide infra*) loss of λ_a and λ_d ($\phi < 0.01$), attributed to hydrogen abstraction from λ . Photoexcited *m*-methoxyacetophenone (which is inefficient at photoreduction²⁷) caused no change in λ_a or λ_d .

Anthracene singlet states are quenched by amines, including aromatic amines such as *N,N*-dimethylaniline (DMA).^{6f,n,28} Plots of ϕ_0/ϕ vs. $[\text{DMA}]$ were linear for the quenching of photoisomerization and fluorescence of λ . Emission quenching was accompanied by the appearance of a broad structureless new emission for the amine exciplex²⁸ ($\lambda_{\text{max}} = 490 \text{ nm}$). The quenching rate constants obtained from the Stern Volmer slopes ($k_q\tau$) and lifetime data (Table 1) are at the limit for diffusion controlled quenching of $\lambda_{a,b,d}$ ($k_q = 0.9 - 1.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$). The quenching rate is diminished for 10,10'-substituted linked anthracenes (λ_c and λ_e , $k_q \leq 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$). The photoisomerization of the nonfluorescent paracyclophane λ_g can be partially quenched; a fluorescent amine exciplex was not observed in this case. Using the limited Stern-Volmer data and assuming $k_q = 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, a lifetime of about 30 psec for λ_g can be calculated.

Values of $k_q\tau$ for quenching of photoisomerization and fluorescence of λ are virtually identical, suggesting that emission and photoreaction have a

common origin in excited singlet I_1 . The data suggest further that the amine exciplexes do not give significant amounts of photodimer, in contrast with reports of anthracene-amine exciplex photoreactivity.⁶ⁿ Conjugated dienes are known to enhance anthracene photodimerization.²⁶ In experiments with I_b , I_d , and I_g , however, 1,3-cyclohexadiene did not alter (within experimental error) the quantum yield of photoisomerization.

Saturation of solutions of I_a and I_d with oxygen, an efficient scavenger of anthracene triplets,²⁹ did not significantly affect the rate of disappearance of I or the chemical yield of photoisomer. Oxygen saturation weakly quenched ($\sim 5\%$) the fluorescence of I_a and I_d . Significant involvement of oxygen in the formation of photoproducts (endoperoxides²⁹) was excluded by repeated photoisomerization to high conversion in oxygen saturated solutions. After reduction of anthracene absorption to $< 0.1\%$ of its original value, the original spectrum could be restored entirely by thermal reversion of the photoisomer. The rate of reversion was identical to that for the pure photoisomer. By conservative estimate, the triplet yield for I_a and I_d is no more than 10%.

Thermal Back Reaction, Storage Enthalpies and Kinetics. The thermal cycloreversion of photoisomers was studied in several cases. Linked anthracenes were regenerated quantitatively on pyrolysis of 2a and 2d ($120 - 150^\circ$) and 2g ($50 - 70^\circ$) in benzene or o-dichlorobenzene (10^{-4} M solutions). The reactions were followed spectrophotometrically and shown to be first order. Arrhenius parameters and relative rates are shown in Table 2 along with heat of reaction data obtained by differential scanning calorimetry. The heating of crystalline photoisomers in sealed pans produced exotherms over the temperature ranges given; melting endotherms were observed at higher temperatures. Samples which remained solid during thermal reaction were shown spectrophotometrically to have been isomerized. Due to the very low solubility of photoisomers, the heats of reaction in solution could not be determined by DSC.

Table 2. Heats of Reaction and Kinetic Parameters for Thermal Reversion of Anthracene Photocycloadducts.

	ΔH , kcal/mol ^a (temp., °C)	Arrhenius Parameters		
		E_a (kcal/mol)	Log A	k_{rel} (130°)
$2a \rightarrow 1a$	17.3 (176 - 202°)	32.7	15.4	4.0
$2d \rightarrow 1d$	14.6 (165 - 190°)	32.8	15.9	13.
$2g \rightarrow 1g$	8.5 (125 - 135°)	22.3	12.2	4400.
$13a \rightarrow 12a$ ^b	15.6 (25°) ^c	37.1	14.0	.0007
	8.4 (220 - 250°) ^d			
$13b \rightarrow 12b$ ^b	20.0 (125 - 150°) ^e	30.9	14.8	11.
$13c \rightarrow 12c$	19.7 (35 - 65°) ^e			

^aHeats of reaction determined by differential scanning calorimetry on solid samples (temperature ranges for exotherms as shown) unless otherwise indicated. Cracking reactions $13 \rightarrow 12$ correspond to the reversion of photodimers of (a) anthracene, (b) 9-cyanoanthracene, and (c) 9-acetoxy-10-cyanoanthracene.

^bRef 3e.

^cFrom heats of combustion for anthracene and photodimer, ref 30.

^dRef 7b.

^eRef 31.

Two features of the thermolysis data are striking. Fusion of a small ring onto photodimers does not accelerate the thermal back reaction to the extent that might have been expected (activation energies for all cases so far measured, excepting 2g - linked and unlinked photodimers, Table 2 and ref 3e - fall between 30 and 37 kcal/mol).³² As suggested by Greene^{3e} the rate determining step does not appear to include opening of the bridging (small) ring, since a release of ring strain (up to 25 kcal/mol) is not manifest in a substantially lowered activation energy. The data require a non-synchronous mechanism the leading portion of which is cleavage of the bond connecting 10,10' positions (vide infra). The sensitivity of the reaction rate to modification of Y substituents (the relative instability of 2e ³³ and 2g) is consistent with this view.

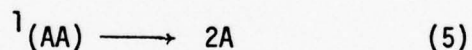
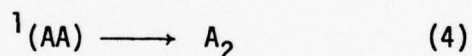
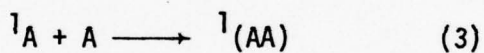
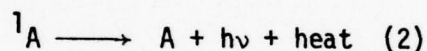
The heat of reaction data are puzzling due to the absence of any exothermic component associated with small ring cleavage for 1 . These ring strain increments which permissibly fail to lower kinetic stability must be important in determining the overall heat of back reaction. Bond energy calculations do not provide reliable reference points due to the unusual bond lengths³⁴ and angles³⁵ present in photodimer structures. Further problems arise in comparing reaction enthalpies determined by scanning calorimetry of solid samples. Reaction temperature differences and differential heat capacities obscure true differences in standard heats.^{7c} In addition, crystal packing forces (differential heats of sublimation for reactants and products^{3e}) cannot be neglected. We conclude that the available thermochemical data only crudely reflect the amount of latent heat which is stored in anthracene photodimers in solution.³⁶⁻³⁸

General Discussion

Anthracene photodimerization has been almost universally understood in recent years⁶ in terms of the mechanism shown in Scheme I, where A and A₂

symbolize anthracene monomer and photodimer, respectively. Support for the intervention of excimers (step 3) rests in a complementarity of spectroscopic and photochemical results. For a number of systems, excimer formation and photodimerization are parallel observations, and for others a lack of correspondence can be reasonably explained.^{6a} Low temperature,^{6k} quenching⁶ⁱ and temperature dependence^{6l} data permit that excimers are intermediates in photodimerization, and recent strongly worded arguments^{6e} point to their necessity for photoreaction.³⁹

Scheme I



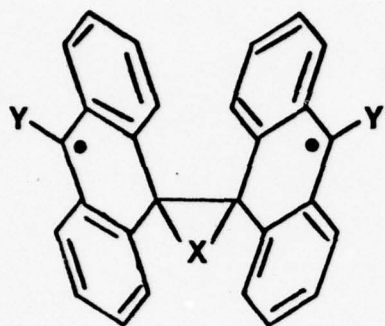
Accepting that anthracene pairs interacting in the excited state seek out energy minima with sandwich geometries which may lead to photodimer, several important questions of detail remain. (1) What range of interaction geometries is acceptable for photodimerization (i.e., are "edge to edge" and other arrangements of anthracene molecules subject to penalty in rate of cycloaddition)? (2) Besides minima associated with excimerization, what are the other important features of the reaction coordinate? What are the geometric details for further movement away from an initial (e.g., plane parallel) geometry and intersection

with the ground surface? Are other minima involved? Do one or more bonding steps lead to photodimer? (3) What is the nature of unreactive radiationless decay and is it closely associated with decay to photodimer?

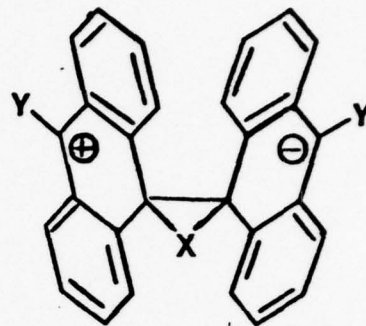
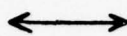
The value of linked systems in defining the dependences of photophysical and photochemical properties on geometry is apparent in recent reviews.⁴⁰ Two principal findings from our study of $\lambda \rightleftharpoons \zeta$ focus on structure-reactivity characteristic for the one- and two-atom linked systems (note again the divisions in Table I). (1) Excited singlet states for the dianthrylmethanes λ_{a-c} and -ethanes $\lambda_{d,e,g}$ are very short lived ($\tau_f \leq 2$ nsec). Photophysical processes (e.g., fluorescence, intersystem crossing, $k \leq 10^8 \text{ sec}^{-1}$) and direct formation of valence isomers ζ ($\phi_{12} < 1.0$) cannot account for such rapid decay. Required then is the intervention of at least one photochemical intermediate, formation of which is lifetime limiting and partitioning of which (to λ and to ζ) is quantum yield determining. The uncoupling of steps is especially apparent in the lack of correlation between ϕ_{12} and τ_f for the series. (2) Rapid decay of excited singlets λ is not a function of any expected or observed tendency for the linked systems to form excimers. The high reactivity of the dianthrylmethanes ($\tau_f \leq 1$ nsec) is especially notable.

\mathcal{H} The effective quenching of "monomer" fluorescence does not require the attainment of a sandwich configuration. Paths for photoreactive decay for anthracene pairs with overlapping edges (or overlapping points) are at least as favorable as geometries with two overlapping parallel or nearly parallel planes. Indeed, measured fluorescence lifetimes are relatively long for a number of substituted anthracene excimers (e.g., 9-methylanthracene, $\tau_f = 13.4$ nsec, 9-ethylanthracene, $\tau_f = 22$ nsec)^{3b} which show by their spectral shifts a high degree of stabilization (a large equilibrium constant for excimerization due to the accessibility of sandwich geometries). Likewise, the rather stable linked excimer of \mathcal{g} is long lived at room temperature ($\tau_f = 37$ nsec).²⁰ The lifetime of the parent anthracene excimer, which should display the least inhibition for reaction from a parallel plane geometry, is 1.5 nsec.⁴¹ Since steps for singlet decay and photoisomer formation remain uncoupled for the short lived dianthrylmethanes, a photochemical intermediate other than an excimer must be considered.

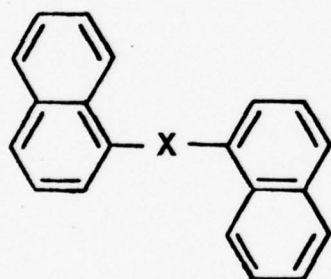
The geometrical constraint for the dianthrylmethanes provides a clue to the nature of a sufficient intermediate for photoisomerization (photodimerization). 9,9'-Positions in \mathcal{I}_{a-c} are very near bonding distance (2.1 Å) at an equilibrium (ground state) geometry. A slight attractive and buckling movement of the rings results in formation of species \mathcal{I}_4 . Biradicals of this sort, in which odd electron centers are weakly coupled (open shell systems with degenerate sets of essentially non-bonding orbitals) have been the subject of much recent discussion.⁴² Biradical geometries require a set of rather closely lying electronic states in the singlet manifold with varying contributions from canonical forms ($\mathcal{I}_{4a} \leftrightarrow \mathcal{I}_{4b}$).^{42a,b,43} The potential importance of biradicals, which results from the avoided crossing of ground and excited surfaces, in most organic photochemical reactions (a general biradical theory of reactive radiationless decay) is now well recognized.^{42b,c,44} Michl has provided a preliminary application of the theory to anthracene photodimerization.^{44a}



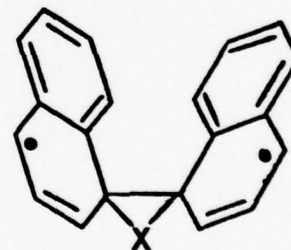
14a



14b



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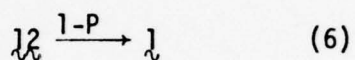
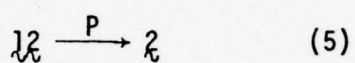
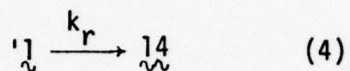
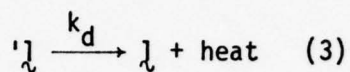
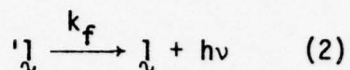
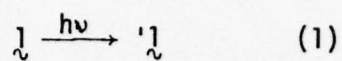


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The simplest mechanism for photoisomerization of 1 , incorporating 14 as an intermediate, is shown in Scheme II. Rate constants and partition factors can be calculated using the relationships, $k_f = \phi_f/\tau_f$, $k_r + k_d = 1 - \phi_f/\tau_f$, and $P = \phi_{12}/k_r\tau_f$, and assuming $k_d \cong 10^8 \text{ sec}^{-1} \ll k_r$. Notable features of the resultant data, shown in Table III include the following: (1) k_f 's fall in the range ($\sim 10^8 \text{ sec}^{-1}$) expected for substituted anthracenes ^{3b,c} (2) Reactive decay (k_r) is a dominant and increasing portion of non-radiative decay ($k_r + k_d$) in the series carbonate ($1f$), ethanes ($1d-e$), methanes ($1a-c$), paracyclophanes ($1g$). (3) Partition factors fail to match measured quantum efficiencies for photoisomerization only to the extent that fluorescence of 1 is competitive. (4) The carbinols $1b,c$ show several peculiarities; non-radiative decay is especially rapid and partitioning factors show both favor ($1b$) and disfavor ($1c$) for photoisomers.

The most plausible effect of hydroxy group substitution in $1b,c$ on biradical formation and partitioning (excepting some artifact of intramolecular hydrogen bonding) involves the influence of an electron donating substituent on the strength of cyclopropane ring bonds. Hoffmann⁴⁵ originally proposed, on the basis of qualitative molecular orbital considerations and extended Huckel calculations, that an electron donating substituent should weaken the transannular bond of a cyclopropane ring. Recent experimental results on norcaradiene-cycloheptatriene equilibria and theoretical considerations by Staley⁴⁶ suggest to the contrary that groups such as amino or hydroxyl contribute a resistance to cyclopropane ring opening. The observed accelerated biradical formation (cyclopropane ring closure to give 14) observed for $1b,c$ and the high partitioning factor in favor of photoisomer for $1b$ are consistent with the latter view of the substituent effect.⁴⁷

Scheme II



The mechanism in Scheme II requires elaboration with regard to the photoisomerization of dianthrylethanes and other systems with longer links (e.g., $\overset{\sim}{\lambda}g, \overset{\sim}{\lambda} - \overset{\sim}{\lambda}l$). The dynamics of myriad interconverting conformations must be considered, and computed rate constants represent composites of the decay of a number of geometries (energy minima) which may emit or react. We have not attempted a dissection of this more complicated scheme but note that, for $\overset{\sim}{\lambda}d$ and $\overset{\sim}{\lambda}e$, a final solution will contend with the room temperature, single exponential but "dual" emission which, according to a generous interpretation of the spectral data, involves two conformations with similar fluorescence yields.^{48,49}

Table III. Kinetic Parameters for Photoisomerization of λ .^a

	k_f	$k_r + k_d$	ρ^b
λ_a	0.55	8.6	0.16
λ_b	0.67	33.	0.29
λ_c	0.67	33.	0.05
λ_d	0.94	4.9	0.31
λ_e	0.70	4.3	0.05
λ_f	0.57	1.3	---- ^c
λ_g	(1.0)	~300.	0.36

^aRate constants $\times 10^{-8} \text{ sec}^{-1}$.

^bCalculated assuming $k_r \gg k_d$.

^cNot calculated since $k_r \sim k_d$.

Surface relationships for the diradical photoisomerization mechanism including experimental points for $\lambda_a \rightleftharpoons \lambda_a$ are shown in Figure 2. Focus on the biradical as the central mechanistic feature⁵² not only accounts for the "reduced" geometric requirement for photoisomerization, and the uncoupling of excited state depleting and product forming steps. Other economies obtain if the biradical is considered a common intermediate for forward and back photoreactions. Kaupp has proposed¹³ that merging, two directional photochemical mechanisms involving biradicals may be generally important. The requirement that quantum yields of fluorescence emission and photoreaction sum to unity is met reasonably well for $\lambda \rightleftharpoons \lambda$. Additional consistency is found

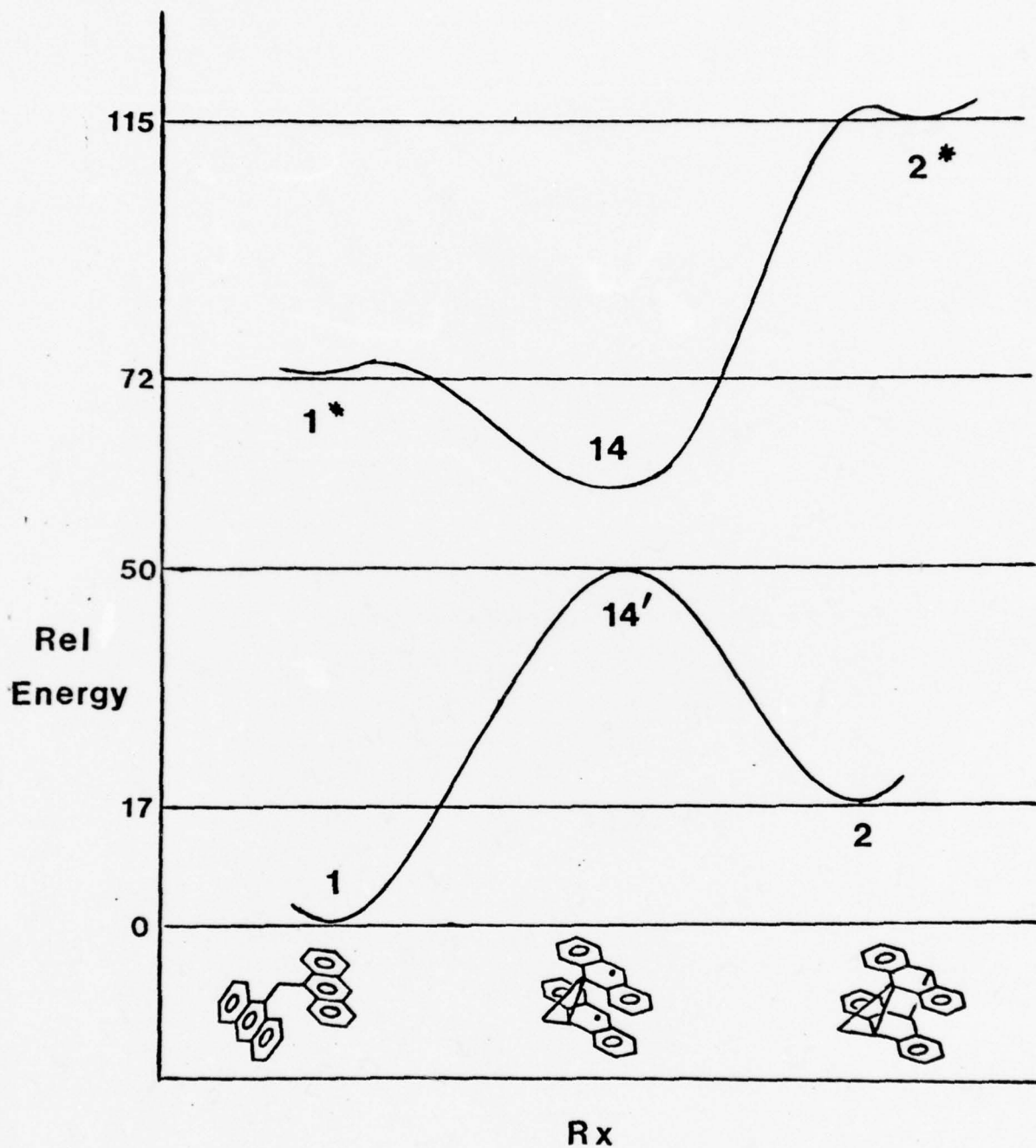


Figure 2. Energy surface relationships for valence isomerization of linked anthracenes including all experimental quantities for the inter-conversions $1a \rightleftharpoons 2a$. Relative energies derive respectively from heat of reaction (solid state only) and activation energy for $2a \rightarrow 1a$, the zero-zero transition for $1a$ from excitation and emission spectra, and absorption data for $2a$.

in the kinetics data for the thermal back reaction. Theory requires that the transition state for the ground surface and the biradical minimum in the excited surface have similar geometries ($14'$ and 14 - figure 2 - are, respectively, the biradical ground and first excited states).^{42b,c,44} The independence of the rate of back reaction on the fusion of small rings onto dianthracenes is the result of this discontinuity in bondbreaking (rate limiting formation of $14'$) on the ground state surface. Fused small rings in ζ remain intact at the biradical transition state.

Important unresolved issues are the lifetime and spectroscopic properties of (excited) biradical 14 . Some insight is provided from the elegant experiment by Forster in which the excited photodimer of 9-methylanthracene was shown to lead directly to 9-methylanthracene fluorescence.⁵⁴ This demonstration of adiabatic photochemistry suggests the permissibility of the path, ${}^1\zeta + 14 + {}^11$ (i.e., that at least a portion of the path which is common to photoreaction in both directions is on an excited surface).

Although the biradical mechanism (with its subordination of the role of excimers) should be general for aromatic photodimerization, the results of Davidson and Whelan⁵⁵ concerning linked naphthalenes do not readily provide support. For a series for 1- and 2-substituted naphthalenes with varying (one- to nine-atom) links, they find a correspondence among internal quenching of monomer fluorescence, formation of excimers, and photoisomerization.⁵⁶ In contrast to the linked anthracenes, dinaphthylmethanes and ethanes show normal yields of fluorescence ($\phi = 0.2 - 0.3$) (their singlets are presumably long-lived); i.e., under demanding geometrical constraint, the linked naphthalenes do not exhibit rapid singlet decay ascribable to something other than excimer formation (generation of biradicals). The data for the linked naphthalenes, in permitting

the intermediacy of excimers, do not exclude the central role of biradicals in radiationless decay in cases where photoisomerization takes place. Biradical formation is not revealed, exclusive of excimerization, for $\lambda\lambda$ ($X =$ one- and two-carbon links) (indeed, photoreaction is not observed) probably due to energetic prohibition. The cost of ring closure ($\lambda\lambda \rightarrow \lambda\lambda$) where small rings are formed is forbidding when added to the rather expensive loss of resonance energy (delocalization energy for one naphthalene ring is 50% higher than that for the central ring of anthracene⁵⁷).

In summary, we conclude that excimerization and photodimerization of anthracenes have different geometrical requirements. The finding that "edge to edge" arrangements of proximal anthracenes are entirely appropriate for photodimerization reveals a significant discontinuity in bond forming steps. The formation and partitioning of biradicals ($\lambda\lambda$) account for all significant non-radiative decay of excited anthracene pairs. The data further suggest that excimers are not sufficient or necessary but permissible intermediates in the self-quenching of aromatic fluorescence and in photodimerization; indeed, they constitute attractive minima (for plane-parallel encounters of anthracene molecules) on the excited surface, staging areas for the crucial disposition of meso positions for biradical formation. The biradical partitioning mechanism and its geometrical requirement has significance for diverse observations including (1) the relatively short life of the "55° dimer" of anthracene at low temperatures,²² (2) the portion of concentration quenching of anthracene fluorescence which is not due to excimer formation,⁵⁸ and (3) the stereochemical adaptation of disordered regions of anthracene crystals for photodimerization in the solid state.⁵⁹

Experimental Section

General. Linked anthracene starting materials were purchased from Aldrich Chemical Co. The 2-methyltetrahydrofuran was obtained from Other chemicals were reagent, analytical or spectro grade. N,N-dimethyl aniline was treated with acetic anhydride and distilled (center cut); benzene was treated with H₂SO₄, washed with distilled water, dried (MgSO₄) and distilled. Decalin was passed through alumina (activity grade 1). Elemental analyses were performed by Galbraith Laboratories, Nashville, Tennessee. Melting points are uncorrected.

Bis(9-anthryl)methane (1a) was prepared by the method of Applequist.^{23a} 1,2-Bis(9-anthryl)ethane (1d) and 1,2-bis(10-methyl-9-anthryl)ethane (1e) were prepared by the method of Stewart,⁶⁰ noting the identifications made by Bouas-Laurent.⁶¹ Tetrabenz[2.2]paracyclophane (1g) was prepared according to the procedure by Golden^{12a} and purified by successive recrystallization from benzene/chloroform, and methylene chloride. Bis(9-anthryl)carbonate (1f) was a gift from Professor D. E. Applequist.

Bis(9-anthryl)carbinol (1b). Addition of 11.3 ml (22.6 mmol) of a 2.0 M butyllithium solution to a dry ether solution of 5.80 g (22.6 mmol) of 9-bromoanthracene⁶³ in 150 ml of ether gave a yellow orange heterogeneous mixture. A solution of 4.65 g of 9-anthraldehyde was added and the mixture stirred for 1.5 hr. After partitioning with aqueous NH₄Cl, the dried (MgSO₄) ether extract was evaporated to give 8.8 g of a yellow solid, mp 170-195°. Two recrystallizations from benzene afforded pale yellow needles, mp 209-211° (lit.⁶² 190-199°).

(10-methoxy-9-anthryl)-9-anthrylcarbinol (1c). 9-Methoxy-10-bromoanthracene⁶⁴ was prepared from 9-methoxyanthracene⁶⁵ and converted into 1c using the procedure described for bis(9-anthryl)carbinol (1b). Crystals from benzene, mp 211-14°; ir (CHCl₃) 3660 sp, 2850 sp, 1452 m, 1370 m, 1100 m; nmr (diglyme d₁₄) 3.40 (1H, d, J = 5Hz, -OH), 4.05 (3H, s, -OCH₃), 5.30 (1H, d, J = 5Hz, -CH-),

7.00-9.00 (17H, m, aromatic) uv (ϕ H) (essentially a composite of 9-methyl-10-methoxyanthracene and 9-methylanthracene), see Table 3. Anal. C, H.

Preparative Photoisomerization of Linked Anthracenes.²³ Samples of 1 (0.2 - 1.0 g in 300 - 500 ml of benzene) were irradiated with Pyrex-filtered light from a 450 W medium pressure mercury lamp in a standard immersion well. The reaction was followed spectrophotometrically and the irradiation terminated when the 350 - 400 nm absorption was reduced to a minimum (usually 1 - 2 hr). Solutions were reduced in volume by 90% by evaporation in vacuo. White crystals which formed were filtered, washed, and dried. Melting points compared favorably with literature data;²³ for $2c$, mp

Purity of Samples. Photopurification. Samples of linked anthracenes proved difficult to purify rigorously. Contamination by unlinked anthracene derivatives was especially worrisome although not readily apparent by analysis of melting point and simple uv absorption. Samples were evaluated by irradiation of deoxygenated solutions at low concentration ($\sim 10^{-4}$ M). Samples were considered of high quality if the absorption in the 300 - 400 nm region could be reduced to 0.5% of an initial value without modification of characteristic peak shapes as a function of irradiation time. Unlinked anthracenes are photostable under these (dilute solution) conditions.

Linked anthracenes $1a$ and $1c$ were further purified by photolysis and crystallization of photoproducts 2 . The photoisomers were heated to the melting point (to regenerate 1) and cooled; the residue was recrystallized once or twice from benzene. This photopurification method gave samples of $1a$ and $1c$ of highest purity (most reproducible fluorescence).

Ultraviolet Spectra. Absorption spectra (Table 4) of benzene solutions of the linked anthracenes were recorded on a Cary 14 spectrophotometer.

Fluorescence Spectra. Emission spectra (Table 4) were recorded using a Hitachi Perkin-Elmer MPF 2A fluorescence spectrophotometer. Low temperature spectra were recorded for samples in 3 mm quartz tubes using a phosphorimetry cryostate accessory (no chopping). Broken dimers were prepared^{15,16} by dissolution in quartz tubes of samples of photoisomers \mathcal{Z} in 2-methyltetrahydrofuran or in 3:2 methylcyclohexane/decalin, glass formation at 77°K and insertion of the phosphoroscope into a semimicro photochemical reactor (Bradford Scientific, Inc.) for irradiation at 254 nm. Fluorescence quantum yields were determined relative to a 9-methylanthracene standard (benzene solution, ϕ_f taken to be 0.49^{6a}).

Fluorescence Lifetimes. Kinetic spectrofluorimetry was carried out on benzene solutions at room temperature using single-photon counting apparatus⁶⁵ and methods⁶⁷ previously described. Emission decay for the linked anthracenes was cleanly first order. Broad band cut-off filters were used, and error limits for lifetimes under these conditions were estimated to be $\pm 10\%$ for $\tau > 1.0$ nsec and ± 0.1 nsec for $\tau < 1.0$ nsec.

Quantum Counting Apparatus. Photochemical Quantum Yields. Apparatus consisted of a Bausch and Lomb High Intensity Monochromator, a super pressure mercury arc point light source, flexible quartz optical fiber light conductors, irradiation cells, and a Rhodamine B quantum counter (with amplifier and recorder) as previously described in part.^{9a} The monochromator exit casing was modified to accept one 2 x 250 mm and one 4 x 250 mm light conductor (Schott Optical Glass, Inc.) which connected respectively the quantum counter and the irradiation cells. The latter were 1 cm quartz cuvettes. The quantum counter employed Rhodamine B/ethylene glycol solution.⁶⁸ Ferrioxalate actinometer was used to calibrate the apparatus (i.e., to determine relative intensities from the 2 and 4 mm light pipes). Irradiations were performed at 366 nm and the

ferrioxalate quantum efficiency at this wavelength was assumed to be 1.21.⁶⁹ Care was taken to match optical densities for calibration and sample solutions.

Quantum yields for isomerization of the linked anthracenes were determined by irradiating 10^{-3} M nitrogen purged benzene solutions with simultaneous monitoring of light intensity. The disappearance of linked anthracene was monitored spectrophotometrically with reference to the intense absorption at ~ 400 nm and other characteristics in this region. Percent conversion to photoproduct was typically 25%. Duplicate measurements indicated a variance of 10 - 15% in absolute quantum efficiency. Similar procedures were used for measurement of the quantum yields for back reaction ($\phi_{\lambda} \rightarrow \phi_{\lambda}$). Benzene solutions of the photoisomers were irradiated at 285 nm and the apparatus was calibrated at this wavelength (ferrioxalate quantum yield assumed to be 1.25).⁶⁹

Relative quantum efficiencies in quenching studies were obtained using a Rayonet RPR - 204 reactor equipped with RVL 3500A lamps and a merry-go-round attachment. Nitrogen purged solutions of the linked anthracenes (10^{-3} M in benzene with added quencher) were irradiated simultaneously in cylindrical 15 mm stoppered tubes (temperature in the irradiation chamber about 32°) and the samples analyzed spectrophotometrically as before. Standard deviations in the slopes and intercepts of plots of ϕ_0/ϕ vs. [quencher] were typically less than 10%.

Table 4. Spectral Characteristics of λ .

Compound	Absorption		Emission	
	λ_{\max}	$\epsilon \times 10^4$	λ_{\max}	λ_{\max} 77°K
λ_a	395	2.45	407	
	374		425	
	355		451	
	334		478	
λ_b	395	2.00	395	
	374		415	
	355		441	
	334		465	
λ_c	405	1.36	419	415
	394		440 broad	438
	387			465
λ_d	395	2.60	409	409
	374		422 broad	423
	355			450
	334			
λ_e	409	2.07	428 broad	416
	385			441
	363			470
	346			
λ_f	388	1.80	395	
	368		415	
	349		440	
	333		464	
λ_g	456 sh	1.05		
	420			
	388			
	383			
	375 sh			
	366			
	342			
315				

Pyrolysis Kinetics. The general procedure involved introduction of solid samples of photoisomers \mathcal{Z} to 25 - 40 ml of redistilled o-dichlorobenzene in a stoppered 50 ml amber Erlenmeyer flask which had been equilibrated at the desired temperature (constant temperature salt bath and apparatus as previously described⁷⁰). The solid samples were rapidly dissolved at bath temperature; resulting solutions were $\sim 10^{-4}$ M. At appropriate intervals 3 ml aliquots were withdrawn and analyzed spectrophotometrically. The appearance of linked anthracene absorption at 350 - 400 nm was monitored as a function of time, and conventional graphical analysis produced excellent first order plots. The procedure was modified for \mathcal{J}_g , \mathcal{Z}_g . Solutions (10^{-4} M) of \mathcal{J}_g in benzene were evacuated and sealed in rectangular 1 cm cuvettes. Irradiation at 365 nm (Bradford Reactor) reduced the paracyclophane absorption in the 400 - 500 nm to a minimum. The cell was placed in a constant temperature water bath ($\pm 0.2^\circ$) and removed periodically for analysis. The appearance of \mathcal{J}_g was monitored at 383 or 420 nm.

First order rate constants for pyrolysis of \mathcal{Z} are tabulated in Table 5. Activation energies and preexponential factors (Table 2) were computed using a least squares program. Errors were estimated⁷¹ for k ($\pm 5\%$), E_a (± 1.5 kcal/mol) and log A (± 1.0).

Thermochemistry. Enthalpies of reaction of \mathcal{Z}_a , \mathcal{Z}_d , and \mathcal{Z}_g were measured using a Perkin-Elmer Differential Scanning Calorimeter Model DSC-1B with an L & N Model W recorder. Solid samples (~ 5 mg) were sealed in standard aluminum volatile sample pans. Thermograms included exotherms corresponding to heats of reaction of samples below the melting point and melting endotherms (in the region of the mp of the reaction product, Fig. 3). Heats were calculated from the integrated areas under curves and calibrated against the melting curve for indium metal according to standard procedures.⁷¹ Spectrophotometric analysis showed that reaction products were the linked anthracenes \mathcal{J} .

Table 5. Kinetics Data for Thermal Isomerization of Photoisomers \mathcal{Z} .

Isomerization	Temp. (°C)	k (sec ⁻¹)
$\mathcal{Z}_a \rightarrow \mathcal{I}_a$	130.0	6.60×10^{-5}
	135.0	1.33×10^{-4}
	140.8	2.67×10^{-4}
	145.0	3.00×10^{-4}
	150.0	4.82×10^{-4}
$\mathcal{Z}_d \rightarrow \mathcal{I}_d$	100.0	7.33×10^{-6}
	120.0	7.72×10^{-5}
	130.0	2.23×10^{-4}
	135.0	3.02×10^{-4}
$\mathcal{Z}_g \rightarrow \mathcal{I}_g$	30.0	2.17×10^{-6}
	35.4	3.95×10^{-6}
	48.0	1.85×10^{-5}
	57.0	3.10×10^{-5}
	61.5	8.43×10^{-5}
	65.0	9.75×10^{-5}

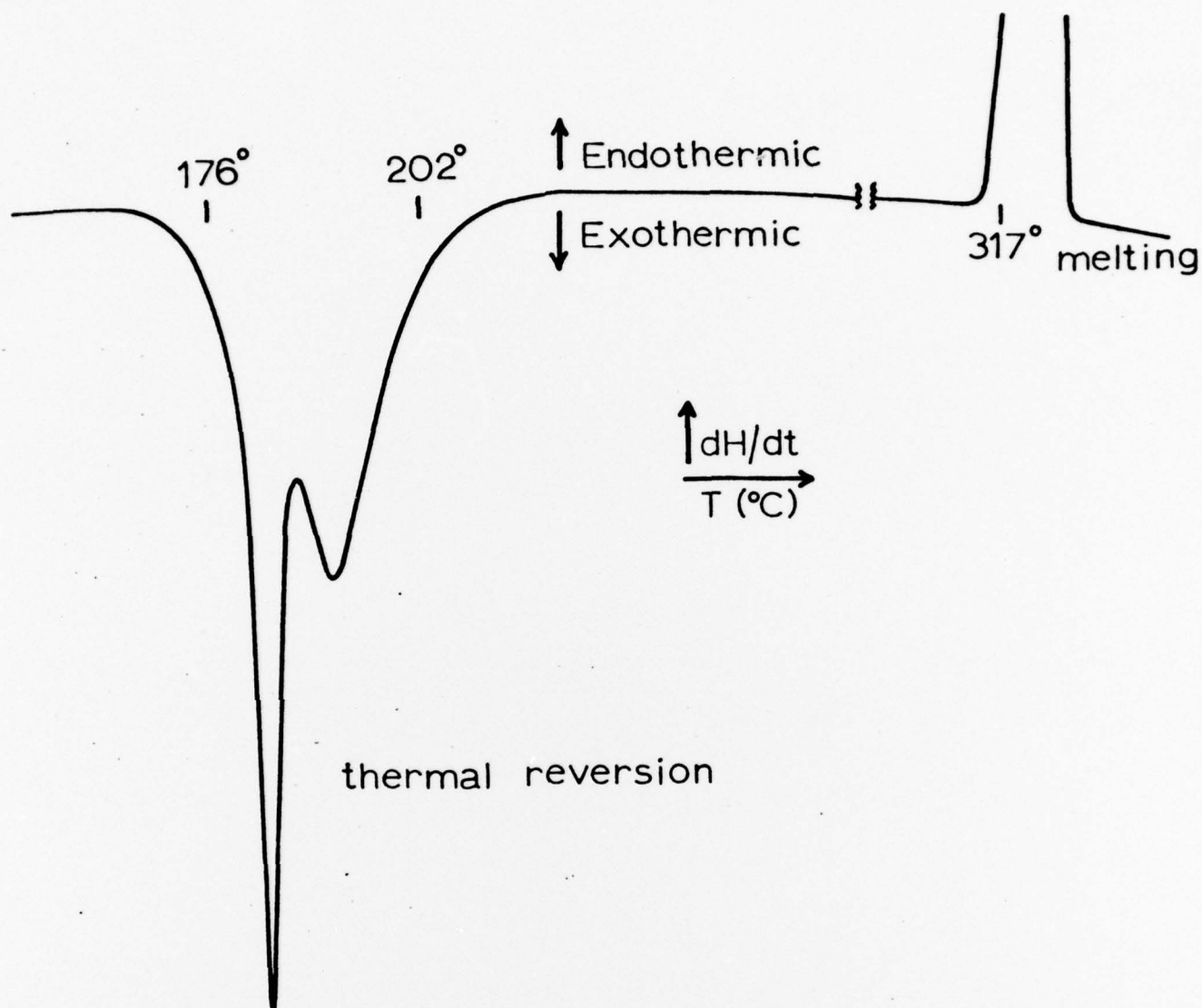


Figure 3. A typical thermogram for solid state thermal reversion of linked anthracene photoisomers. Here a 3.2 mg sample of **2a** is heated at 20°/min. The shape of the curve depends on the heating rate and on the physical characteristics of the sample. The "structure" of the exotherm may be due to differential rates of isomerization and reorganization of the crystal lattice (see ref 31b).

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