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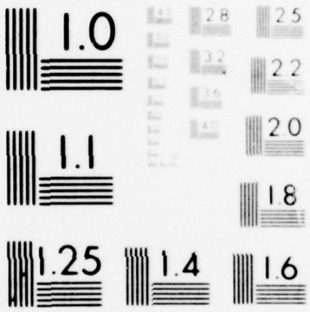

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PHOTOISOMERIZATION OF LINKED ANTHRACENES. A DEMANDING TEST OF MOLECULAR GEOMETRY FOR INTERMEDIATES IN PHOTODIMERIZATION

by

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Valence photoisomerization and photophysical properties of a series of dianthrylethanes, dianthrylmethanes, and tetrabenzo(2.2)paracyclophane are reported. Flourescence lifetimes and quantum yields depend upon the nature of the linkage between anthracene moieties. Quantum efficiency for photoisomerization depends on the substitution pattern at 10,10 Prime positions. Sandwich dimers with excimer-like interaction are generated on low temperature photolysis in glasses of dianthrylethane but not dianthrylmethane. It is concluded that geometrical requirements for excimerization and photodimerization are quite different.

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PHOTOISOMERIZATION OF LINKED ANTHRACENES. A DEMANDING TEST OF MOLECULAR GEOMETRY FOR INTERMEDIATES IN PHOTODIMERIZATION

ABSTRACT

Valence photoisomerization and photophysical properties of dianthrylmethanes, (1c-e), dianthrylethanes (1a,b), and tetrabenzo(2.2)paracyclophane (1f) have been examined. Flourescence yields and lifetimes are significantly a function of the bridging group for the linked anthracenes [e.g., τ_f(ethanes) > τ_f(methanes)]. Quantum yields for photoisomerization (ϕ_{12}), on the other hand, appear to be more a function of the 9' substituent group Y. Evidence for emission from a weakly stabilized excimer-like state is presented for 1a, whereas similar experiments on 1c-e in which "sandwich dimers" are produced by 254 nm photolysis at 77 K reveal only normal anthracene flourescenece. The effects of structure on photoreactivity and signlet excited state decay for the linked anthracenes are mechanistically consistent with singlet lifetime-limiting formation of diradical intermediates which partition to reactant and photoisomer. The geometrical requirements for excimerization exceed those for photoreaction of proximal anthracenes, suggesting a subordinate role for excimers in photodimerization.

Photoisomerization of Linked Anthracenes. A Demanding Test of Molecular Geometry for Intermediates in Photodimerization.

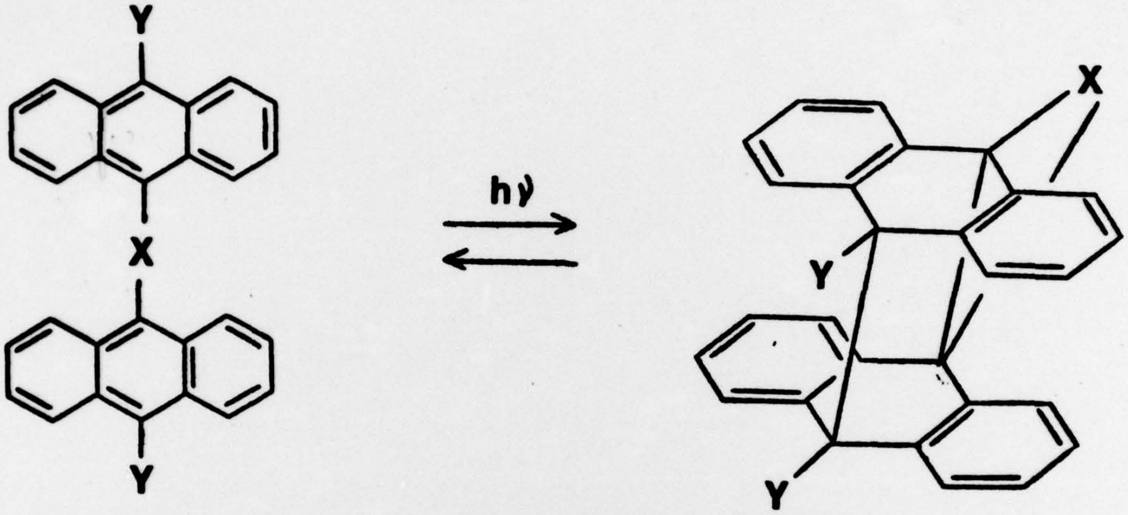
Sir:

We have examined the photoisomerization and emission characteristics of linked anthracenes **1**, which represent a graded series of molecular constriction ending with the rigid tetrabenzo[2.2]paracyclophane, **1f**. Our results are informative with regard to the nature of necessary intermediates in anthracene photodimerization. The data are presented in Table I.

Excimers. Sandwich-like excimer states have long been assumed (by virtue of similarity in structure to photodimers) to be intermediates in anthracene photodimerizations, and a number of experiments have been interpreted as supporting this view.[4] Examination of models of the linked systems **1**, in particular those with a one-carbon bridge (**1c-e**), reveals that the intramolecular counterparts to excimers should be strained, beyond the normally expected[4d] 5-10 kcal/mol excimer binding energy if they assume a sandwich-like geometry.

The synthesis of sandwich dimers is possible using the clever experimental approach of Chandross and Ferguson[5] involving photolysis of anthracene photodimers at 77°K. We have applied this procedure to compounds **1c-e** and find only normal fluorescence (that observed for **1c-e** in glasses at 77°K) after irradiation (254 nm) of photoisomers **2c-e** in 2-methyltetrahydrofuran glasses. Unusual or long wavelength excimer emission found for a number of sandwich dimers[5,6] is not observed, even on using a more rigid hydrocarbon glass[6] (3:2, methylcyclohexane/decalin).

Rather different results are provided by 1,2-bis(9-anthryl)ethane, **1a**. After its photoisomer **2a** is irradiated at 254 nm in a rigid glass at 77°K, a strong emission is observed, the major part of which is very similar to the normal 77°K emission spectrum except for an 8 nm red-shift. Melting and refreezing the glass restores the normal spectrum. We interpret the red-shifted emission as resulting from an eclipsed conformation of **1a**. This interpretation is supported by the observation that the 25°C



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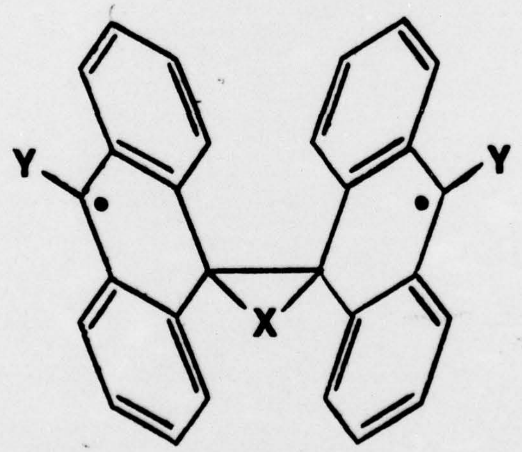

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Table I. Photochemical and Photophysical Data for Linked Anthracenes **1**.

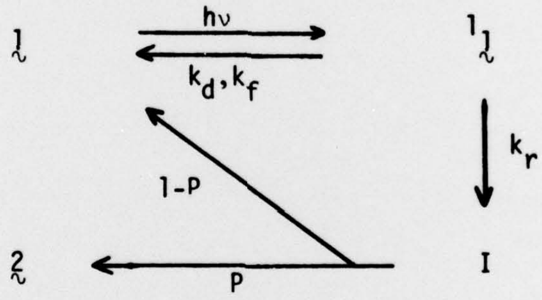
	X	Y	Φ_{12}^{a}	Φ_{21}^{a}	Φ_{f}^{b}	τ_{f}^{b}(nsec)
(a)	CH_2CH_2	H,H	0.26	0.55	0.16	1.7
(b)	CH_2CH_2	CH_3,CH_3	0.04	---	0.14	2.0
(c)	CH_2	H,H	0.15	0.76	0.06	1.1
(d)	CHOH	H,H	0.29	0.81	0.02	0.3
(e)	CHOH	H,OCH_3	0.05	---	0.02	0.3
(f)	CH_2CH_2	CH_2CH_2	0.36	0.60[c]	< 0.001[d]	(~0.01)[e]

[a] Isomerization quantum yield, benzene, 25°; **1** → **2**, 366 nm, **2** → **1**, 285 nm. [b] Fluorescence yield and lifetime in benzene, 25° (single photon counting measurements except where noted). [c] Ref. 1. [d] Ref. 2. [e] From dimethylaniline quenching of photoisomerization (k_q assumed $\cong 10^{10}\ M^{-1}\ sec^{-1}$ as shown for **1a, c, d**).

fluid solution fluorescence spectrum of **1a** is abnormally broad and doesn't clearly show the characteristic vibrational bands noted in most anthracenes and in **1c-e**.[7] The ambient temperature spectrum is presumably that of averaged conformations. The observations concerning **1a** are consistent with low temperature studies recently reported,[8] in which two excimer-like conformations were assigned geometries with different degrees of interchromophore interaction.[9]

We conclude that linked anthracenes **1c-e** are negligibly stabilized in the excited state due to interaction of the aromatic rings. On the other hand, a geometry which is nominally acceptable for excimerization is available to **1a**. The striking result is that photoisomerization proceeds readily for these diverse systems (including **1f**, where a high degree of chromophore interaction is revealed in absorption[3]), without significant penalty for geometrical constraint in quantum efficiency or reaction rate.[10] *We conclude that a sandwich-like excimer state is not a necessary intermediate for anthracene photodimerization.*

Diradicals. Linked anthracenes **1** have relatively short fluorescence lifetimes. The results in Table I show moreover that the rate of excited state decay is dependent on structure. With increasing anthracene proximity (note Table divisions), singlet lifetimes fall, but not in a way that can be rationalized by the yield of photoproduct. A mechanism, which accounts economically for the results, involves formation of an intermediate which partitions to reactant and photoisomer.



The ensuing kinetic relationships are $k_f = \Phi_f/\tau_f$, $k_r + k_d = 1 - \Phi_f/\tau_f$, and $P = \Phi_{12}/k_r\tau_f$, where k_f, k_r, and k_d are rate constants for fluorescence and reactive[12] and unreactive radiationless decay, respectively, and where P is a partition factor. If k_d is $< 10^8 \text{sec}^{-1}$ (normally associated with intersystem crossing and triplet decay),[4d,11,13] then reactive decay (k_r) is lifetime limiting and intermediate partitioning largely controls quantum efficiency.

The variety of geometrical constraints offered by the linked anthracenes (which significantly affects excited state decay rate but not quantum yield[14]), provides a clue to the nature of a sufficient intermediate for photoisomerization. Differences in the arrangement of anthracene moieties largely disappear with the formation of a 9,9' bond. Identification of intermediate I as diradical **3** would provide a unifying mechanism consistent with (1) singlet lifetime dependence on X, (2) lifetime independence on Y, and (3) quantum wastage. In short, the strict requirement for high

Table II. Kinetic Parameters for Photoisomerization of **1**.[a]

	k_f	$k_r + k_d$	P[b]
1a	0.94	4.9	0.31
1b	0.70	4.3	0.05
1c	0.55	8.6	0.16
1d	0.67	33	0.29
1e	0.67	33	0.05
1f	< 1.0	∿1000	0.36

[a] Rate constants X 10^{-8} sec^{-1}. [b] Calculated assuming $k_r \gg k_d$.

reactivity does not include a sandwich arrangement of aromatic rings or even a particular inter-ring dihedral angle, but more a proximity of two meso positions for sigma-bond formation. It follows that quantum efficiency for internal cycloaddition will depend largely on the nature of Y, and the effects observed in **1b**, **e**, and **f** are not surprising.

The proposal of diradical as sufficient intermediate in anthracene cycloaddition is supported by current theories concerning reactive radiationless decay.[15] Intermediate **3** is presumably the "pericyclic minimum" available to S_1 as the result of attempted crossing of ground and doubly excited states for the system. The theory permits that diradical **3** be a common intermediate for **1** → **2** and **2** → **1**, in which case $\Phi_f + \Phi_{12} + \Phi_{21} = 1$[1] (excluding unreactive decay of **2**). Within experimental error, our results are consistent with this scheme.[16]

That the geometrical requirements for excimerization[17] exceed those for photoreaction of the linked anthracenes suggests a subordinate role for excimers in photodimerization but does not exclude their intermediacy in the general case. The data speak more to the nature of reactive decay of proximal anthracenes, whatever the degree of overall excited state stabilization of aromatic moieties due to excitation resonance[4d] or other factors. The issues are: what is the minimum arrangement of anthracenes necessary for rapid photoreaction and, given that a number of geometries may be acceptable, is photodimer formation a one- or two-step process? The observed structure-reactivity relationships for the linked anthracenes provide valuable insight for both of these questions.

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(1) (a) G. Kaupp, *Ann.*, 844 (1974); (b) G. Kaupp, *Angew. Chem. Intl. Ed.*, *11*, 313 (1972).

(2) We observe (benzene solutions, in agreement with Kaupp[1]) neither the fluorescence nor the wavelength dependence in photoisomerization quantum yield reported by Shizuka, *et al.*[3] for THF solutions of **1f**.

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(4) (a) M. D. Cohen, A. Ludmer, and V. Yakhot, *Chem. Phys. Letters*, *38*, 3908 (1976);(b) A. Castellan, R. Lapouyade, and H. Bouas-Lourent, *Bull. Soc. Chim. France*, 210 (1976); (c) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, *45*, 3564 (1966); (d) J. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, NY (1970) ch. 7; (e) J. Ferguson and A. W.-H. Mau, *Mol. Phys.*, *27*, 377 (1974); (f) J. Ferguson and S. E. H. Miller, *Chem. Phys. Lett.*, *36*, 635 (1975); and (g) B. Stevens, *Adv. in Photochem.*, *8*, 161 (1971).and (h) N.C. Yang, D.M. Shold, and B. Kim, *J. Am. Chem. Soc.*, **98** 6587 (1976).

(5) (a) E.A. Chandross, J. Ferguson, and E.G. McRae, *J. Chem. Phys*. *45*, 3546 (1966);
(b) E.A. Chandross and J. Ferguson, *J. Chem. Phys.*, *45*, 3554 (1966).

(6) J. Ferguson, A. W.-H. Mau, and J. M. Morris, *Aust. J. Chem.*, *26*, 91, 102 (1973).

(7) Room temperature solution absorption spectra for **1a-e** are nearly identical to that of 9-methylanthracene (or composite with 9-methoxy-10-methylanthracene) with slight alterations in vibronic intensities.

(8) (a) J. Ferguson, M. Morita, and M. Puza, *Chem. Phys. Lett.*, *42*, 288 (1976); (b) T. Hayashi, N. Mataga, Y. Sakata, S. Misumi, M. Morita, and J. Tanaka, *J. Amer. Chem. Soc.*, *98*, 5910 (1976).

(9) In addition to the structured "P band"[8a] we have also observed the broad, structureless but very weak emission which occurs at longer wavelengths noted by Ferguson[8a] and Mataga.[8b]

(10) Compare, for example, phenomenological rate constants for photoisomerization of **1c-e** (Φ_{12}/τ_f, $0.1 - 1.0 \times 10^9 \text{ sec}^{-1}$) with pseudo first order rate constants for photodimerization of anthracene and 9-substituted anthracenes,[11] $0.4 - 1.0 \times 10^9 \text{ sec}^{-1}$ 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).

(11) R. S. Shon, D. O. Cowan and W. W. Schmiegel, *J. Phys. Chem.*, *79*, 2087 (1975).

(12) For **1a,b** k_r is a composite of conformer equilibrium constant and the rate constant for internal cycloaddition.

(13) Sensitization and quenching experiments confirm that the involvement of triplets for **1** is minimal.

(14) The trend in fluorescence quantum yield and lifetime continues for a three atom linked system, 9,9'-dianthrylcarbonate ($\Phi_{12} = 0.02$, $\tau_f = 5.3$ nsec, $\Phi_f = 0.30$). In this case, however, the yield of photoisomer is depleted significantly by competitive fluorescence and perhaps intersystem crossing. Presumably, diradical formation is slow due to an unfavorable entropy factor; i.e., in this case anthracene-anthracene orientation is important but more the availability than type of interchromophore arrangement. Excimer-type fluorescence was not observed for the carbonate.

(15) (a) J. Michl, *Top. in Current Chem.*, *46*, 1 (1974); (b) W. G. Dauben, L. Salem, and N. J. Turro, *Accounts Chem. Research*, *8*, 41 (1975).

(16) Other features of the reaction coordinate include data for the thermal back reaction for selected systems: **2a**, $E_a = 32.8$, $\Delta H = -14.6$; **2c**, $E_a = 32.7$, $\Delta H = -17.3$; **2f**, $E_a = 22.3$, $\Delta H = -8.2$ (all in kcal/mol). The reaction enthalpies were determined by differential scanning calorimetry for isomerization in the solid state.

(17) Chandross and Dempster[18] have shown that geometrical requirements are quite strict for excimerization of dinaphthylpropanes.

(18) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, *92*, 3586 (1970).

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