

ON THE RELATIONSHIP BETWEEN MOLECULAR GEOMETRY AND EXCITED STATE REACTIVITY.
ADIABATIC PHOTOREACTIONS INVOLVING ANTHRACENES

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Abstract - The effects of molecular geometry on the formation of electronically excited products have been studied in a series of bichromophoric compounds. In linked anthracenes, steric factors noticeably affect the radiative deactivation. In the case of diastereoisomeric dianthrylmethyl ethers, only the d,l compounds form luminescent intramolecular excimers. The intramolecular deactivation of photo-excited anthracenes by ground state aromatic ketones in non-polar solvents proceeds by endothermic singlet energy transfer. In polar solvents, the main process leads to the formation of intramolecular luminescent exciplexes in which the donor and acceptor can be in mutually perpendicular arrangement. - Differences between ground state geometry and the geometry of the singlet excited state of sterically hindered 9-anthrylethylenes are responsible for remarkably large energy gaps between absorption and emission maxima. - The reversible adiabatic generation of anthracene:olefin exciplexes by photolytic retro-Diels-Alder reaction of lepidopterenes has been studied. - The relationship between ground state molecular geometry and excimer and exciplex luminescence of crystals is discussed on the basis of X-ray diffraction analyses.

INTRODUCTION

In 1970, at the III IUPAC Symposium on Photochemistry, Förster suggested that those photoreactions be termed adiabatic in which the conversion of an electronically excited reactant R into a chemical product P occurs on the same potential energy surface (Ref. 1). By this definition, the P* product configuration corresponds to a minimum on the excited electronic energy surface from which deactivation to P proceeds. The typical, and virtually only, examples of adiabatic photoreactions then known were intramolecular and intermolecular proton transfer reactions, as well as the formation of excimers and exciplexes, all of which are detectable by their characteristic fluorescence (Ref. 2). Significantly, one feature common to all these reactions is their ground state reversibility, or the presence of a low activation barrier between R and P, as shown in Fig. 1a. Unknown at the time of Förster's proposal were adiabatic photoreactions characterized by high barriers of activation between R and P, as shown in Fig. 1b (Ref. 3 & 4).

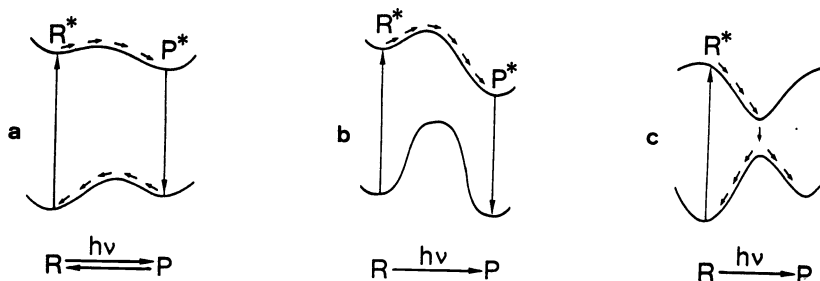


Fig. 1. Adiabatic (a, b) and diabatic (c) photochemical conversion of R into P.

Most "well-behaved" photoreactions of organic molecules in condensed phases, it was recognized, proceed diabatically, i.e. the formation of the reaction product P is an event which takes place subsequent to electronic deactivation of R* and does not involve the intermediacy of the P* state (see Fig. 1c). The apparent scarcity of adiabatic photochemical processes has provided a stimulus for research in this area of photochemistry (Ref. 5). The search for intramolecular adiabatic photoreactions such as fragmentations, rearrangements, or geometrical isomerizations has been as challenging as tedious, but the didactic usefulness of the classification of photoreactions as suggested by Förster is obvious (Ref. 6 & 7).

Interestingly, the anthracene fluorophore has played a prominent role in the search for adiabatic photoreactions. Early attempts to detect the formation of electronically excited anthracene or its excimer by photolytic dissociation of dianthracene were largely unsuccessful and discouraging. For example, adiabatic generation of 9-methylanthracene from its photodimer was found to proceed with a quantum yield of only 0.0004 (Ref. 4). At low temperatures, excimer formation may be more easily detectable (Ref. 8), but most recent results indicate that the photodissociation of anthracene photodimers is anything but a simple process (Ref. 9) which becomes even more complicated at low temperatures (Ref. 10).

Concerning the photodissociation of other suitable anthracene precursors, attempts to detect the formation of electronically excited 9,10-diphenylanthracene by adiabatic photofragmentation of 9,10-diphenyl-1,4-dihydroanthracene-1,4-dicarboxylic anhydride (or the corresponding 9,10-isomer) were virtually unsuccessful (Ref. 11). On the other hand, adiabatic photolytic cycloreversion of 9,10-diphenylanthracene endoperoxide to give singlet molecular oxygen ($\Phi = 0.28$) has been accomplished by irradiation of the $S_0 \rightarrow S_2$ transition (Ref. 12). Direct evidence has also been obtained for the adiabatic generation of 1,4-dimethyl-9,10-diphenylanthracene by photolysis of its 1,4-endoperoxide (Ref. 13). Other examples of adiabatic photolytic cycloreversions proceeding by the reaction path outlined in Fig. 1b were reported most recently. The photodissociation of the formal $4\pi+4\pi$ cycloadduct of benzene to anthracene was found to proceed largely (>90%) adiabatically, but the efficiency of the adiabatic formation of anthracene from the corresponding formal $4\pi+2\pi$ cycloadduct was considerably lower (Ref. 14). Likewise, the quantum yield of adiabatic photodissociation of the $4\pi+4\pi$ cycloadduct derived from 9-cyanoanthracene and 1,3-cyclohexadiene is larger than 10%, but the photoexcited $4\pi+2\pi$ cycloadduct derived from 9-cyanoanthracene and 1,3-hexadiene deactivates mainly by fluorescence in competition with the formation of a biradical state (Ref. 15).

We have investigated the excited state properties of a variety of novel substituted anthracenes. Most of these compounds are bichromophoric, as the substituent incorporates another π -system. Bichromophoric compounds, in general, have been and continue to be of considerable photochemical and photophysical interest (Ref. 16-22). In our studies, we were mainly concerned with the potential effects of molecular geometry on their excited state properties as revealed by their fluorescence, or reflected by their photochemical reaction products. In particular, we have investigated the following topics summarized in this paper.

- I. Steric and electronic effects on the photochemical and photophysical properties of linked anthracenes.
- II. Intramolecular deactivation of electronically excited anthracenes by ground state aromatic ketones.
- III. The effect of molecular geometry on the luminescence properties of 9-anthrylethylenes.
- IV. Formation of luminescent anthracene:olefin exciplexes by adiabatic cycloreversion of lepidopterenes.
- V. Crystal luminescence studies of excimer and exciplex geometries.

I. STERIC AND ELECTRONIC EFFECTS ON THE PHOTOCHEMICAL AND PHOTOPHYSICAL PROPERTIES OF LINKED ANTHRACENES

Intramolecular photoreactions of α,ω -di(9-anthryl)alkanes and related linked anthracenes have attracted considerable attention in the past (Ref. 23-28), and have been reviewed at the VIII IUPAC Symposium on Photochemistry (Ref. 29). One feature typical of many of these compounds is the absence of excimer emission in non-polar solvents at room temperature. It is assumed that the deactivation of excimers by intramolecular $4\pi+4\pi$ cycloaddition efficiently competes with their deactivation by luminescence. We have investigated a series of substituted 1,2-dianthrylethanes 1, and our results (see Table I) are complementary insofar as they show that sterically demanding substituents which impair the cycloaddition reaction to give 2 do enhance the radiative deactivation from the locally excited state (Ref. 30).

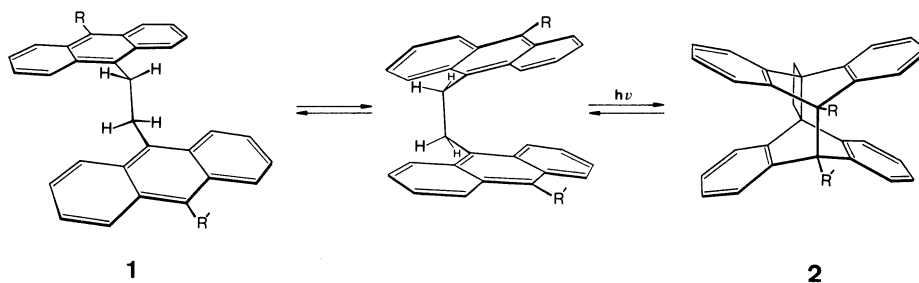


TABLE 1. Quantum yields of deactivation of photo-excited dianthrylethanes **1** by intramolecular cycloaddition (Φ_R) to give **2**, and by fluorescence (Φ_F) in cyclohexane.

R	H	H	H	H	H	CH ₃	OCH ₃	OCH ₃	OAc	n-C ₄ H ₉	C ₆ H ₅
R'	H	CH ₃	OCH ₃	OAc	C ₆ H ₅	CH ₃	OCH ₃	OAc	OAc	n-C ₄ H ₉	C ₆ H ₅
Φ_R	0.26	0.26	0.24	0.14	0.034	0.14	0.11	0.068	0.015	<<0.015	<<0.015
Φ_F	0.20	0.15	0.14	0.40	0.61	0.16	0.30	0.45	0.74	0.70	0.79

In a related study, we investigated the spectroscopic and photochemical properties of diastereoisomeric α,α' -disubstituted bis-9-anthrylmethyl ethers **3** (R = methyl or phenyl) and found that the photophysical consequences of their conformational differences are visibly detectable (Ref. 31). The meso compounds may assume a molecular geometry which is characterized by mirror plane symmetry and perfectly overlapping anthracene moieties. The corresponding d,l-diastereoisomers, for steric reasons (see Ref. 31), assume a conformation which is characterized by a twofold axis of symmetry. Interestingly, both the meso and d,l-diastereoisomers cyclomerize, similar to the previously investigated parent compound (Ref. 29), with a quantum yield of about 0.25. However, while the meso compounds are virtually non-fluorescent at room temperature in solution, the d,l-diastereoisomers deactivate radiatively both from the locally excited state and from an excimer state (Fig. 2). Thus, the molecular geometry of the emitting excimer state of linked anthracenes appears to be one in which the two aromatic moieties are only partially overlapping, and they may be in an angular arrangement. Previous investigations of sterically crowded linked anthracenes (Ref. 32 & 33) and of various anthracenophanes (Ref. 34-38) are in line with this interpretation. Apparently, the formation of luminescent excimers from bichromophoric aromatic compounds is associated with perfectly overlapping π -systems only when intramolecular cycloaddition is an inefficient process (cf. Ref. 39-45).

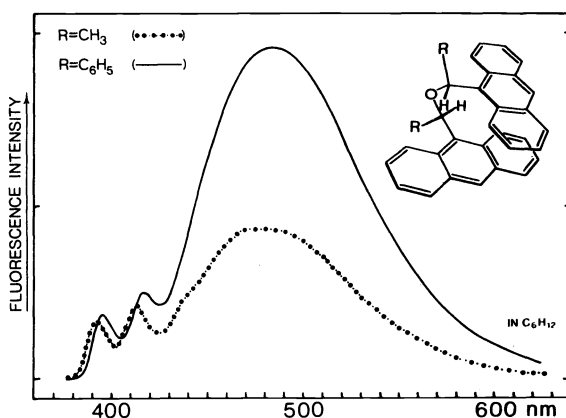
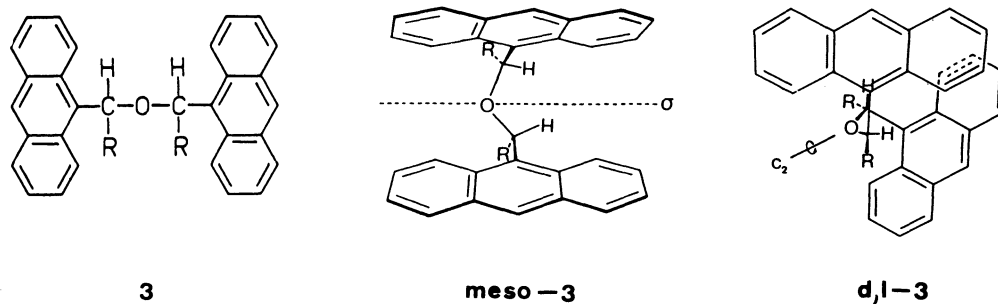


Fig. 2. Emission spectra of d,l-diastereoisomeric bis-9-anthrylmethyl ethers **3** in cyclohexane at room temperature.

As for the series of C_3 -linked anthracenes 4-7, none of these compounds gives rise to luminescent intramolecular excimers at room temperature (Ref. 46). The quantum yields of fluorescence and of formation of the corresponding intramolecular cycloaddition products 8-11 (see Table 2) vary greatly. The quantum yield of cycloaddition of 1,3-dianthrylpropanone 5 is remarkably high. Significantly, oxygen quenching experiments indicate that the photochemical cycloaddition of 5 predominantly involves the triplet excited state. In the case of 6 and 7, the intramolecular $4\pi+4\pi$ cycloaddition has to be preceded by geometrical isomerization of the olefinic double bond. Interestingly, irradiation of the C_3 -linked anthracene 12 does not give a structurally feasible intramolecular $4\pi+4\pi$ cycloaddition product derived from the *cis,cis*-isomer. Apparently, in the intermediate *cis,trans*-isomer, the proximity of the *trans*-ethylenic double bond above the anthracene system favors the formation of the intramolecular Diels-Alder adduct 13.

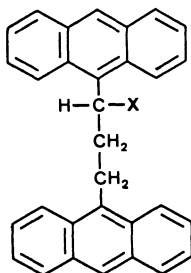
TABLE 2. Photophysical and photochemical properties of C_3 -linked anthracenes 4-7 at room temperature.

	$\frac{4}{X = H}$	$\frac{4}{X = OH}$	$\frac{4}{X = OAc}$	<u>5</u>	<u>6</u>	<u>7</u>
$\Phi_F^a)$	0.47 ^{c)}	0.27	0.20	0.00026	0.13	<0.0001
$\Phi_R^b)$	0.14 ^{c)}	0.14	0.20	0.65	<0.001	<0.005

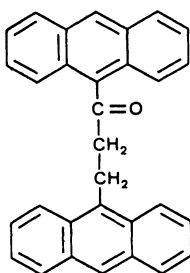
a) Fluorescence quantum yields in cyclohexane

b) Quantum yields of disappearance in benzene

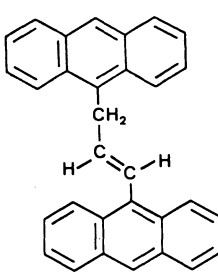
c) In methylcyclohexane (from Ref. 29)



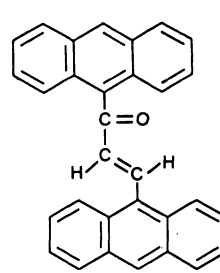
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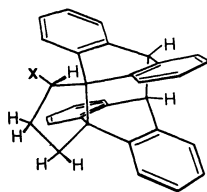
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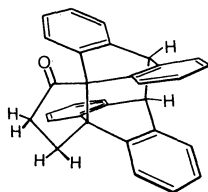
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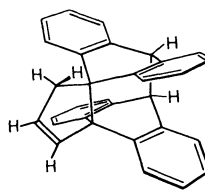
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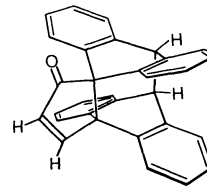
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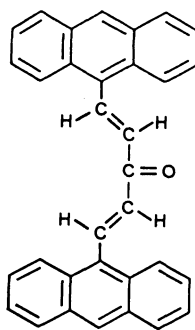
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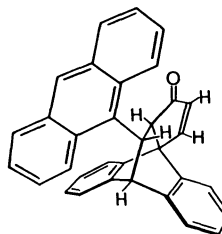
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II. INTRAMOLECULAR DEACTIVATION OF ELECTRONICALLY EXCITED ANTHRACENES BY GROUND STATE AROMATIC KETONES

Geometrical aspects of the intramolecular deactivation of photo-excited anthracenes by electron donors, such as amines, have been studied extensively (Ref. 47-53), but little appears to be known about the geometrical and electronic prerequisites for conceivable interactions between photo-excited anthracenes and electron acceptors, such as ketones. We have investigated a series of bichromophoric compounds consisting of an anthracene and an aromatic ketone whose singlet excited energy lies above that of the anthracene (Ref. 54). As a measure of the degree of interaction between the two non-conjugated chromophores, we have taken the quantum yield of fluorescence from the locally excited anthracene. The results listed in Table 3 for ω -(9-anthryl)propiophenones **14a-d** in cyclohexane solution leave no doubt about the existence of an intramolecular quenching process which, interestingly, is governed by the remote substituent R of the aromatic ketone. In the case of R = methoxy, the fluorescence quantum yield is 0.20, it is 0.08 for R = H, 0.03 for R = phenyl, and in the case of R = acetyl, the quantum yield has decreased to 0.0006. A rationale for the quenching process can be found in the effect of substituents on the absorption spectra of acetophenones (Fig. 3). Thus, the onset of absorption shifts hypsochromically in the order R = acetyl, phenyl, H, methoxy, suggesting that the excited singlet energies of substituted acetophenones **14** increase in the same order. As the anthracene absorption spectrum remains unaffected by the substituent R of the acetophenone, it apparently is the energy gap between the singlet excited states of the two chromophores which determines the degree of fluorescence quenching in ω -anthrylpropiophenones **14**. Consequently, the efficiency of endothermic intramolecular singlet energy transfer from the anthracene to the ketone should decrease in the order R = acetyl, phenyl, H, methoxy. The singlet excited ketone, in turn, will undergo efficient intersystem crossing, so that the quenching of the anthracene fluorescence in ω -anthrylpropiophenones in non-polar solvents is explicable in terms of an intramolecular triplet sensitization. In support of this explanation, we find that the fluorescence quantum yields of ketone-substituted anthracenes **15a-e** also vary distinctly (see Table 5). In this case, the energy of the singlet excited ketone remains unchanged while the energy level of the singlet excited anthracene is lowered successively by the substituent R in the order of H, acetoxy, methyl, methoxy, trimethylsiloxy (see Table 4). The observed temperature dependence of the emission from the locally excited anthracene moiety is in quantitative agreement with the fluorescence quenching by endothermic singlet energy transfer to the carbonyl chromophore, as outlined schematically in Fig. 4. Exothermic intramolecular singlet energy transfer from a carbonyl chromophore to an aromatic hydrocarbon has been substantiated spectroscopically in a related study (Ref. 55). Likewise, intramolecular exothermic triplet energy transfer from a spiro-substituted anthrone to a naphthalene moiety has been investigated previously (Ref. 56-58).

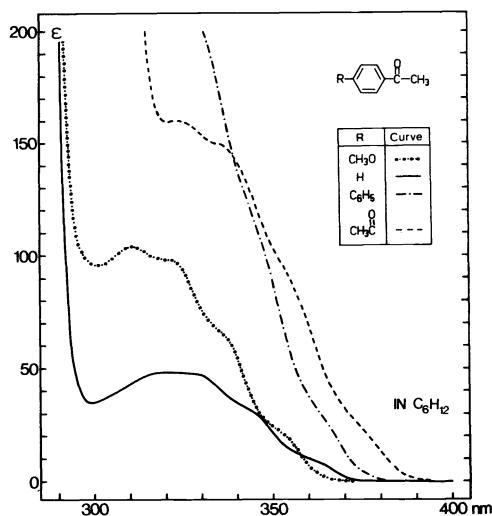


Fig. 3. The effect of substituents on the electronic absorption spectra of acetophenones (in cyclohexane).

TABLE 3. Fluorescence quantum yields of anthracenes **14**.

	a	b	c	d
R	OCH ₃	H	C ₆ H ₅	COCH ₃
Φ_F	0.20	0.082	0.031	0.00059

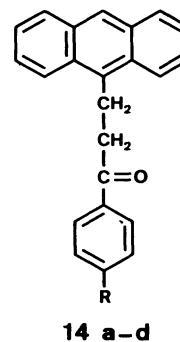
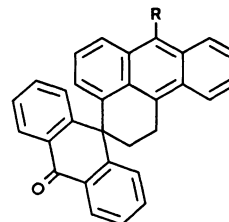


TABLE 4. Substituent effects on singlet excited state energies of anthracenes **15**.

	R	E_S (kcal/mol)
a	H	72.2
b	CH ₃ COO	70.8
c	CH ₃	70.2
d	CH ₃ O	69.8
e	(CH ₃) ₃ SiO	67.7



The deactivation mechanism outlined in Fig. 4 applies to anthracene-ketone bichromophores in cyclohexane solution. In polar solvents, the intramolecular deactivation of photo-excited anthracenes by aromatic carbonyl compounds may take a rather different course. For example, the quantum yield of emission from the locally excited state in 14d in chloroform decreases to 0.0001 as a new broad, structureless emission around 580 nm appears. We explain the dominant red-shifted emission by the radiative deactivation of an intramolecular exciplex state. Similar quenching in polar solvents of the anthracene fluorescence in conjunction with the appearance of exciplex emission is observed for 14c, and for spiro-anthranyl substituted anthracenes 15a-e (see Table 5, and Fig. 5), suggesting that the electron-withdrawing properties of the carbonyl compound are utilized in the exciplex formation, and that the photo-excited anthracene functions as electron donor. The formation of luminescent exciplexes from anthracenes 15 is of particular interest because the donor and acceptor moieties are virtually in perpendicular arrangement (cf. Ref. 54). It has been recognized in previous studies concerning the formation of intramolecular exciplexes that the geometrical requirements may be less stringent than they are for the formation of excimers (Ref. 48, 59-62). The role of polar solvents in assisting exciplex formation in bichromophores 14 and 15 may be such as to cause state inversion, as has been observed previously for intramolecular anthracene-aniline exciplexes (Ref. 47). A similar role of solvent polarity is known for aromatic compounds which may give rise to twisted internal charge transfer states (Ref. 2, 50, 63-67). In the case of intramolecular exciplexes derived from photo-excited anthracenes and aromatic ketones, the nature of the solvent primarily affects the electronic structure of the carbonyl moiety, rather than that of the aromatic hydrocarbon. The net effect will be the stabilization of the intramolecular charge transfer state. The data summarized in Table 5 indicate that other solvent properties than just the dielectric constant (cf. Ref. 68) contribute to exciplex stabilization.

TABLE 5. The effect of solvents and substituents on the quantum yields of emission from the locally excited state of anthracenes 15. The numbers in parenthesis are the ratios of quantum yields in oxygen-free and air-saturated solution. E indicates detected exciplex luminescence. λ_{\max} refers to the longest wavelength absorption band in cyclohexane.

R	λ_{\max} (nm)	C ₆ H ₁₂	C ₆ H ₅ CH ₃	CHCl ₃	CH ₂ Cl ₂	C ₆ H ₅ CF ₃	CH ₃ COCH ₃	CH ₃ CN
H	396	0.037 (1.05)	0.014 (1.03)	0.0021 (1.61)E	0.00058 (1.47)E	0.0054 (1.99)E	0.00031 (1.26)E	0.00016 (1.07)E
CH ₃ COO	404	0.34 (1.21)	0.20 (1.15)	0.083 (1.97)E	0.017 (1.57)E	0.10 (1.43)E	0.0057 (1.58)E	0.00046 (1.14)E
CH ₃	407	0.34 (1.27)	0.20 (1.22)	0.00093 (1.63)E	0.00029 (1.13)E	0.015 (4.37)E	0.00022 (1.10)E	0.00010 (1.06)E
CH ₃ O	410	0.47 (1.32)	0.35 (1.32)	0.00093 (1.30)E	0.00026 (1.10)E	0.0078 (2.18)E	0.00022 (1.10)E	0.00009 (1.00)
(CH ₃) ₂ SiO	422	0.66 (1.51)	0.66 (1.80)	0.00051 (1.14)E	0.00012 (1.05)E	0.0024 (1.54)E	0.00015 (1.01)E	0.00006 (1.00)

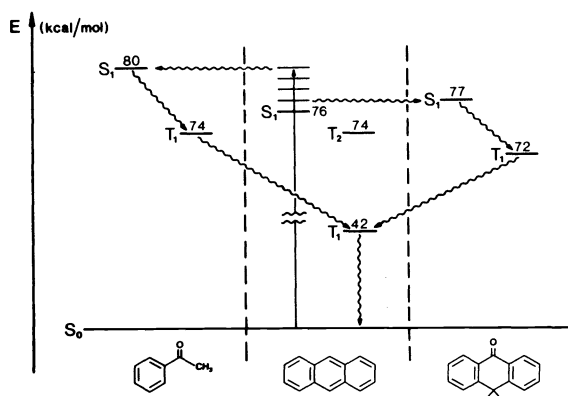


Fig. 4. Schematic representation of fluorescence quenching by intramolecular endothermic singlet energy transfer in bichromophoric anthracenes 14 and 15.

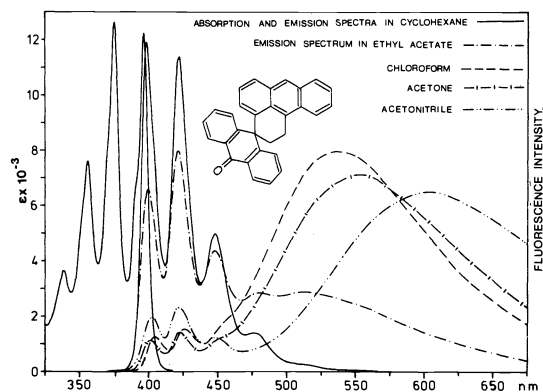


Fig. 5. Solvent-assisted intramolecular exciplex formation in spiro-anthranyl substituted anthracene 15a.

Seemingly subtle structural changes of the ketone also may alter its electronic properties. In cyclohexane, for example, intramolecular quenching of fluorescence from the locally excited anthracene is less efficient in compound 16 than it is in the related compound 17. By the same token, intermolecular exciplex formation is more pronounced in 17 than it is in 16 (see Fig. 6). The differences between the electronic structures of the anthrone moieties in 16 and 17 can be deduced from a comparison of their electronic absorption spectra which suggest that 10-hydroxy-10-methylanthrone is a better electron acceptor than anthrone or its 10,10-diethyl derivative. The importance of geometrical factors in the intramolecular deactivation of electronically excited anthracenes by ketones is apparent in the exceptionally high exciplex luminescence quantum yields which are characteristic of methano-linked anthranyl-anthracene 18 (see Fig. 7) in comparison with those of its ethano-analogue 19 (see Table 6). We know from X-ray structure analyses (cf. Section V) that the molecular geometry of 18 differs significantly from that of 19 (Ref. 69).

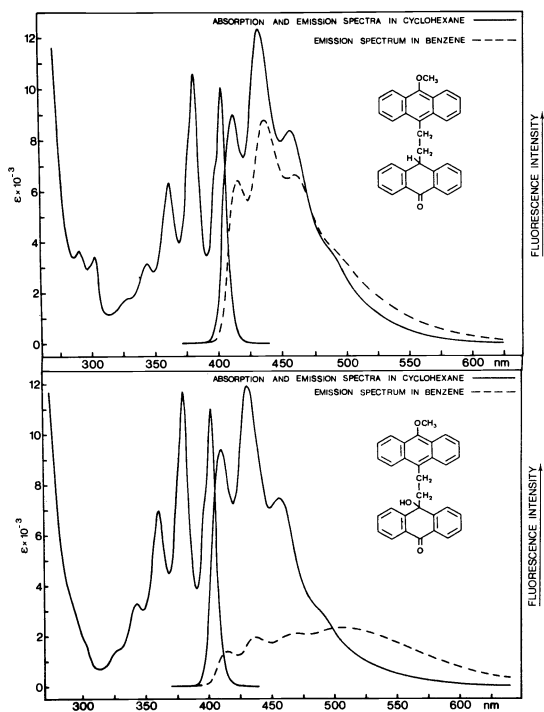


Fig. 6. Absorption and emission spectra of anthracenes 16 and 17 in cyclohexane (solid curves) and benzene (dashed curves).

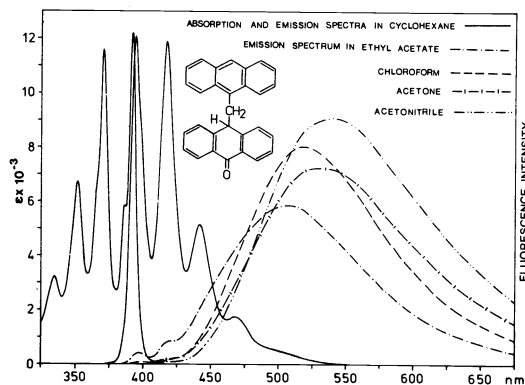
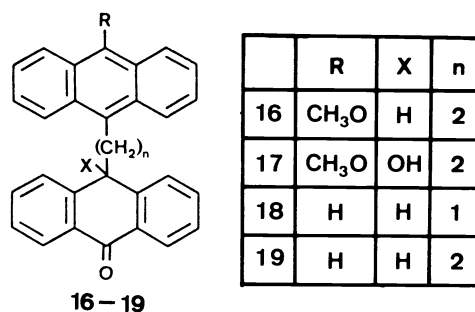


Fig. 7. Solvent effects on the exciplex emission of methano-linked anthranyl anthracene 18.

TABLE 6. Exciplex emission quantum yields and wavelengths for anthracenes 18 and 19. F_0/F is the ratio of quantum yields in oxygen-free and air-saturated solution.

Solvent	<u>18</u>			<u>19</u>		
	Φ_F	F_0/F	λ_{\max}^{em} (nm)	Φ_F	F_0/F	λ_{\max}^{em} (nm)
C ₆ H ₅ CH ₃	0.016	1.50	a)	b)	b)	b)
CHCl ₃	0.27	1.81	510	0.063	1.58	495
CH ₂ Cl ₂	0.26	1.56	520	0.041	1.54	517
C ₆ H ₅ CF ₃	0.22	2.03	485	0.12	2.71	466
CH ₃ COCH ₃	0.15	2.26	515	0.017	1.24	535
CH ₃ CN	0.11	2.19	540	0.0018	1.10	590

a) maximum not discernible; b) exciplex emission not detectable

III. THE EFFECT OF MOLECULAR GEOMETRY ON THE LUMINESCENCE PROPERTIES OF 9-ANTHRYL-ETHYLENES

Molecular models of 9-anthryl substituted ethylenes as well as their electron spectra are suggestive of steric impairment of conjugation in the electronic ground state. Photoexcitation of 9-anthryl substituted ethylenes, however, results in a change of molecular geometry, and the differences between the ground state and the singlet excited state geometries are readily apparent from a comparison of absorption and emission spectra. For example, the fluorescence spectrum of 9-methylanthracene in cyclohexane at room temperature is characterized by a Stokes shift of only 130 cm^{-1} , but the emission spectrum of 9-vinylanthracene has a Stokes shift of $1,200\text{ cm}^{-1}$ (see Fig. 8). Likewise, *trans*-1,2-di(9-anthryl)ethylenes **20** in their electronic ground state cannot be planar, and the remarkably large shift of $10,000\text{ cm}^{-1}$ between absorption and emission maxima suggests that the emitting singlet excited state has a more planar geometry than the electronic ground state. We conclude from the excitation wavelength dependence and from the solvent viscosity dependence of the emission spectra (Ref. 70) that various rotamers of dianthrylethylenes **20** are in conformational equilibrium (see Fig. 9; cf. also Ref. 71 & 72). The *cis*-1,2-di(9-anthryl)ethylenes **21**, whose molecular geometry is characterized by mirror plane symmetry, are non-fluorescent in solution at room temperature. The unexpected low quantum yield for the geometrical isomerization ($\Phi = 0.0007$) and for the intramolecular cycloaddition to give **22** ($R = \text{H}$; $\Phi = 0.0007$) appears to be a consequence of its unique molecular geometry (Ref. 70 & 73).

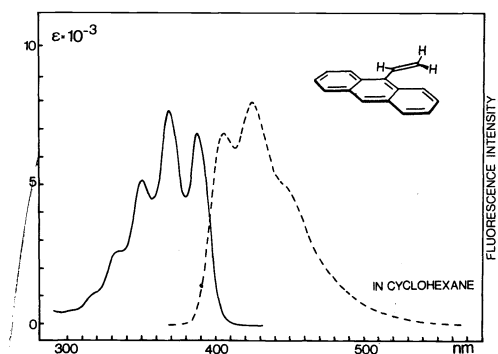


Fig. 8. Absorption and emission spectra of 9-vinylanthracene in cyclohexane.

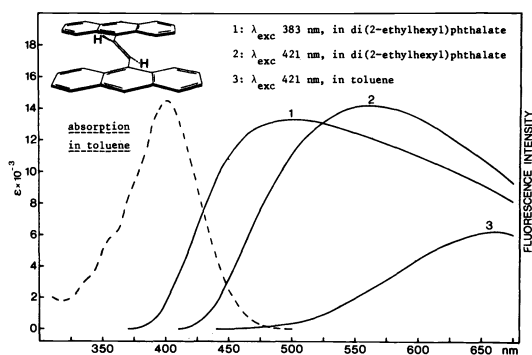
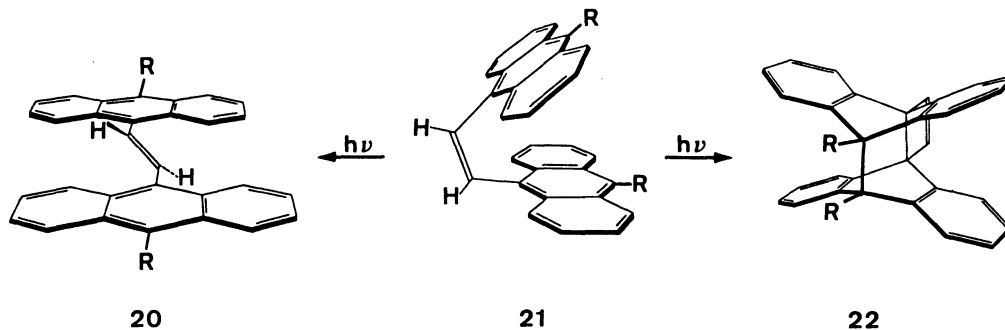


Fig. 9. Excitation wavelength dependence of *trans*-1,2-di(9-anthryl)ethylene emission at $0\text{ }^{\circ}\text{C}$.



In order to assess the geometrical differences between the electronic ground state and the emitting singlet excited state we have studied the luminescence properties of the symmetrically substituted 9-anthrylethylenes **23** in cyclohexane solution at room temperature. Two features become apparent from the data listed in Table 7. First, we observe an increase in Stokes shift from 900 cm^{-1} in the case of **23b**, to $10,700\text{ cm}^{-1}$ in the case of **23e** as the degree of conjugation in the excited state increases (see Fig. 10). Second, we note that the fluorescence quantum yields in cyclohexane vary dramatically with the nature of the substituents R^1 and R^2 . Thus, "aliphatically" substituted **23a** and **23b** fluoresce with quantum yields of 0.63 and 0.64, respectively. Diphenyl-substituted **23c** has a decreased fluorescence quantum yield of 0.29. If the two phenyl moieties are joined by a methylenecarbon, as in **23e**, the quantum yield drops to 0.015. In the conformationally more rigid **23d**, in which the ground state geometry may be such as to have the anthracene and the substituted ethylene in mutually perpendicular arrangement, the fluorescence quantum yield has decreased to 0.0003.

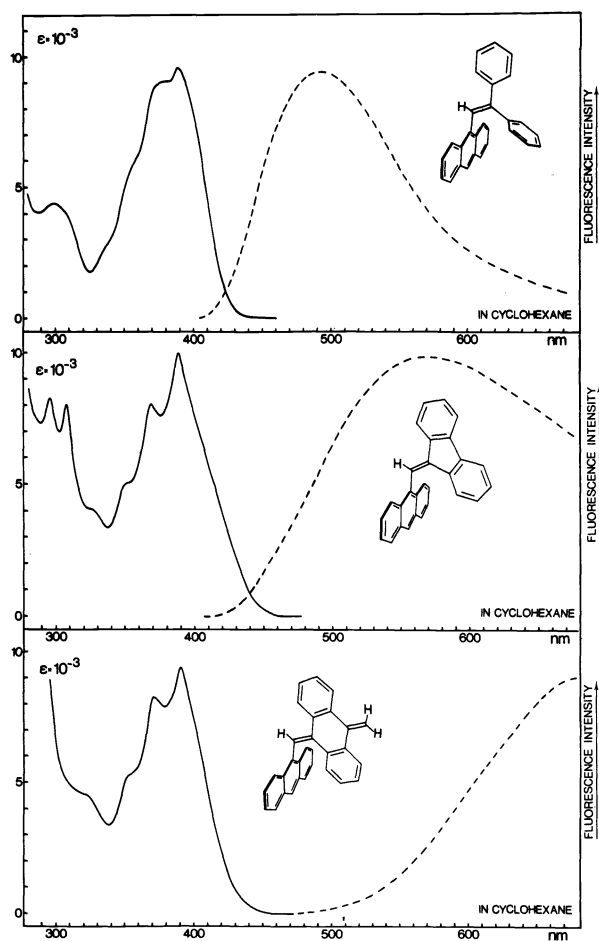
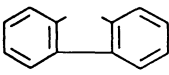
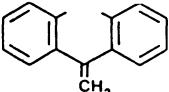
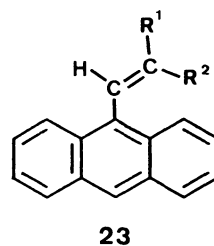


Fig. 10. Absorption spectra (solid curves) and emission spectra (dashed curves) of sterically hindered 9-anthrylethylenes 23c, 23d, and 23e in cyclohexane.

TABLE 7. Absorption and emission spectroscopic data of 9-anthrylethylenes 23.

<u>23</u>	R ¹	R ²	abs λ_{\max} (nm)	em λ_{\max} (nm)	$\Delta\nu'$ (cm ⁻¹)	Φ_F in	
						C ₆ H ₁₂	CH ₃ CN
a	H	H	386	405	1 200	0.63	0.72
b	CH ₃	CH ₃	386	400	900	0.64	0.50
c	C ₆ H ₅	C ₆ H ₅	388	495	5 600	0.29	0.00033
d			388	565	8 100	0.0003	<0.0001
e			390	670	10 700	0.015	<0.0001



Significantly, in the electronic absorption spectra of 23c-e, transitions due to the aryl-substituted ethylene moiety are clearly noticeable, and we may view vinylanthracenes 23c-e as bichromophoric compounds. Most likely, the quenching of the fluorescence is explicable in terms of an intramolecular electron transfer process. In support of this assumption, we find that the fluorescence of 23c-e, but not that of 23a and 23b, is drastically quenched in polar solvents. For example, the fluorescence of 23c decreases by three orders of magnitude in acetonitrile (see Table 7), and both 23d and 23e are non-fluorescent in most solvents which are more polar than cyclohexane (Ref. 74).

IV. FORMATION OF LUMINESCENT ANTHRACENE:OLEFIN EXCIPLEXES BY ADIABATIC CYCLOREVERSION OF LEPIDOPTERENES

The fluorescence of anthracenes can be quenched by intermolecular interaction with conjugated olefins, but exciplex luminescence under these conditions is rarely observed (Ref. 75-78). A successful approach to the formation of intramolecular anthracene-olefin exciplexes was found in the photolysis of lepidopterene (L, Y = H) which we reported in 1978 (Ref. 79). Photo-excitation of L around 275 nm gives rise to the electronically excited cycloreversion product E^* whose deactivation to ground state is associated with strong emission ($\Phi = 0.58$) around 600 nm (see Fig. 11). The subsequent spontaneous intramolecular Diels-Alder reaction of "E" smoothly regenerates L. In principle, all lepidopterenes of general structure L undergo this type of reversible adiabatic photolysis with an efficiency of about 90% and, in all cases, the radiative deactivation of the exciplex state is the most prominent process (Ref. 80 & 81; cf. Table 8). Significantly, in their electronic ground state, lepidopterenes L are in equilibrium with their cycloreversion products of structure A which are spectroscopically detectable by their typical anthracene absorption and by the corresponding fluorescence of mirror image relationship. The importance of molecular geometry in excited state processes is borne out by the fact that photo-excited A^* deactivates predominantly by emission to its Franck-Condon ground state. In the case of the parent compound A (Y = H), the quantum yield of emission from the locally excited state is 0.84 at room temperature in cyclohexane.

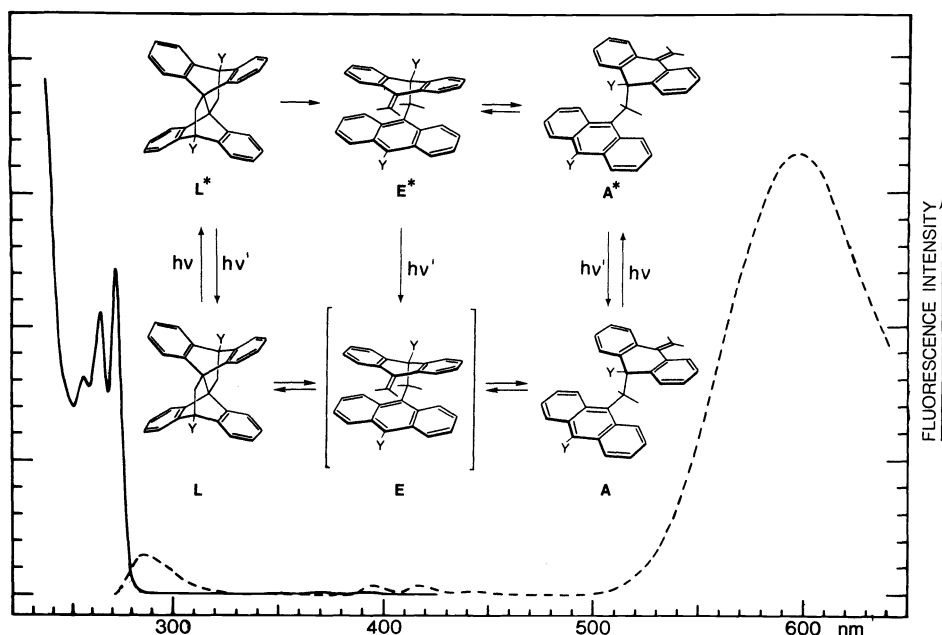


Fig. 11. Absorption spectrum (solid curve) and triple emission spectrum (dashed curve) of lepidopterene in cyclohexane at room temperature.

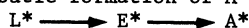
TABLE 8. Ground state and excited state properties of lepidopterenes (cf. Fig. 11).

Y	H	CH ₃	C ₂ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₅	β-styryl	α-naphthyl-CH ₂
equilibrium ratio [L]:[A] at 298 K	630	>10 ⁷	>2x10 ⁶	3x10 ⁵	2x10 ⁴	>10 ⁶	>10 ⁶
quantum yield of emission from L*	0.005	0.013	0.025	0.003	0.003	-	-
quantum yield of emission from E*	0.58	0.54	0.28	0.34	0.52	0.07	0.16
λ _{max} of emission from E* state (nm)	597	573	573	584	607	608	577
λ _{exc} (nm)	273	273	273	273	273	210	210

The adiabatic process



involves an activation energy of 10.3 kcal/mol and proceeds at room temperature with a quantum yield of only 0.005. Photo-excitation of dimethyllepidoptere (L, Y = methyl) gives rise to triple emission, and the adiabatic formation of A^* according to the sequence



has been established by oxygen quenching experiments (cf. Ref. 81). The activation energy associated with the generation of A^* from E^* is 9.3 kcal/mol.

Chloro substitution of lepidopterenes was found to affect their excited state properties in a distinct manner. When the chloro substituents are pointing outwards from the lepidoptere skeleton as in peri-tetrachloro-L, the photophysical properties resemble those of the parent compound. In dichloro-L and tetrachloro-L, the chloro substituents are located so as to poke into the aromatic π -system, and the quantum yields of emission from L^* and E^* are reduced, (see Table 9), probably due to enhanced intersystem crossing. Also, the exciplex emission quantum yield increases with increasing excitation energy, suggesting that adiabatic cycloreversion from higher vibronic levels of the singlet excited state competes more efficiently with radiationless deactivation processes of L^* . Moreover, chloro substitution lowers the activation barrier of the adiabatic generation of E^* from its rotamer A^* . Thus, the activation energy associated with the formation of dichloro- E^* from dichloro- A^* is 5.7 kcal/mol. The activation energy associated with the formation of tetrachloro- E^* from tetrachloro- A^* is as low as 4 kcal/mol. Consequently, exciplex formation by selective excitation of tetrachloro-A around 380 nm is easily demonstrated (see Fig. 12). Because of the substitution pattern in dichloro-L and tetrachloro-L, two structurally different exciplexes may be generated.

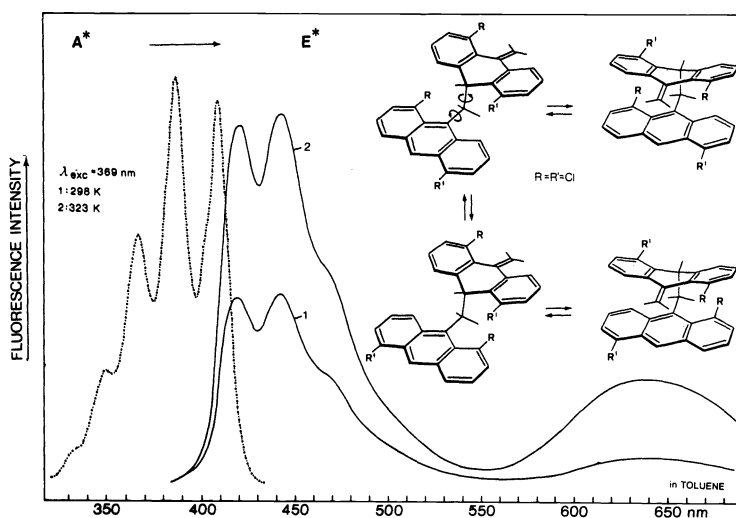


Fig. 12. Absorption spectrum and dual emission spectra of tetrachloro-A in toluene at 298 K (curve 1) and at 323 K (curve 2).

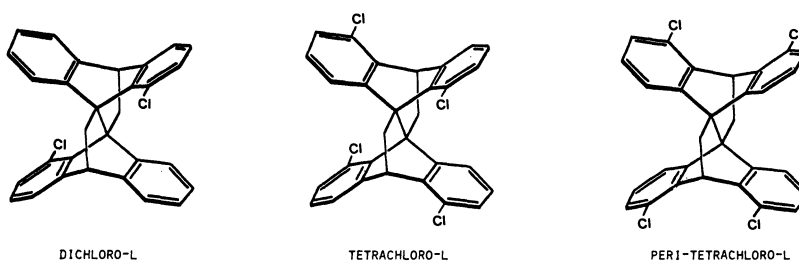


TABLE 9. Ground state and excited state properties of chloro-lepidopterenes.

	Dichloro-L	Tetrachloro-L	peri-Tetrachloro-L
quantum yield of emission from L^*	$<10^{-4}$	$<10^{-4}$	2×10^{-3}
quantum yield of emission from E^*	0.009 0.15	0.016 0.17	0.39 (λ_{exc} 280 nm) 0.39 (λ_{exc} 230 nm)
λ_{max} of emission from E^* state (nm)	628	628	610
equilibrium ratio [L]:[A] at 298 K	63	790 (in toluene solution)	3×10^4

The excited state properties of chromophorically substituted lepidopterenes L ($Y = \alpha$ -naphthylmethyl, $Y = \beta$ -styryl, $Y =$ benzoyl) are those of bichromophoric compounds, i.e. intramolecular energy transfer reactions from the lepidopterene chromophore to the substituent chromophore are feasible processes. For example, dibenzoyl-L is virtually non-fluorescent (Ref. 82), presumably because of efficient triplet state formation. Excitation of the L-chromophore in di-(α -naphthylmethyl)lepidopterene gives rise to triple emission, namely, emission from E^* , A^* , and from the electronically excited naphthalene moiety (cf. Fig. 13). From the excitation wavelength dependence of the E^* emission quantum yield we conclude that the adiabatic cycloreversion from higher vibronic levels of the L^* state competes more efficiently with intramolecular energy transfer to the naphthalene moiety. We can also conclude that energy transfer from the second singlet excited state of the naphthalene to the lepidopterene chromophore can compete with internal conversion to the first singlet excited state of the naphthalene moiety.

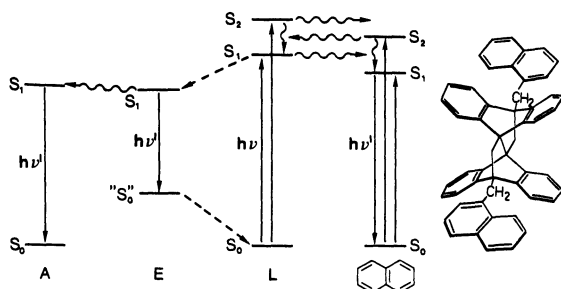


Fig. 13. Schematic representation of adiabatic photoreactions of di(α -naphthylmethyl)lepidopterene.

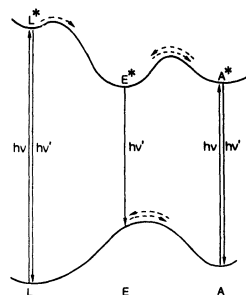


Fig. 14. Energy diagram correlating ground state and excited state reactions of lepidopterenes.

The results of our studies suggest that the geometrical prerequisites for adiabatic photochemical cycloreversion are ideal in the lepidopterene skeleton. The high efficiency of the process may indicate that the geometry of the exciplex state resembles more closely that of the L^* state (see Fig. 14), than it resembles the geometry of the transition complex involved in the ground state intramolecular Diels-Alder reaction. As to whether exciplex formation, either from L^* or from A^* , is preceded on the excited state potential energy surface by a minimum corresponding to a "tight complex" (cf. Ref. 83) cannot be determined on the basis of our steady state measurements.

V. CRYSTAL LUMINESCENCE STUDIES OF EXCIMER AND EXCIPLEX GEOMETRIES

The existence of a relationship between crystal luminescence and intermolecular geometry was noted in conjunction with the formation of excimers in solution (Ref. 84 & 85). By and large, the crystal fluorescence spectrum of an anthracene resembles that of a dilute solution if the intermolecular geometry in the crystal lattice is characterized by large spatial separation so as to make π -orbital interactions negligible. Parallel alignment of adjacent molecules with high degree of π -orbital interaction, generally characterized by interplanar separations of about 3.5 Å between eclipsed molecules, gives rise to excimer-like emission spectra which are structureless and red-shifted with respect to the structured monomer spectra. Numerous papers on crystal fluorescence spectra and on solid-state photochemistry substantiate the importance of intermolecular geometry in the deactivation pathways of electronically excited anthracenes (Ref. 86-89).

Our interest in crystal luminescence phenomena was greatly stimulated by the observation that deviations from perfect excimer geometry in crystalline dianthronylidene ethane drastically affected fluorescence yields (Ref. 90 & 91). Moreover, many of the anthracenes which we had synthesized for solution studies were found to crystallize in more than one modification, which were visibly distinguishable by their crystal luminescence properties. The evaluation of a series of X-ray structure analyses suggests that differences in excimer emission energies are attributable mainly to the differences in intermolecular overlap, characterized by shifts along to two symmetry axes of the anthracene moiety, rather than to varying degrees of interplanar spacing (Ref. 69, 92, 93). The examples shown in Figures 15, 16, 17 illustrate this point. We assume that the crystal luminescence of the benzoate in Fig. 15 reflects the higher degree of intermolecular π -orbital overlap compared to that found in the acetate. Increased shifts along the molecular axes of the anthracene moiety, generally, are associated with an increase in excimer emission energy. Thus, the structureless emission of the β -phase of 1,2-bis(10-acetoxy-9-anthryl)ethane is virtually similar in energy to that of the structured monomer emission (see Fig. 17) which is associated with the α -phase and its intermolecular geometry of negligible overlap (Ref. 94).

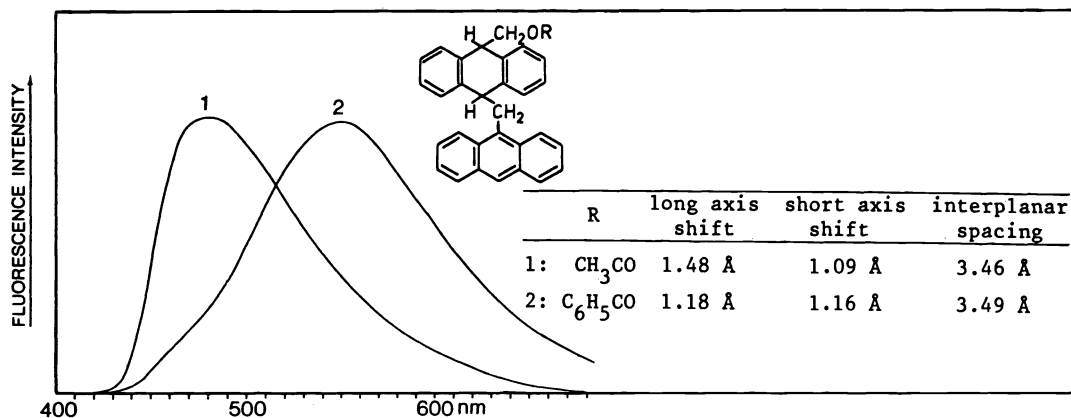


Fig. 15. Crystal luminescence spectra of substituted anthracenes and their different excimer geometries.

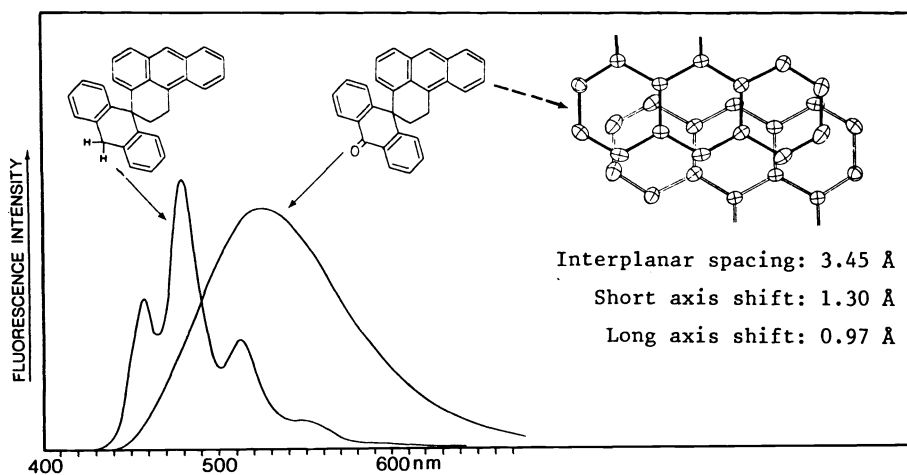


Fig. 16. Crystal luminescence and excimer geometry of spiro-anthranyl substituted anthracene 15a, and the monomer-like crystal luminescence of the corresponding hydrocarbon.

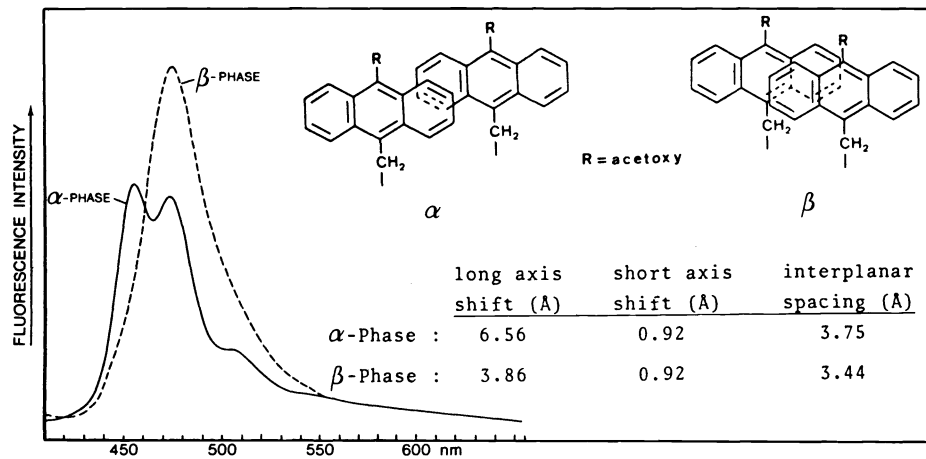


Fig. 17. The effects of intermolecular shifts and interplanar spacing of parallel arranged molecules on the crystal luminescence of two modifications of 1,2-bis(10-acetoxy-9-anthryl)ethane.

The structureless crystal luminescence of those anthronyl-substituted anthracenes which we investigated by X-ray diffraction also was found to be attributable to intermolecular excimer arrangements, rather than to conceivable intramolecular exciplex formation (Ref. 69 & 92; see Fig. 16). Intimate intramolecular anthrone-anthracene interaction, as found in crystalline 18, appears to result in fluorescence quenching. Interestingly, however, the lepidoptere exciplex luminescence discussed in the preceding Section is not limited to solutions but is associated with the crystalline state as well. Thus, the parent compound (L) and its derivatives such as dimethyllepidoptere (DML) or tetrachlorolepidoptere ($\text{Cl}_4\text{-L}$) give rise to structureless crystal luminescence spectra. Significantly, different crystal modifications of the same lepidoptere are clearly distinguishable by their different exciplex emission energy. The evaluation of crystal structure analyses (Ref. 94) in terms of molecular geometry suggests that, for polymorphs of a given lepidoptere, smaller angles between upper and lower pairs of aromatic "wings" give rise to lower exciplex emission energy. As summarized in Table 10, the lower exciplex emission energy is associated with the metastable crystal phases in which the butterfly-shaped exciplex precursors are characterized by more compressed molecular geometry. Other factors such as lattice constraints may affect the luminescence energy of crystals (cf. Ref. 95), but the X-ray analyses of the lepidopteres leave little doubt that the major differences between two polymorphs of the same lepidoptere are the differences in their molecular geometry.

TABLE 10. Molecular geometry and exciplex crystal luminescence of lepidoptere (L), dimethyllepidoptere (DML), and tetrachlorolepidoptere ($\text{Cl}_4\text{-L}$).

Angle (deg) between rings	DML	L, stable phase		L, metastable phase			$\text{Cl}_4\text{-L}$, stable phase	$\text{Cl}_4\text{-L}$, meta- stable phase	
		L-1	L-2	L-1	L-2	L-3		L-1	L-2
A : B	125.2	126.5	127.9	134.0	130.9	132.4	125.2	128.7	123.7
C : D	125.2	126.5	127.9	132.1	130.8	127.9	125.2	128.7	123.7
A : C	54.8	53.5	52.1	48.4	42.2	45.1	54.8	51.3	56.3
B : D	54.8	53.5	52.1	45.5	55.9	54.4	54.8	51.3	56.3
Central bond length (Å)	1.636	1.639	1.645	1.65	1.61	1.65	1.66	1.67	1.67
$\lambda_{\text{max}}^{\text{em}}$ (nm)	540	560		580			575	590	

CONCLUSION

Ten years ago, not much was known about the geometry of exciplexes, or about excimers deviating from perfect sandwich geometry (Ref. 96). As the involvement of excited state complexes in photobiological and photochemical reactions has become indisputable (Ref. 97 & 98), it is obvious that we should know about the geometrical prerequisites of their formation. The luminescence phenomena of the bichromophoric compounds described in this paper have given us some insight into the relationship between molecular geometry and excited state reactivity.

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