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# Unimolecular Photochemistry of Anthracenes

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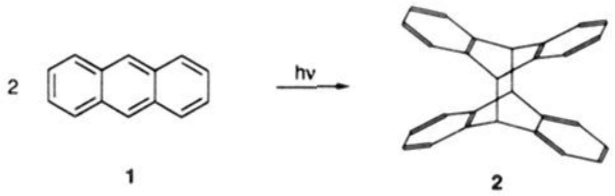
## Contents

Hans-Dieter Becker was born in Germany in 1931. He studied chemistry from 1951 to 1959 at the University of Göttingen, where he did his doctoral research under the direction of G. O. Schenck on benzophenone-sensitized photochemical autoxidations of organic compounds. After post-doctoral studies at Chalmers University of Technology in Gothenburg, Sweden (1959–1960), the University of Wisconsin in Madison (1960–1961), and Iowa State University in Ames (1961–1962), he joined the General Electric Research Laboratory in Schenectady, New York, in 1963. He left GE in 1970 to assume a research position at the Department of Organic Chemistry at Chalmers University of Technology and the University of Gothenburg. His experimental engagement during the past 15 years in the synthesis, structural studies, and photochemistry of chromophorically substituted anthracenes has been summarized recently in a contribution to the *Advances in Photochemistry*. His previous investigations have dealt with photochemical reactions involving phenols, the oxidation of phenols and phenolic benzyl alcohols, quinone dehydrogenations, and photochemical isomerizations of spiro-epoxy-substituted 2,4-cyclohexadienones, and their various Diels–Alder products.

## I. Introduction

During the course of his studies on solid hydrocarbons that were obtainable from coal tar by distillation, J. Fritzsche discovered in 1866 that saturated solutions of anthracene (**1**) upon exposure to sunlight gave a colorless crystalline precipitate which regenerated anthracene upon melting.[1,2] The dimeric nature of the photoproduct was established in 1891 by molecular weight determination, and the correct structure was proposed before the turn of the century.[3-5] Mechanism studies on the photochemical formation of dianthracene (**2**) commenced as early as 1905.[6] In particular, the photophysical aspects and the reversibility of the reaction were studied during the following 50 years.[7-19]



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Between 1955 and 1965, concomitant with the renewed interest in organic photochemistry, many of the easily available substituted anthracenes were investigated, mainly in order to establish the scope of the dimerization. Also, research was focused on the structure and stereochemistry of the photoproducts, which were generally found to be derived by head-to-tail $4\pi + 4\pi$ cycloaddition involving the central ring of the anthracene $\pi$-system.[20-36]

The essentials of anthracene photochemistry as seen by 1963/1964 were the subject of a contribution to the first volume of the *Advances in Photochemistry* and were discussed in a review of photochemical reactions or organic molecules.[37] A large number of subsequent detailed studies on the mechanism of dimerization, and on the deactivation of photoexcited anthracenes by fluorescence and phosphorescence then provided fundamentally important results,[38-55] which were reviewed in a textbook on organic photochemistry published in 1976.[56] By that time, much of our present-day knowledge about intramolecular energy-transfer processes had been gained by investigating bichromophoric compounds in which the anthracene chromophore was one of the two interacting $\pi$-systems.[57-59] Moreover,

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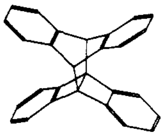
the photochemistry of anthracene derivatives, in conjunction with elegant ground-state reactions, had enriched organic chemistry with some remarkable novel structures, namely, 9,10-dehydrodianthracene (3), 9,10′-dehydrodianthracene (4), 9,9′-didehydrodianthracene (5), and 9,9′,10,10′-tetradehydrodianthracene (6).[23,60–62]



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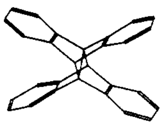

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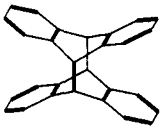

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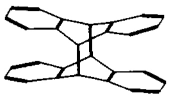

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The present review deals with *unimolecular* photochemical reactions of anthracene derivatives, including intramolecular reactions of bichromophoric anthracenes, most of which were studied during the past 20 years. The limitation of the scope of the review by excluding *bimolecular* photochemistry was deemed mandatory in view of the overwhelming number of articles dealing with addition reactions, and with the photophysical consequences of bimolecular interactions. For several topics involving electronically excited anthracenes, such as the formation of intramolecular exciplexes, twisted intramolecular charge transfer (TICT) states, adiabatic cycloreversions, and rotational isomerism in anthryl-substituted ethylenes, comprehensive reviews have been published previously.[63–66] Likewise, the role of anthracene derivatives in photochromic systems has been treated elsewhere.[67]

## II. Electron Spectral Properties of Anthracenes

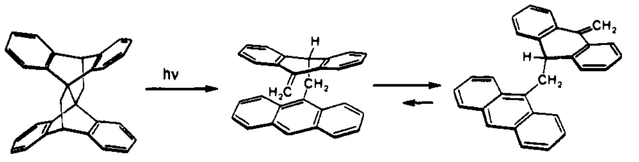
The electronic absorption and emission spectra of anthracene are being described in detail in most textbooks and monographs on photochemistry and spectroscopy.[68–72] Therefore, this section will be limited to a brief outline of only those spectroscopic features which are of direct relevance to the unimolecular photochemistry of anthracenes.

For anthracene, the electronic absorption of photochemical interest is characterized by a series of vibrationally spaced bands around 350 nm. The longest wavelength transition near 380 nm has an extinction of about 9 000 $M^{-1}$ $cm^{-1}$. The short wavelength absorption around 254 nm, having an extinction of about 200 000 $M^{-1}$ $cm^{-1}$, is hardly ever utilized in photochemical context for practical reasons, since electronic excitation of the photoproducts, generally absorbing light in this region of the spectrum, is undesirable. It is worth noting that irradiation of solutions of anthracene in cyclohexane with unfiltered light from a mercury lamp does not give dianthracene, as had been claimed,[73] but yields a degradation product of unknown structure.[39]

The energy difference between the electronic ground state ($S_0$) of anthracene and its first excited singlet state ($S_1$) is 76 kcal/mol. The energy level of the lowest triplet state ($T_1$) is 42 kcal/mol above that of $S_0$. Significantly, the second triplet state ($T_2$) of anthracene lies 74 kcal/mol above $S_0$, i.e. 2 kcal/mol below $S_1$, and intersystem crossing from the $S_1$ state to the triplet state proceeds efficiently with a quantum yield of 0.7. The quantum yield of fluorescence is 0.3, and it has been established for numerous substituted anthracenes that the sum of quantum yields of fluorescence and of intersystem crossing to the triplet state typically is unity. Thus, for many anthracene derivatives, deactivation of the $S_1$ state by internal conversion is negligible.[45–49]

The effects of substituents on the electronic absorption and emission spectra of anthracenes have been of longstanding interest, and the fluorescence properties of substituted anthracenes have been studied in detail.[74–91] Substitution of the anthracene chromophore lowers the $S_1$ energy level, thus changing the excited-state properties by affecting the energy gap between the $S_1$ and $T_2$ states and, consequently, the quantum yield of intersystem crossing. By the same token, the quantum yields of fluorescence at room temperature vary greatly for the multitude of known anthracene derivatives. For example, 9,10-diphenylethynyl-substituted anthracene fluoresces with a quantum yield of about unity, while the quantum yield of fluorescence for 9-bromoanthracene, in which the halogen may enhance the rate of intersystem crossing, is about 0.01.[76,82,89] 9-Carbonyl-substituted anthracene derivatives, in general, are nonfluorescent due to efficient population of the triplet state.[92] For a variety of substituted anthracenes, such as 9-anthramide, interaction with polar solvents will alter the nature of the lowest excited state, as can be evidenced from the marked solvent dependence of the fluorescence spectrum, and in solvent dependent photochemistry.[80,86] In some cases, such as that of 9-*tert*-butylanthracene discussed in section III, the low fluorescence quantum yield (0.011) is associated with the deactivation of the $S_1$ state by both internal conversion and intramolecular chemical reaction, rather than with intersystem crossing to the triplet state.[82] The fluorescence quenching of anthracene by carbon tetrachloride is due to intermolecular reaction of photoexcited anthracene with the solvent.[42,44,77,93]

The relationship between molecular geometry and electron spectral properties has been investigated both experimentally and theoretically. Of particular interest are $\pi$-chromophorically substituted anthracenes, such as 9-phenylanthracene, in which coplanarity of the two $\pi$-systems, i.e. conjugation in the electronic ground state, is precluded for steric reasons.[94–99] In general, the shape of the fluorescence spectrum and the shape of the absorption spectrum are characterized by a mirror-image relationship, and Stokes shifts typically are about 150 $cm^{-1}$, if the differences between the geometry of the electronic ground state $S_0$ and the emitting excited state $S_1$ are small. Large Stokes shifts of up to 10 000 $cm^{-1}$, indicative of large differences between the geometry of the $S_0$ state and that of the $S_1$ state, have been found to characterize the luminescence of various 9-anthrylethylene derivatives and 1,2-di-9-anthrylethylenes, which cannot assume a planar ground-state geometry for steric reasons.[100–109] Moreover, topologically facilitated intramolecular charge-transfer interactions between a photoexcited anthracene $\pi$-system and an electron donor or acceptor moiety may give rise to an exciplex which is characterized by red-shifted structureless emission.[65,110] For example, the anthracene derivative **9** in cyclohexane solution is characterized by a structured fluorescence spectrum ($\Phi_F$ = 0.84) around 425 nm, while its electronically excited rotamer **8**, generated by photolytic cycloreversion of **7**, gives rise to a broad structureless exciplex emission ($\Phi_F$ 0.8) around 600 nm.[111-115]



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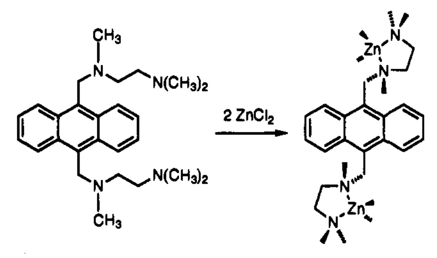
The chromophoric and fluorophoric properties of anthracene derivatives have long been of practical interest in analytical context, and numerous chemically reactive anthracene derivatives, such as isocyanates or acid chlorides, are being utilized as labeling agents for the detection and estimation of UV transparent substrates.[116-121] However, most recent interest in the fluorescence properties of substituted anthracenes derives from their application as probes and chemosensors.[123-138] Numerous examples of anthracene derivatives, particularly anthryl-substituted crown ethers and cryptands, whose fluorescence properties may be drastically affected by the environment, have been investigated in recent years. Complexation by metal ions, or protonation, typically will enhance the fluorescence quantum yield, as fluorescence quenching due to intramolecular electron transfer will no longer be operative. Thus, for 9,10-diaminoalkyl-substituted anthracene **10**, chelation with zinc chloride leading to the binuclear complex **11** was found to enhance the intensity of fluorescence by a factor of about 1000.[128]

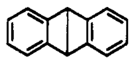


10 11

The cation-sensitive fluorescence properties of bisanthraceno crown ethers and cryptands have been studied in detail in conjunction with their photochemistry (cf. section VIII.A), and the subject has been reviewed recently.[139]

## *III. Photochemistry of Nonplanar Anthracenes*

Sterically demanding substituents, which cause the ground-state geometry of aromatic hydrocarbons to deviate from planarity, generally are a prerequisite for photochemical valence isomerizations. Therefore, neither 9,10-Dewar anthracene (**12**) nor 1,4-Dewar anthracene (**13**) are accessible by direct photochemical isomerization of anthracene, although both have been prepared by multistep syntheses.[140,141] Dewar isomers **12** and **13** revert to anthracene in a thermal reaction which is associated with an activation barrier of 21.6 and 26.5 kcal/mol, respectively. For the 1,4-Dewar isomer **13**, it has been established that the photolytic electrocyclic ring opening, proceeding with a quantum yield of 0.41, in part affords electronically excited anthracene ($\Phi$ ~0.1) in an adiabatic cycloreversion.[141] The photolytic aromatization of 1,4-Dewar naphthalene also proceeds adiabatically.[142-144]



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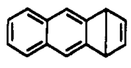

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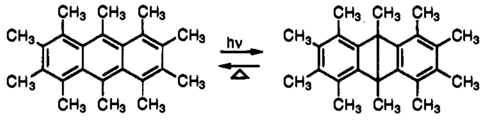
Decamethylanthracene (**14**), for which an X-ray diffraction analysis indicates the lateral benzene rings to assume boat conformations, smoothly yields the Dewar isomer **15** by direct irradiation at room temperature with Pyrex-filtered light in degassed solution.[145] Dewar anthracene **15** has been isolated and characterized, and its thermal reversion to **14** has been established. However, as is typical of sterically crowded 9-methylanthracenes, decamethylanthracene also is prone to isomerize by 1,5-hydrogen migration in a reaction which is catalyzed by traces of acid.[146-148] The analogous isomerization of 6-methylpentacene (**16**) into **17** has been reported to be a photochemical reaction.[149]



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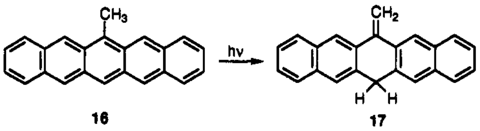

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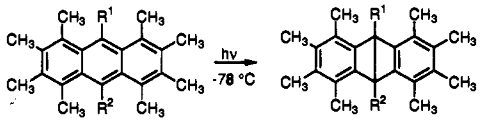
9-Methoxyoctamethylanthracene **18a** as well as 9,10-dialkoxyoctamethylanthracenes **18b–d** are seemingly photostable at room temperature. Upon irradiation at −78 °C, however, anthracenes **18a–d** are found to react smoothly, giving the corresponding Dewar isomers **19**, whose structures were deduced from NMR and electron spectral data. Dewar anthracenes **19** were not isolable, as they reverted to their anthracene isomers above −30 °C.[150]

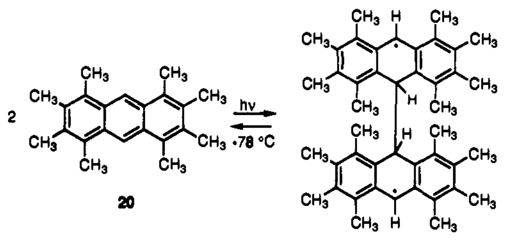


18 19

a: $R^1$ = methoxy; $R^2$ = H
b: $R^1$ = $R^2$ = methoxy
c: $R^1$ = $R^2$ = ethoxy
d: $R^1$ = $R^2$ = isopropoxy

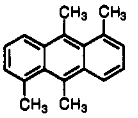
Significantly, irradiation of octamethylanthracene **20** at −78 °C did not yield any Dewar isomer but produced a radical species, suggested to have structure **21**, from which octamethylanthracene **20** was regenerated above −30 °C.[150]

Neither 1,5,9,10-tetramethylanthracene (**22**) nor 1,8,9,10-tetramethylanthracene (**23**) isomerize upon irradiation, although their facile autoxidation under ambient



conditions leading to endoperoxides indicates that the anthracene $\pi$-system is geometrically distorted.[150] Similar easy autoxidation characterizes various (9,10)-anthracenophanes in which the anthracene $\pi$-system severely deviates from planarity.[151,152]

Remarkably, 9-methoxyanthracene has recently been suggested to isomerize photochemically to give 9-methoxy(Dewar anthracene) (24), since it had been found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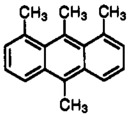
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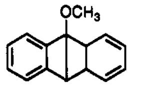
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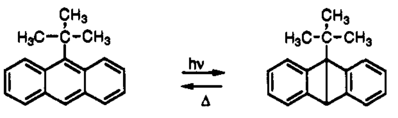
that 9-methoxyanthracene in solution disappears upon photoexcitation, and the reaction turned out to be thermally reversible.[153] The photochemical formation of 9-methoxy(Dewar anthracene) would be unique insofar as the anthracene $\pi$-system in 9-methoxyanthracene is virtually planar, the folding angle about the 9,10 axis being only 178.6°. It appears to be more reasonable to assume that the spectroscopically detected reversible process is attributable to the photochemical formation of a thermally labile head-to-head dimer of 9-methoxyanthracene, which in solution at room temperature dissociates to regenerate 9-methoxyanthracene. The formation of a head-to-tail dimer (35% yield) by irradiation of 9-methoxyanthracene ($\sim 10^{-2}$ M) in ether solution has been reported earlier.[28]

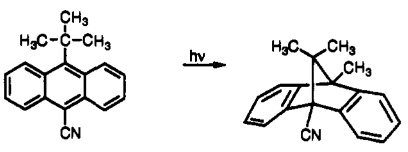
Most detailed and quantitative data are available on the thermally reversible photochemical conversion of 9-*tert*-butylanthracene (25) into 9-*tert*-butyl-9,10-(Dewar anthracene) (26).[154-159] Moreover, the structures of both isomers in question have been analyzed by X-ray diffraction.[160] Thus, the aromatic $\pi$-system in 9-*tert*-butylanthracene deviates from planarity by a folding angle of 166.2° about the molecular short axis. In the [2.2.0]bicyclohexadiene moiety of the Dewar isomer 26, the dihedral angle about the photochemically formed bond (1.623 Å) is 113°.



Unique photochemical properties of 9-*tert*-butylanthracene are indicated by its exceptionally low fluorescence quantum yield at room temperature and by negligible intersystem crossing to the triplet state. The photochemical isomerization of 9-*tert*-butylanthracene in dilute solution into the Dewar anthracene 26 proceeds with a quantum yield of about 0.016. Thus, at room temperature in fluid solution, internal conversion from the excited singlet state to ground state appears to be the main mode of deactivation. In viscous solvents, the observed double-exponential fluorescence decay has been attributed to the involvement of an undefined intermediate precursor of 9-*tert*-butyl-9,10-(Dewar anthracene).[161]

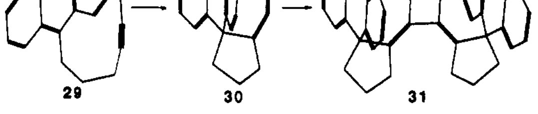
Photoexcitation of 9-*tert*-butyl-9,10-(Dewar anthracene) results in cycloreversion with a quantum yield of 0.35.[156,157] The activation energy associated with the thermal regeneration of 9-*tert*-butylanthracene from 26 is 22.3 kcal/mol.[158]

The only other geometrically distorted anthracene thus far found to be photochemically convertible ($\Phi$ = 0.016) into its Dewar isomer is 9-*tert*-pentylanthracene ($\Phi_F$ = 0.008).[157,158] Unexpectedly, irradiation of 9-*tert*-butyl-10-cyanoanthracene (27) in acetonitrile at 0 °C does not give the corresponding Dewar anthracene but yields the isomeric dibenzonorbornadiene derivative 28, whose formation involves the skeletal rearrangement of the *tert*-butyl group.[162] At room temperature, 9-*tert*-butyl-10-cyanoanthracene in fluid solution is virtually nonfluorescent ($\Phi$ < 0.001), and investigation of photoexcited 27 between 77 K and 163 K in a poly(methyl methacrylate) matrix by single-photon counting indicates multiexponential decay.[163]



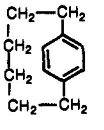
The photochemistry of 9-(trifluoromethyl)anthracene has been studied, and it was found to dimerize by $4\pi + 4\pi$ cycloaddition upon irradiation at 0 °C, even at low concentration ($<10^{-4}$ M). The head-to-tail structure of the dimer was established by X-ray diffraction analysis.[164] Neither 9-(dimethylphenylsilyl)anthracene ($\Phi_F$ = 0.86) nor 9-(trimethylsilyl)anthracene ($\Phi_F$ = 0.79) led to Dewar isomers upon irradiation at low concentration in hydrocarbon solvents.[158] At high concentration in non-polar solvents, 9-trimethylsilylanthracene does undergo dimerization by $4\pi + 4\pi$ cycloaddition.[165]

A most remarkable photochemical reaction has been observed for [10](9,10)anthracenopha-4,6-diyne (29) which upon exposure to sunlight is smoothly converted into the radialene derivative 31.[166] A spectroscopic investigation has revealed that the photochemical step involves singlet state isomerization of 29 to the strained cumulene 30, which dimerizes to give 31 in a thermal reaction.[167]



Recently, [6](1,4)anthracenophane (34) has been synthesized, and its bent molecular geometry has been established by X-ray diffraction.[168] Different from [6]-paracyclophane (32) and [6](1,4)naphthalenophane

(33), which are photochemically converted into the corresponding Dewar isomers, anthracenophane 34 does not isomerize photochemically but yields dimeric products by $2\pi + 2\pi$ cycloaddition involving the 1,2 bond.[169-171] The photochemical dimerization of 34 is suggested to proceed via an excited triplet state.[169] It is worth noting that the 1,2 bond in anthracenophane 34 also is highly reactive in ground-state reactions with electrophiles.[172,173]



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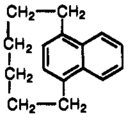

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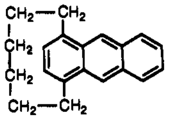

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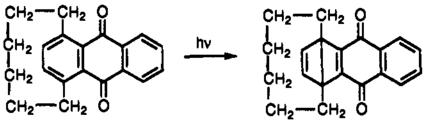
Various geometrically distorted 9,10-anthraquinone derivatives have been synthesized in recent years, and their photochemical isomerization has been investigated. Thus, [6]-1,4-cyclophaneanthraquinone (35) upon irradiation in deuteriochloroform or methylcyclohexane solution, using light of wavelengths >400 nm, smoothly yields the Dewar isomer 36, which is characterized by a half-life of 10 min at 80 °C.[174] Analogous Dewar isomers were formed ($\Phi = 0.03$) by irradiation of 1,2,3-tri-*tert*-butyl- and 1,2-di-*tert*-butyl-3-(trimethylsilyl)anthraquinone. An apparent prerequisite for the valence isomerization of anthraquinone derivatives is the $\pi\pi^*$ nature of the excited state involved in the reaction.[175] If the lowest excited state of *tert*-butyl-substituted anthraquinones is $n\pi^*$ in nature, their unimolecular photochemistry will be characterized by intramolecular hydrogen atom transfer reactions.



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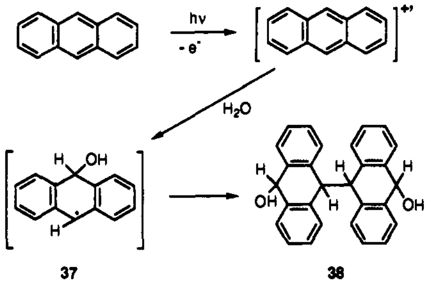
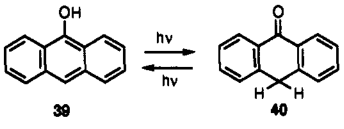
## IV. Photolytic Transformations of Anthracenes

Unimolecular transformations of unsubstituted anthracene have not been reported yet. However, the photolysis of anthracene in very dilute aqueous solution ($3 \times 10^{-7}$ M; argon purged; λ 350 nm) has recently been found to give as main products three stereoisomers of 10,10′-dihydroxy-9,9′,10,10′-tetrahydro-9,9′-bianthryl (38). The result has been rationalized by the intermediacy of the anthracene cation radical, followed by reaction with water, and dimerization of radical 37.[176]



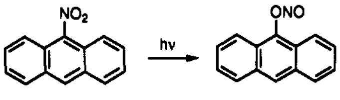
37 38

For substituted anthracenes, the course of their intramolecular photolytic transformations is governed by the nature of the substituent and by their excited-state interactions with the anthracene π-system. The examples of unimolecular photochemistry thus are limited to those anthracene derivatives in which the substituent typically is characterized by lone-pair electrons. Frequently, primary products of unimolecular photochemical reactions of anthracenes are unstable and may react further, particularly by oxidation or dimerization. For example, the photochemistry of 9-hydroxyanthracene (39) is complicated not only because of the solvent-dependent ground-state equilibrium with anthrone (40), but also by the facile formation of various autoxidation products.[177-181] The photochemical tautomerization of 9-anthrone to give 9-hydroxyanthracene, in turn, is complicated by the unfavorable electron spectral differences between the two isomers and by inadvertent intermolecular hydrogen atom abstraction reactions by the photoexcited anthrone.[182] Laser flash investigations have revealed that triplet-excited 9-hydroxanthracene is formed from triplet-excited 9-anthrone by way of bimolecular energy transfer.[183] Although the triplet energy of 9-anthrone (71.5 kcal/mol) is considerably higher than that of 9-hydroxyanthracene (about 43 kcal/mol), direct population of the triplet state of 9-hydroxyanthracene by excitation of 9-anthrone has not been observed in picosecond laser experiments.[184]



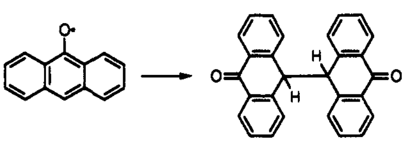
39 40

Considerable efforts have been devoted to investigating the photochemistry of 9-nitroanthracene (41).[185-194] The virtual lack of 9-nitroanthracene fluorescence is indicative of efficient intersystem crossing from the lowest excited $\pi\pi^*$ singlet state to an upper $n\pi^*$ triplet state.[187,188] The weak luminescence with maxima around 685 and 760 nm observed at 77 K in a solid matrix has been attributed to 9-nitroanthracene phosphorescence.[189,190] However, luminescence observed in solid matrices also can arise from various photoproducts of 9-nitroanthracene, particularly 9,10-anthraquinone, which may be formed from photoexcited 9-nitroanthracene with high quantum efficiency (0.7) due to the presence of oxygen.[192,193] A holographic study has revealed that 9-nitroanthracene in a polymer matrix disappears upon irradiation at 458 nm to give 9-hydroxyanthracene (39) with a quantum yield of about 0.01.[194]



41 42

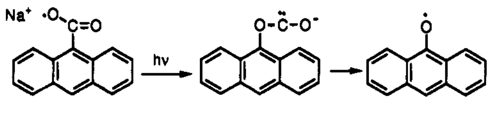
Evidence for the photolytic decomposition of 9-nitroanthracene was obtained in an early investigation in which irradiation with light of wavelengths of 370–410 nm was found to give nitric oxide and 10,10′-bianthronyl (44), while excitation at longer wavelengths (420–530 nm) yielded the $4\pi + 4\pi$ head-to-tail cyclodimer of 9-nitroanthracene.[32,186] In a subsequent detailed preparative study, the intramolecular reaction of an upper $n\pi^*$ triplet state of nitroanthracene was suggested to lead to 9-anthryl nitrite (**42**) via an oxaziridine intermediate.[185] The observed formation of **44** was accounted for by cleavage of 9-anthryl nitrite leading to nitric oxide and 9-anthryloxy radical **43**, which can dimerize or give anthraquinone monoxime via a radical recombination process.



**43** **44**

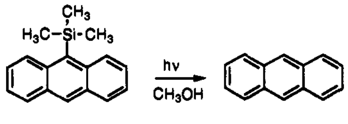
In a series of spectroscopic investigations on 9-nitroanthracene, 9-benzoyl-10-nitroanthracene, and 9-cyano-10-nitroanthracene, the photochemical formation of 9-anthryloxy radicals as primary products has been confirmed, including by electron-spin resonance spectra. Moreover, the kinetics of pico- and nanosecond spectroscopic experiments indicate that, following excitation to the $S_1(\pi\pi^*)$ singlet state, the lowest excited triplet state $(T_1(\pi\pi^*)$ is populated via the internal conversion of $T_n(n\pi^*)$.[187,191]

In terms of unimolecular phochemistry, the excited-state properties of sodium 9-anthracenecarboxylate (**45**) resemble those of 9-nitroanthracene insofar as 10,10′-bianthronyl (**44**), as well as anthracene, can be formed as byproducts, depending on reaction conditions.[195] Dimerization by $4\pi + 4\pi$ cycloaddition generally is the predominant photochemical reaction of sodium 9-anthracenecarboxylate.[51] Irradiation in degassed solution has been found to give carbon monoxide and the anion of 9-hydroxyanthracene (**47**) whose formation has been rationalized by the intermediacy of **46**.[195]



**45** **46** **47**

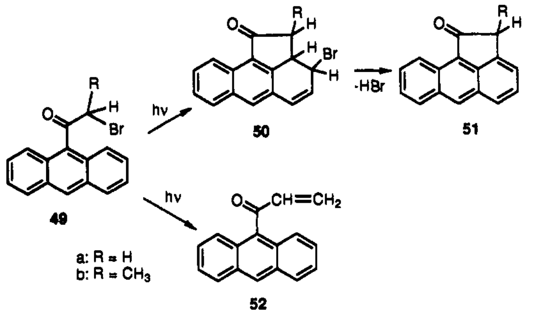
9-(Trimethylsilyl)anthracene (**48**) has been found to undergo smooth photolytic protodesilylation in methanol solution, yielding anthracene with a quantum yield of ~0.1. It is worth noting that the desilylation competes efficiently with the photochemical dimerization even at fairly high concentrations of **48**. The result has been attributed to solvent interaction by hydrogen bonding with the $S_1$ state of **48**.[196]



**48**

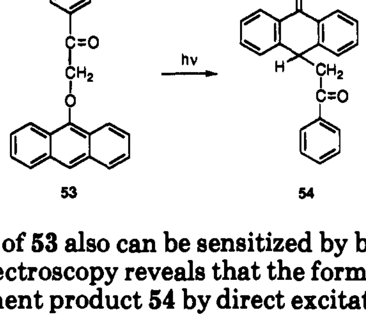
As for 9-anthryl ketones in their electronic ground state, their molecular geometry is such as to have the anthracene and the carbonyl $\pi$-systems in mutually perpendicular arrangement, so that electronic conjugation is negligible.[197,198] In their photoexcited state, by contrast, 9-anthryl ketones can assume a geometry in which the torsional angle between the anthracene and the carbonyl group is drastically reduced, and intramolecular reactions involving the anthracene and the carbonyl substituent become feasible.[199] In fluid solution, 9-anthryl ketones typically are nonfluorescent because of efficient intersystem crossing to the triplet state.[92] Picosecond laser experiments indicate that deactivation of the excited singlet state $(\pi\pi^*)$ of 9-anthryl ketones to the lowest excited triplet state $(T_1\pi\pi^*)$ involves very fast intersystem crossing from $S_1\pi\pi^*$ to an upper triplet state with $n\pi^*$ character.[200]

Within the group of carbonyl-substituted anthracenes, 9-anthryl $\alpha$-bromoalkyl ketones are unique insofar as the $\alpha$-bromoalkyl ketone moiety is characterized by a photochemically labile carbon–halogen bond. Thus, the unimolecular photochemistry of both 9-($\omega$-bromoacetyl)anthracene (**49a**) and 9-($\alpha$-bromopropionyl)anthracene (**49b**) involves cleavage of the carbon–bromine bond. Photoexcited **49a** isomerizes mainly by carbon–halogen addition to the 1,2-bond to give the labile primary product **50a**, from which hydrogen bromide is eliminated either photochemically or thermally. Byproducts formed in the photolysis of (bromoacetyl)anthracene **49a** are 9-bromoanthracene, 9-acetylanthracene, and anthracene. In the case of 9-($\alpha$-bromopropionyl)anthracene, the main photoproducts isolated were 2-methyl-1-aceanthrenone (**51b**; 43%) and 9-anthryl vinyl ketone (**52**, 42%). At −196 °C, irradiation of **49b** leads exclusively to **52**, suggesting that changes in the molecular geometry of **49b** are important for the formation of the intermediate **50b**.



**49**

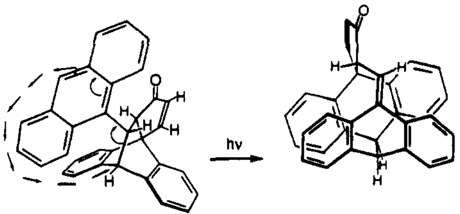
Unequivocal evidence for the involvement of radicals has been obtained in the photolysis of $\alpha$-(9-anthryloxy)acetophenone (**53**), which was found to disappear with a quantum yield of 0.24 upon irradiation in methanol solution.[204] The CIDNP spectrum in acetonitrile ($\lambda_{exc}$ 308 nm) reveals as minor products acetophenone, its enol, and 1,2-dibenzoylethane. The main photoproduct of **53** has not been isolated, but the CIDNP spectrum observed during the photolysis is in agreement with the structure of the anthrone derivative **54**, which is formed by radical coupling. The photochemical rearrangement of **53** also can be sensitized by biacetyl, but CIDNP spectroscopy reveals that the formation of the rearrangement product **54** by direct excitation of $\alpha$-(9-anthryloxy)acetophenone involves the excited singlet



**53** **54**

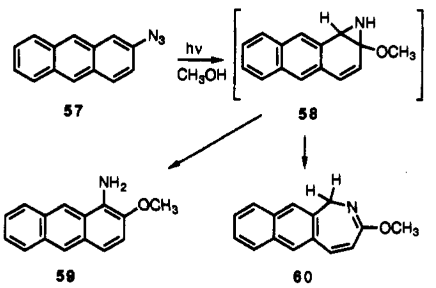
rather than the triplet state. An analogous mechanism applies to the photolytic β-cleavage of other (α-aryloxy)-acetophenones.[205]

The rearrangement of the anthracene derivative **55** by direct excitation to give the dearomatized product **56**, formally, also proceeds by way of β-bond cleavage and may be rationalized in terms of an intramolecular triplet sensitization by the cyclopentenone moiety. In line with the arguments presented in section V.A for interactions between photoexcited anthracenes and aromatic ketones, intramolecular singlet–singlet energy transfer from the anthracene chromophore to the cyclopentenone in **55** is energetically feasible because of the favorable electron spectral overlap of the anthracene absorption around 380 nm, and the absorption due to the cyclopentenone n–π* transition. The subsequent intersystem-crossing step is assumed to be an efficient process, as may be deduced from the relatively low fluorescence quantum yield of **55** (0.05).[206] Other examples of photochemical dearomatization of 9-alkyl-substituted anthracenes characterized by a weak β-bond have been reported.[207]

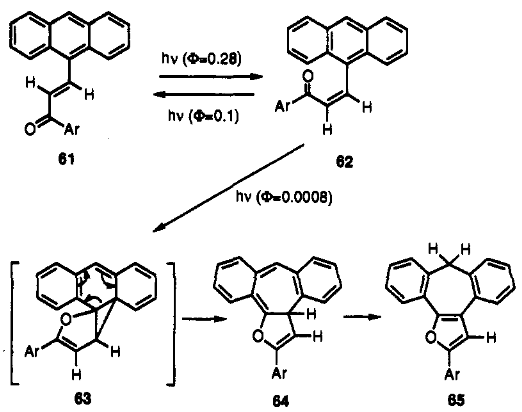


**55** **56**

Irradiation of 2-azidoanthracene (**57**) in dioxane–methanol containing potassium methoxide yields, depending on the workup conditions, either 1-amino-2-methoxyanthracene (**59**) or the azepine derivative **60** in excellent yields. The aziridine derivative **58**, deriving from the primarily formed nitrene, is assumed to be the reactive intermediate.[208] The products deriving from the carbene formed by photolytic decomposition of di-9-anthryldiazomethane have not been investigated.[209]



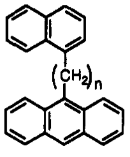
The photochemical isomerization of 1-(9-anthryl)-2-benzoylethylenes **61**/**62** leading to 5*H*-dibenzo[*a*,*d*]-cycloheptenes **65** proceeds smoothly, albeit with low quantum efficiency, as a process competing with geometrical cis–trans isomerization. The enlargement of the central ring of the anthracene π-system has been rationalized by a 4π + 2π cycloaddition leading to **65** via intermediates **63**/**64**.[210]



## V. Intramolecular Energy Transfer in Substituted Anthracenes

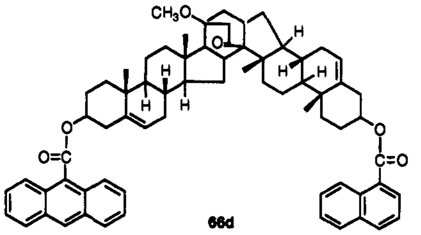
### A. Photophysical Effects

Intramolecular energy-transfer reactions involving the anthracene π-system as one of the participating chromophores have been investigated mainly by emission spectroscopy, and the results have provided basic information about the dependence of the rate of energy transfer on the distance between the donor and acceptor moieties.[57–59] For α-(9-anthryl)-ω-(1-naphthyl)alkanes **66a–c**, the efficiencies of singlet energy transfer from the naphthalene to the anthracene were found to be identical for methano-, ethano-, and propano-separated π-systems.[57] In model compound **66d**, where the donor and acceptor π-chromophores are separated by about 20 Å, the singlet–singlet energy-transfer efficiency was found to be about 0.84.[58] By contrast, evidence for triplet–triplet energy transfer in **66** was not obtained.[59]



n = 1,2,3

**66a–c**



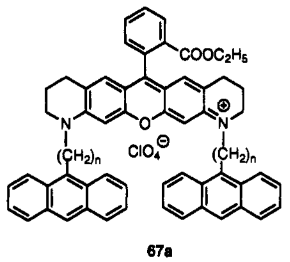
**66d**

Reviews on various aspects of energy transfer have been published previously, and intramolecular energy transfer continues to be a topic of general interest.[211–216] The following discussion will be limited to recent results on the photophysical and photochemical consequences of singlet and triplet energy-transfer reactions involving anthracene derivatives.

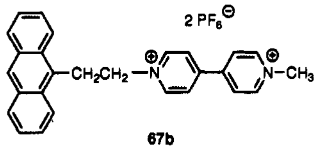
#### 1. Anthracene-Tethered Dyes

Intramolecular singlet energy transfer from anthracene to Rose Bengal has been established in an emission spectroscopic investigation of anthracene-tethered derivatives.[217] The increase of the Rose Bengal fluorescence intensity was found to be less than expected from the degree of quenching observed for the emission from the locally excited anthracene. The excitation spectra for the emission from anthracene-tethered Rose Bengal derivatives differ from the corresponding absorption spectra, indicating the formation of intramolecular complexes. In those ground-state complexes, the two chromophores are suggested to be in a proximate geometry conducive to fluorescence quenching. Intramolecular complex formation has also been deduced from the emission spectral properties of the 9-anthrylmethyl ester of fluorescein, for which the efficiency of singlet energy transfer from the anthracene to the dye chromophore was calculated to be 0.38.[218]

In a recent study of $\pi$-chromophorically substituted rhodamine dyes, energy transfer from the anthracene to the rhodamine in trichromophores **67a** was found to be associated with unexpected quenching of the rhodamine fluorescence.[219] In the rhodamine model lacking the anthracene antenna, the fluorescence quantum yield is 0.96. The quantum yield decreases to 0.22 in **67a** when $n = 1$, and to 0.07 when $n = 2$. Structural details about the ground-state geometry of anthracene substituted rhodamine derivatives **67a** are not available, but it seems reasonable to assume that increased flexibility of the linking chain facilitates an intramolecular arrangement of the donor and acceptor $\pi$-systems to the effect of fluorescence quenching, conceivably by way of electron transfer. The decrease in fluorescence quantum yield observed by tethering the anthracene fluorophore to viologens such as in **67b** also has been attributed to intramolecular electron transfer.[220]



**67a**



**67b**

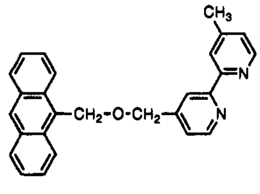
Evidence for singlet energy transfer from the anthracene to the tetraphenylporphyrin $\pi$-system was obtained by emission spectroscopy for terminally substituted polyenes.[221] This finding is unique insofar as selective excitation of the anthracene $\pi$-system around 256 nm is possible, and singlet energy transfer apparently proceeds along the fully conjugated spacer.

### 2. Energy Transfer Involving Metal Complexes

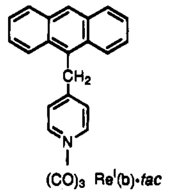
Intramolecular energy-transfer reactions of metal complexes containing covalently bound anthracene have been investigated in recent years in conjunction with the growing interest in electron transfer processes. In a study on the photoproduction of hydrogen from water by irradiation of anthracene-tethered hexaaza–cobalt cage complexes, the aromatic $\pi$-system was found to serve as an antenna sensitizer for the reduction of Co(III) to Co(II).[222,223] The fluorescence quenching observed in the ruthenium complex of substituted bipyridyl **68** was found to be due to efficient intramolecular triplet energy transfer to the anthracene from the metal-to-ligand charge transfer state.[224] Likewise, in rhenium carbonyl complexes **69**, the metal-to-ligand excited state was found to be efficiently deactivated by strongly exothermic energy transfer to the lowest triplet state of the anthracene.[225]

**Table I. Fluorescence Quantum Yields of ω-(9-Anthryl)propiophenones 70a–e in Cyclohexane and Acetonitrile**

| compd | R | R′ | $\Phi_F$ $C_6H_{12}$ | $\Phi_F$ $CH_3CN$ |
|---|---|---|---|---|
| **70a** | H | $C_6H_5$ | 0.41 | 0.066 |
| **70b** | $CH_3O$ | H | 0.20 | 0.075 |
| **70c** | H | H | 0.082 | 0.016 |
| **70d** | $C_6H_5$ | H | 0.04 | 0.0014 |
| **70e** | $CH_3CO$ | H | 0.00056 | 0.00008 |



**68**

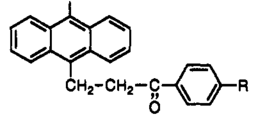


**69**

### 3. Anthracene–Aryl Ketone Interactions

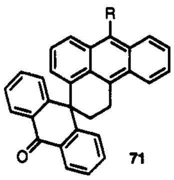
Excited-state interactions between anthracenes and aromatic ketones have been studied mainly in bichromophoric compounds such as **70** and **71**, in which the energy gap between the two interacting $\pi$-systems, and the relative disposition of their excited-state energy levels may be manipulated by appropriate substitution.[65,110] In both **70** and **71**, the absorption spectral properties of the aromatic carbonyl chromophores are such as to preclude their selective excitation and to make the transfer of energy from the photoexcited anthracene to the ketone an endothermic process.

For ω-(9-anthryl)propiophenones **70** in nonpolar solvents, the decrease of the fluorescence quantum yield from 0.40 for **70a** to $<10^{-3}$ in **70e** is associated with the decrease in energy gap between the $S_1$ states of the two interacting $\pi$-systems. In polar solvents, the electron acceptor properties of the arylcarbonyl moiety are enhanced to the effect of facilitating fluorescence quenching by electron transfer, as is evident from the drastically reduced fluorescence quantum yields in acetonitrile (see Table I).[65]



**70a–e** (see Table I)

Analogous substituent- and solvent-dependent fluorescence properties have been found for spiroanthronyl anthracenes **71**.[65] Moreover, in both **70** and **71**, the charge-transfer mode of deactivation in polar solvents is evident from the appearance of exciplex-like lumi-

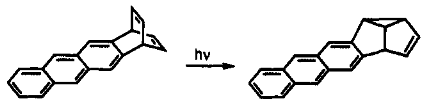


71

nescence. For example, the fluorescence quantum yield for the locally excited anthracene in 71, R = methoxy, decreases from 0.47 in cyclohexane to <0.001 in chloroform, and the formation of an electronically excited complex is indicated by a structureless emission around 560 nm.[65,110] The geometrical aspects of excited-state complex formation from fairly rigid spiro compounds 71 are of particular interest, as any sandwich arrangement of donor and acceptor moiety is precluded for structural reasons, and the excited-state geometry should closely resemble the geometry of the electronic ground state.[226,227]

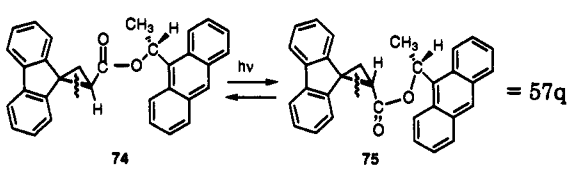
## B. Isomerizations Involving Energy Transfer

Chemical transformations by way of intramolecular energy transfer generally involve the triplet state of the anthracene chromophore. The photochemical di-$\pi$-methane rearrangement of 2,3-anthrabarrelene (72) to give 2,3-anthrasemibullvalene (73) with a quantum yield of 0.25 represents an interesting example of an isomerization which proceeds by intramolecular transfer of excitation energy from a higher triplet state of the anthracene chromophore to the substituting divinylmethane moiety.[228] It is worth noting that the skeletal rearrangement does not proceed by aryl–vinyl bridging, that the isomerization cannot be sensitized by biacetyl ($E_T$ = 55 kcal/mol), and that the $T_1$ state of 2,3-anthrabarrellene (~43 kcal/mol) is unreactive. Most likely, energy transfer occurs from the $T_2$ state of the anthracene ($E_T \approx$ 74 kcal/mol) to the di-$\pi$-methane moiety ($E_T \approx$ 57 kcal/mol) undergoing vinyl–vinyl bridging.



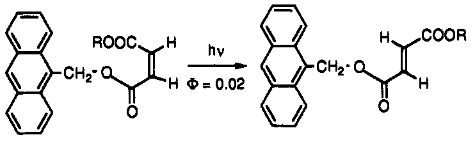
72 73

Photoexcitation of the anthracene $\pi$-system in diastereomeric (9-anthrylethyl)spiro[cyclopropane-1,9′-fluorene]-2-carboxylates 74 and 75 leads to a photostationary state with a 74:75 ratio of 95:5. On the basis of the degree of quenching by oxygen, the isomerization of the cyclopropane stereochemistry has been suggested to involve $T_2$ energy transfer from the anthracene to the fluorene and subsequent reversible cleavage of the cyclopropyl bond.[229] Photochemical isomerization experiments with 74/75 prepared from optically active $\alpha$-(9-anthryl)ethanol provided evidence for asymmetric induction by intramolecular $T_2$ energy transfer due to geometrically enhanced interaction between the anthracene and fluorene $\pi$-systems in one of the two diastereomers.



74 75

The photochemical isomerization of 9-anthrylmethyl methyl maleate (76) in benzene solution to give 9-anthrylmethyl methyl fumarate (77) with a quantum yield of 0.02 has been rationalized in terms of a triplet state reaction.[230] Since the energy of the triplet state of the maleate chromophore is assumed to be about 72–77 kcal/mol, triplet sensitization by intramolecular energy transfer from the photoexcited anthracene would have to involve its $T_2$ state.[231,232]

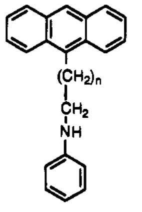


76 77

## VI. Chemical Consequences of Intramolecular Electron Transfer

During recent years, a multitude of reviews on photoinduced electron-transfer reactions have been published.[233-237] Therefore, the discussion in this section will be limited to some recent examples of intramolecular electron transfer induced photochemical transformations of anthracene derivatives.

Most spectroscopic studies of intramolecular electron transfer involving photoexcited anthracenes have been devoted to the formation of exciplexes with aromatic amines.[63,238] Irreversible chemical transformations by intramolecular electron transfer will lead to addition products derived from initially formed radical ions. Thus, irradiation of 9-(2-anilinoethyl)anthracene (78; $n$ = 1) in benzene gives in 58% yield the dihydroanthracene derivative 79, whose formation resembles an electrophilic substitution of the anilino moiety. Only minor amounts of the amination product 80 are formed in the photolysis of the (anilinoethyl)anthracene. Irradiation of 9-(3-anilinopropyl)anthracene (78; $n$ = 2) was found to give intramolecular addition products 81–83, although in low yield only (25%, 4%, and 4%, respectively).[239]



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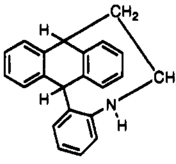

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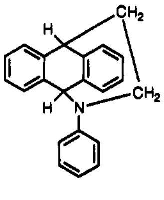

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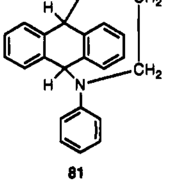

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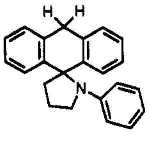

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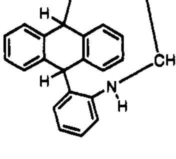
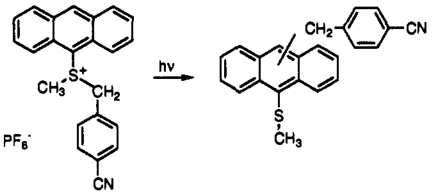
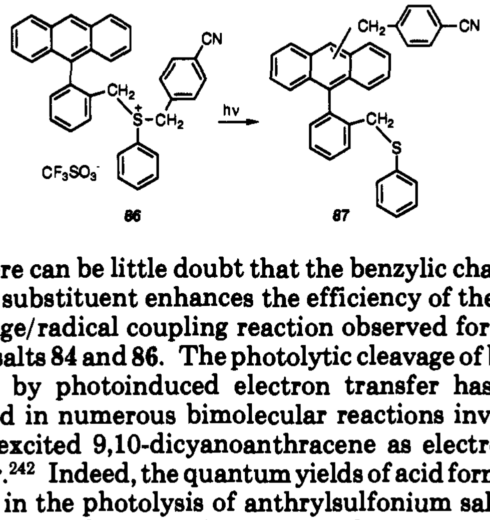


83

The chemical consequences of intramolecular photoinduced electron transfer involving the excited singlet state of the anthracene $\pi$-system as donor moiety, and sulfonium groups as electron acceptors are rearrangement and solvolysis reactions. For example, photoexcitation of the anthracene chromophore in (*p*-cyanobenzyl)methyl(9-anthryl)sulfonium hexafluorophosphate (**84**) in acetonitrile ($\lambda > 400$ nm) gives hexafluorophosphoric acid (100% yield) with a quantum yield of 0.77, and all five regioisomeric (*p*-cyanobenzyl)-substituted 9-(methylthio)anthracenes **85** (56% yield) with a quantum yield of 0.43. The relative preponderance of the 9,10 isomer (68%) over the 1,9 (15%), 2,9 (10%), 3,9 (2%), and 4,9 isomers (5%) has been attributed to a 9,10-bridged sulfonium ion intermediate. Solvolytic formation of 9-(methylthio)anthracene and the *N*-acetyl derivative of *p*-cyanobenzylamine, proceeding with a quantum yield of 0.34, competes with the photochemical rearrangement. Likewise, irradiation of the 9-phenylanthracene derived sulfonium salt **86** in acetonitrile was found to give rearrangement products **87** ($\Phi = 0.15$) and the corresponding solvolysis products ($\Phi = 0.17$).[240,241]

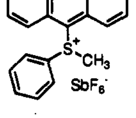


**84** **85**

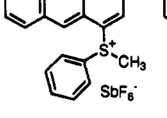


**86** **87**

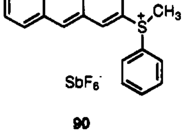
There can be little doubt that the benzylic character of the substituent enhances the efficiency of the bond cleavage/radical coupling reaction observed for sulfonium salts **84** and **86**. The photolytic cleavage of benzyl bonds by photoinduced electron transfer has been studied in numerous bimolecular reactions involving photoexcited 9,10-dicyanoanthracene as electron acceptor.[242] Indeed, the quantum yields of acid formation found in the photolysis of anthrylsulfonium salts **88**–**90** lacking the benzyl moiety are quite low (~0.1–2%).[243] Moreover, the quantum yields are dependent on the excitation wavelength.



**88**

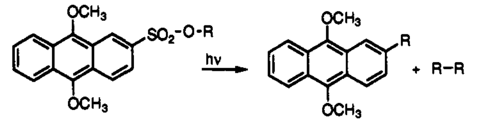


**89**



**90**

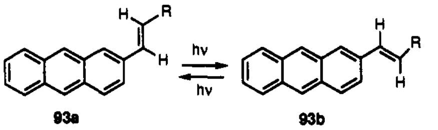
The formation of 9,10-dimethoxyanthracene-2-sulfonic acid ($\Phi = 0.10$), *p,p'*-dinitrobibenzyl, and 9,10-dimethoxy-2-(*p*-nitrobenzyl)anthracene (**92**) by photoexcitation of the anthracene chromophore in *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (**91**) in acetonitrile solution is typical of radical ion chemistry. The presence of an electron-withdrawing substituent in the para position of the benzyl moiety appears to be a prerequisite for the cleavage to occur, as benzyl 9,10-dimethoxyanthracene-2-sulfonate was found to be photostable.[244,245]



**91** R = *p*-nitrobenzyl **92**

## VII. Excited-State Reactions of Anthryl-Substituted Alkenes, Azomethines, and Azines

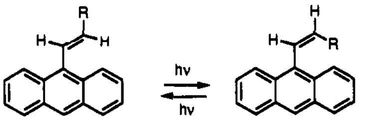
Photochemical transformations of anthryl-substituted alkenes, particularly their geometrical isomerization, have been investigated extensively during the past 10 years, since it was found that various anthryl-substituted *trans*-alkenes resist photochemical conversion to the cis isomer.[100,102,246,247] The mechanistic aspects of photochemical "one-way" isomerization of aromatic olefins are being reviewed elsewhere in the current issue of *Chemical Reviews*. As for the photochemical s-cis/s-trans isomerization (rotamerization) of anthryl-substituted alkenes such as **93a**/**93b**, this topic has recently been treated comprehensively and will not be considered here.[66,248]



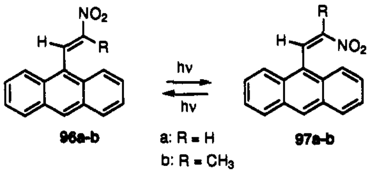
**93a** **93b**

### A. Geometrical Isomerization and Cycloaddition Reactions

Upon irradiation in dichloromethane solution, (9-anthryl)alkenes **94**–**97**, in which the alkene is conjugatively substituted by either carbonyl or nitro groups, undergo reversible geometrical isomerization in dichloromethane solution (see Table II). In the case of the nitrovinyl substituted anthracenes **96**/**97**, the quantum yields of geometrical isomerization are markedly solvent dependent. In benzene solution, $E \rightarrow Z$ isomerization of **96a** and **96b** proceeds with quantum yields of 0.20 and 0.14, respectively.[249,250]



**94a-b** a: R = $CH_3CO$ **95a-b**
b: R = $C_6H_5CO$



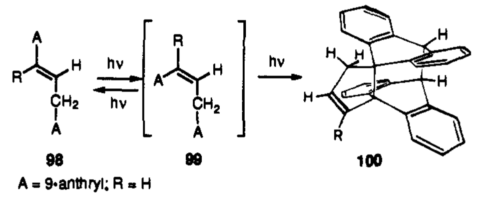
**96a-b** a: R = H **97a-b**
b: R = $CH_3$

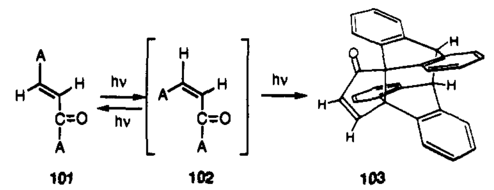
Geometrical isomerization and competing intramolecular cycloaddition reactions characterize the photochemistry of (9-anthryl)alkenes which contain an additional anthracene chromophore (cf. section VIII.B). Thus, irradiation of *trans*-1,3-di(9-anthryl)propene (**98**)

**Table II. Quantum Yields of $E/Z$ Isomerization of (9-Anthryl)alkenes 94–97 in Dichloromethane**

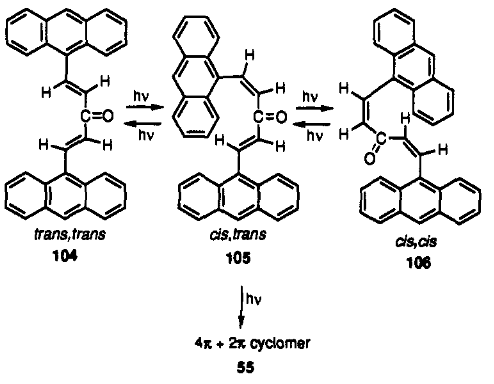
| compd | R | Φ | | ref |
|---|---|---|---|---|
| | | $E \rightarrow Z$ | Z-E | |
| **94a/95a** | $CH_3CO$ | 0.39 | 0.32 | 102 |
| **94b/95b** | $C_6H_5CO$ | 0.28 | 0.1 | 102 |
| **96a/97a** | H | 0.008 | 0.005 | 249 |
| **96b/97b** | Me | 0.055 | 0.004 | 250 |

in benzene smoothly gives the cycloaddition product **100**, albeit with low quantum yield (<0.001). Attempts to detect by absorption spectroscopy the intermediate cis isomer **99** during the course of the reaction have not been successful, because the quantum yield of intramolecular cycloaddition of **99** is far higher (0.25).[102] Similar features characterize the photochemical isomerization of *trans*-1,3-di(9-anthryl)propenone (**101**).

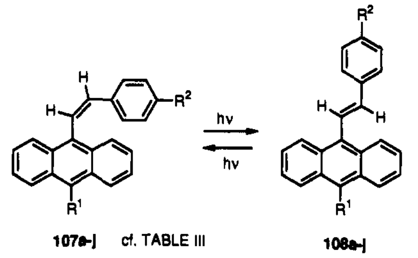




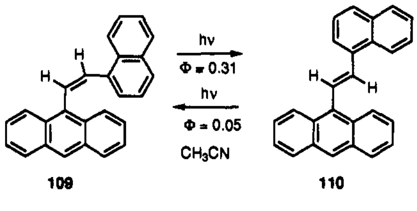
*trans,trans*-Dianthrylpentadienone **104** isomerizes photochemically in oxygen-saturated solution to give a mixture of cis,trans isomer **105** and the cis,cis isomer **106**. However, irradiation of **104** under nitrogen smoothly leads via the cis,trans isomer **105** to the cyclomer **55**. Its formation from **105** involves the Diels–Alder addition of the trans-(9-anthryl)alkene double bond to the central ring of the other anthracene moiety. The quenching by oxygen suggests that the $4\pi + 2\pi$ cycloaddition proceeds as a triplet-state reaction, while the geometrical isomerization of **105**/**106** involves the excited singlet state.[102] (For the photolytic rearrangement of **55**, see section IV.)



Considerable experimental and theoretical efforts have been devoted to the photochemistry of styrylanthracenes.[251-257] It has been established for both *cis*- and *trans*-9-styrylanthracene (**107a**/**108a**) that steric repulsions involving the vinyl group and H-1/H-8 of the anthracene preclude planar ground-state conformations, so that electronic conjugation of the styryl and anthracene π-systems is impaired even for the trans isomer **108a**.[103] In cyclohexane solution, *cis*-9-styrylanthracene (**107a**) is photochemically converted into the trans isomer **108a** with a quantum yield of 0.22, but the reaction is irreversible, i.e. trans → cis isomerization is not observed in cyclohexane, although **108a** reacts slowly (Φ = 0.0014) to give some unidentified product.[207,251] Time-resolved fluorescence decay measurements reveal the photochemical cis → trans isomerization of 9-styrylanthracenes to proceed adiabatically. Significantly, polar solvents and polar substitutents in the para position of the styryl group (see Table III) have been found to facilitate the photochemical trans → cis isomerization of 9-styrylanthracenes, conceivably by way of intramolecular electron-transfer processes. For the *N,N*-dimethylamino derivative **108b**, trans → cis isomerization is remarkably efficient in cyclohexane. The trans → cis isomerization of the nitro derivative **108h** is worth noting, as it proceeds with lower quantum efficiency in acetonitrile than in cyclohexane. Formyl substitution of the 10-position of the anthracene moiety virtually quenches trans → cis isomerization in **108i**, possibly by altering the character of the lowest excited state.



Even in the absence of polar substituents, trans → cis isomerization can be enhanced in polar solvents. The trans isomeric anthryl naphthyl ethylene **110** cannot be converted into its cis isomer **109** by irradiation in cyclohexane, but the trans → cis isomerization proceeds smoothly in acetonitrile, albeit with low quantum efficiency.

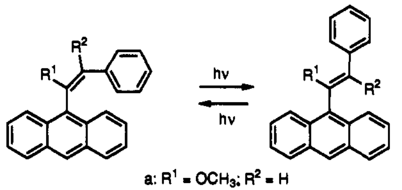


Substitution of the carbon–carbon double bond in 9-styrylanthracene by either methoxy or nitro groups also was found to facilitate photochemical $E \rightarrow Z$ isomerization. For example, the photochemical conversion of the **111a,b** into their corresponding $Z$ isomers **112a,b** proceeds in cyclohexane solution with quantum yields of 0.23 and 0.14, respectively. The corresponding quantum yields for the reverse reaction are 0.23 and 0.045, respectively.

The photochemistry of the parent *trans*-1,2-di(9-anthryl)ethylene (**114a**) resembles that 9-styrylanthracene **108a** insofar as geometrical isomerization of the ethylene double bond is not observed. Surprisingly, the cis isomer **113a** also is characterized by extremely

**Table III. Quantum Yields of Geometrical Isomerization of Substituted 9-Styrylanthracenes 107/108 in Cyclohexane and in Acetonitrile[251,257]**

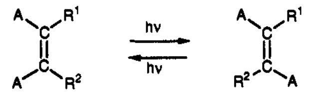
| | | | $\Phi$ | |
|---|---|---|---|---|
| | $R^1$ | $R^2$ | cis→trans ($C_6H_{12}/CH_3CN$) | trans→cis ($C_6H_{12}/CH_3CN$) |
| **107a/108a** | H | H | 0.22/0.41 | <0.01/0.003 |
| **107b/108b** | H | $NMe_2$ | 0.18/0.40 | 0.24/0.22 |
| **107c/108c** | H | OMe | 0.17/0.25 | 0.02/0.33 |
| **107d/108d** | H | Me | 0.19/0.36 | <0.01/0.18 |
| **107e/108e** | H | CN | 0.47/0.46 | <0.01/0.41 |
| **107f/108f** | H | CHO | 0.70/0.35 | 0.02/0.38 |
| **107g/108g** | H | $C_6H_5CO$ | 0.45/0.32 | 0.20/0.26 |
| **107h/108h** | H | $NO_2$ | 0.51/0.05 | 0.13/0.02 |
| **107i/108i** | CHO | H | 0.41/0.34 | 0/0 |
| **107j/108j** | CHO | $C_6H_5CO$ | ? | 0/0 |



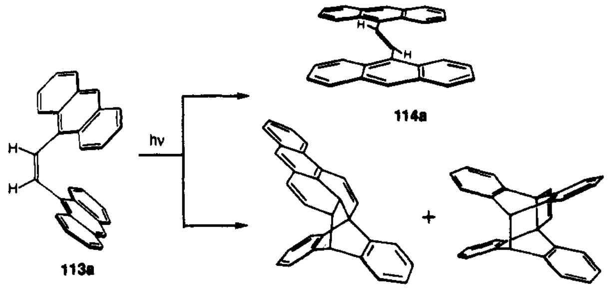
a: R¹ = OCH₃; R² = H
b: R¹ = H; R² = NO₂

**111a-b** **112a-b**

inefficient photochemistry. The conversion of **113a** into the trans isomer **114a** proceeds in cyclohexane with a quantum yield of only 0.0007, (0.015 in chloroform), and equally inefficient is the isomerization of **113a** by $4\pi + 2\pi$ cycloaddition to give **115** ($\Phi = 0.0007$), and by $4\pi + 4\pi$ cycloaddition to give **116** ($\Phi < 0.0007$).[258,259]



**113a-f** A = 9-anthryl **114a-f**
(see Table IV)

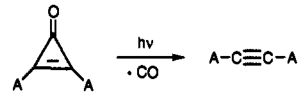


**113a** **114a** **115** **116**

**Table IV. Quantum Yields of Geometrical Isomerization and Cycloaddition for 1,2-Di(9-anthryl)ethylenes 113/114 (in $C_6H_{12}$)**

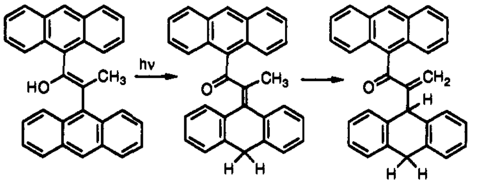
| 113/114 | $R^1$ | $R^2$ | 114→113 | 113→114 | 113→cycl | addition |
|---|---|---|---|---|---|---|
| a | H | H | ≪0.0001 | 0.0007 | 0.0007 | $4\pi + 2\pi$ |
| b | H | CHO | 0.22 | 0.015 | <0.001 | $4\pi + 2\pi$ |
| c | H | MeOCO | 0.20 | 0.015 | <0.001 | $4\pi + 2\pi$ |
| d | H | MeO | 0.088 | 0.053 | 0.0012 | $4\pi + 4\pi$ |
| e | MeO | MeO | 0.26 | 0.049 | 0.0025 | $4\pi + 4\pi$ |
| f | Me | MeO | ? | <0.01 | 0.20 | $4\pi + 4\pi$ |

Substitution of the ethylene bond profoundly affects the excited-state properties of 1,2-dianthrylethylenes **113**/**114**, as it changes their ground-state molecular geometry to the effect of increasing the dihedral angle between the ethylene and anthracene $\pi$-systems.[109] Significantly, trans to cis isomerization is observed, the cis isomer is favored at the photostationary state, and quantum yields may be as high as 0.26 (see Table IV). Moreover, as the dihedral angle between the ethylene and anthracene $\pi$-system increases by substitution, photochemical isomerization of *cis*-dianthrylethylenes by Diels–Alder reaction becomes negligible, and intramolecular $4\pi + 4\pi$ cycloaddition is predominant. Dianthrylethylene **113f**, for which electronic absorption and emission spectra, as well as X-ray diffraction data indicate enhanced intramolecular interaction of the two anthracene $\pi$-systems, undergoes intramolecular $4\pi + 4\pi$ cycloaddition with a quantum yield of 0.20.[108] Irradiation of di-9-anthrylcyclopropenone (**117**) in cyclohexane, by contrast, does not result in dianthrylethylene photochemistry, but decarbonylation smoothly leads to di(9-anthryl)acetylene (**118**) with a quantum yield of 0.14.[108,260]



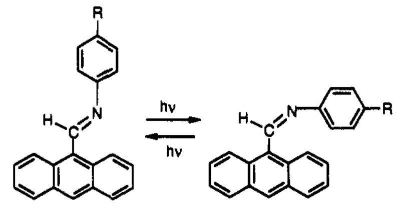
**117** A = 9-anthryl **118**

Unexpectedly, the photochemical isomerization of the 9-anthryl-substituted enol **119** in dichloromethane gives the 9,10-dihydroanthracene derivative **121** ($\Phi$ = 0.18). It has been suggested that the photochemical step leads to the intermediate ketone **120** which isomerizes by way of a ground-state 1,7-hydrogen shift.[108]

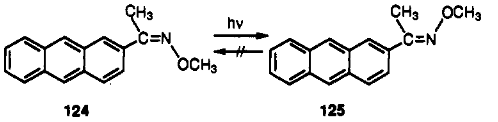


**119** **120** **121**

The photophysical and photochemical properties of 9-anthryl-substituted azomethines **122**/**123** (R = H, Br, $NO_2$) have recently been investigated. For R = $NO_2$, the involvement of the excited triplet state in the geometrical isomerization has been suggested.[261] The excited-state properties of (*E*)- and (*Z*)-*N*-methoxy-1-(2-anthryl)ethanimine (**124**/**125**) have recently been studied in detail with respect to both geometrical and rotational isomerism.[262]



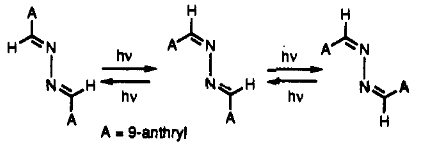
**122** **123**



**124** **125**

The photochemical geometrical isomerization of various 9-anthryl-substituted azines has been of interest in conjunction with their photochromic properties.[263-265]

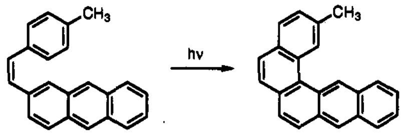
The distinctly different emission spectral properties of the photochemically interconvertible three isomeric 9-anthraldehyde azines **126**–**128** are attributed to differences in their molecular geometry.[266]



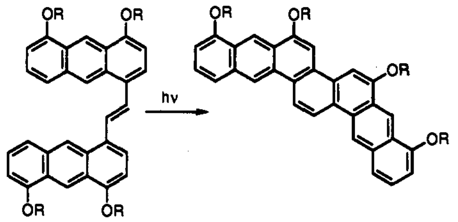
**126** **127** **128**

## B. Dehydrocyclizations

Intramolecular photochemical dehydrocyclizations of anthracene-related compounds are well known for bianthrone and similar stilbene-like anthrone derivatives.[267–271] In recent years, several examples of styryl-substituted anthracenes undergoing photochemical dehydrocyclization have been reported. Irradiation of styryl-substituted anthracene **129** in xylene for 60 h gave **130** in 15% yield.[272,273] The photochemical conversion of the tetradecyloxy-substituted 1,2-di(1-anthryl)ethylene **131** into the dibenzopicene **132** (15% yield) is of interest because the conceivable isomerization of **131** by $4\pi + 4\pi$ cycloaddition was not observed.[274]

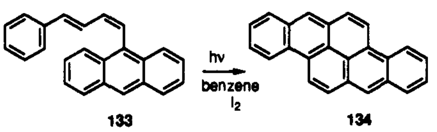


**129** **130**



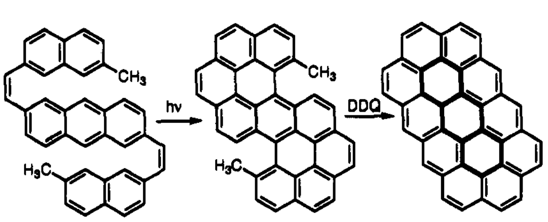
**131** R = n-$C_{10}H_{21}$ **132**

The conversion 1-(9′-anthryl)-4-phenyl-1,3-butadiene (**133**) leading to the dibenzopyrene **134** (7% yield) by



**133** **134**

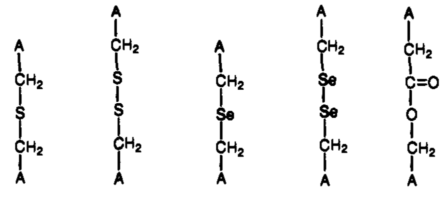
way of two consecutive cyclization and dehydrogenation steps requiring 84 h of irradiation obviously is very inefficient.[275] By contrast, irradiation of **135** in toluene in the presence of iodine in an argon atmosphere afforded **136** in 93% yield by a remarkable 4-fold cyclodehydrogenation. The reaction is of considerable synthetic interest because dehydrogenation of **136** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) proceeds smoothly to give circumanthracene (**137**).[276]



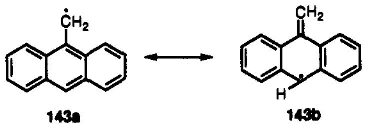
**135** **136** **137**

## VIII. Isomerization of Non-Conjugatively Linked Bichromophoric Anthracenes

Photoexcited bichromophoric anthracenes characterized by a weak link in the connecting chain of atoms may deactivate by way of fragmentation. For example, irradiation of (9-anthryl)methyl sulfides, disulfides, selenides, and diselenides (**138**–**141**; A = 9-anthryl) leads to the $4\pi + 4\pi$ photoisomer of 1,2-di(9-anthryl)ethane and to lepidopterene (see below), i.e. products derived by dimerization of (9-anthryl)methyl radical **143a**/**143b**.[277,278] Photoexcitation of (9-anthryl)methyl (9-anthryl)acetate (**142**) also gives (9-anthryl)methyl radicals by way of decarboxylation, and the high quantum yield of disappearance of **142** ($\Phi$ = 0.38) probably is attributable to the formation of the 1,2-di(9-anthryl)ethane photoproduct and lepidopterene, rather than an intramolecular $4\pi + 4\pi$ cycloaddition product of (9-anthryl)methyl (9-anthryl)acetate, as has been suggested.[279,280]

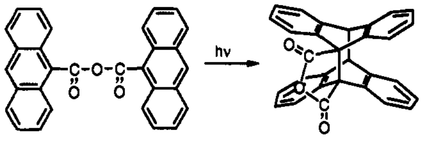


**138** **139** **140** **141** **142**

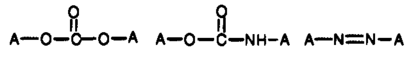


**143a** **143b**

Unimolecular photochemistry of compounds containing two anthracene moieties frequently involves isomerization by intramolecular $4\pi + 4\pi$ cycloaddition, as was first observed by the conversion of 9-anthroic anhydride (**144**) into **145**.[21,32] Structurally similar compounds such as the carbonate **146**, amide **147**, and the azo compound **148** (A = 9-anthryl) were found to



**144** **145**



$A{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}A \quad A{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}A \quad A{-}N{=}N{-}A$

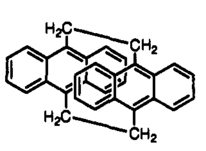
**146** **147** **148**

undergo intramolecular $4\pi + 4\pi$ cycloaddition in the same fashion.[281] In principle, the photochemical isomerization of bichromophoric anthracenes thus resembles the bimolecular reaction of anthracene. However, subsequent systematic studies on bichromophoric anthracenes have revealed that other modes of cycloaddition than $4\pi + 4\pi$ "head-to-head dimerization" are possible. By and large, the unimolecular photochemistry of non-conjugatively linked bichromophoric anthracenes is found to be intimately related to their ground-state molecular geometry and may also be governed by substituents which affect the intrinsic quantum yield of intersystem crossing from the excited singlet to the triplet state.

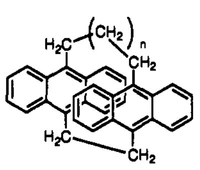
## A. Anthracenophanes and Anthraceno Crown Ethers

The spectroscopic and photochemical properties of anthracenophanes, crown ethers, and cryptands have been reviewed previously, so that only some principal features of their photochemistry are outlined below.[139,283]

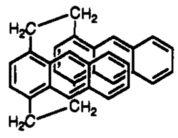
The thermally reversible photochemical isomerization of [2.2](9,10)anthracenophane (**149**) has been investigated most thoroughly, and the structures of both **149** and its photoisomer formed by intramolecular $4\pi + 4\pi$ cycloaddition have been established by X-ray diffraction.[282-290] The anthracene skeletons in **149** were found to be bent about the 9,10-axis by 19° (161°), and the distance between the bond-forming carbon atoms (9,9′:10,10′) is only 2.77 Å.[289] Photochemical isomerization of **149** proceeds even in rigid matrix at 4 K. In solution at room temperature (and at 77 K), anthracenophane **149** is nonfluorescent, there is no excimer state observable, and the quantum yield of photochemical isomerization is 0.36. Evidence for biradical intermediates in the photochemical reaction and the thermal cycloreversion has not been obtained.[282,288]



**149**



**150a-b** a: n = 1
b: n = 2



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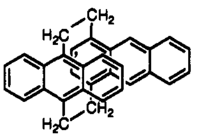

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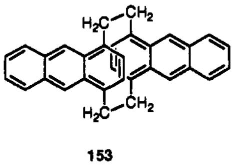

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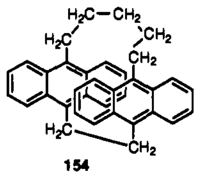
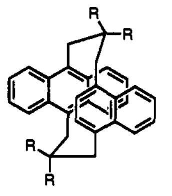


**154**

Other anthracenophanes undergoing photochemical isomerization by $4\pi + 4\pi$ cycloaddition are [2.3](9,10)anthracenophane (**150a**), [2.4](9,10)anthracenophane (**150b**), *syn*-[2.2](1,4)anthracenophane (**151**), and [2.2](1,4)(9,10)anthracenophane (**152**).[285,288,291,292] For anthracenophane **151**, excimer fluorescence has been detected in rigid solution, and it has been established, that the cycloaddition reaction involves deactivation of the excimer state.[285] In a process competing with the intramolecular $4\pi + 4\pi$ cycloaddition, **151** undergoes geometrical isomerization to give *anti*-[2.2](1,4)anthracenophane (**153**) which is characterized by structured fluorescence ($\Phi = 0.27$).[285] Probably due to steric constraints, [2.5](9,10)anthracenophane (**154**) does not isomerize photochemically by cycloaddition.[292]

Several [3.3](1,4)naphthaleno(9,10)anthracenophanes and diaza[3.3]paracyclo(9,10)anthracenophanes such as **155** and **156** have been found to undergo thermally reversible photoisomerization by $4\pi + 4\pi$ cycloaddition with quantum yields of about 10–30%.[293-296] As for dithia[3,3]paracyclo(9,10)anthracenophanes, their photochemistry is characterized by sulfur extrusion, as exemplified by the conversion of **157** into **158**.[297] This type of reaction has been of value in cyclophane synthesis. However, attempts to extrude sulfur by irradiation of dithia[3,3](2,7)anthracenophane have not been successful.[298]



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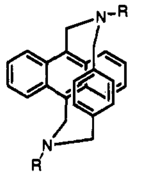
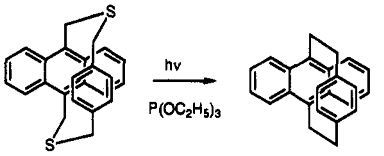
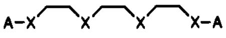


**156**



**157** **158**

The photochemical isomerization of polyether-linked bichromophoric anthracenes such as **159** (X = O) has been studied extensively.[67,299-305] Quantum yield measurements have revealed that $\alpha,\omega$-dianthryl polyethers may isomerize much more efficiently than the corresponding $\alpha,\omega$-dianthrylalkanes. For example, the $\alpha,\omega$-di-9-anthryl-substituted polyether **159** (X = O) isomerizes upon irradiation in benzene by $4\pi + 4\pi$ cycloaddition with a quantum yield of 0.32 to give a thermally labile cyclomer ($t_{1/2}$ ca. 3 min).[299] By contrast, photoexcited 1,10-di(9-anthryl)decane (**159**; X = $CH_2$) in benzene disappears with a quantum yield of $<10^{-4}$, conceivably in a bimolecular reaction (see section VIII.B).



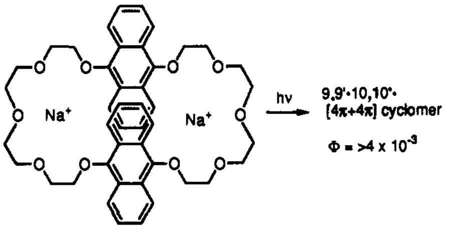
**159** A = 9-anthryl

Due to changes in molecular geometry, the course of the photochemical isomerization of anthraceno crown ethers may be affected by the presence of complexed metal ions. Thus, irradiation of the sodium ion complexed bis(anthraceno) crown ether **160** affords the 9,9′:10,10′-symmetrical isomer formed by $4\pi + 4\pi$ cycloaddition, while irradiation in the absence of sodium ions leads to the dissymmetrical isomer formed by 1,9′:4,10′ $4\pi + 4\pi$ cycloaddition.[127] For more rigidly linked anthraceno crown ethers of limited intramolecular mobility, such as **161**, metal complexation has been

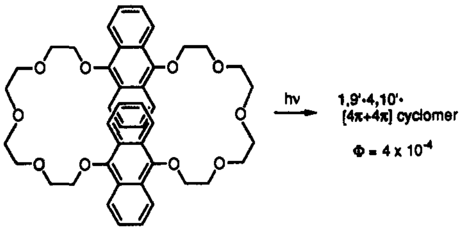
**Table V. Quantum Yields of Fluorescence ($\Phi_F$) and Isomerization ($\Phi_R$) for Di-(9-anthryl)methane Derivatives 162, 164, and 166**

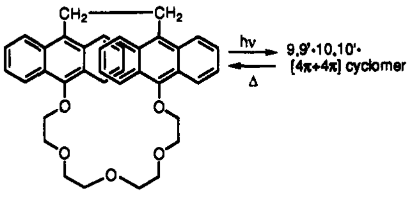
| compd | $\Phi_F$ | $\Phi_R$ | solvent | cycloaddition |
|---|---|---|---|---|
| **162a** | 0.06 | 0.15 | benzene | $4\pi + 4\pi$ |
| **162b** | 0.02 | 0.29 | benzene | $4\pi + 4\pi$ |
| **162c** | 0.02 | 0.05 | benzene | $4\pi + 4\pi$ |
| **164** | 0.18 | 0.45 | toluene | $4\pi + 2\pi$ |
| **166** | <0.0001 | 0.0003 | benzene | $4\pi + 2\pi$ |

found to be without effect on the efficiency of photochemical isomerization by intramolecular $4\pi + 4\pi$ cycloaddition.[301]



**160**

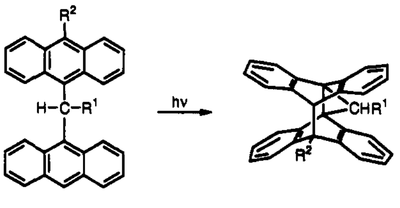




**161**

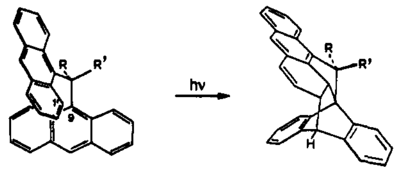
## B. Dianthrylalkanes and Their Derivatives

Pertinent excited-state properties of di(9-anthryl)methane derivatives **162** are summarized in Table V. Both di(9-anthryl)methane (**162a**) and di(9-anthryl)methanol (**162b**), and its 10-methoxy derivative **162c**, isomerize photochemically by $4\pi + 4\pi$ cycloaddition to give the corresponding cyclopropane derivatives **163a–c**.[282] By contrast, the photochemical isomerization of the methyl ester of 9-anthrilic acid (**164**) proceeds by $4\pi + 2\pi$ cycloaddition to give **165**.[306] The observed quantum efficiency of 0.45 is exceptionally high for a photochemical Diels–Alder reaction involving two anthracene π-systems, and may be compared to the quantum yield of 0.0003 which characterizes the analogous photochemical intramolecular Diels–Alder reaction of di(9-anthryl) ketone (**166**) leading to **167**.[307]

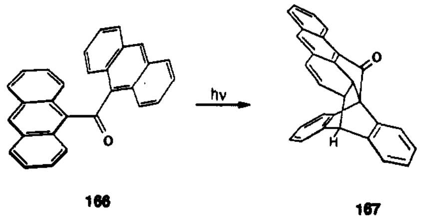


**162a-c** **163a-c**

a: $R^1 = R^2 = H$
b: $R^1 = OH$; $R^2 = H$
c: $R^1 = OH$; $R^2 = OCH_3$



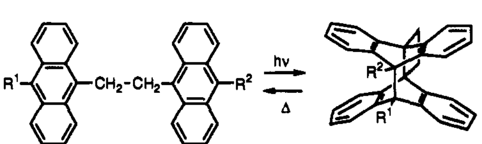
**164** $R = OH$; $R' = COOCH_3$ **165**



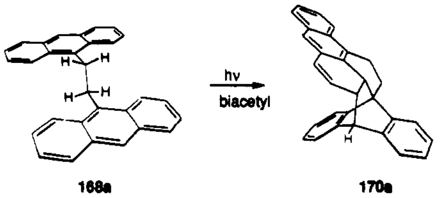
**166** **167**

The ground-state structures of **162a,b**, **164**, and **166** have been analyzed by X-ray diffraction, and the topological differences between dianthrylmethanol and dianthryl ketone were found to be insufficiently small to account for the difference in the observed mode of photochemical isomerization.[99,308,308] Since the isomerization of dianthryl ketone also was found to proceed in a biacetyl-sensitized reaction ($\Phi_R$ = 0.005), the observed $4\pi + 2\pi$ cycloaddition by direct excitation of **166** probably is due to an excited triplet state reaction. As for the $4\pi + 2\pi$ cycloaddition mode of **164**, the reaction apparently does not involve the excited triplet state, since its quantum efficiency is virtually unaffected by the presence of molecular oxygen. It is worth noting that the distance between the Diels–Alder termini C-9 and C1′ in **164** is as short as 2.86 Å and that the $4\pi + 2\pi$ cycloaddition of **164** also can be brought about in a thermal reaction.[309]

The excited state properties of 1,2-di(9-anthryl)ethane (**168a**) have been most frequently and thoroughly investigated during the past 25 years.[282,310-316] Deactivation of the first excited singlet state by fluorescence and by intramolecular $4\pi + 4\pi$ cycloaddition to give **169a** proceeds with quantum yields of 0.20 and 0.26, respectively.[282,310,314] Oxygen quenching experiments indicate that the triplet state may contribute slightly to the isomerization in thoroughly degassed solution.[310] Significantly, biacetyl-sensitized isomerization of dianthrylethane **168a** has been found to involve $4\pi + 2\pi$ (rather than $4\pi + 4\pi$) cycloaddition to give **170a** with a quantum yield of 0.1.[316] However,



**168a-i** **169a-i**



**168a** **170a**

**Table VI. Substituent Effects on the Quantum Yields of Fluorescence ($\Phi_F$) and Isomerization of Dianthrylethanes 168 by Cycloaddition ($\Phi_R$) in Cyclohexane**[314]

| 168 | $R^1$ | $R^2$ | $\Phi_F$ | $\Phi_R$ | $t_{1/2}$ of 169[a] |
|---|---|---|---|---|---|
| a | H | H | 0.20 | 0.26 | 385 years |
| b | H | $CH_3$ | 0.15 | 0.26 | 38 years |
| c | H | $CH_3O$ | 0.14 | 0.24 | 39 years |
| d | H | $CH_3COO$ | 0.40 | 0.14 | 130 years |
| e | H | $C_6H_5$ | 0.61 | 0.034 | 187 days |
| f | $CH_3$ | $CH_3$ | 0.16 | 0.14 | 33 min |
| g | $CH_3O$ | $CH_3O$ | 0.30 | 0.11 | 142 min |
| h | $CH_3COO$ | $CH_3O$ | 0.45 | 0.068 | 260 min |
| i | $CH_3COO$ | $CH_3COO$ | 0.74 | 0.015 | 234 min |

[a] $t_{1/2}$ is the half-life in solution at 25 °C.

**Table VII. Quantum Yields of Fluorescence ($\Phi_F$) in Cyclohexane and Quantum Yields of Isomerization by 4π + 4π Cycloaddition ($\Phi_R$) in Benzene for 1,3-Di(9-anthryl)propane Derivatives**[322]

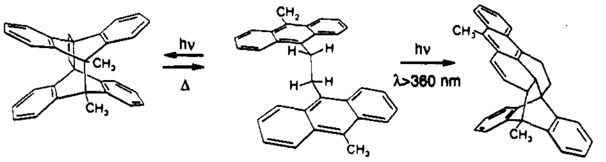
| propano-linked anthracene | $\Phi_F$ | $\Phi_R$ |
|---|---|---|
| 1,3-di(9-anthryl)propane | 0.47[a] | 0.14[a] |
| 1,3-di(9-anthryl)-1-propanol | 0.27 | 0.14 |
| 1,3-di(9-anthryl)-2-propanol | 0.48 | 0.046 |
| 1,3-di(9-anthryl)-2-methyl-2-propanol | 0.24 | 0.021 |
| 1,3-di(9-anthryl)-2-propanone | 0.009 | 0.25 |
| 1,3-di(9-anthryl)-2-butanone | 0.007 | 0.22 |
| 1,3-di(9-anthryl)-1-butanone | <0.001 | 0.40 |
| 1,3-di(9-anthryl)-1-propanone | <0.001 | 0.65 |
| 1,3-di(9-anthryl)-2-methyl-1-propanone | <0.001 | 0.72 |

[a] In methylcyclohexane; from ref 311.

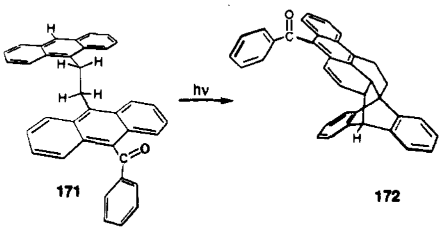
triplet-sensitized isomerizations of non-conjugatively linked anthracenes will proceed by 4π + 4π cycloaddition, if the molecular geometry of the electronic ground state facilitates parallel alignment of overlapping anthracene moieties, as is typical for propano-linked aromatic π-systems (see below).

The effects of 10,10′ substitution on the quantum yields of fluorescence and 4π + 4π cycloaddition of dianthrylethanes and on the stability of the photoisomers are summarized in Table VI.[314] For the isomerization of dianthrylethanes 168, a quantum yield of 0.26 appears to be the upper limit. Fluorescence quantum yields increase noticeably as quantum yields for isomerization decrease due to steric impairment by substitution. The fluorescence quantum yield of the 10,10′-diphenyl derivative of dianthrylethane is as high as 0.79, and photochemical isomerization has not been detected.[314]

The short half-life at room temperature of the dimethyl substituted 4π + 4π cyclomer **169f** is worth noting in conjunction with the fact that irradiation of **168f** at 70 °C affords the thermally more stable photoisomer **170f**, which derives from dianthrylethane **168f** by a competing photochemical 4π + 2π cycloaddition reaction of low quantum efficiency.[317] It is conceivable that the photochemical isomerization of **168f** by 4π + 2π cycloaddition involves the excited triplet state. The photochemical isomerization of 10-benzoyl-1,2-di(9-anthryl)ethane (**171**; $\Phi_F$ = 0.002) leading to the 4π + 2π cyclomer **172** also proceeds with low quantum yield (0.005), and evidence for a triplet-state reaction in that case has been obtained by biacetyl sensitization.

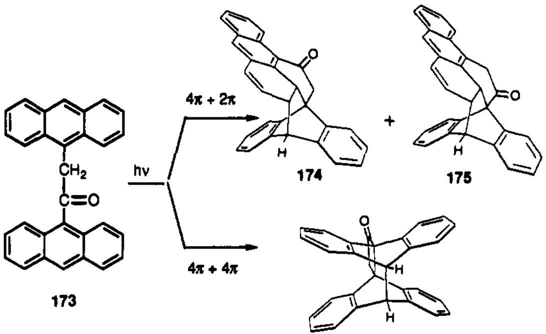


169f 168f 170f



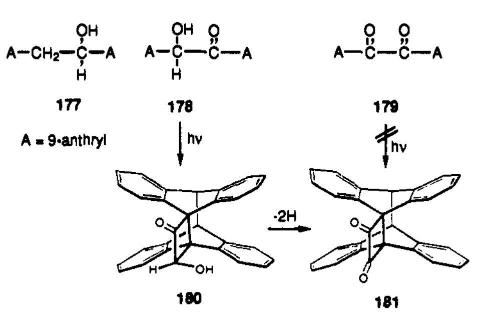
171 172

For photoexcited 1,2-di(9-anthryl)ethanone (**173**), the mode of isomerization by intramolecular cycloaddition has been found to be concentration dependent. Irradiation of **173** at low concentration (0.00003 M) affords mainly the two Diels–Alder products **174** and **175**, while the 4π + 4π cyclomer **176** is formed nearly exclusively by irradiation at higher concentration (0.0075 M). Dianthrylethanone is virtually nonfluorescent, and the quantum yield of intersystem crossing has been estimated to be about 0.6. Therefore, the 4π + 2π cycloadditions conceivably involve the triplet state. The 4π + 4π cyclomer **176** has been suggested to derive from the excited singlet state whose population at higher concentration could be attributable to triplet–triplet annihilation.[307,318]

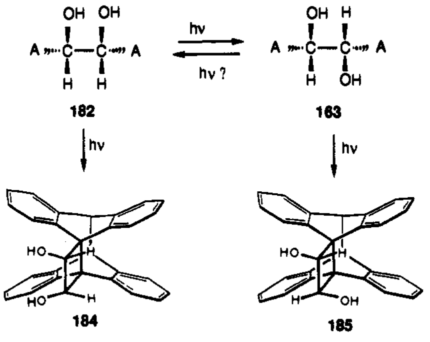


173 174 175 176

The photochemical isomerization of various other ethano-linked anthracenes has been investigated. Both 1,2-di(9-anthryl)ethanol (**177**) and 9,9′-anthroin (**178**) isomerize by 4π + 4π cycloaddition with quantum yields of 0.34 and 0.21, respectively.[307,319–321] Di(9-anthryl)ethanedione (**179**; 9,9′-anthril) upon irradiation gives, among various decomposition products, an isomer derived by intramolecular Diels–Alder reaction.[320] However, the 1,2-cyclobutanedione **181** is accessible from the anthroin photoisomer **180**.

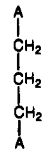


*meso*-Hydro-9,9′-anthroin (**182**) isomerizes photochemically ($\Phi = 0.15$) by 4π + 4π cycloaddition, but gives two stereoisomeric (cis and trans) 1,2-cyclobutanediols **184**/**185**. The formation of the trans isomer **185** indicates photoexcited *meso*-hydro-9,9′-anthroin undergoes stereoisomerization to give racemic *d*,*l*-hydro-9,9′-anthroin (**183**) by reversible scission of the central single bond.



**182** **183** **184** **185**

The photochemical isomerization of propano-linked bisanthracenes **186**–**195** (A = 9-anthryl) has been found to occur exclusively by 4π + 4π cycloaddition, and typical quantum yields of reaction and fluorescence are summarized in Table VII.[322] Both 1,3-di(9-anthryl)-1-butanols **190a** (1*R*,3*S*/1*S*,3*R*) and **190b** (1*R*,3*R*/1*S*,3*S*) isomerize with identical quantum yields (0.23), but stereochemical differences may be reflected in the different quantum yields of fluorescence (0.15 and 0.07, respectively). Photochemical isomerization of racemic 1,3-di(9-anthryl)propan-1-ol (**187**) in a chiral matrix of poly(methyl L-glutamate) was found to proceed enantioselectively. At 90% conversion, an enantiomeric excess of more than 30% was observed. In a separate experiment, it was established that the *l* isomer of **187** undergoes intramolecular 4π + 4π cycloaddition about 20% faster than the *d* isomer.[323]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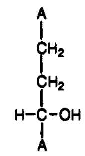
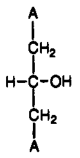
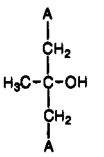
**186**


$\begin{array}{c}A\\|\\CH_2\\|\\CH_2\\|\\H-C-OH\\|\\A\end{array}$

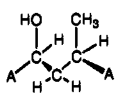
**187**


$\begin{array}{c}A\\|\\CH_2\\|\\H-C-OH\\|\\CH_2\\|\\A\end{array}$

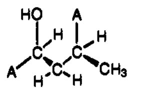
**188**


$\begin{array}{c}A\\|\\CH_2\\|\\H_3C-C-OH\\|\\CH_2\\|\\A\end{array}$

**189**

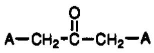


**190a**

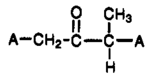


**190b**

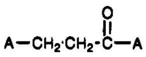
The involvement of the excited triplet state in the isomerization by 4π + 4π cycloaddition has been established by oxygen quenching and sensitization experiments for nonfluorescent propano-linked anthracenes **193**–**195** which are characterized by the presence of a 9-anthroyl group. The highly efficient isomerization of 1,3-di(9-anthryl)-1-propanone (**193**; $\Phi_R = 0.65$) and its 2-methyl derivative **195** ($\Phi_R = 0.72$) probably reflects an excimer geometry of parallel aligned overlapping anthracene π-systems. Spatially more crowded diastereomeric 1,3-di(9-anthryl)-2-methyl-1-butanones **196** (2*R*,3*S*/2*S*,3*R*) and **197** (2*R*,3*R*/2*S*,3*S*) undergo intramolecular 4π + 4π cycloaddition with quantum yields of 0.19 and 0.17, respectively.


$A-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-A$

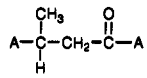
**191**


$A-CH_2-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{H}{C}}-A$

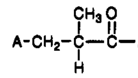
**192**


$A-CH_2\cdot CH_2-\overset{O}{\overset{\|}{C}}-A$

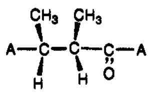
**193**


$A-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-A$

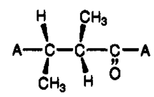
**194**


$A-CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-A$

**195**



**196**

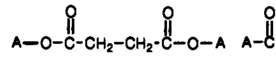


**197**

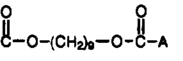
Photochemical isomerization by intramolecular 4π + 4π cycloaddition has been established for 1,4-di(9-anthryl)butane ($\Phi_R = 0.061$), but not for any of the higher α,ω-di(9-anthryl)alkane homologues. It is obvious from the quantum yields of reaction ($\Phi_R$), of fluorescence from the locally excited state ($\Phi_{FM}$), and of excimer fluorescence ($\Phi_{Fexc}$) listed in Table VIII that deactivation of the first excited singlet state by fluorescence becomes dominant when intramolecular cycloaddition becomes less favorable.[311] In line with earlier observations on a series of α,ω-dipyrenyl alkanes, quantum yields of excimer luminescence vary with the length of the alkane chain.[324] For 1,2-di(9-anthryl)ethane and 1,3-di(9-anthryl)propane, the question of excimer formation continues to be of interest, although excimer emission has been detectable only under special environmental conditions.[325–331]

In a recent emission spectroscopic investigation of α,ω-di(9-anthryl)alkanes of varying chain length ($C_3$, $C_5$, $C_7$, $C_{10}$, $C_{12}$, $C_{14}$, and $C_{18}$), picosecond time-resolved measurements have revealed intramolecular "excitation hopping" for photoexcited 1,7-di(9-anthryl)heptane and its higher homologues.[332]

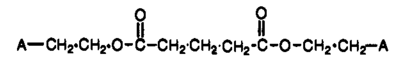
It should be pointed out that the quantum yields of disappearance of α,ω-di(9-anthryl)alkanes are not to be considered quantum yields of isomerization, because *inter*molecular cycloaddition may become an important competing reaction if *intra*molecular cycloaddition proceeds with low quantum yield. Thus, irradiation of di-9-anthryl succinate (**198**) was found to give a polymer by intermolecular head-to-tail 4π + 4π cycloaddition.[32] Polymer formation by intermolecular 4π + 4π cycloadditions of various linked bis-anthracenes has been studied in some detail.[333–337] For a series of bisanthracenes derived from 1-anthracene- and 2-anthracenecarboxylic acid, such as **199**, irradiation was found to give both intramolecular head-to-head and head-to-tail 4π + 4π cycloaddition products.[337] The photochemical isomerization of di-9-anthryl glutarate (**200**) has been found to involve a head-to-tail 4π + 4π cycloaddition, although another major photoproduct of unknown structure is formed as well.[338]


$A-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-A$

**198** A = 9-anthryl


$A-\overset{O}{\overset{\|}{C}}-O-(CH_2)_9-O-\overset{O}{\overset{\|}{C}}-A$

**199** A = 2-anthryl


$A-CH_2\cdot CH_2\cdot O-\overset{O}{\overset{\|}{C}}-CH_2\cdot CH_2\cdot CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2\cdot CH_2-A$

**200** A = 9-anthryl

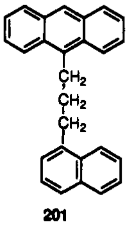
The problem of intermolecular reactions competing with intramolecular photochemistry of bichromophoric

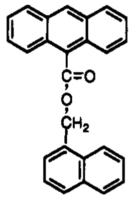
Table VIII. Quantum Yields of Reaction ($\Phi_R$), Monomer Fluorescence ($\Phi_{Fm}$), and Excimer Fluorescence ($\Phi_{Fexc}$) for $\alpha,\omega$-Di(9-anthryl)alkanes in Methylcyclohexane[a]

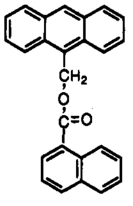
| alkane | $\Phi_R$ | $\Phi_{Fm}$ | $\Phi_{Fexc}$ |
|---|---|---|---|
| butane | 0.061 | 0.34 | 0.02 |
| pentane | 0.0011 | 0.31 | 0.16 |
| hexane | 0.0011 | 0.38 | 0.06 |
| heptane | 0.0012 | 0.37 | 0.04 |
| octane | 0.0011 | 0.33 | 0.14 |
| nonane | 0.0006 | 0.30 | 0.21 |
| decane | 0.0004 | 0.39 | 0.08 |

[a] From ref 311.

compounds can be circumvented by irradiation of very dilute solutions, as was noted for photochemical isomerization of 1-(9-anthryl)-3-(1-naphthyl)propane (201).[339-343] Irradiation at low concentration ($2 \times 10^{-5}$ M) smoothly gives the intramolecular $4\pi + 4\pi$ cyclomer, while irradiation at concentrations higher than $10^{-3}$ M results in intermolecular $4\pi + 4\pi$ cycloaddition involving two anthracene moieties. This finding suggests that $4\pi + 4\pi$ cycloadditions of anthracene to naphthalene proceed with low quantum yield. It is worth noting that neither **202** nor **203** isomerize upon irradiation, but undergo intermolecular anthracene–anthracene cycloaddition.[339]


**201**

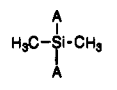

**202**


**203**

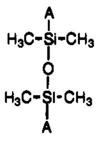
The mechanism of photochemical intramolecular $4\pi + 4\pi$ cycloaddition of linked anthracenes, and that of the photolytic cycloreversion, has been a subject of considerable interest with respect to the involvement of excimers and biradicals as intermediates.[312,313] In several electron spectroscopic studies on 1,2-di(9-anthryl)ethanes, evidence has been obtained for more than one excimer geometry, and for the existence of anti and gauche conformers.[285,314,325,330,331] Geometrically different excimers also have been detected spectroscopically for photoexcited 1,2-di(1-anthryl)ethane which undergoes intramolecular $4\pi + 4\pi$ cycloaddition involving the 9,10 positions of both anthracene moieties.[285] The polar character of the excimer state of dianthrylethanes is borne out in the dependence of its electronic structure on solvent polarity.[325] Moreover, results obtained by time-resolved picosecond laser spectroscopy indicate the formation of a common intermediate in the photochemical cycloaddition and cycloreversion, and it has been established spectroscopically that intramolecular electron transfer between the two aromatic moieties is involved in both the cycloaddition and cycloreversion process.[315,344]

## C. Dimethylsilyl-Linked Bichromophoric Anthracenes

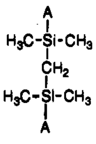
The effects of molecular geometry on the course of unimolecular photochemistry of bichromophoric anthracenes are particularly evident in the excited-state properties of bisanthracenes **204–207**, in which sub-


$A{-}Si(CH_3)_2{-}A$

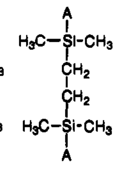
**204**


$A{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}A$

**205**

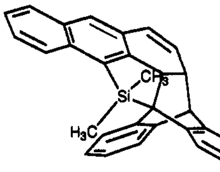

$A{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}A$

**206**

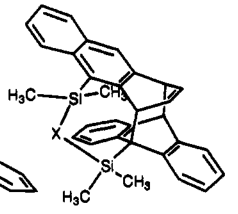

$A{-}Si(CH_3)_2{-}CH_2{-}CH_2{-}Si(CH_3)_2{-}A$

**207**

stitution of the 9,9′ positions by dimethylsilyl groups makes photochemical isomerization of di(9-anthryl) compounds by symmetrical $4\pi + 4\pi$ cycloadditions highly unfavorable for steric reasons. Thus, di(9-anthryl)dimethylsilane (**204**) isomerizes by $4\pi + 2\pi$ cycloaddition, involving as Diels–Alder termini the 9,10 and 1′,2′ positions of the two anthracene $\pi$-system, to give **208**.[345,346] Di(9-anthryl)dimethylgermane has been reported to react in the same manner.[346] The photochemical isomerization of 1,3-di(9-anthryl)-1,1,3,3-tetramethyldisiloxane (**205**), bis[(9-anthryl)dimethylsilyl]methane (**206**), and 1,2-bis[(9-anthryl)dimethylsilyl)]ethane (**207**) does proceed by $4\pi + 4\pi$ cycloaddition, but the reaction involves the 9,10-carbon atoms of one anthracene, and the 1,4-carbon atoms of the other, giving the corresponding cyclomers of structure **209**.[305,347,348] By this *dissymmetrical* mode of $4\pi + 4\pi$ cycloaddition, spatial overcrowding in the photoproducts due to interaction of the methyl groups and the proximate aromatic hydrogen atoms is decreased.



**208**



**206**

Excited-state properties of silyl-hinged bisanthracenes **204–207** in terms of reaction and fluorescence quantum yields are listed in Table IX. Significantly, photoexcited silicon-linked bis-anthracenes **205–207** exhibit both monomer fluorescence, i.e. emission from the locally excited state, and emission from an excimer state. For anthryl-substituted disiloxane **205**, the quantum yield of excimer emission is remarkably high. It has been established in a detailed spectroscopic investigation that isomerization by cycloaddition and fluorescence from the excimer state are competing processes, and the photoreactive excimer is suggested to be characterized by unsymmetrical arrangement of overlapping anthracene $\pi$-systems.[349]

## D. Anthrylalkyl Ethers

The intramolecular $4\pi + 4\pi$ cycloaddition of numerous bichromophoric (9-anthryl)methyl ethers has been extensively investigated in conjunction with their potential use as photochromic materials.[67,165,302,350-353] The effects of substituents on the excited state properties of bis[(9-anthryl)methyl] ethers **210a–f** in terms of quantum yields of cycloaddition and fluorescence in methylcyclohexane at room temperature are summarized in Table X. Quantum yields of reaction range from an optimal value of 0.32 for the parent compound **210a**, to 0.16 for disubstituted **210f** ($R^1$ = cyano; $R^2$ = phenyl). Slightly higher cyclization quantum yields

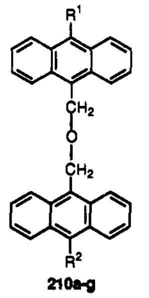
**Table IX. Quantum Yields of Isomerization ($\Phi_R$), Monomer Fluorescence ($\Phi_{Fm}$), and Excimer Fluorescence ($\Phi_{Fexc}$) for Silicon-Linked Bisanthracenes**

| compd | $\Phi_R$ | $\Phi_{Fm}$ | $\Phi_{Fexc}$ | cycloaddition |
|---|---|---|---|---|
| **204** | 0.05 | 0.45 | | $4\pi + 2\pi$ |
| **205** | 0.13 | 0.02 | 0.13 | dissymm $4\pi + 4\pi$ |
| **206** | 0.002 | 0.03 | 0.02 | dissymm $4\pi + 4\pi$ |
| **207** | 0.0008 | 0.085 | 0.025 | dissymm $4\pi + 4\pi$ |

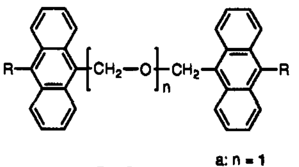
**Table X. Substituent Effects on the Quantum Yields of Fluorescence ($\Phi_F$) and Isomerization by Cycloaddition ($\Phi_R$) of Bis[(9-anthryl)methyl] Ethers 210 in Methylcyclohexane[350]**

| 210 | R¹ | R² | $\Phi_F$ | $\Phi_R$ |
|---|---|---|---|---|
| **a** | H | H | 0.03 | 0.32 |
| **b** | H | $CH_3$ | 0.07 | 0.32 |
| **c** | H | $C_6H_5$ | 0.09 | 0.19 |
| **d** | H | Br | 0.03 | 0.18 |
| **e** | $CH_3$ | CN | 0.05 | 0.25 |
| **f** | $C_6H_5$ | CN | 0.05 | 0.16 |

have been observed in acetonitrile.[350] Fluorescence quantum yields generally are <0.10.



**210a-g**
(see Table X)

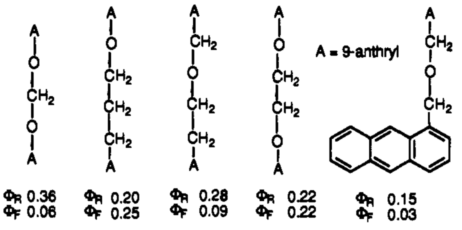


**211a-b** (R = $C_6H_5$)
a: n = 1
b: n = 2

Analogous to the 10,10′-diphenyl derivative of 1,2-di(9-anthryl)ethane **168** mentioned above (section VIII.B), photoexcited bis[(10-phenyl-9-anthryl)methyl] ether (**211a**; $n = 1$) does not isomerize, but is characterized by high fluorescence quantum yield of 0.55. More important, **211a** in fluid solution at room temperature exhibits both structured fluorescence, from the locally excited state ($\Phi = 0.21$), and red-shifted broad excimer emission ($\Phi = 0.34$), indicating geometrically favored intramolecular interaction of overlapping anthracene moieties.[350] The fluorescence properties of **211a** are dependent on solvent viscosity and have been exploited in probing molecular motions in polymers.[354]

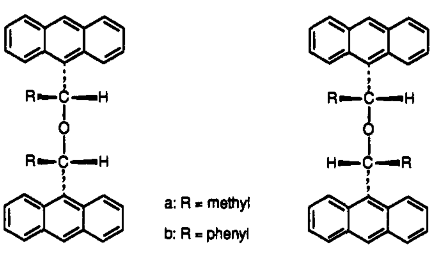
Dual emission in solution at room temperature also characterizes the excited state properties of the bis(10-phenyl-9-anthryl) ether **211b** ($n = 2$). However, extending the methyl ether linkage in **211a** by an oxymethylene group markedly alters the kinetics of excimer formation. Thus, the quantum yield of excimer emission has decreased to 0.21, and emission from the locally excited state of **211b** is as high as 0.69.[355]

For the series of 9-anthryl-substituted ethers **212**–**215**, quantum yields for the photochemical isomerization by $4\pi + 4\pi$ cycloaddition ($\Phi_R$) and fluorescence ($\Phi_F$) have been determined. In general, the ether-linked bis-anthracenes isomerize with higher quantum efficiency than the corresponding $\alpha,\omega$-di(9-anthryl)alkanes. The (9-anthryl)methyl ether of (1-anthryl)methanol (**216**) isomerizes with a quantum yield of 0.15 by dissymmetrical $4\pi + 4\pi$ cycloaddition involving the 9,10 and 1′,4′ positions of the 9-anthryl and 1-anthryl moieties, respectively.[165] Intramolecular $4\pi + 4\pi$ cycloaddition also characterizes the photochemistry of (9-anthryl)methyl ethers of (1-naphthyl)methanol and of furfuryl alcohol.[302,351] By contrast, irradiation of (9-anthryl)methyl ethers of (2-naphthyl)methanol, (9-phenanthryl)methanol, and (1-pyrenyl)methanol gave mixtures of intermolecularly formed head-to-head and head-to-tail dimers involving only the anthracene π-systems.[352]



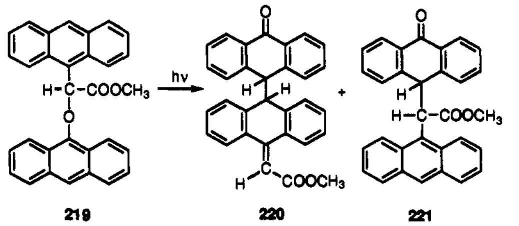
**212** **213** **214** **215** **216**

As for diastereomeric $\alpha,\alpha'$-disubstituted (9-anthryl)methyl ethers **217a,b** and **218a,b**, the *meso* form **217** and *d,l* form **218** have been found to isomerize by $4\pi + 4\pi$ cycloaddition with equal quantum efficiency ($\Phi = 0.25$).[356] However, the conformational differences between the *meso* and *d,l* forms are borne out in their distinctly different fluorescence properties. The *meso* form, which may assume a conformation of fully eclipsed parallel aligned anthracene π-systems, was found to be nonfluorescent. By contrast, the *d,l* diastereomers in cyclohexane solution at room temperature are fluorescent ($\Phi \sim 0.01$), and the emission derives mainly from an excimer state ($\lambda_{max}$ ~480 nm). Since a sandwich arrangement of two anthracene moieties in the *d,l* diastereomers **218** is precluded for structural reasons, the geometry of the luminescent excimer most likely is characterized by only partially overlapping anthracene π-systems.[356,357]



**217a-b** **218a-b**

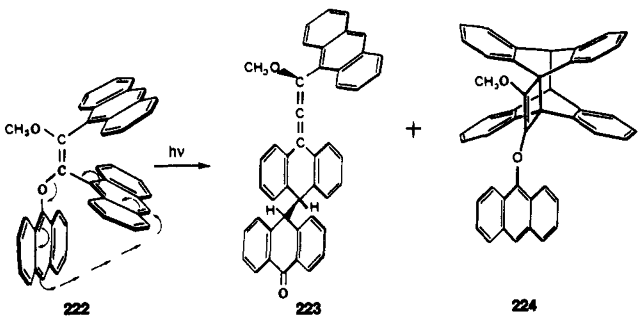
Some 9-anthryl (9-anthryl)methyl ethers have only recently become available and were found to isomerize photochemically by way of rearrangement to give 10-substituted 9-anthrones.[306] Thus, photoexcited **219** in toluene solution disappears with a remarkably high quantum yield of 0.57. Preparative irradiations, carried out in ethyl acetate solution with light of wavelengths > 400 nm, lead to anthrone derivatives **220** and **221** in



**219** **220** **221**

an approximate ratio of 4:1. In view of the CIDNP evidence obtained for the photochemical homolytic $\beta$-cleavage of (9-aryloxy)acetophenones (see section IV), the photochemical formation of the minor product **221** by an analogous radical mechanism appears probable. As for the major product, namely, anthronyl-substituted dihydroanthracene derivative **220**, another conceivable pathway may involve an intramolecular $4\pi + 4\pi$ cycloaddition of **219**, leading to an oxymethylene annelated dianthracene. Cleavage of the oxetane moiety in a thermal reaction would account for the observed product **220**.

Indications for the involvement of a cycloaddition step in the migratory rearrangement of 9-anthryloxy compounds to 9-anthrones has been obtained in an investigation of the trichromophoric anthracene **222**, which isomerizes with a quantum yield of 0.16.[306] For **222**, there are two intramolecular $4\pi + 4\pi$ cycloaddition reactions possible, and two isomeric photoproducts have been isolated. Photoisomer **224** deriving by intramolecular $4\pi + 4\pi$ cycloaddition of the *cis*-dianthrylethylene moiety in **222** is formed in only 13% yield. The major product, isolated in 67% yield, is the allene derivative **223**. Its stereochemistry about the allene moiety indeed is such as to have the methoxy group and the 9-anthronyl moiety cis oriented, as would be expected from either a concerted rearrangement of **222**, or from ring opening of a thermally labile oxetane intermediate.



**222** **223** **224**

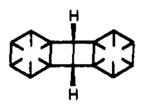
## IX. Retrospective Contemplations and Conclusions

In the realm of organic photochemistry, Fritzsche's name is intimately associated with the dimerization of anthracene.[358] However, Fritzsche himself emphatically rejected the idea that the hydrocarbon, which he had isolated from coal tar about 10 years before he described its "peculiar behavior towards sunlight", and which he had left unnamed, should be called *anthracene*.[2,359,360] He was aware of "paranaphthaline", melting around 180 °C, which Dumas and Laurent in 1832 had isolated from coal tar and which Laurent in 1837 had named "anthracène".[361,362] Fritzsche also knew the paper on "anthracene or paranaphthaline", which Anderson in Glasgow had published in 1861.[363] Anderson and his contemporaries active in the area of hydrocarbon chemistry, namely, Limpricht in Greifswald, Berthelot in Paris, and Graebe and Liebermann in Berlin, all considered Fritzsche's hydrocarbon and anthracene to be identical, though none of them ever noted its sensitivity toward light.[364-366] Fritzsche, by contrast, considered the photochemical properties and the fluorescence, which he discussed in detail, to be characteristic of his compound.[367] In a comprehensive paper published in two parts in 1868/1869, Fritzsche proposed that his hydrocarbon $C_{14}H_{10}$, melting at 210–212 °C, should be called photene ("Photen").[368] For another hydrocarbon, of somewhat lower melting point (195 °C), but very similar photochemical properties, he proposed the name phosene ("Phosen"), "to indicate both their behavior towards light, and their close relationship". For the photoproducts of photene and phosene, Fritzsche suggested the names paraphotene and paraphosene, respectively, and he had some experimental evidence to presume that "paraphosene maybe is formed from two molecules of phosene, and heat only halves paraphosene" ("peut-être, le paraphosène serait-il formé par deux molécules de phosène, et la chaleur ne faisait-elle que dédoubler le paraphosène").[368b,369] Fritzsche also remarked on a light-sensitive impurity he named "Chrysogen", which caused the yellow color of crude photene.

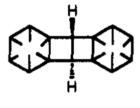
As for "artificially prepared anthracene", Fritzsche found the samples he had obtained from his "revered friend Limpricht", and from "Messrs. Gräbe and Liebermann" to be "photene, contaminated by a small amount of phosene". Fritzsche also checked a sample of Berthelot's anthracene, and proclaimed it to be "pure photene". This belated and seemingly obstinate claim to the name "photene" may seem remarkable, but should be seen in light of the significance which anthracene had gained in 1868 by its preparation from alizarin.[366] The discovery of the synthesis of alizarin from anthracene only one year later, when the structure of anthracene was still unknown, was to become the foundation of a chemical industry.[370]

Concerning phosene, Barbier in 1874 concluded from a reinvestigation that it was a mixture of anthracene and phenanthrene, which in 1872, the year after Fritzsche's death, had been discovered in crude anthracene.[371-373] Since phenanthrene does not dimerize upon irradiation, Fritzsche's "paraphosene" thus must have been dianthracene.

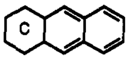
Ironically, the proposal of the correct structure of dianthracene (**2**) by Orndorff and Cameron in 1895 is based on their assumption that anthracene existed in cis and trans stereoisomeric forms **225a**/**225b**.[5] Armstrong's correct anthracene structure **226** of 1890, "wherein C is the nucleus of benzene", was rejected because it did not represent the chemical conduct of anthracene.



**225a**



**225b**



**226**

To paraphrase Armstrong, "such speculations, even if proved to be entirely false, at least served to suggest fresh lines of experimental inquiry, and on this account were not only permissible but also desirable".[374] In 1920, by comparison of refraction measurements on a substituted anthracene and its 9,10-dihydro derivative, von Auwers ruled out the commonly accepted 9,10-bridged anthracene structure, and confirmed Armstrong's "quinoid" structure **226**.[375] Nevertheless, as late as 1956, C. K. Ingold argued "that the pecularities of anthracene chemistry could not be explained away by double bond conjugation without bridged structures", and that "the 9:10-bridge must be of outstanding importance in anthracene".[376] The problem of "bridged anthracene" was finally settled in 1982, when Pritschins and Grimme accomplished the synthesis of 9,10-Dewar anthracene.[140]

Chrysogen, the yellow trace impurity in anthracene, which Fritzsche had found to undergo "a similar light-induced transformation as photene and phosene" deserves a comment.[1,2,377] Its structure remained a mystery until 1934, when the chromatographic separation of chrysogen from anthracene was accomplished in connection with cancer research. Chrysogen turned out to be identical with naphthacene (tetracene).[378] As a vindication of Fritzsche's original observations, the blue fluorescence of crystalline anthracene was found to be "nearly totally quenched by addition of 1/100 000%" of naphthacene. The phenomenon of energy transfer in crystalline anthracene and "anthracene-type" hydrocarbons containing small amounts of naphthacene was to be investigated in 1940 by Weigert, whose first fundamental contribution to the photochemistry of anthracene had been published 35 years earlier.[6,379] As for the photochemical properties of naphthacene, they are indeed similar to those of anthracene, and they are still being investigated.[380-384]

Perusal of the recent literature suggests that the anthracene chromophore will continue to play a prominent role in the development of organic photochemistry. The anthracene $\pi$-system remains to be a most useful auxiliary, be it in probing the photochemistry in micelles or cyclodextrins,[385-387] in structural studies on lipid membranes,[388] or the investigation of energy transfer in DNA.[389] Numerous new anthracene derivatives of potential photochemical and photophysical interest are being synthesized.[390-392] Their investigation by sophisticated experimental techniques should lead to a better understanding of excited-state reactions.

## X. References

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