

Unimolecular Photochemistry of Anthracenes

Hans-Dieter Becker

Department of Organic Chemistry, Chalmers University of Technology, and University of Gothenburg, S-412 96 Gothenburg, Sweden

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Contents

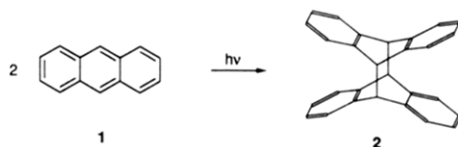
I. Introduction	145
II. Electron Spectral Properties of Anthracenes	146
III. Photochemistry of Nonplanar Anthracenes	147
IV. Photolytic Transformations of Anthracenes	149
V. Intramolecular Energy Transfer in Substituted Anthracenes	151
A. Photophysical Effects	151
B. Isomerizations Involving Energy Transfer	153
VI. Chemical Consequences of Intramolecular Electron Transfer	153
VII. Excited-State Reactions of Anthryl-Substituted Alkenes, Azomethines, and Azines	154
A. Geometrical Isomerization and Cycloaddition Reactions	154
B. Dehydrocyclizations	157
VIII. Isomerization of Non-Conjugatively Linked Bichromophoric Anthracenes	157
A. Anthracenophanes and Anthraceno Crown Ethers	158
B. Dianthrylalkanes and Their Derivatives	159
C. Dimethylsilyl-Linked Bichromophoric Anthracenes	162
D. Anthrylalkyl Ethers	162
IX. Retrospective Contemplations and Conclusions	164
X. References	165



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



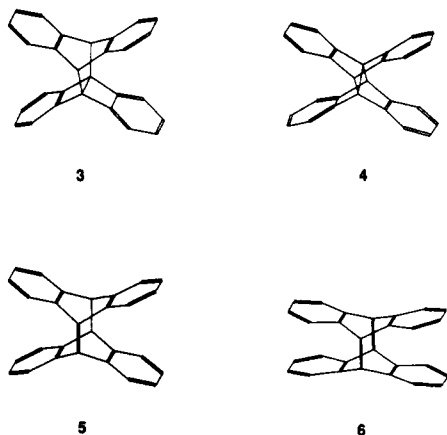
photoproduct was established in 1891 by molecular weight determination, and the correct structure was proposed before the turn of the century.^{3–5} Mechanism studies on the photochemical formation of dianthracene (2) commenced as early as 1905.⁶ In particular, the photophysical aspects and the reversibility of the reaction were studied during the following 50 years.^{7–19}

Between 1955 and 1965, concomitant with the renewed interest in organic photochemistry, many of the easily available substituted anthracenes were investi-

gated, 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 π -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 of 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 π -systems.^{57–59} Moreover,

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'-tetrahydrodianthracene (6).^{23,60-62}



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 $9\,000\text{ M}^{-1}\text{ cm}^{-1}$. The short wavelength absorption around 254 nm, having an extinction of about $200\,000\text{ M}^{-1}\text{ cm}^{-1}$, 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

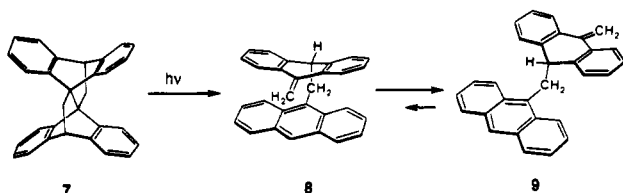
The energy difference between the electronic ground state (S_0) of anthracene and its first excited singlet state

(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

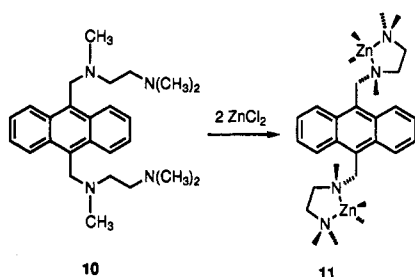
The effects of substituents on the electronic absorption and emission spectra of anthracenes have been of longstanding interest, and the fluorescence properties of substituted anthracenes have been studied in detail.⁷⁴⁻⁹¹ Substitution of the anthracene chromophore lowers the S_1 energy level, thus changing 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 π -chromophorically substituted anthracenes, such as 9-phenylanthracene, in which coplanarity of the two π -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 $10\,000\text{ cm}^{-1}$, 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 inter-

actions between a photoexcited anthracene π -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



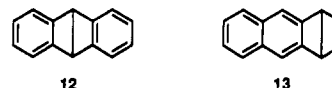
The chromophoric and fluorophoric properties of anthracene derivatives have long been of practical interest in analytical context, and numerous chemically reactive anthracene derivatives, such as isocyanates or acid chlorides, are being utilized as labeling agents for the detection and estimation of 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



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

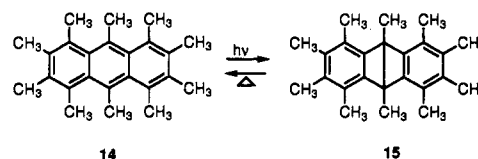
III. Photochemistry of Nonplanar Anthracenes

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

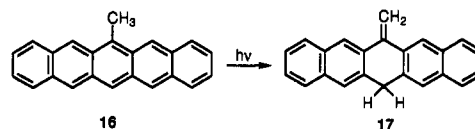


isomerization of anthracene, although both have been prepared by multistep syntheses.^{140,141} Dewar isomers **12** and **13** revert to anthracene in a thermal reaction which is associated with an activation barrier of 21.6 and 26.5 kcal/mol, respectively. For the 1,4-Dewar isomer **13**, it has been established that the photolytic electrocyclic ring opening, proceeding with a quantum yield of 0.41, in part affords electronically excited anthracene ($\Phi \sim 0.1$) in an adiabatic cycloreversion.¹⁴¹ The photolytic aromatization of 1,4-Dewar naphthalene also proceeds adiabatically.¹⁴²⁻¹⁴⁴

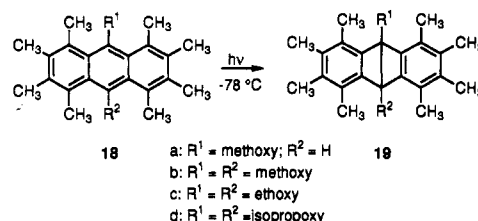
Decamethylanthracene (**14**), for which an X-ray diffraction analysis indicates the lateral benzene rings to assume boat conformations, smoothly yields the Dewar isomer **15** by direct irradiation at room temperature with Pyrex-filtered light in degassed solution.¹⁴⁵ Dewar anthracene **15** has been 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

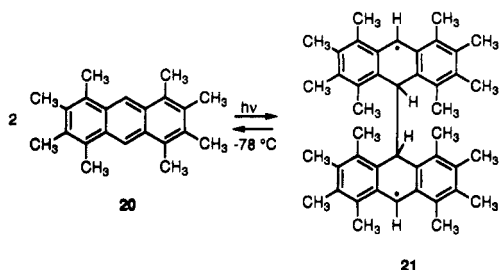


9-Methoxyoctamethylanthracene **18a** as well as 9,10-dialkoxyoctamethylanthracenes **18b-d** are seemingly photostable at room temperature. Upon irradiation at -78°C , however, anthracenes **18a-d** are found to react smoothly, giving the corresponding Dewar isomers **19**, whose structures were deduced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



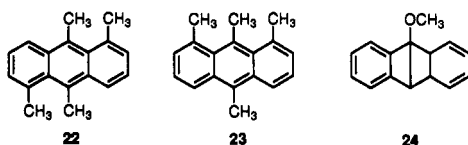
Significantly, irradiation of octamethylanthracene **20** at -78°C did not yield any Dewar isomer but produced a radical species, suggested to have structure **21**, from which octamethylanthracene **20** was regenerated above -30°C .¹⁵⁰

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



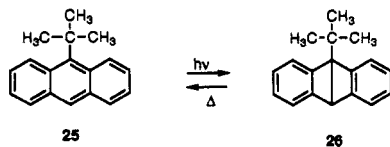
conditions leading to endoperoxides indicates that the anthracene π -system is geometrically distorted.¹⁵⁰ Similar easy autooxidation characterizes various (9,10)-anthracenophanes in which the anthracene π -system severely deviates from planarity.^{151,152}

Remarkably, 9-methoxyanthracene has recently been suggested to isomerize photochemically to give 9-methoxy(Dewar anthracene) (24), since it had been found



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 π -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 π -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°.

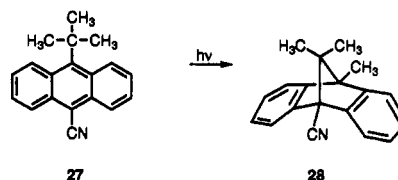


Unique photochemical properties of 9-*tert*-butylanthracene are indicated by its exceptionally low fluorescence quantum yield at room temperature and by negligible intersystem crossing to the triplet state. The photochemical isomerization of 9-*tert*-butylanthracene in dilute solution into the Dewar 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

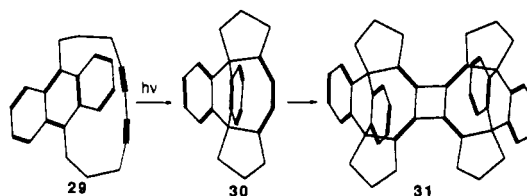
The only other geometrically distorted anthracene thus far found to be photochemically convertible ($\Phi = 0.016$) into its Dewar isomer is 9-*tert*-pentylanthracene ($\Phi_F = 0.008$).^{157,158} Unexpectedly, irradiation of 9-*tert*-butyl-10-cyanoanthracene (27) in acetonitrile at 0 °C does not give the corresponding Dewar anthracene but yields the isomeric dibenzonorborene 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

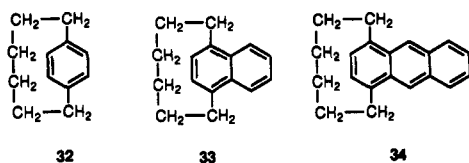
The photochemistry of 9-(trifluoromethyl)anthracene has been studied, and it was found to dimerize by $4\pi + 4\pi$ cycloaddition upon irradiation at 0 °C, even at low concentration ($< 10^{-4}$ M). The head-to-tail structure of the dimer was established by X-ray diffraction analysis.¹⁶⁴ Neither 9-(dimethylphenylsilyl)anthracene ($\Phi_F = 0.86$) 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)anthracenophane-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

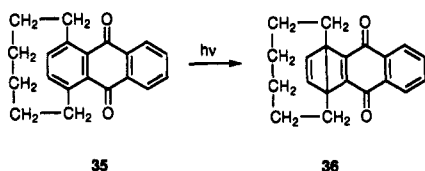


Recently, [6](1,4)anthracenophane (34) has been synthesized, and its bent molecular geometry has been established by X-ray diffraction.¹⁶⁸ Different from [6]-paracyclophane (32) and [6](1,4)naphthalenophane

(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}

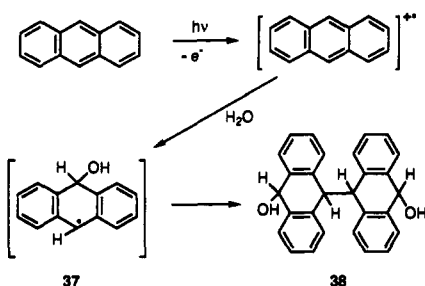


Various geometrically distorted 9,10-anthraquinone derivatives have been synthesized in recent years, and their photochemical isomerization has been investigated. Thus, [6]-1,4-cyclophaneanthraquinone (35) upon irradiation in deuteriochloroform or methylcyclohexane solution, using light of wavelengths >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.

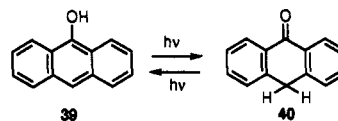


IV. Photolytic Transformations of Anthracenes

Unimolecular transformations of unsubstituted anthracene have not been reported yet. However, the photolysis of anthracene in very dilute aqueous solution (3×10^{-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

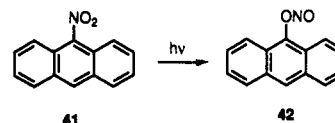


For substituted anthracenes, the course of their intramolecular photolytic transformations is governed by the nature of the substituent and by their excited-state interactions with the anthracene π -system. The examples of unimolecular photochemistry thus are limited to those anthracene derivatives in 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 autooxidation 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-hydroxyanthracene 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

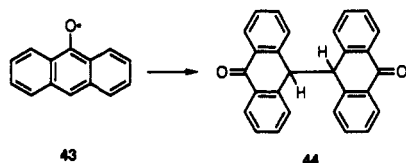
Considerable efforts have been devoted to investigating the photochemistry of 9-nitroanthracene (41).¹⁸⁵⁻¹⁹⁴ The virtual lack of 9-nitroanthracene flu-



orescence 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

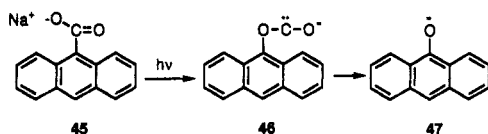
Evidence for the photolytic decomposition of 9-nitroanthracene was obtained in an early investigation in which irradiation with light of wavelengths of 370–410 nm was found to give nitric oxide and 10,10'-bianthronyl (44), while excitation at longer wavelengths (420–530 nm) yielded the $4\pi + 4\pi$ head-to-tail cycloclodimer 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.



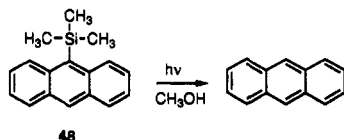
In a series of spectroscopic investigations on 9-nitroanthracene, 9-benzoyl-10-nitroanthracene, and 9-cyano-10-nitroanthracene, the photochemical formation of 9-anthryloxy radicals as primary products has been confirmed, including by electron-spin resonance spectra. Moreover, the kinetics of pico- and 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 photochemistry, the excited-state properties of sodium 9-anthracenecarboxylate (45) resemble those of 9-nitroanthracene insofar as 10,10'-bianthranyl (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

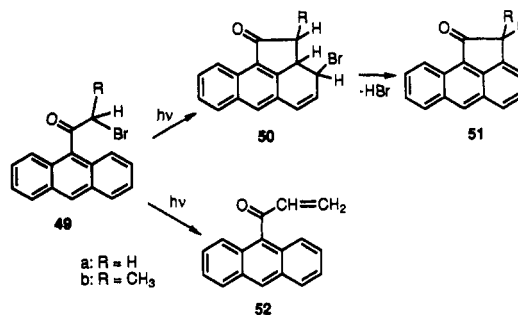
9-(Trimethylsilyl)anthracene (48) has been found to undergo smooth photolytic protodesilylation in methanol solution, yielding anthracene with a quantum yield of ~ 0.1 . It is worth noting that the desilylation competes efficiently with the photochemical dimerization even at fairly high concentrations of 48. The result has been attributed to solvent interaction by hydrogen bonding with the S_1 state of 48.¹⁹⁶



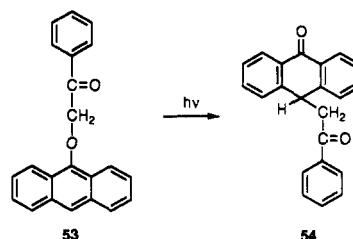
As for 9-anthryl ketones in their electronic ground state, their molecular geometry is such as to have the anthracene and the carbonyl π -systems in mutually perpendicular arrangement, so that electronic conjugation is negligible.^{197,198} In their photoexcited state, by contrast, 9-anthryl ketones 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 α -bromoalkyl ketones are unique insofar as the α -bromoalkyl ketone moiety is characterized by a photochemically labile carbon-halogen bond. Thus, the unimolecular photochemistry of both 9-(ω -bromoacetyl)anthracene (49a) and 9-(α -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-(α -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.



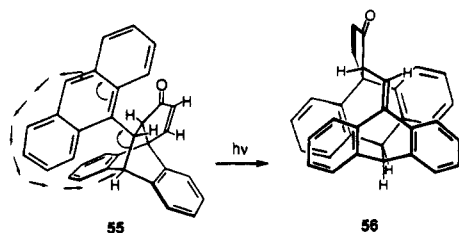
Unequivocal evidence for the involvement of radicals has been obtained in the photolysis of α -(9-anthryloxy)acetophenone (53), which was found to disappear with a quantum yield of 0.24 upon irradiation in methanol solution.²⁰⁴ The CIDNP spectrum in acetonitrile (λ_{exc} 308 nm) reveals as minor products acetophenone, its enol, and 1,2-dibenzoylthane. 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 rear-



range of 53 also can be sensitized by biacetyl, but CIDNP spectroscopy reveals that the formation of the rearrangement product 54 by direct excitation of α -(9-anthryloxy)acetophenone involves the excited singlet

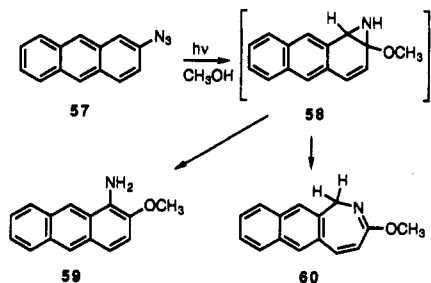
rather than the triplet state. An analogous mechanism applies to the photolytic β -cleavage of other (α -aryloxy)-acetophenones.²⁰⁵

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

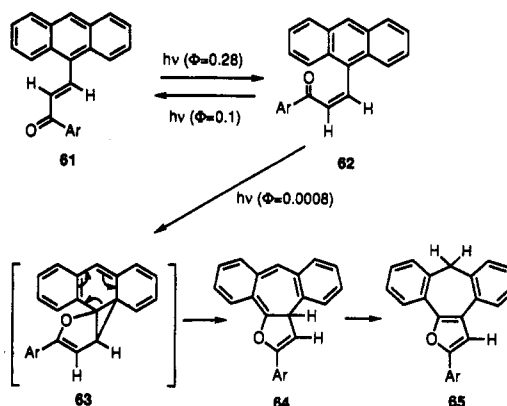


and may be rationalized in terms of an intramolecular triplet sensitization by the cyclopentenone moiety. In line with the arguments presented in section V.A for interactions between photoexcited anthracenes and aromatic ketones, intramolecular singlet-singlet energy transfer from the anthracene chromophore 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 $n\text{-}\pi^*$ 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

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



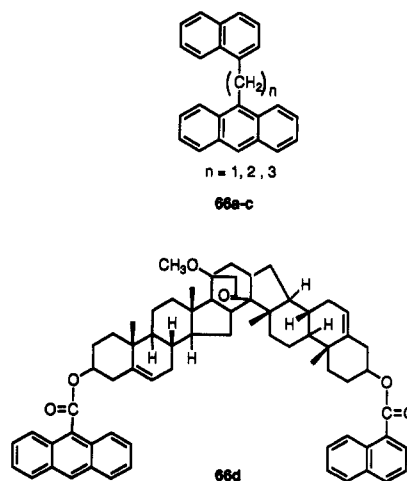
The photochemical isomerization of 1-(9-anthryl)-2-benzoyl ethylenes **61/62** leading to 5*H*-dibenzo[*a,d*]-cycloheptenes **65** proceeds smoothly, albeit with low quantum efficiency, as a process competing with geometrical *cis-trans* isomerization. The enlargement of the central ring of the anthracene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



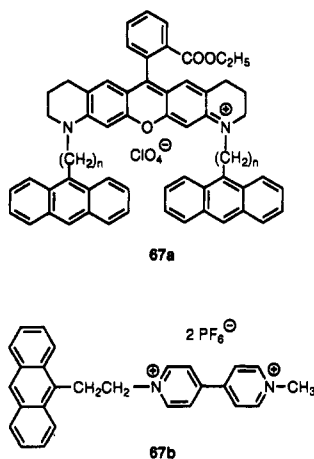
Reviews on various aspects of energy transfer have been published previously, and intramolecular energy transfer continues to be a topic of general interest.²¹¹⁻²¹⁶ The following discussion will be limited to recent results on the photophysical and photochemical consequences of singlet and triplet energy-transfer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



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

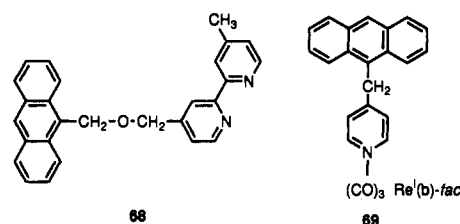
2. Energy Transfer Involving Metal Complexes

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

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

compd	R	R'	Φ_F	
			C ₆ H ₁₂	CH ₃ CN
70a	H	C ₆ H ₅	0.41	0.066
70b	CH ₃ O	H	0.20	0.075
70c	H	H	0.082	0.016
70d	C ₆ H ₅	H	0.04	0.0014
70e	CH ₃ CO	H	0.00056	0.00008

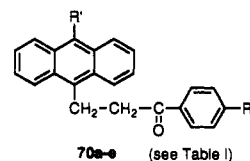
cage complexes, the aromatic π -system was found to serve as an antenna sensitizer for the reduction of Co(III) to Co(II).^{222,223} The fluorescence quenching observed in the ruthenium complex of substituted bipyridyl **68** was found to be due to efficient intramolecular triplet energy transfer to 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



3. Anthracene-Aryl Ketone Interactions

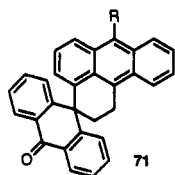
Excited-state interactions between anthracenes and aromatic ketones have been studied mainly in bichromophoric compounds such as **70** and **71**, in which the energy gap between the two interacting π -systems, and the relative disposition of their excited-state energy levels may be manipulated by appropriate 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 π -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

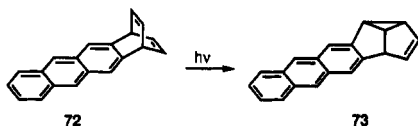
Analogous substituent- and solvent-dependent fluorescence properties have been found for spiroanthronyl anthracenes **71**.⁶⁵ Moreover, in both **70** and **71**, the charge-transfer mode of deactivation in polar solvents is evident from the appearance of exciplex-like lumi-



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}

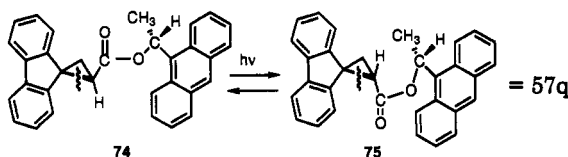
B. Isomerizations Involving Energy Transfer

Chemical transformations by way of intramolecular energy transfer generally involve the triplet state of the anthracene chromophore. The photochemical di- π -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 divinyl-methane 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-anthrabarrelene (~ 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- π -methane moiety ($E_T \approx 57$ kcal/mol) undergoing vinyl-vinyl bridging.

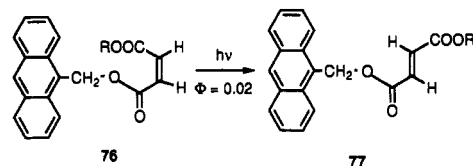
Photoexcitation of the anthracene π -system in diastereomeric (9-anthrylethyl)spiro[cyclopropane-1,9'-fluorene]-2-carboxylates 74 and 75 leads to a photo-stationary state with a 74:75 ratio of 95:5. On the basis



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 α -(9-anthryl)ethanol provided evidence for asymmetric induction by intramolecular T_2 energy transfer due to geometrically enhanced interaction between the an-

thrancene and fluorene π -systems in one of the two diastereomers.

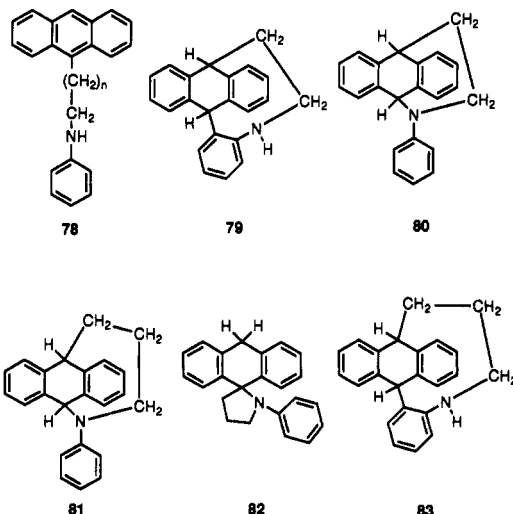
The photochemical isomerization of 9-anthrylmethyl methyl maleate (76) in benzene solution to give 9-anthrylmethyl methyl fumarate (77) with a quantum yield of 0.02 has been rationalized in terms of a triplet state reaction.²³⁰ Since the energy of the triplet state of the maleate chromophore is assumed 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}



VI. Chemical Consequences of Intramolecular Electron Transfer

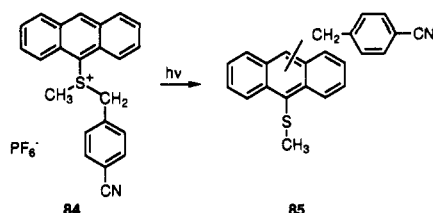
During recent years, a multitude of reviews on photoinduced electron-transfer reactions have been published.^{233–237} Therefore, the discussion in this section will be limited to some recent examples of intramolecular electron transfer induced photochemical transformations of anthracene derivatives.

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

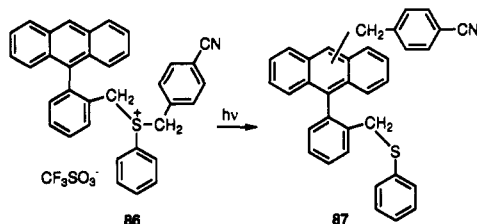


The chemical consequences of intramolecular photoinduced electron transfer involving the excited singlet state of the anthracene π -system as donor moiety, and

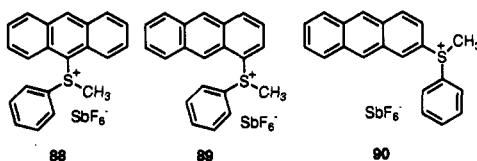
sulfonium groups as electron acceptors are rearrangement and solvolysis reactions. For example, photoexcitation of the anthracene chromophore in (*p*-cyanobenzyl)methyl(9-anthryl)sulfonium hexafluorophosphate (**84**) in acetonitrile ($\lambda > 400$ nm) gives hexafluorophosphoric acid (100% yield) with 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}

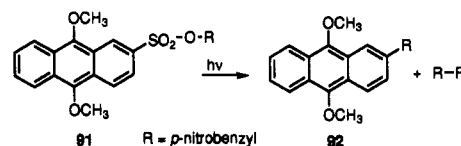


There can be little doubt that the benzylic character of the substituent enhances the efficiency of the bond cleavage/radical coupling reaction observed for sulfonium salts **84** and **86**. The photolytic cleavage of benzyl bonds by photoinduced electron transfer has been studied in numerous bimolecular 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.



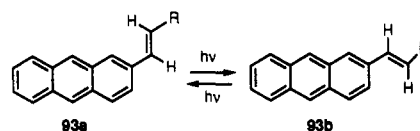
The formation of 9,10-dimethoxyanthracene-2-sulfonic acid ($\Phi = 0.10$), *p,p'*-dinitrobenzyl, and 9,10-dimethoxy-2-(*p*-nitrobenzyl)anthracene (**92**) by photoexcitation of the anthracene chromophore in *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (**91**) in acetonitrile solution is typical 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}



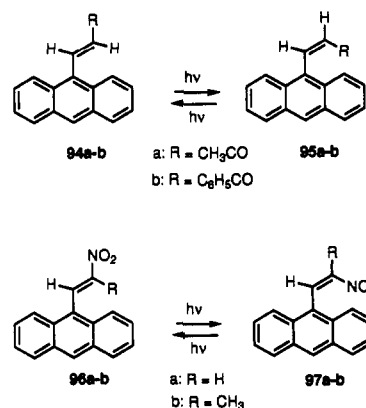
VII. Excited-State Reactions of Anthryl-Substituted Alkenes, Azomethines, and Azines

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}



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}

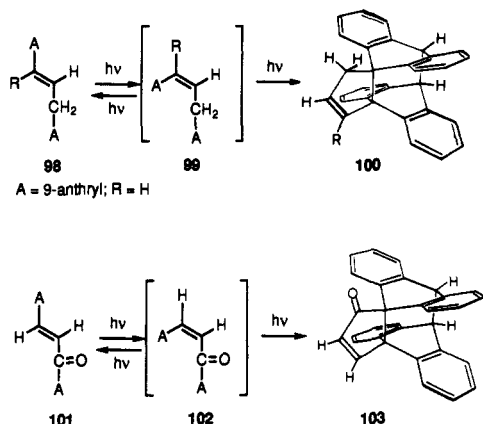


Geometrical isomerization and competing intramolecular cycloaddition reactions characterize the photochemistry of (9-anthryl)alkenes which contain an additional anthracene chromophore (cf. section VIII.B). Thus, irradiation of *trans*-1,3-di(9-anthryl)propene (**98**)

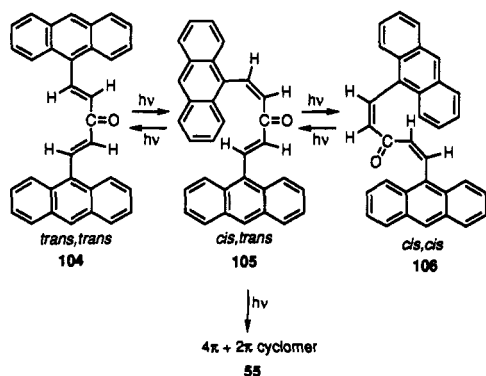
Table II. Quantum Yields of *E/Z* Isomerization of (9-Anthryl)alkenes 94–97 in Dichloromethane

compd	R	Φ		ref
		<i>E</i> → <i>Z</i>	<i>Z</i> → <i>E</i>	
94a/95a	CH ₃ CO	0.39	0.32	102
94b/95b	C ₆ H ₅ CO	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**).

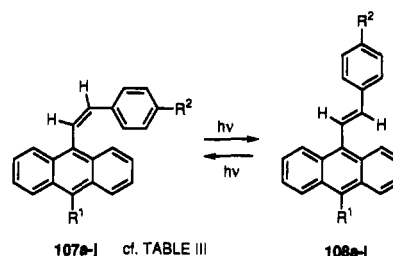


trans,trans-Dianthrylpentadienone **104** isomerizes photochemically in oxygen-saturated solution to give a mixture of *cis,trans* isomer **105** and the *cis,cis* isomer **106**. However, irradiation of **104** under nitrogen smoothly leads via the *cis,trans* isomer **105** to the cyclomer **55**. 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.)



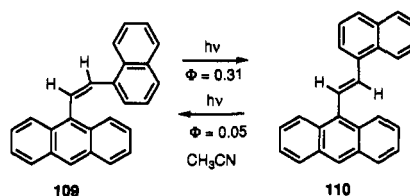
Considerable experimental and theoretical efforts have been devoted to the photochemistry of styryl-anthracenes.^{251–257} It has been established for both *cis*- and *trans*-9-styrylanthracene (**107a/108a**) that steric repulsions involving the vinyl group and H-1/H-8 of

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-styryl-



anthracene (**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 ($\Phi = 0.0014$) 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 substituents 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.

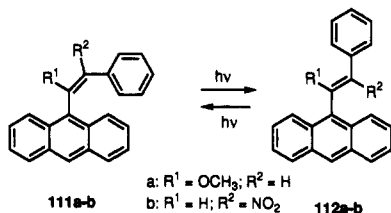


Substitution of the carbon–carbon double bond in 9-styrylanthracene by either methoxy or nitro groups also was found to facilitate photochemical *E* → *Z* isomerization. For example, the photochemical conversion of the **111a,b** into their corresponding *Z* isomers **112a,b** proceeds in cyclohexane 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.

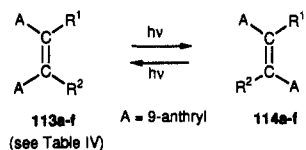
The photochemistry of the parent *trans*-1,2-di(9-anthryl)ethylene (**114a**) resembles that 9-styrylanthracene **108a** insofar as geometrical isomerization of the ethylene double bond is not observed. Surprisingly, the *cis* isomer **113a** also is characterized by extremely

Table III. Quantum Yields of Geometrical Isomerization of Substituted 9-Styrylanthracenes 107/108 in Cyclohexane and in Acetonitrile^{251,257}

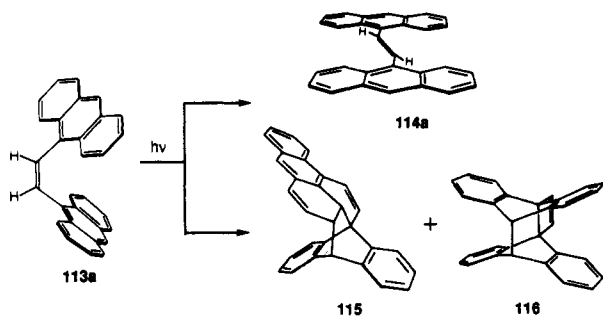
	R ¹	R ²	Φ	
			cis→trans (C ₆ H ₁₂ /CH ₃ CN)	trans→cis (C ₆ H ₁₂ /CH ₃ CN)
107a/108a	H	H	0.22/0.41	<0.01/0.003
107b/108b	H	NMe ₂	0.18/0.40	0.24/0.22
107c/108c	H	OMe	0.17/0.25	0.02/0.33
107d/108d	H	Me	0.19/0.36	<0.01/0.18
107e/108e	H	CN	0.47/0.46	<0.01/0.41
107f/108f	H	CHO	0.70/0.35	0.02/0.38
107g/108g	H	C ₆ H ₅ CO	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 ₆ H ₅ CO	?	0/0



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 π + 2 π cycloaddition to give 115 (Φ = 0.0007), and by 4 π + 4 π cycloaddition to give 116 (Φ < 0.0007).^{258,259}

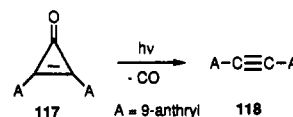


Substitution of the ethylene bond profoundly affects the excited-state properties of 1,2-dianthrylethylenes 113/114, as it changes their ground-state molecular geometry to the effect of increasing the dihedral angle between the ethylene and anthracene π -systems.¹⁰⁹ Significantly, trans to cis isomerization 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 π -system increases by substitution, photochemical isomerization of *cis*-dianthrylethylenes by Diels–Alder reaction becomes negligible, and intramolecular 4 π + 4 π 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

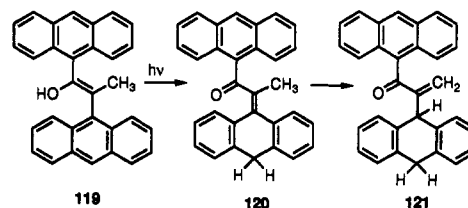
Table IV. Quantum Yields of Geometrical Isomerization and Cycloaddition for 1,2-Di(9-anthryl)ethylenes 113/114 (in C₆H₁₂)

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

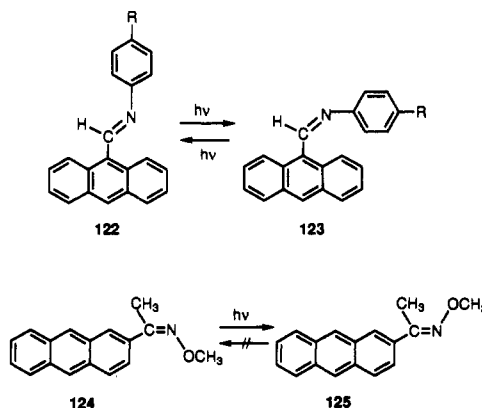
anthracene π -systems, undergoes intramolecular 4 π + 4 π cycloaddition with a quantum yield of 0.20.¹⁰⁸ Irradiation of di-9-anthrylcyclopropanone (117) in cyclohexane, by contrast, does not result in dianthrylethylene photochemistry, but decarbonylation smoothly leads to di(9-anthryl)acetylene (118) with a quantum yield of 0.14.^{108,260}



Unexpectedly, the photochemical isomerization of the 9-anthryl-substituted enol 119 in dichloromethane gives the 9,10-dihydroanthracene derivative 121 (Φ = 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

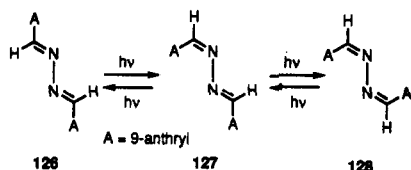


The photophysical and photochemical properties of 9-anthryl-substituted azomethines 122/123 (R = H, Br, NO₂) have recently been investigated. For R = NO₂, the involvement of the excited triplet state in the geometrical isomerization has been suggested.²⁶¹ The excited-state properties of (*E*)- and (*Z*)-*N*-methoxy-1-(2-anthryl)ethanimine (124/125) have recently been studied in detail with respect to both geometrical and rotational isomerism.²⁶²



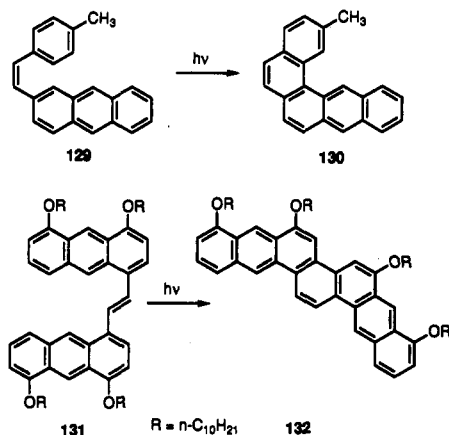
The photochemical geometrical isomerization of various 9-anthryl-substituted azines has been of interest in conjunction with their photochromic properties.^{263–265}

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

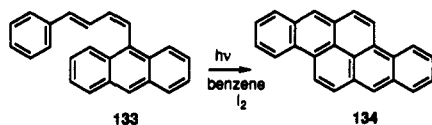


B. Dehydrocyclizations

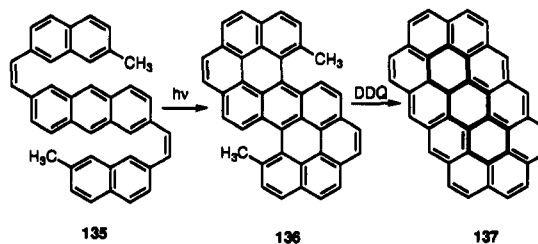
Intramolecular photochemical dehydrocyclizations of anthracene-related compounds are well known for bianthrone and similar stilbene-like anthrone derivatives.^{267–271} In recent years, several examples of styryl-substituted anthracenes undergoing photochemical dehydrocyclization have been reported. 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



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

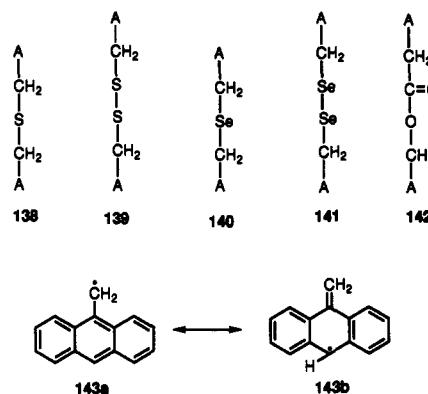


way of two consecutive cyclization and dehydrogenation steps requiring 84 h of irradiation obviously is very inefficient.²⁷⁵ By contrast, irradiation of 135 in toluene in the presence of iodine in an argon atmosphere afforded 136 in 93% yield by a remarkable 4-fold cyclodehydrogenation. The reaction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

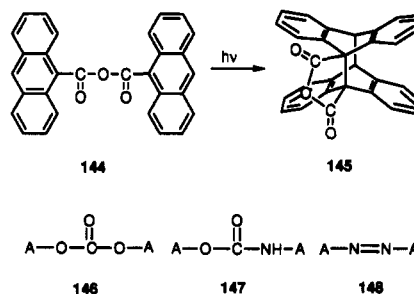


VIII. Isomerization of Non-Conjugatively Linked Bichromophoric Anthracenes

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 lepidoptere (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 lepidoptere, rather than an intramolecular $4\pi + 4\pi$ cycloaddition product of (9-anthryl)methyl (9-anthryl)acetate, as has been suggested.^{279,280}



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-anthracic 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



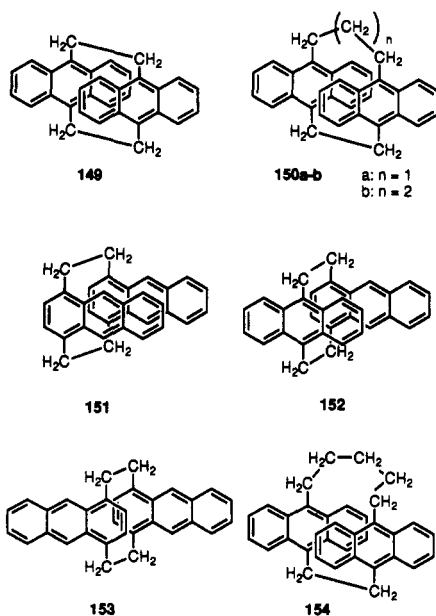
undergo intramolecular $4\pi + 4\pi$ cycloaddition in the same fashion.²⁸¹ In principle, the photochemical isomer-

ization 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

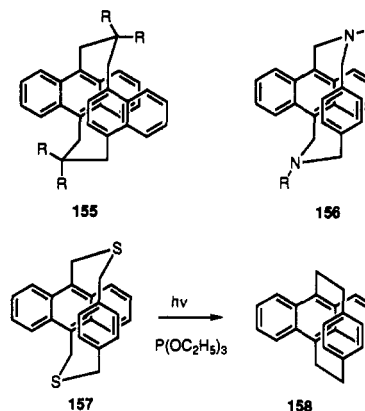


intermediates in the photochemical reaction and the thermal cycloreversion has not been obtained.^{282,288}

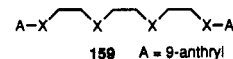
Other anthracenophanes undergoing photochemical isomerization by $4\pi + 4\pi$ cycloaddition are [2.3](9,10)anthracenophane (150a), [2.4](9,10)anthracenophane (150b), syn-[2.2](1,4)anthracenophane (151), and [2.2](1,4)(9,10)anthracenophane (152).^{285,288,291,292} For anthracenophane 151, excimer fluorescence 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



The photochemical isomerization of polyether-linked bichromophoric anthracenes such as 159 (X = O) has been studied extensively.^{87,299-305} Quantum yield measurements have revealed that α,ω -dianthryl polyethers may isomerize much more efficiently than the corresponding α,ω -dianthrylalkanes. For example, the α,ω -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 = CH₂) in benzene disappears with a quantum yield of $<10^{-4}$, conceivably in a bimolecular reaction (see section VIII.B).

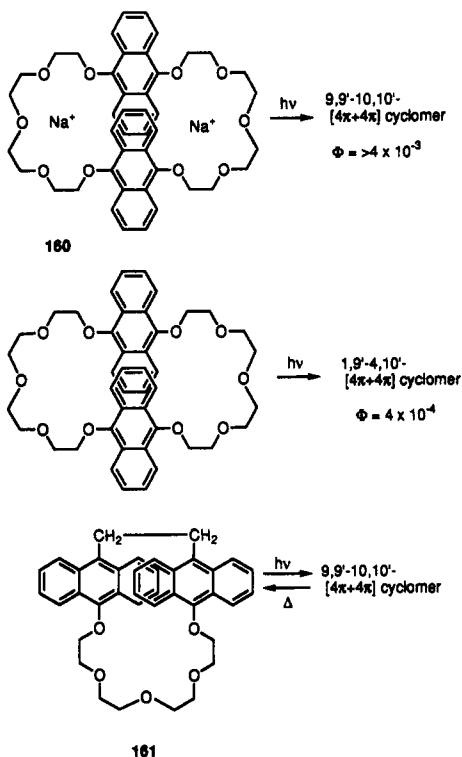


Due to changes in molecular geometry, the course of the photochemical isomerization of anthraceno crown ethers may be affected by the presence of complexed metal ions. Thus, irradiation of the sodium ion complexed bis(anthraceno) crown ether 160 affords the 9,9':10,10'-symmetrical isomer formed by $4\pi + 4\pi$ 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 (Φ_F) and Isomerization (Φ_R) for Di-(9-anthryl)methane Derivatives 162, 164, and 166

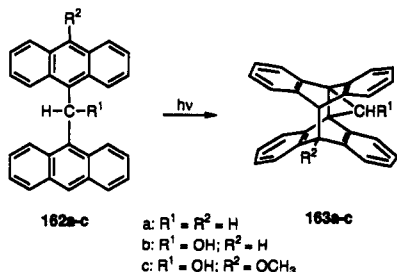
compd	Φ_F	Φ_R	solvent	cycloaddition
162a	0.06	0.15	benzene	$4\pi + 4\pi$
162b	0.02	0.29	benzene	$4\pi + 4\pi$
162c	0.02	0.05	benzene	$4\pi + 4\pi$
164	0.18	0.45	toluene	$4\pi + 2\pi$
166	<0.0001	0.0003	benzene	$4\pi + 2\pi$

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

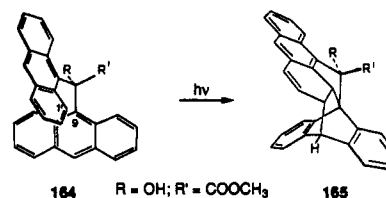


B. Dianthrylalkanes and Their Derivatives

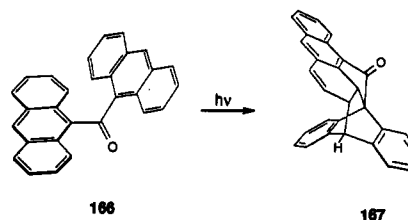
Pertinent excited-state properties of di(9-anthryl)methane derivatives 162 are summarized in Table V. Both di(9-anthryl)methane (162a) and di(9-anthryl)methanol (162b), and its 10-methoxy derivative 162c, isomerize photochemically by $4\pi + 4\pi$ cycloaddition to give the corresponding cyclopropane 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 anal-

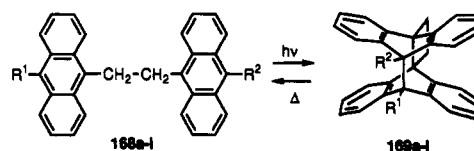


ogous photochemical intramolecular Diels–Alder reaction of di(9-anthryl) ketone (166) leading to 167.³⁰⁷



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.^{99,308,309} 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,

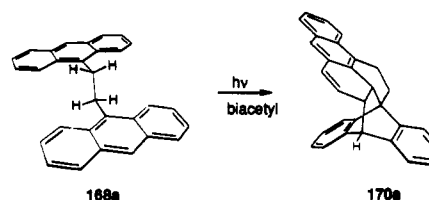


Table VI. Substituent Effects on the Quantum Yields of Fluorescence (Φ_F) and Isomerization of Dianthrylethanes 168 by Cycloaddition (Φ_R) in Cyclohexane³¹⁴

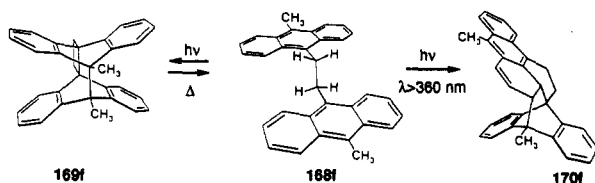
168	R ¹	R ²	Φ_F	Φ_R	$t_{1/2}$ of 169 ^a
a	H	H	0.20	0.26	385 years
b	H	CH ₃	0.15	0.26	38 years
c	H	CH ₃ O	0.14	0.24	39 years
d	H	CH ₃ COO	0.40	0.14	130 years
e	H	C ₆ H ₅	0.61	0.034	187 days
f	CH ₃	CH ₃	0.16	0.14	33 min
g	CH ₃ O	CH ₃ O	0.30	0.11	142 min
h	CH ₃ COO	CH ₃ O	0.45	0.068	260 min
i	CH ₃ COO	CH ₃ COO	0.74	0.015	234 min

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

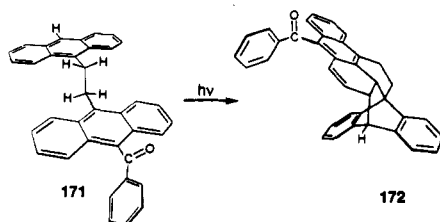
triplet-sensitized isomerizations of non-conjugatively linked anthracenes will proceed by $4\pi + 4\pi$ cycloaddition, if the molecular geometry of the electronic ground state facilitates parallel alignment of overlapping anthracene moieties, as is typical for propano-linked aromatic π -systems (see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

The effects of 10,10' substitution on the quantum yields of fluorescence and $4\pi + 4\pi$ 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 $4\pi + 4\pi$ 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 $4\pi + 2\pi$ cycloaddition reaction of low quantum efficiency.³¹⁷ It is



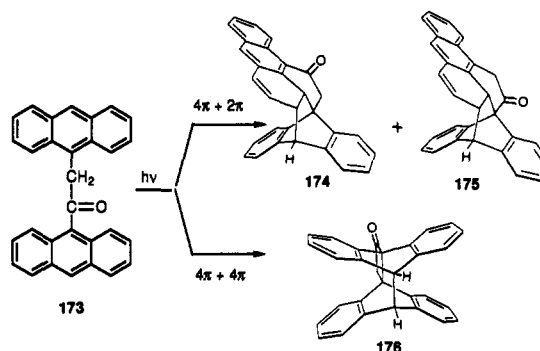
conceivable that the photochemical isomerization of 168f by $4\pi + 2\pi$ cycloaddition involves the excited triplet state. The photochemical isomerization of 10-benzoyl-1,2-di(9-anthryl)ethane (171; $\Phi_F = 0.002$) leading to the $4\pi + 2\pi$ cyclomer 172 also proceeds with low quantum yield (0.005), and evidence for a triplet-state reaction in that case has been obtained by biacetyl sensitization.

**Table VII. Quantum Yields of Fluorescence (Φ_F) in Cyclohexane and Quantum Yields of Isomerization by $4\pi + 4\pi$ Cycloaddition (Φ_R) in Benzene for 1,3-Di(9-anthryl)propane Derivatives³²²**

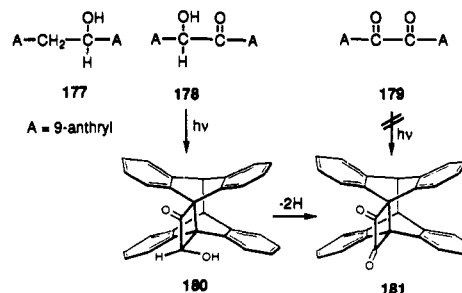
propano-linked anthracene	Φ_F	Φ_R
1,3-di(9-anthryl)propane	0.47 ^a	0.14 ^a
1,3-di(9-anthryl)-1-propanol	0.27	0.14
1,3-di(9-anthryl)-2-propanol	0.48	0.046
1,3-di(9-anthryl)-2-methyl-2-propanol	0.24	0.021
1,3-di(9-anthryl)-2-propanone	0.009	0.25
1,3-di(9-anthryl)-2-butanone	0.007	0.22
1,3-di(9-anthryl)-1-butanone	<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.

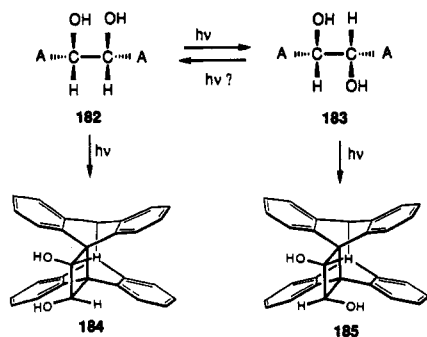
For photoexcited 1,2-di(9-anthryl)ethanone (173), the mode of isomerization by intramolecular cycloaddition has been found to be concentration dependent. Irradiation of 173 at low concentration (0.00003 M) affords mainly the two Diels-Alder products 174 and 175, while the $4\pi + 4\pi$ cyclomer 176 is 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 $4\pi + 2\pi$ cycloadditions conceivably involve the triplet state. The $4\pi + 4\pi$ 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}



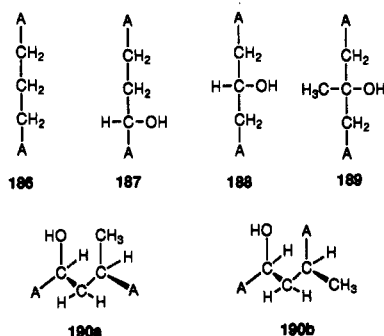
The photochemical isomerization of various other ethano-linked anthracenes has been investigated. Both 1,2-di(9-anthryl)ethanol (177) and 9,9'-anthroin (178) isomerize by $4\pi + 4\pi$ cycloaddition with quantum yields of 0.34 and 0.21, respectively.^{307,319-321} Di(9-anthryl)ethanedione (179; 9,9'-anthril) 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 $4\pi + 4\pi$ 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.

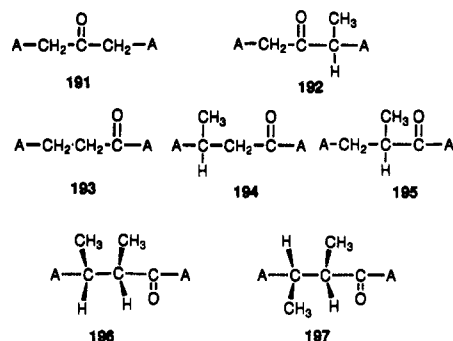


The photochemical isomerization of propano-linked bisanthracenes 186–195 (A = 9-anthryl) has been found to occur exclusively by $4\pi + 4\pi$ cycloaddition, and typical quantum yields of reaction and fluorescence are summarized in Table VII.³²² Both 1,3-di(9-anthryl)-



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 $4\pi + 4\pi$ cycloaddition about 20% faster than the *d* isomer.³²³

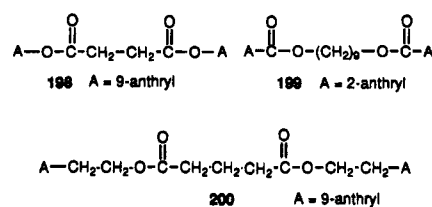
The involvement of the excited triplet state in the isomerization by $4\pi + 4\pi$ cycloaddition has been established by oxygen quenching and sensitization experiments for nonfluorescent propano-linked anthracenes 193–195 which are characterized by the presence of a 9-anthroyl group. The highly efficient 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 $4\pi + 4\pi$ cycloaddition with quantum yields of 0.19 and 0.17, respectively.



Photochemical isomerization by intramolecular $4\pi + 4\pi$ 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 (Φ_R), of fluorescence from the locally excited state (Φ_{FM}), and of excimer fluorescence ($\Phi_{F_{exc}}$) 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 intermolecular cycloaddition may become an important competing reaction if intramolecular 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 $4\pi + 4\pi$ cycloaddition.³² Polymer formation by intermolecular $4\pi + 4\pi$ 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-anthracene-carboxylic acid, such as 199, irradiation was found to give both intramolecular head-to-head and head-to-tail $4\pi + 4\pi$ cycloaddition products.³³⁷ The photochemical isomerization of di-9-anthryl glutarate (200) has been found to involve a head-to-tail $4\pi + 4\pi$ cycloaddition, although another major photoproduct of unknown structure is formed as well.³³⁸



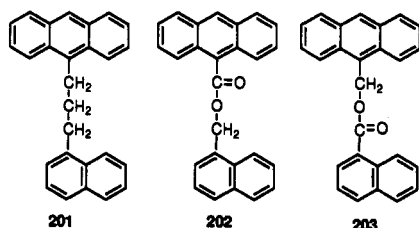
The problem of intermolecular reactions competing with intramolecular photochemistry of bichromophoric

Table VIII. Quantum Yields of Reaction (Φ_R), Monomer Fluorescence (Φ_{FM}), and Excimer Fluorescence (Φ_{Fexc}) for α,ω -Di(9-anthryl)alkanes in Methylcyclohexane^a

alkane	Φ_R	Φ_{FM}	Φ_{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.

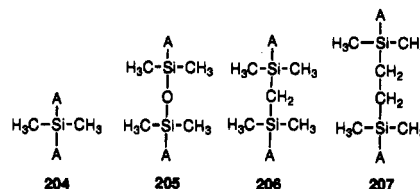
compounds can be circumvented by irradiation of very dilute solutions, as was noted for photochemical isomerization of 1-(9-anthryl)-3-(1-naphthyl)propane (201).³³⁹⁻³⁴³ Irradiation at low concentration (2×10^{-5} M) smoothly gives the intramolecular $4\pi + 4\pi$ cycloaddition, while irradiation at concentrations 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



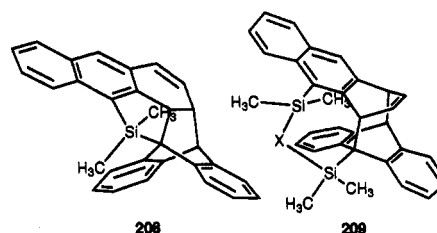
The mechanism of photochemical intramolecular $4\pi + 4\pi$ cycloaddition of linked anthracenes, and that of the photolytic cycloreversion, has been a subject of considerable interest with respect to the involvement of excimers and biradicals as intermediates.^{312,313} In several electron spectroscopic 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-



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 π -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.



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 π -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.^{87,165,302,350-353} 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

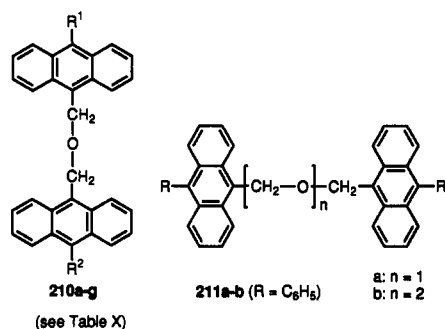
Table IX. Quantum Yields of Isomerization (Φ_R), Monomer Fluorescence (Φ_{FM}), and Excimer Fluorescence (Φ_{Fexc}) for Silicon-Linked Bisanthracenes

compd	Φ_R	Φ_{FM}	Φ_{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 (Φ_F) and Isomerization by Cycloaddition (Φ_R) of Bis[(9-anthryl)methyl] Ethers 210 in Methylcyclohexane³⁵⁰

210	R ¹	R ²	Φ_F	Φ_R
a	H	H	0.03	0.32
b	H	CH ₃	0.07	0.32
c	H	C ₆ H ₅	0.09	0.19
d	H	Br	0.03	0.18
e	CH ₃	CN	0.05	0.25
f	C ₆ H ₅	CN	0.05	0.16

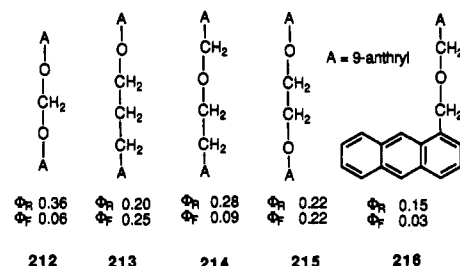
have been observed in acetonitrile.³⁵⁰ Fluorescence quantum yields generally are <0.10.



Analogous to the 10,10'-diphenyl derivative of 1,2-di(9-anthryl)ethane 168 mentioned above (section VI.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

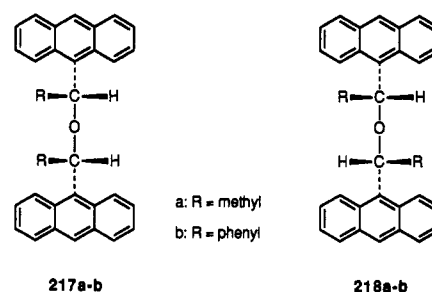
Dual emission in solution at room temperature also characterizes the excited state properties of the bis-(10-phenyl-9-anthryl) ether 211b ($n = 2$). However, extending the methyl ether linkage in 211a by an oxymethylene group markedly alters the kinetics of excimer formation. Thus, the quantum yield 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 (Φ_R) and fluorescence (Φ_F) have been determined. In general, the ether-linked bis-anthracenes isomerize with higher quantum efficiency than the corresponding α,ω -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



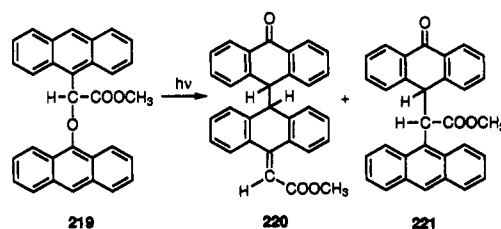
moieties, respectively.¹⁶⁵ Intramolecular $4\pi + 4\pi$ cycloaddition also characterizes the photochemistry of (9-anthryl)methyl ethers of (1-naphthyl)methanol and of furfuryl alcohol.^{302,351} By contrast, irradiation of (9-anthryl)methyl ethers of (2-naphthyl)methanol, (9-phenanthryl)methanol, and (1-pyrenyl)methanol gave mixtures of intermolecularly formed head-to-head and head-to-tail dimers involving only the anthracene π -systems.³⁵²

As for diastereomeric α,α' -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



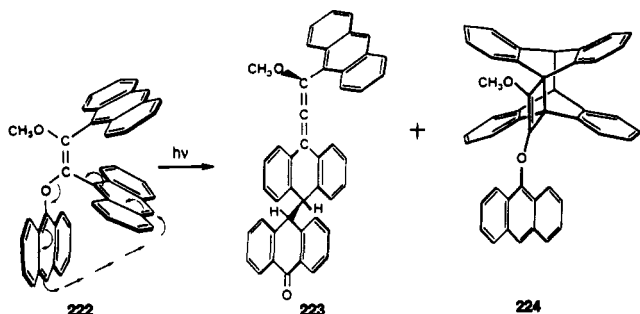
between the *meso* and *d,l* forms are borne out in their distinctly different fluorescence properties. The *meso* form, which may assume a conformation of fully eclipsed parallel aligned anthracene π -systems, was found to be nonfluorescent. By contrast, the *d,l* diastereomers in cyclohexane solution at room temperature are fluorescent ($\Phi \sim 0.01$), and the emission derives mainly from an excimer state ($\lambda_{max} \sim 480$ 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}

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-anthrone.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



an approximate ratio of 4:1. In view of the CIDNP evidence obtained for the photochemical homolytic β -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, anthranyl-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-anthrone 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-anthranyl moiety *cis* oriented, as would be expected from either a concerted rearrangement of 222, or from ring opening of a thermally labile oxetane intermediate.



IX. Retrospective Contemplations and Conclusions

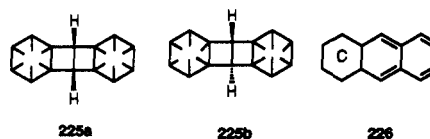
In the realm of organic photochemistry, Fritzsche's name is intimately associated with the dimerization of anthracene.³⁶⁸ However, Fritzsche himself emphatically rejected the idea that the hydrocarbon, which he had isolated from coal tar about 10 years before he described its "peculiar behavior towards sunlight", and which he had left unnamed, should be called *anthracene*.^{2,359,360} He was aware of "paranaphthalene", 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 paranaphthalene", 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 charac-

teristic 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.



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 peculiarities 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 π -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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