lap integrals and the use of separate parameters for different types of bonds in place of the approximations of eq 35 and 46. We are studying these and other analogous possibilities, and we are also extending our treatment to include all integrals involving one-center differential overlap (NDDO approximation[5]) in case this should prove necessary in treating molecules containing heteroatoms.

Reversible Photoisomerization of 1,2-Bis(9-anthryl)ethane[1]

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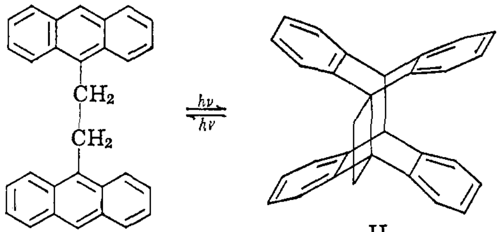
Abstract: The hydrocarbon 1,2-bis(9-anthryl)ethane (I) is photoisomerized efficiently and reversibly. The isomeric product (II) does not absorb appreciably at wavelengths longer than 260 mμ. The quantum yields of the forward and back reactions (0.19 and 0.42, respectively) are independent of the concentration of the reactant. Compound I is strongly fluorescent with maxima at 408, 436, and 460 mμ, and a fluorescent quantum yield of about 0.37. Flash illumination of its deoxygenated solutions produces an absorption transient, similar to but not identical with the lowest triplet of anthracene. No attempt was made to observe the fluorescence or triplet formation of the isomer (II).

The hydrocarbon 1,2-bis(9-anthryl)ethane (I) is efficiently and reversibly photoisomerized.[3] The detailed structure of the photoproduct (II) has not been established definitely. However, as was clearly stated by Roitt and Waters,[3a] its ultraviolet absorption spectrum is in general similar to that of dianthracene,[4] demonstrating that in II the conjugation of the anthracene rings is interrupted. It was postulated[3a] that II is a dimer of I, but molecular weight determinations (with a Mechrolab osmometer[3b]) prove that it is an isomer rather than a dimer of I. Our present finding, that the quantum yields of the photochemical reactions are independent of the concentrations of the reactants, confirms this conclusion unambiguously. Physical evidence (nmr, infrared, and mass spectrographic measurements[5]) is consistent with formula II.



I II

Compound II is stable at room temperature (in the absence of ultraviolet radiation) but isomerizes at its melting point, re-forming I.

Since the product II does not absorb appreciably at wavelengths longer than 260 mμ, the quantum yield of the forward reaction was measured directly, using light of 365 mμ. The quantum yield of the reverse reaction was estimated from the extinction coefficients, the quantum yield of the forward reaction, and the composition of a steady-state mixture, prepared by prolonged exposure to 254 mμ.

Experimental Section

Methods and Materials. Materials. The 1,2-bis(9-anthryl)-ethane was furnished by Dr. S. Fenton (University of Minnesota). It was recrystallized from *n*-hexane before use. The cyclohexane was Fisher Spectro Grade and was used without further purification.

Determination of Quantum Yields. The intensity of the absorbed light was determined by the use of a ferrioxalate actinometer, following the procedure outlined by Parker.[6] The absorption of the incident light was practically complete, except for those experiments made with the most dilute solutions; for these, the per cent absorption was calculated from the extinction coefficients. Light of the required wavelengths was isolated from the radiation of a Hanovia S-100 mercury arc, using combinations of glass, solution, and Cl_2 gas filters.[7]

Optical Measurements. The absorption spectra were measured with a Cary 15 spectrophotometer. The fluorescence spectrum was measured by T. Bednar of this department, using a deaerated, 5×10^{-6} *M* solution of I in cyclohexane and exciting light of 370 mμ. The fluorescence was observed at right angles to the exciting beam. The spectral resolution of the fluorimeter was estimated to be 10 A. The spectrum was corrected for variation of the sensitivity of the apparatus with wavelength but not for reabsorption, which probably seriously distorted the curve at wavelengths shorter than 400 mμ. Qualitatively similar results were obtained by K. S. W., using a manually operated spectrofluorimeter.[7]

Results

The absorption and fluorescence spectra of I are shown on Figure 1; the absorption spectrum of its isomer (II) is shown on Figure 2. The quantum yield of fluorescence of I was estimated to be 0.37, by comparing its total emission to that from anthracene, for which the fluorescence yield (measured under similar conditions) is 0.31.[8]

Carefully deoxygenated, 10^{-5} *M* solutions of I exhibited large transient changes in absorption, when

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[2] Author to whom inquiries should be sent.

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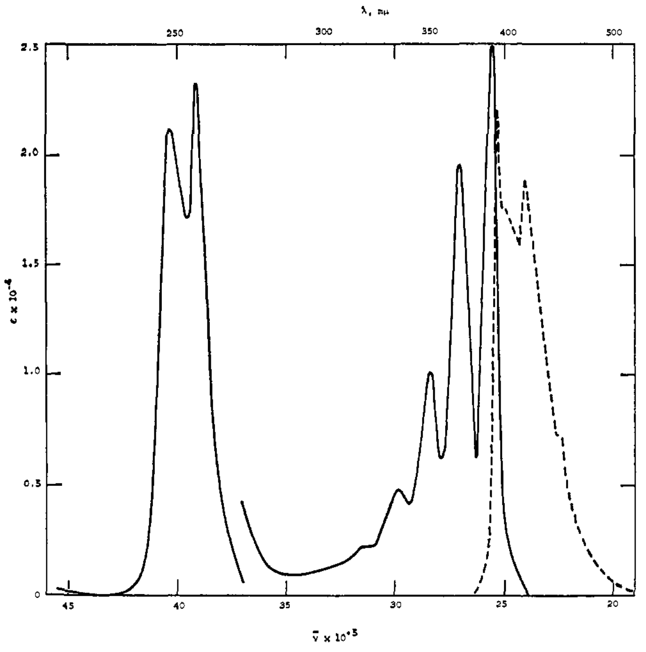

Figure 1. Absorption and emission spectra of 1,2-bis(9-anthryl)-ethane in cyclohexane. The scale for absorption between 220 and 270 mμ is reduced by a factor of 10. The emission spectrum is plotted as intensity in arbitrary units. It is corrected for variation of instrumental sensitivity with wavelength but not for reabsorption, which seriously distorts the curve at wavelengths shorter than 400 mμ. Absorption is indicated by a solid line, emission by a dash line.

subjected to flash illumination, under conditions which have been described elsewhere.[9] The maximum of this transient occurred at 445 mμ, about 15 mμ longer than the wavelength of the maximum of the anthracene triplet. The half-life of the transient was approximately 1.5×10^{-3} sec. An anthracene solution, prepared in a similar way, showed a half-life of 3.0×10^{-3} sec. These half-lives are minimum values and are probably much shorter than the values which correspond to the spontaneous unimolecular decay of the triplet state.[10] The observed difference between the values of the half-lives for anthracene and I is probably due to differences in the residual oxygen concentration in the two solutions.

Quantum yields of isomerization of I, in cyclohexane, are summarized in Table I. Generally similar results were obtained using benzene as the solvent. Over a 20-fold range the yield is independent of the concentration of the reactant. The apparent dependence on temperature is of doubtful significance but, if real, corresponds to an energy of activation of about 400 cal/mole. Oxygen has a small but definite inhibiting effect. This effect cannot be explained as due to peroxide formation, since its occurrence would increase the apparent quantum yield of dimerization.

Table I. Quantum Yields of Isomerization of 1,2-Bis(9-anthryl)ethane[a]

[A], M	[O$_2$], M	Temp, °C	φ
5.0×10^{-6}	2.0×10^{-4}	25	0.18
1.0×10^{-5}	2.0×10^{-4}	25	0.18
2.0×10^{-5}	2.0×10^{-4}	25	0.21
6.0×10^{-5}	2.0×10^{-4}	25	0.19
1.0×10^{-4}	2.0×10^{-4}	25	0.19
1.0×10^{-4}	2.0×10^{-4}	10	0.18
1.0×10^{-4}	2.0×10^{-4}	35	0.19
1.0×10^{-4}	2.0×10^{-4}	70	0.21
1.0×10^{-4}	$<10^{-6}$	25	0.26
1.0×10^{-4}	1.0×10^{-3}	25	0.17

[a] Solvent, cyclohexane, λ 365 mμ.

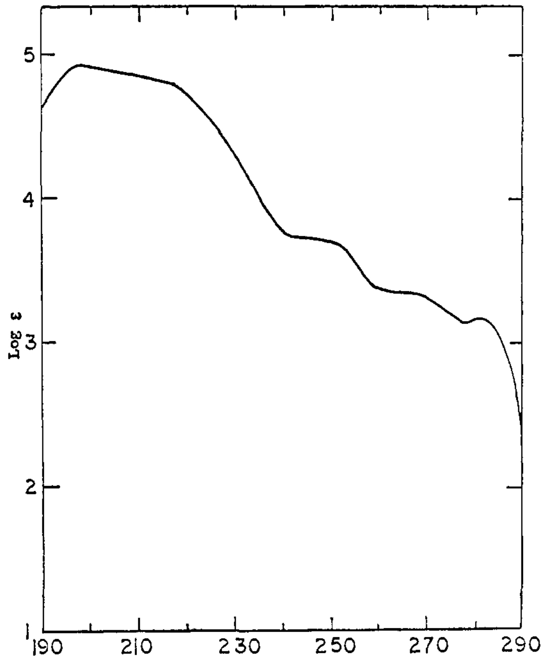

Figure 2. Absorption spectrum of the isomer (II) of 1,2-bis(9-anthryl)ethane in n-hexane.

Quantum yields for the back reaction, which are listed in Table II, were calculated from the steady-state compositions; they depend on the measured values of the extinction coefficients, the quantum yield of the forward reaction, and the assumption that this yield is the same for 365 and 254 mμ. Light of 254 mμ was used to produce the steady state. Effects of the reactant concentration, oxygen, and temperature are similar to those observed for the forward reaction.

Table II. Steady-State Composition and Quantum Yields of the Reverse Isomerization[a]

[A]^0, M	[O$_2$], M	Temp, °C	Steady-state mole % of I	Quantum yield
1.0×10^{-6}	2.0×10^{-4}	25	4.5	0.42
5.0×10^{-6}	2.0×10^{-4}	25	4.1	0.37
1.0×10^{-5}	2.0×10^{-4}	25	4.5	0.41
1.0×10^{-5}	2.0×10^{-4}	10	4.8	0.44
1.0×10^{-5}	2.0×10^{-4}	35	4.8	0.45
1.0×10^{-5}	2.0×10^{-4}	70	5.3	0.49
1.0×10^{-5}	$<10^{-6}$	25	5.4	0.51

[a] Solvent, cyclohexane; λ 254 mμ.

Discussion

The observation that the quantum yield of isomerization is not affected by a 20-fold change in the concentration of the reactant indicates that the reaction is a

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unimolecular rearrangement of the electronically excited molecule. This unimolecular reaction must compete with the spontaneous (radiative and nonradiative) decay of the excited state and with its quenching by oxygen. Measurements, made by M. Walker of this department with a phase shift apparatus[11] using a deaerated 5×10^{-5} *M* solution of I in cyclohexane, indicate a mean lifetime of fluorescence of 2.5×10^{-9} sec. The rate constants for the spontaneous decay of the triplet and for the oxygen quenching of the first excited singlet and the lowest triplet have not been determined for I. It is plausible that they are in general similar to the corresponding values for anthracene, which are as follows: first-order decay of the triplet, 30 sec^{-1};[12] second-order (oxygen) quenching of the excited singlet,[8] 2.3×10^{10} l./mole sec; second-order quenching of the triplet,[12] 2.3×10^{9} l./mole sec. Values of these orders of magnitude preclude the possibility that the active intermediate for isomerization is exclusively the triplet state. The postulate that the observed reaction is the result of a spontaneous rearrangement of the fluorescent state is consistent with the observed values for air- and oxygen-saturated solutions. However, the relatively high value obtained for deoxygenated solutions is incompatible with this mechanism. This value, if correct, suggests that both the excited singlet and the triplet states can isomerize, but that the triplet state contributes significantly to the reaction only in deoxygenated solutions.

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Electron Spin Resonance Studies on Ion Pairing in Semiquinone–Alkali Metal Systems

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Abstract: Esr spectra from semiquinone anion radicals produced by alkali metal reduction of parent quinones in ether solvents have been investigated. The results reveal large changes in the spin density distribution in the semiquinone rings as a consequence of association of the anion with alkali metal cations. Ion pairs with different amounts of solvation have been detected, and the results have been interpreted in terms of an ion-pair equilibrium model. Alternating line-width effects have also been observed in the semiquinone–alkali metal system. This arises from the time-dependent modulations of the isotropic ring proton splitting constants resulting from an equilibrium between "solvated" and "intimate" ion pairs in which the metal cation does not drift away from the radical anion.

There has been considerable interest in the experimental and theoretical investigations of the electron spin resonance (esr) of semiquinones in the recent past. The semiquinones form a convenient system for such investigations for various reasons, like ease of producing radicals using different methods and the simplicity of their esr spectra. *p*-Benzosemiquinone (PBSQ), which forms the simplest member of the semiquinone type of radicals, has been investigated extensively, and accurate data are available for hyperfine splittings from protons[1–12] and carbon-13[13–20] and oxygen-17[21,22] nuclei. From these data a good deal of information is available[14,19,20,22] as regards the unpaired electron density distribution in the molecule and the solvent-induced perturbations on the distribution of the π density.

In the past, semiquinone ion radicals have been produced by air oxidation of the hydroquinone in alkaline solvents,[1–11,13–17] by electrolytic methods[18–22] and by ultraviolet irradiation methods.[23] However, a very

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