# Reversible Photochemistry and Photocyclization of 10*H*,10'*H*-Bianthrylidene

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The photochemistry of 10,*H*,10'*H*-bianthrylidene was extensively studied over a wide temperature range. Two photoisomers, C and E, are formed, both reverting thermally to the parent modification A. The C isomer is a cyclization product of the 4a,4b-dihydrophenanthrene type, whereas the E isomer results from *cis–trans*-isomerization about the central double bond together with additional torsions about the four single bonds of the 9,9'-ethylene system. The A, E, and C modifications are oxidized by atomic iodine. The dependence of the quantum yield of fluorescence on temperature indicates that intersystem crossing is an activated process above a certain critical temperature (*ca.* −130°) and non-activated at lower temperatures. The C modification is formed from the excited singlet and the E isomer from the triplet state.

Two main types of reversible photoisomerizations were observed in irradiated solutions of bianthrone (1a) and bixanthylidene (1b).† (a)Torsion about the 9,9' double bond produces the conformational B photoisomer.[1] (b) 1,1' Photocyclization, produces a 4a,4b-dihydrophenanthrene-like C isomer.[2] The thermochromic and photochromic properties of (1a and b) are lost [3] upon replacement of the C=O or O bridging group by an S or $NCH_3$ group. However, in these systems a new labile modification E is formed which absorbs at shorter wavelengths [4] and reverts thermally to the starting form A. The proposed structures of (2A and E) (shown in Figure 1) were previously calculated by the CFF-π-electron CI method.[4] We now report on the reversible photochemistry and the photodehydrogenation of compounds (2) and (3a and b), in which the C=O group in (1a) is replaced by a methylene ($CH_2$) or a hydroxymethylene (CHOH) bridge.

(A) *Photoformation of the E and C Modifications.*—Two photoisomers, the light stable E and the photolabile C isomer, are formed by the u.v. irradiation of solutions of (2) and (3a) at low temperatures. The absorption spectra of these two isomers are shown in Figure 2, curve E, and in Figure 3, curves 2 and 3. These modifications are obtained both in nonpolar methylcyclohexane (MCH)–methylcyclopentane (MCP) (1 : 1) and in polar propan-1-ol (1-P)–propan-2-ol (2-P) (2 : 3). Both E and C revert thermally in a first order reaction to the parent modification A at temperatures above −80°. Relevant data are summarized in Figure 4 as Arrhenius plots. The corresponding Arrhenius parameters are summarized in Table 1.

The initial ratio (2C) : (2E) decreases sharply on cooling so that at −160° (2E) is the only photoisomer formed. The E photoisomers are light stable, and therefore the photoconversion A ⟶ E approaches completion after sufficient irradiation. The absorption spectra of (2E)

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† Compounds (1a and b) are also known as dianthrone and dixanthylidene. The different modifications are denoted by capital letters. A is the fundamental modification, B, the twisted and C the cyclic form.

[1] R. Korenstein, K. A. Muszkat, and S. Sharafi-Ozeri, *J. Amer. Chem. Soc.*, 1973, **95**, 6177.

[2] R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv. Chem.* 1970, **53**, 2101.

[3] G. Kortum, W. Theilacker, and G. Schreyer, *Z. Phys. Chem. (Frankfurt)*, 1957, **11**, 182.

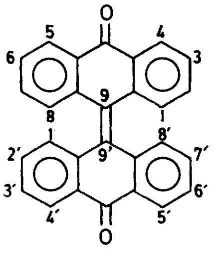
[4] R. Korenstein, G. Seger, and K. A. Muszkat, *J.C.S. Perkin II*, in the press; R. Korenstein, K. A. Muszkat, and E. Fischer, *J. Photochem.*, 1976, **5**, 345, 447.

and (3aE) were determined in this way. The quantum yields $\phi_{A\to C}$ and $\phi_{A\to E}$ decrease as the temperature is lowered (Figure 5). In (3b) the photocyclization process is the only photoreaction observed. Thus in this case it is possible to study the temperature dependence of the A ⟶ C photoconversion without interference from the competing A ⟶ E photoisomerization. $\phi_{A\to C}$ is constant (0.51) down to $-100°$ and then drops sharply down to 0.05 at $-160°$. The photoreversal C ⟶ A with 365 nm light is quite efficient, $\phi_{A\to C}$ 0.3—0.2 in the range $-100$ to $-160°$. Thus the photochemical ring opening is virtually temperature independent in marked contrast to the photochemical ring closure. The same trends of $\phi_{A\to C}$ and $\phi_{C\to A}$ were also observed in (2) and (3a). In this respect these systems resemble the simpler systems derived from 1,2-diarylethylenes.[5,8]

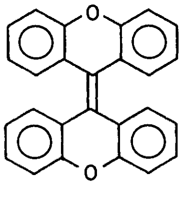
TABLE 1

Activation energies $E_a$ (kcal mol$^{-1}$), pre-exponential factors $A$(s$^{-1}$), and rate constants $k$(s$^{-1}$) for the C ⟶ A and E ⟶ A processes

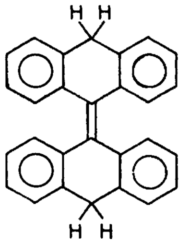
| | C ⟶ A | | | E ⟶ A | | |
|---|---|---|---|---|---|---|
| Compound | $E_a$ | $A$ | $k$ ($-20°$) | $E_a$ | $A$ | $k$ ($-40°$) |
| (2) | 12.6 | $10^{11}$ | 0.75 | | | |
| (3a) | 14.7 | $10^{12}$ | 0.42 | 12.4 | $10^{13}$ | $1 \times 10^{-3}$ |
| (3b) | 15 | $10^{13}$ | 1.33 | | | |



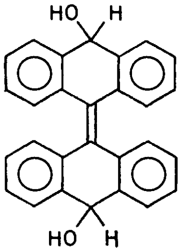
(1a)



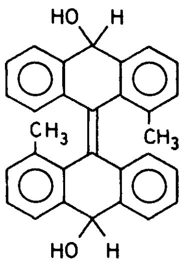
(1b)



(2)



(3a)



(3b)

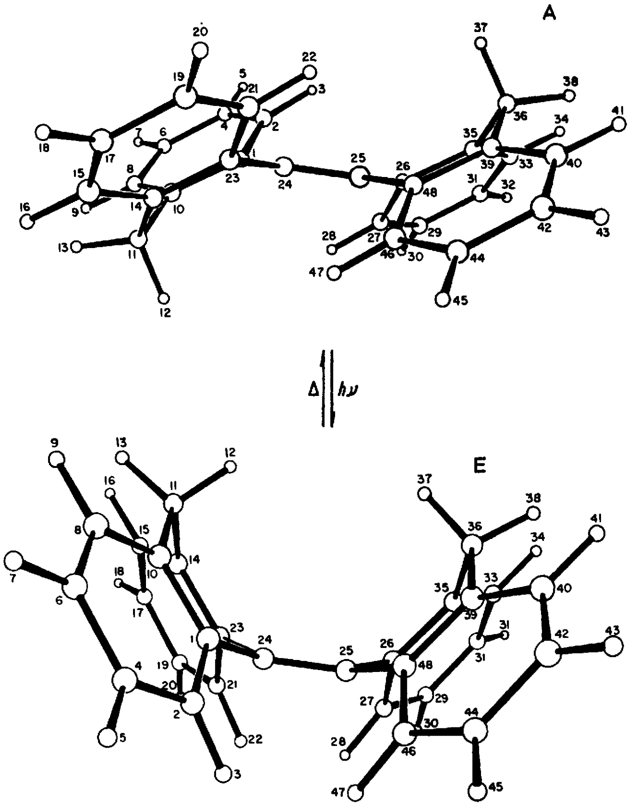


FIGURE 1 Proposed molecular structures for the A and the E forms of (2) and (3a)

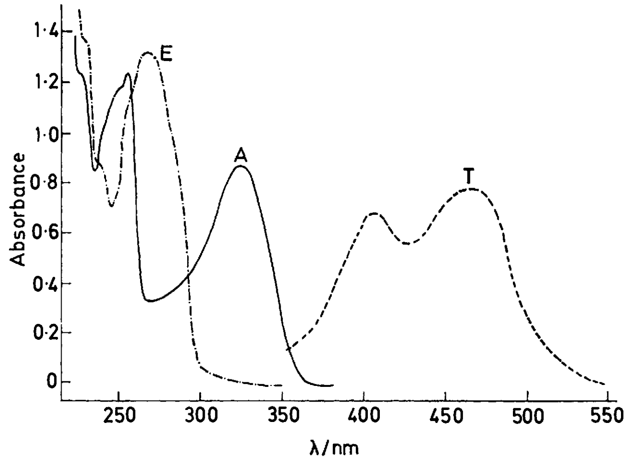


FIGURE 2 Curves A and E, absorption spectra of the A and E isomers of (3a) in 1-P-2-P (2 : 3) at $-160°$; Curve T, the proposed triplet–triplet absorption of (3aA) at $-190°$ in the same solvent

(B) *Flash Photolysis Studies*.—Flash photolysis of (3a) in a 1-P-2-P glass at $-190°$ results in the formation of a transient, denoted T, absorbing in the 400—500 nm region (Figure 2, Curve T). By analogy with the situation in the bianthrone[6] series (see below) we deduce that

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[5] T. Wismonski-Knittel, G. Fischer, and E. Fischer, *J.C.S. Perkin II*, 1974, 1930.

[6] T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, 1970, **24**, 531.

this transient is the triplet $^3$(3aA). The kinetics of the thermal decay of this transient are given in Figure 4. T decays to E at temperatures above −167° and to A at lower temperatures. Two Arrhenius curves with different slopes are thus obtained. An energy of activation $E_a$ of 5 kcal mol$^{-1}$ and a frequency factor $A$ of $10^{12}$ were found for the T ⟶ E process. For the T ⟶ A process the corresponding values are $E_a$ 0.8 kcal mol$^{-1}$ and $A$ $10^3$. The T ⟶ E process can be observed at temperatures at which the photoisomerization of A into E takes place with an appreciable quantum yield. These features are closely similar to those observed in the bianthrone series,[6] differing only in the structure of the photoisomer formed, B in bianthrones and E in (2) and (3a). Thus in bianthrones at temperatures below about −174° T ⟶ A is the major path of disappearance of T ($E_a$ 1.3 kcal mol$^{-1}$) while at higher temperatures the T ⟶ B process gradually takes over ($E_a$ 11.5 kcal mol$^{-1}$).

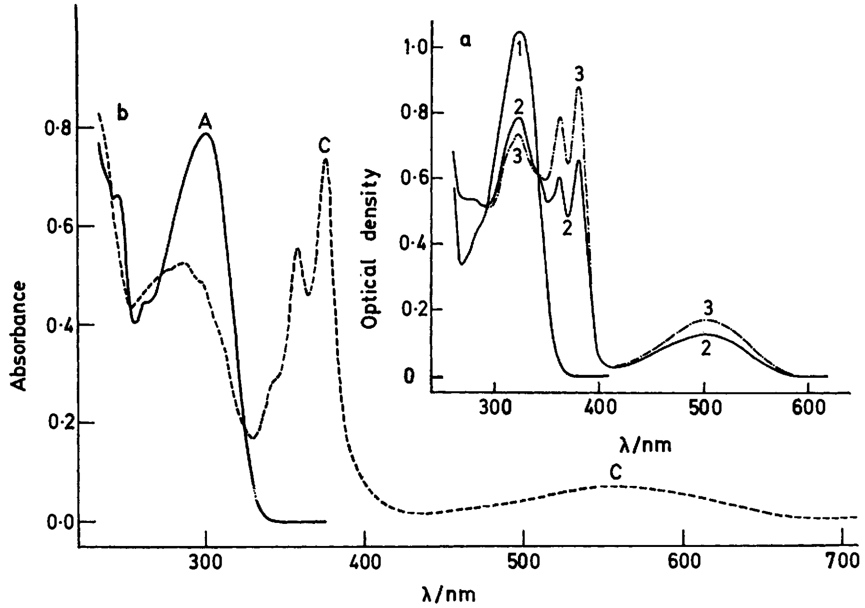

FIGURE 3 a, Absorption spectra of A and C forms of (2) in MCH–MCP (1 : 1) at −120°. Curve 1, A form; Curve 2, C form where the conversion of A→C is *ca.* 75%; Curve 3, absorption spectrum of pure C extrapolated from Curve 2. b, Absorption spectra of A and C isomers of (3b) in 1-P–2-P (2 : 3) at −130°. Curve A, A form; Curve C, C form at the photostionary concentration

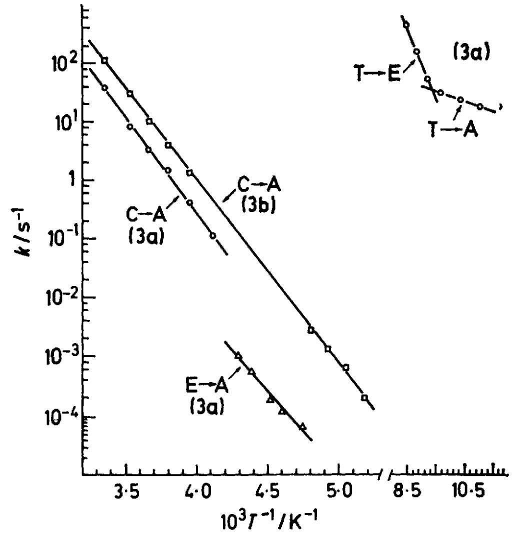

FIGURE 4 Arrhenius plots for the C ⟶ A, E ⟶ A, T ⟶ E, and T ⟶ A processes. (3a and b) *ca.* 4 × $10^{-5}$M in 1-P–2-P (2 : 3)

In the present cases we were not able to follow the formation of E at 260 nm (Figure 2, Curve E) where E has a high extinction coefficient, because of the absorption overlap with the transient T. An instantaneous absorption increase following excitation is seen at 260nm due to both decay of T and formation of E. The formation of the E isomer from the triplet state was observed in 10,10′-dimethylbiacridan.[7]

(C) *Oxidation of* (2C) *and* (3aC).—Ground state oxidation of (2C) and of (3aC) to the corresponding helianthryls (4) are accomplished by molecular oxygen. Isomer (2C) in MCH–MCP (1 : 1) and (3aC) in 1-P–2-P (2 : 3) were formed at −100° by irradiating argon-flushed solutions with 313 nm light. After obtaining maximal conversion into the C isomer, oxygen was bubbled through the solution. Slow oxidation occurred as shown by the disappearance of the longest absorption band at 500 nm and the appearance of helianthryl (4) band at 380 nm (Figure 6a, Curve 3). As shown previously, [8] the quantitative oxidation of the 4a,4b-dihydrophenanthrene-type photoisomer (DHP) to the corresponding phenanthrene-like compound can serve as an accurate method for determining the extent of photoconversion into the DHP.[5,8] In a similar way, *i.e.* by means of the absorption of the oxidation product (4) we estimated an initial

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[7] R. Korenstein, G. Seger, K. A. Muszkat, and E. Fischer, *J.C.S. Perkin II*, in the press.

[8] K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662.

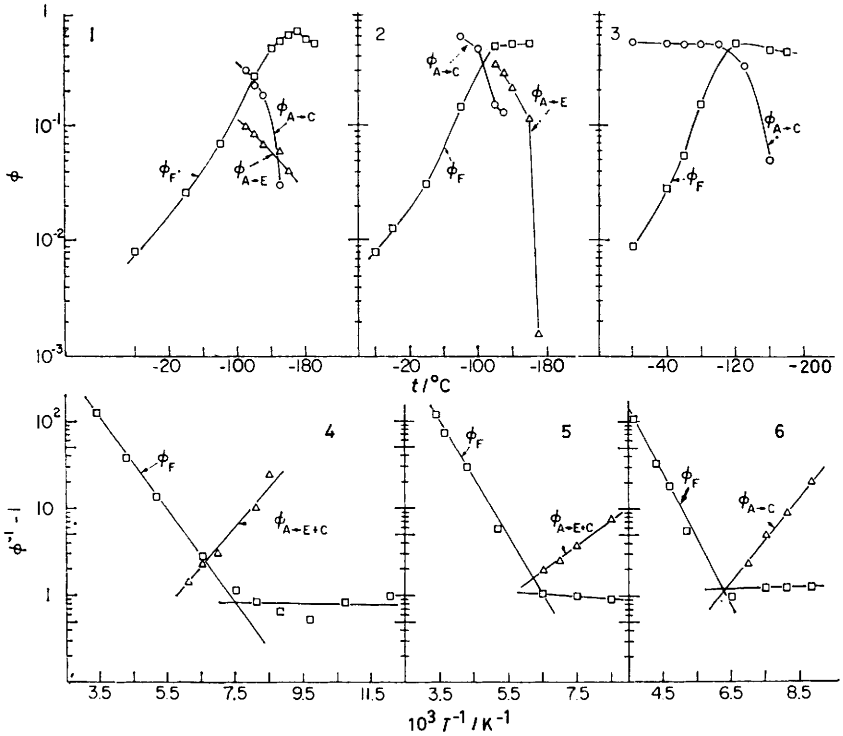
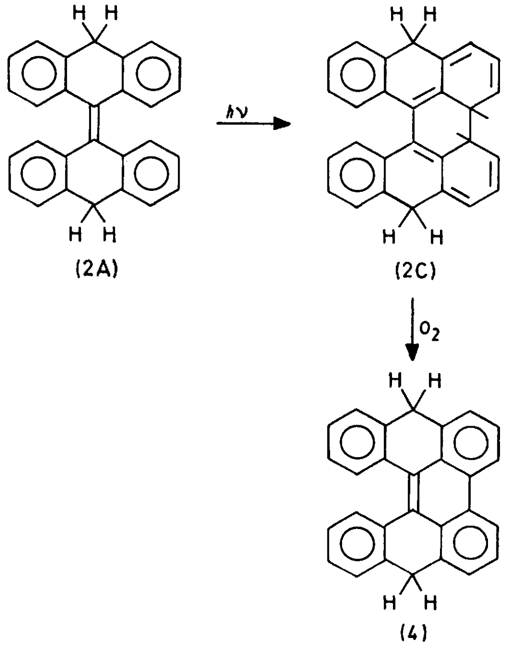


FIGURE 5 Temperature dependence of fluorescence ($\phi_F$) and of photoisomerization quantum yields for A ⟶ C ($\phi_{A\to C}$) and for A ⟶ E ($\phi_{A\to E}$) processes. 1, (2) in MCH–MCP (1 : 1); 2, (3a) in 1-P-2-P (2 : 3); 3, (3b) in 1-P-2-P (2 : 3). Curves 4—6 show the corresponding temperature dependence of $\phi_F$, $\phi_{A\to C}$, and $\phi_{A\to E}$ plotted as log ($\phi^{-1} - 1$) against $T^{-1}$

conversion of 75% of A to C. This result was confirmed using a different method useful in cases where the photoconversion into a mixture of light stable and photolabile isomers such as A ⟶ E + C takes place.[6] In the first step A is almost completely converted into a photoequilibrium mixture of E and C by irradiation at 313 nm. C is then reconverted into A by irradiating at 366 nm and then the cycle is repeated until all molecules are converted into the light stable modification E. Thus the total increment in E after the first step is equivalent to the quantity of C which disappeared. Since the concentration of E is known, that of C can be calculated. The spectrum of pure C (Figure 3, Curve 3) was obtained by extrapolation assuming Curve 2 in Figure 3 to describe a mixture of 75% C and 25% A. The extinction coefficients of (2C) at the absorption maxima calculated in this way are: $\lambda_{max.}$ 363 ($\varepsilon$ 15 850), 380 (17 700), and 500 nm (3 360). Compound (2C) is also dehydrogenated by molecular iodine.



(2A) (2C) (4)

Complete photocyclodehydrogenation of (2A) to the corresponding helianthryl (4) is effected by 313 nm irradiation of (2A) solutions saturated with air or oxygen. The quantum yield for this process at +20° is *ca.* 0.6. Since (2C) is dehydrogenated by iodine at −80°, irradiation at 313 nm of (2A) at −80° in the presence of iodine also causes complete conversion into (4). Figure 6a describes a typical experiment. An MCH solution of iodine (3.7 × $10^{-4}$M) and (2A) (4 × $10^{-5}$M) (curve 1) was flushed with argon and then irradiated at 313 nm. The resulting spectrum (curve 2) is a superposition of the spectra of iodine, helianthryl (4), and probably some iodine complex of (4), possessing a broad absorption in the 400—500 nm region.[9] On warming the solution and removing the iodine with copper foil, a solution of (4) resulted, (curve 3), mechanism (1) seems plausible.

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[9] H. Stegemeyer, T. Wismonski-Knittel, and E. Fischer, unpublished results.

(D) *Dehydrogenations by Atomic Iodine.*—Iodine atoms obtained by photolysis of iodine solutions with u.v. or

$$(2A) \xrightarrow[-80^\circ]{h\nu} (2C) \xrightarrow[-80^\circ]{I_2} [\text{helianthryl–}I_2] \xrightarrow{\Delta} \text{helianthryl} + I_2 \quad (1)$$

visible light are known as effective hydrogen-abstracting agents, and act as such also on (2A and E). Thus, when an MCH solution of (2A) and iodine, *e.g.* curve 1 in Figure 6a, was irradiated at room temperature with 546 and 578 nm light, where only iodine absorbs, oxidation to 9,9′-bianthracenyl (5) identified by its anthracene-like absorption spectrum (Figure 6b, curve 3) takes place and can proceed to completion.

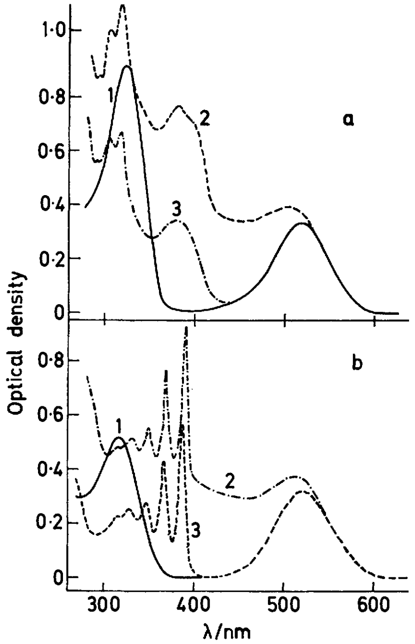
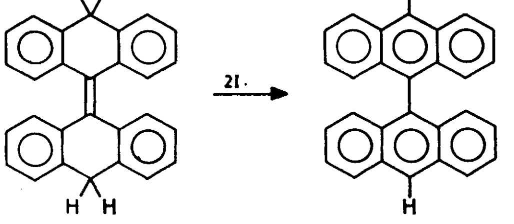


FIGURE 6 a, Compound (2) in MCH, in the presence of iodine. Curve 1, (2aA) before irradiation at −80°; Curve 2, after irradiation at 313 nm to completion; Curve 3, same, warmed to 25°. b, (2) in MCH. Curve 1, (2aA) at −80°; Curve 2, same, following complete conversion into (2E) by irradiation at 313 nm, addition of iodine, and irradiation at 546 nm; Curve 3, spectrum obtained following warming-up to 25°. Band at 520 nm is due to iodine. A similar curve is obtained following 546 nm irradiation, at 25° of a mixture of (2A) ($4 \times 10^{-5}$M) and iodine ($3.7 \times 10^{-4}$M)



(2) (5)

This reaction no longer takes place at −80°. However, when (2A) is first converted into (2E) by u.v. irradiation at this temperature and then irradiation with 546 nm light in the presence of iodine, efficient formation of (5) occurs. This much higher reactivity of (2E), relative to (2A), is in accordance with the results of minimum strain energy calculations [4] which show that the ground state energy of (2E) is higher by 13 kcal mol$^{-1}$ than that of (2A). The low temperature oxidation of (2E) to (5) with atomic iodine involves the formation of an iodine complex, probably with (5), as evidenced by the appearance of a broad absorption in the 400—500 nm region (Figure 6b, curve 3). The similarity to the phenomena accompanying the low temperature dehydrogenation of (2C) with iodine is obvious. We tend to believe that many photo-oxidations with iodine at low temperatures result in the transient formation of complexes of iodine with the polynuclear aromatic oxidation products,[9] characterized by strong broad absorption bands in the 400—500 nm range, and possibly related to similar complexes observed as equilibrium mixtures at room temperature in very concentrated solutions of iodine and the respective aromatic hydrocarbons.[9]

(E) *Temperature Dependence of Fluorescence Quantum Yields.*—The emission and absorption spectra of (2) and (3a and b) are shown in Figure 7. The fluorescence quantum yields $\phi_F$ within the +20 to −180° temperature range in argon-flushed solutions were measured relative to a $\phi_F$ value of unity in 9,10-diphenylanthracene.[10] The results are given in Figure 5, curves 1–3.

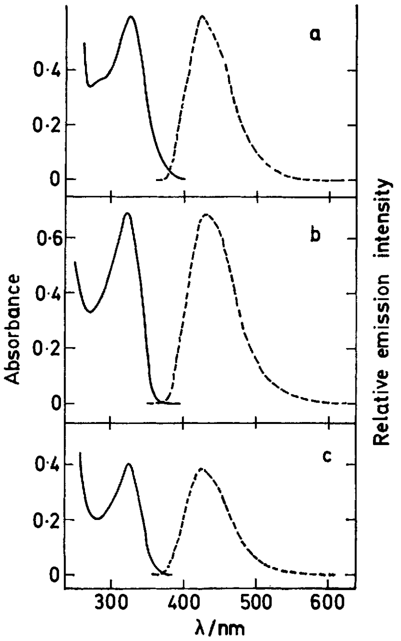


FIGURE 7 Emission and absorption spectra of (2) and (3a and b) at −160°. a, Emission and absorption spectra of (2) in MCH–MCP (1 : 1); b and c, emission and absorption spectra of (3a and b) in 1-P–2-P (2 : 3)

The fluorescence quantum yields decrease, and the

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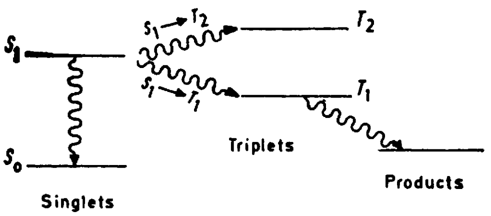
[10] I. B. Berlman, 'Handbook of Fluorescence Spectra,' Academic Press, New York, 1971, 2nd edn.

quantum yields of isomerization A $\longrightarrow$ E and of cyclization A $\longrightarrow$ C increase with rising temperature. Discontinuities in the curves of $\phi_F$ *versus* $T$ and of log $(\phi_F^{-1} - 1)$ *versus* $T^{-1}$ are apparent in all cases [*e.g.* at −140° for (2), at −120° for (3a), and at −114° for (3b)]. The significance of these discontinuities will be examined later.

Previous work[11] has established that in nonrigid aromatic systems (*e.g.* 1,2-diarylethylenes) both intersystem crossing (ISC, $S_1 \longrightarrow T$) and internal conversion (IC, $S_1 \longrightarrow S_0$) are activated processes. The curves of Figure 5 clearly show that the fluorescence and the photoisomerization processes A $\longrightarrow$ C and A $\longrightarrow$ E are inter-related. Thus, though we shall consider only ISC as the E isomers are formed from triplet state molecules, the temperature dependence of $\phi_F$ could also be due in part to the temperature dependence of $\phi_{A\rightarrow C}$ and of IC, the importance of which has only lately been fully appreciated.[11]

According to the conventional approach, the temperature dependence is due to an activated process, the activation energy representing the energy difference between two *electronic* levels.[12-15] Two (at least) ISC crossing processes $S_1 \longrightarrow T$ are assumed: A slow nonactivated process, $S_1 \longrightarrow T_1$,[15] the $T_1$ state lying below the $S_1$ state, and a fast activated process, $S_1 \longrightarrow T_2$ to the $T_2$ state (or to some higher state). These two processes are described by the wavy arrows in the Jablonski diagrams in the scheme. The Scheme implies that as long as the rate of $S_1 \longrightarrow T_2$ is considerably larger than that of $S_1 \longrightarrow T_1$ (*i.e.* at the higher temperatures) intersystem crossing will be a straightforward activated process and the temperature dependence will be described by proportionality (2). At lower temperature, when the rate of $S_1 \longrightarrow T_1$ is larger than that of $S_1 \longrightarrow T_2$, intersystem crossing becomes temperature independent. Indeed both types of behaviour are seen in the curves of log $(\phi_F^{-1} - 1)$ *versus* $T^{-1}$ in Figure 5, curves 4—6.

$$\log(\phi_F^{-1} - 1) \propto T^{-1} \qquad (2)$$



SCHEME

The occurrence of temperature dependent and independent radiationless processes in one molecule, and the transition from one type to the other are of particular significance to recent theoretical work on radiationless transitions.[16] These investigations conclude that radiationless transitions take place through the interaction of the excited states of the solute with the phonon states of the system. They predict temperature independent behaviour at low temperatures and temperature dependent behaviour at higher temperatures. Thus even downhill processes of the $S_1 \longrightarrow T_1$ type are predicted to require activation and there is no longer need to invoke higher energy states in order to explain the observation of activated ISC processes.[16]

## EXPERIMENTAL

Compounds (3a and b) were synthesized according to the literature.[17] Compound (2) was obtained from Dr. G. Seger, Technical University, Berlin. Absorption measurements were performed in a Cary 14 recording spectrometer. Long-necked quartz 1 cm sample cells were used. Variable temperatures[18] down to −193 °C were achieved by passing a slow stream of liquid nitrogen through a windowed copper block surrounding the sample cell. The copper block was placed in a quartz Dewar fitted with polished fused silica windows. The temperature was regulated by a thermocouple thermoregulator. Liquid nitrogen was led through 5 mm Teflon tubing from the metal storage container to the copper block. The flow of liquid nitrogen was maintained by applying a vacuum and stopped for regulation purposes by admitting air through a magnetic valve actuated by the thermoregulator. Variable temperatures in fluorescence and flash photolysis experiments were obtained using the same instrument. Fluorescence measurements were carried out on a 90° set-up. Light from a 450 W d.c. Xenon lamp was passed through a 500 mm Bausch and Lomb grating monochromator and focused on a 1 cm sample cell. The emitted light was focused on the entrance slit of another monochromator of the same type, fitted with a 9558Q EMI photomultiplier the anode current of which was fed to a Kipp and Zonen Micrograph recording galvanometer having a maximum full scale sensitivity of 20 nA. Fluorescence quantum yields were measured by comparison with 9,10-diphenylanthracene.[10] The flash photolysis apparatus consists of two air-filled (5 Torr) quartz 10 cm flash tubes energized by two 1 μF capacitors loaded up to 20 kV. A 100 W 12 V quartz iodine–tungsten monitoring lamp was used with suitable glass light filters. After passing through the sample cell (10—80 mm long) the monitoring beam was led to a photomultiplier monochromator combination as above, the signal being displayed in one or two Tektronix 564 storage oscilloscopes. Unless stated otherwise all solutions were purged at −30° by passing a slow stream of ultrapure argon for 30 min.

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[6/727 *Received*, 13*th April*, 1976]

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[13] K. A. Muszkat, D. Gegion, and E. Fischer, *J. Amer. Chem. Soc.*, 1967, **89**, 4814; 1968, **90**, 12, 3907.

[14] E. C. Lim, D. Laposa, and J. M. H. Yu, *J. Mol. Spectroscopy*, 1966, **19**, 412.

[15] W. G. Herkstroeter and D. S. McClure, *J. Amer. Chem. Soc.*, 1968, **90**, 4522.

[16] See, *e.g.*, V. Yakhot, *Chem. Phys.*, 1976, **14**, 441.

[17] H. Dickert and V. Petsch, *J. prakt. Chem.*, 1935, **143**, 211; K. Glen and S. Nitzsche, *ibid.*, 1939, **153**, 241.

[18] E. Fischer, *Mol. Photochem.*, 1970, **2**, 99.