

THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF 2-STYRYL-ANTHRACENE AND RELATED COMPOUNDS: EXTREME VARIATIONS IN TRIPLET-TRIPLET ABSORPTION SPECTRA WITH THE TEMPERATURE, DECAY ANOMALIES AND TRANS-CIS PHOTOISOMERIZATION†

VALERI KRONGAUZ, NELLY CASTEL and ERNST FISCHER‡

Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot (Israel)

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Summary

Transient triplet-triplet absorption spectra and decay curves of 2-styrylanthracene and four related compounds were determined with conventional microsecond flash spectroscopy over a wide range of temperatures between room temperature and -170°C , in decalin and methyltetrahydrofuran as solvents. The main anomalies observed were as follows: pronounced variation in the triplet absorption spectra with the temperature and, to some extent, with the wavelength of the exciting light; "growing-in"; initial fast decay stages; non-monoexponential decay; variation in the decay rate with the wavelength of measurement. All these were observed at certain temperatures and wavelengths for each compound. Some of these anomalies may be due to the fact that 2-styrylanthracene and its derivatives exist in solution as an equilibrium mixture of two modifications, possibly rotational conformers, both in the ground and in the excited state. Some trans-cis photoisomerization, both direct and sensitized, takes place in all compounds, except possibly in 2-styrylanthracene, and is more pronounced in bromobenzene solutions.

1. Introduction

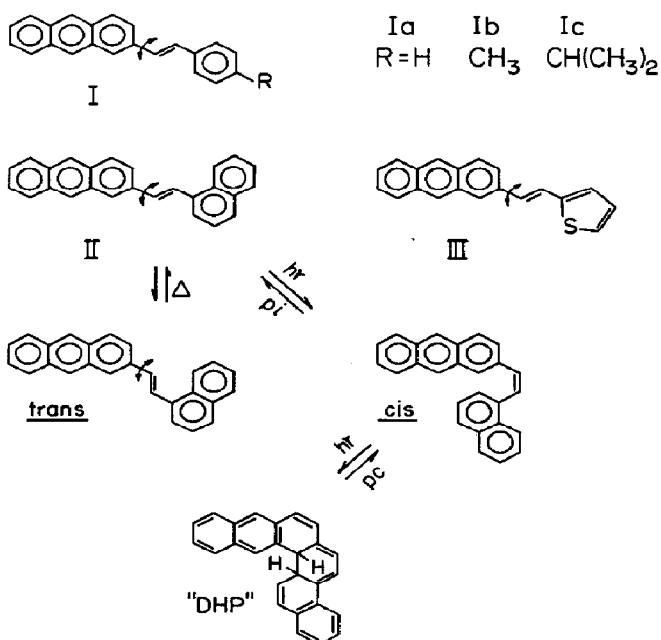
The existence of rotational conformers ("rotamers") in solutions of *trans*-1,2-diarylethylenes ($^1\text{Ar}-\text{CH}=\text{CH}-^2\text{Ar}$) has been demonstrated by our group [1 - 5] and by other groups [6 - 8] using mainly emission spectroscopy and more recently also absorption spectroscopy [3]. 2-Styrylanthracene and related compounds were investigated by us using emission spectroscopy and again showed quite pronounced effects best explained

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‡ Author to whom correspondence should be addressed.

by the rotamer hypothesis [2]. A relevant but much more quantitative study was published recently [9].

In a recent paper [5] we reported low temperature flash photolytic measurements of the triplet-triplet (T-T) absorption spectra of naphthyl derivatives (^1Ar or both ^1Ar and ^2Ar are naphthyl groups). A plausible explanation of the results, in particular those obtained with the freeze-unfreeze method [4], was again the assumption of ground state rotamers differing in their T-T absorption spectra. In the same context we have now investigated the T-T absorption spectra, over a wide temperature range, of 2-styrylanthracene Ia and the related compounds Ib, Ic, II and III



all of which have been studied earlier by emission spectroscopy [2, 3]. The freeze-unfreeze method [4] could not yet be employed with these compounds, since the respective *cis* isomers were not available.

The room temperature T-T absorption spectra of Ia and III obtained in the presence of intersystem crossing enhancers have been reported [10], as has been the direct photoformation of the triplet transients of Ia and the 2-naphthyl analogue of II in benzene solution [11]. Both research groups used laser flash excitation and found these transients to be remarkably long lived (0.1 - 0.2 ms), compared with stilbene and its naphthyl analogues [5].

Our present measurements showed that with all five compounds, the T-T absorption spectra could be observed in a conventional flash photolysis apparatus equipped with a low temperature thermostat, both at room temperature and at low temperatures, down to -170°C . The variation in

the spectra and in the decay behaviour with the temperature proved to be of particular interest. Both "growing-in" and "two-stage decay" were observed under certain conditions.

Concerning the photochemistry, all compounds undergo trans \rightarrow cis photoisomerization to some extent, which is enhanced by sensitizers and by using bromobenzene as the solvent.

2. Experimental details

2.1. Compounds

The compounds have all been described earlier [2]. All but Ib were kindly supplied by Professor Siegrist, Basle. Ib was synthesized by Professor Laarhoven, Nijmegen. The solvents were ethanol 96% "analytical" (Frutarom), methyltetrahydrofuran (MTHF) (Fluka) passed through an alumina (Woelm, basic I) column shortly before use, toluene (Merck) and decalin (Merck), both of which were also passed through alumina columns. Solutions were thoroughly flushed with argon throughout.

2.2. Spectrophotometry

The absorption spectra were measured on a Varian-Cary 2200 instrument and the emission spectra on a Perkin-Elmer MPF-44 spectrofluorimeter. Both instruments were equipped with our usual *in situ* cooling and irradiation arrangements [12]. Flash photolysis was carried out in a home-made more or less conventional apparatus, employing two air-filled flash tubes 10 cm long through which $2 \times 1 \mu\text{F}$ capacitors at 15 - 19 kV were discharged. The optical cells employed in this set-up were made of Suprasil tubing (4 mm \times 16 mm cross-section) [13] and had a light path of 20 mm. They were used inside a Pyrex Dewar vessel equipped with the same cooling arrangements [12]. Corning 7-54 colour filters were placed between the flash tubes and the sample cell, thus effectively limiting the active light to the range 320 - 400 nm. Decay curves were recorded on a Nicolet Explorer III digital oscilloscope. It should be recalled that the observed transient increase in absorbance represents the difference between the absorbance of the ground state and the transient. This is important in the long wavelength edge of the ground state absorption spectrum. Each spectrum involved measuring some 30 decay curves at roughly 10 nm intervals. Solutions were about 2×10^{-5} M.

3. Results

3.1. Triplet-triplet absorption spectra

Solutions in decalin and in MTHF were used for most experiments since these are "good" solvents and can be employed over a wide temperature range, down to -150°C (decalin) or -180°C (MTHF). The spectra observed in the two solvents are rather similar, except that the variation in

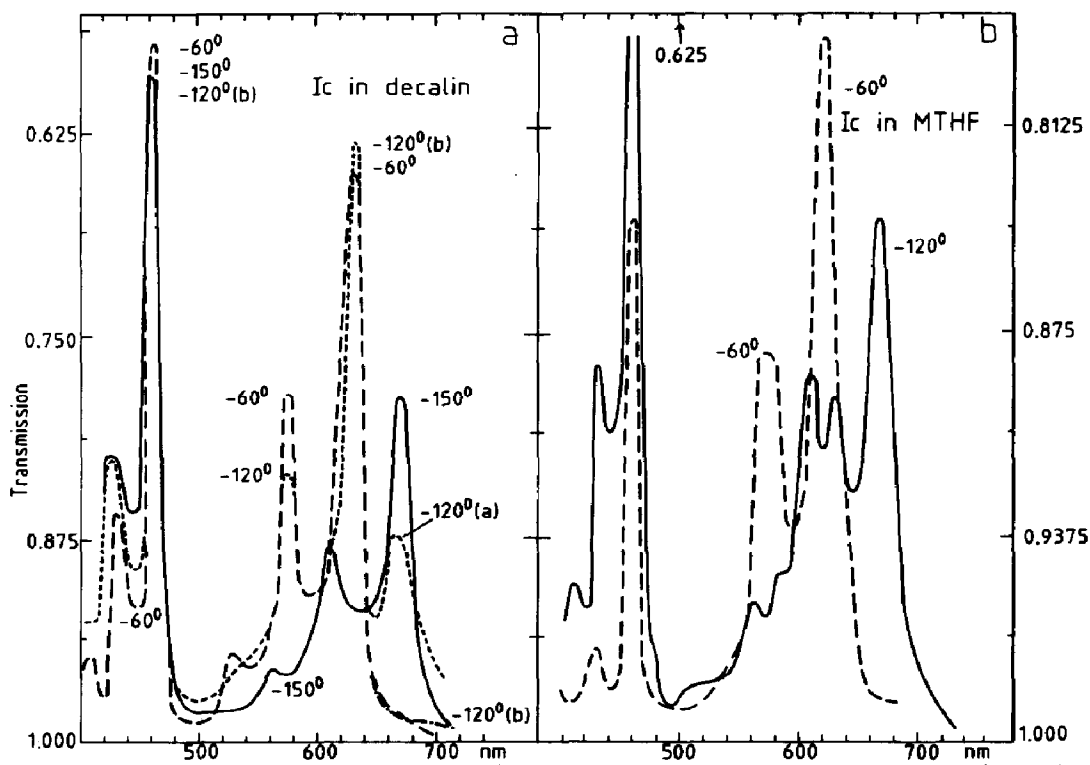


Fig. 1. T-T absorption spectra of Ic in decalin and in MTHF at various temperatures. The transmission at each wavelength was obtained by extrapolation of the decay curve to "zero" time. In (a) at -120°C "a" refers to such an extrapolation from the early part of the decay curve (e.g. broken curves in Fig. 4), while "b" refers to such an extrapolation from the later part (full curves in Fig. 4). See text for spectra at $+20^{\circ}\text{C}$.

the short wavelength peaks with the temperature is much more pronounced in MTHF solutions, as shown in Fig. 1 for compound Ic, which is typical for Ia - Ic. Moreover, the new peak at around 670 nm appears in MTHF already at much higher temperatures than in decalin (about -80°C for Ia - Ic; -70°C for III). Figure 2 describes the spectra observed with II and III in decalin solutions. All the compounds exhibit an extreme variation in the T-T absorption spectra with the temperature. When the spectra at high and low temperatures in each case (the full and broken lines) are compared, the most prominent feature is that cooling causes the disappearance of the peaks around 620 - 630 and 560 - 580 nm and the appearance of a new peak at around 680 nm and also with II at around 470 and 505 nm (Fig. 2(a)). In addition, the short wavelength peaks in decalin solutions are strongly enhanced on cooling. In III the spectra at intermediate temperatures are themselves intermediate, indicating a temperature-dependent equilibrium between two modifications. In other compounds the modification characterized by the spectra at the lower temperatures was observed to be a precursor of the modification stable at the higher

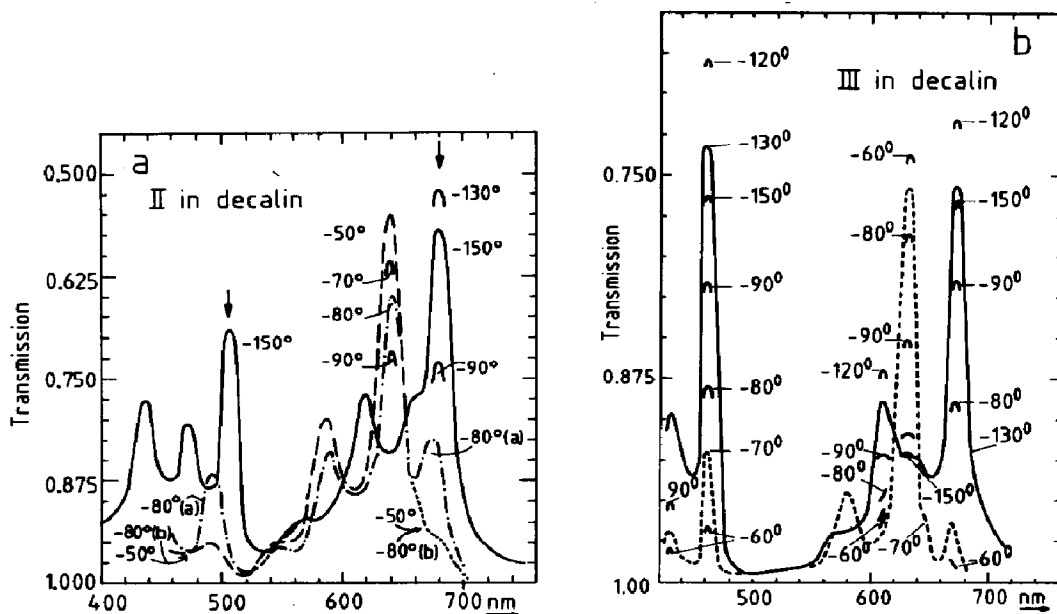


Fig. 2. T-T absorption spectra of II and III in decalin at various temperatures. See also caption to Fig. 1, regarding extrapolation for obtaining the spectra "a" and "b" of II at -80°C . See text for spectra at $+20^{\circ}\text{C}$.

temperature. This is shown in Fig. 1(a) for Ic at -120°C , and in Fig. 2(a) for II at -80°C , and will be discussed in connection with the triplet decay kinetics. The vibrational structure of the spectra is very pronounced. The peaks may be even sharper than shown in Figs. 1 and 2, since the monochromator slits restricted the resolution to about 4 nm. The main temperature effect takes place within the rather narrow temperature range from -60 to -130°C . The room temperature T-T absorption spectra reported for Ia in benzene [11] and for Ia and III in toluene [10] in general resemble our present spectra at -60°C . The 670 - 680 nm band was not observed in those laser flash experiments, in which spectra were taken about 0.001 ms after the excitation flash. Only with III in benzene, in the presence of butyl nitroxide, Wisniewski and Das [10] observed a transient absorbing at 670 nm and decaying with a half-life of about 80 ns (!). Certain discrepancies between the results obtained with our conventional flash and with their laser flash may be due to the rather short lifetime of triplet III at -60°C (less than 0.1 ms), possibly causing some apparent temperature-dependent changes in the spectra in our apparatus. However, the obvious advantages of conventional flash photolysis for transients with half-lives above, say, 0.05 ms are the absence of interference from fluorescence and short-lived (singlet?) transients and the use of cells with longer light paths (20 mm in the present experiments; up to 70 mm in our thermostatted set-up). This fact, and also the probable increase in triplet yields on cooling,

explains why Wisniewski and Das [10] could observe T-T spectra at room temperature only in the presence of intersystem crossing enhancers, while we obtained fairly large signals in argon-flushed solutions without additives,

TABLE 1

Approximate range of decay half-lives $\tau_{1/2}$ of transients at various temperatures for five compounds in the solvents indicated (for anomalies see Table 2)

Temperature (°C)	$\tau_{1/2}$ (ms)	Temperature (°C)	$\tau_{1/2}$ (ms)	Temperature (°C)	$\tau_{1/2}$ (ms)
Ia in MTHF		Ib in MTHF		Ic in MTHF	
-70	0.5 - 0.8 (1.9!)	-60	0.7 - 1	-52	0.7 - 1.5 (3!)
-100	1 - 2 (0.4 at 670 nm)	-80	1 - 3	-80	1.5 - 4
-120	5 - 7.5 (1.3 at 670 nm)	-120	2 - 4 (1.2 at 670 nm)	-120	5 - 8 (1.3 at 670 nm)
-150	26 - 30	-170	28 - 36	-170	30 - 39
Ia in decalin		Ib in decalin		Ic in decalin	
+20	0.10 - 0.13	+20	0.10 - 0.13	+20	0.12 - 0.20
-60	2 - 3	-60	1.2 - 4.2	+8	0.25
-150	30 - 35	-90	7 - 10	0	0.27
		-130	12 (27!) (5 at 670 nm)	-10	0.3
		-150	32 - 36 (59!)	-20	0.35
				-60	0.7 - 0.9 ^a
				-60	2 - 3 ^b
				-90	3.5 - 5
				-120	8 - 10 ^c
				-130	5 - 12
				-150	27 - 33
II in MTHF		III in MTHF		Ic in toluene	
-50	0.3	-50	0.12 ± 0.03	-50	0.6 - 1.4
-80	0.9	-60	0.16 ± 0.04	-90	3 - 4.5
-120	3.4	-70	0.17 ± 0.04		
-170	6 - 8	-100	0.45 ± 0.05		
		-150	1.0 ± 0.2		
		-170	1.2 ± 0.2		
II in decalin		III in decalin		III in ethanol-methanol	
+20	0.03 - 0.04	+20	0.016	-50	0.2
-50	0.2 - 0.26	-60	0.06 - 0.09	-100	0.6
-80	0.4 - 0.5 ^c	-70	0.13 - 0.17 (0.07 at 670 nm)	-150	1.0 ± 0.1
-90	0.6 - 0.7 ^c	-90	0.16 - 0.26 (0.1 at 670 nm)		
-130	3.0 - 3.6	-130	0.8 - 0.9		
-150	11 - 17	-150	1.0 - 1.1		

^aTwo cases.

^bThree different experiments.

^cSecond stage at 660 - 680 nm.

even at room temperature. The room temperature spectra are essentially similar to those at -60°C , except that the ratio between the short and the long wavelength bands decreases with increasing temperature. In addition, we found this ratio also to vary with the wavelength range of the exciting flash light: insertion of a Pyrex filter between the flash lamps and the cell, *i.e.* cutting out light below 310 nm, reduces this ratio by about one-third at room temperature. With III in decalin, the short wavelength component is no longer observed at room temperature, and the only peaks are at 575 and 625 nm. Incidentally, it was a pleasant surprise that it proved to be possible to record this spectrum despite the fast decay (around 0.015 ms). No transients were observed in air- or oxygen-flushed solutions, *i.e.* quenching and/or shortening of transient lifetimes are sufficient to prevent detection.

3.2. Kinetics of formation and decay of the transients

At most wavelengths and temperatures, in both solvents, the transients were observed to be formed "instantaneously", *i.e.* during the flash (about 10 μs), and to decay roughly monoexponentially, at rates varying slightly with temperature in each compound, except that at the lowest temperatures and highest viscosities the decay is slowed down considerably to approximately the same rate in all solvents used, as shown in Table 1. However, at least three anomalies were observed.

(a) At several wavelengths and certain temperatures, the decay rate was less than half, and at others about double that found at the majority of wavelengths (Tables 1 and 2). Thus for Ib in decalin at -130°C , the half-life is about 11 ± 2 ms at 410 - 470 and 560 - 640 nm, but 20 - 30 ms at 490 - 550 nm and 5 - 6 ms at 650 - 690 nm (exceptionally long or short decay time anomaly). The exceptionally short decay time is mostly found in the wavelength range of the longest peak, 660 - 680 nm, characterizing the low temperature spectra (Figs. 1 and 2).

(b) Again, at several wavelengths part of the transient absorption is growing-in at rates much slower than the flash, but much faster than the decay of the transient absorption. In Ia - Ic this is most prominent in decalin solutions at about -130°C , at suitable wavelengths, as shown in Fig. 3. The fraction of absorbance growing-in after the flash, *i.e.* thermally, varies with the wavelength, and is frequently much smaller than that shown in the examples described in Fig. 3 but easily noticeable after horizontal enlargement of the decay curves. Table 2 summarizes the conditions at which pronounced growing-in was observed with Ib, serving as an example. A very rough estimate of the half-time of growing-in is 2 ms for Ib and Ic in decalin at -130°C (growing-in anomaly).

(c) With Ic, pronounced two-stage decay was found from -120 to -130°C for the peak at around 670 nm (Fig. 4(a)), the peak peculiar to the low temperature spectra in Figs. 1 and 2. With II, Fig. 4(b), two-stage decay was observed at -90°C in the 660 - 680 and the 470 - 520 nm regions, both of which characterize the low temperature spectra of II (Fig. 2). In these cases, this behaviour results in transient absorption spectra

TABLE 2

Anomalies in decay behaviour exemplified by Ib: polyexponential decay (ped), fast initial stage (fis), growing-in (gi), exceptionally long (el) or short (es) decay time (temperatures, solvents and wavelengths as indicated; "-" followed by a wavelength means the range between this and the preceding wavelength)

Decalin				MTHF			
λ (nm)	Anomaly	λ (nm)	Anomaly	λ (nm)	Anomaly	λ (nm)	Anomaly
-60 °C		-90 °C		-60 °C		-80 °C	
430 } 450 } 470 }	gi	420 } -470 }	gi	430	el	530 } 570 }	ped
500	ped	-130 °C		590 } 610 }	fis	-650 }	
620 } 630 }	gi	490 } -550 }	el	650 }		660	fis
640 } 660 }	fis	650 } -680 }	es	-120 °C		-170 °C	
-120 °C		-150 °C		410 } 430 } 440 } 450 } 470 }	gi	470	gi
470 } 500 } 530 } 540 } 570 } 630 }	gi	420 } 430 }	gi	530 } 540 } 570 } 580 } 630 }			
		510 } 560 }	ped	600 } 610 }	ped		
		590 } -660 }	fis	660 } -690 }	es		

which differ pronouncedly if taken either soon after the flash, *i.e.* after about 20 - 30 μ s, or by extrapolation to "zero time" of the absorbances from, say, 2 ms onwards (Ic) or 0.5 ms onwards (II). This is shown in Fig. 1(a) for Ic and in Fig. 2(a) for II. The first fast stage has a half-life of about 0.5 ms for Ic in decalin at -120 °C (Fig. 4(a)) and about 0.07 ms for II in decalin at -90 °C (Fig. 4(b)). The second stage is 12 - 20 times slower in both cases (fast initial stage anomaly). When the difference between the rates of the two stages becomes smaller, the result is non-monoexponential decay (polyexponential decay anomaly). Table 2 summarizes these anomalies for Ib, but under appropriate conditions all five compounds display similar behaviour. This holds also for anomaly (a). At the lowest temperatures and highest viscosities (-150 °C in decalin; -170 °C in MTHF) no anomalies were found in decay behaviour.

3.3. Photoisomerization

In view of the recent report [11] that Ia and the 2-naphthyl analogue of II undergo solely *cis* \rightarrow *trans* "one-way isomerization", both directly

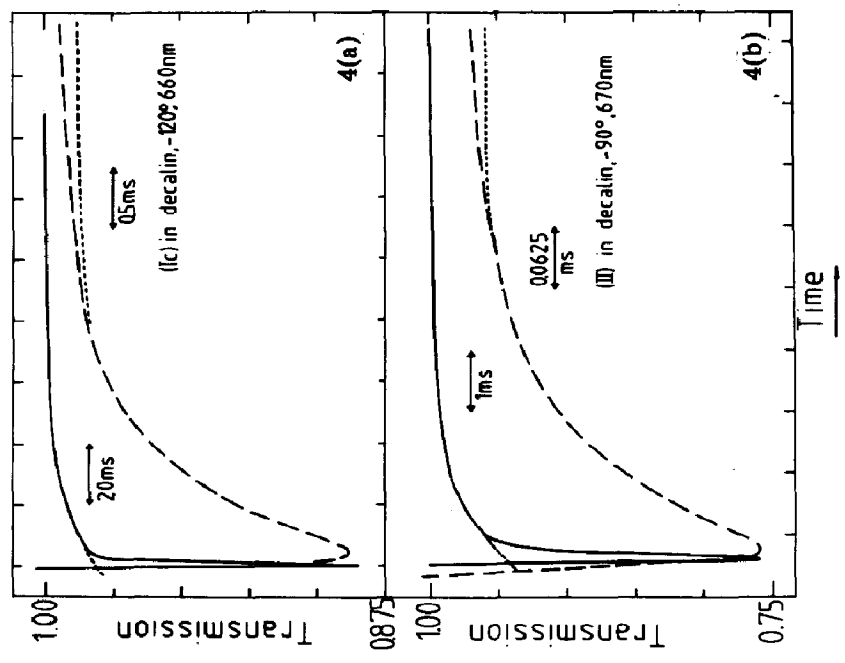


Fig. 3. Decay curves of triplet transients showing the growing-in anomaly on two different time scales. The growing-in half-life is about 2 ms. Both Figs. 3 and 4 show the original decay curves (transmission vs. time) observed on the scope screen. (At these transmission values, $(1 - Tr)$ is roughly proportional to the concentration of the transients.)

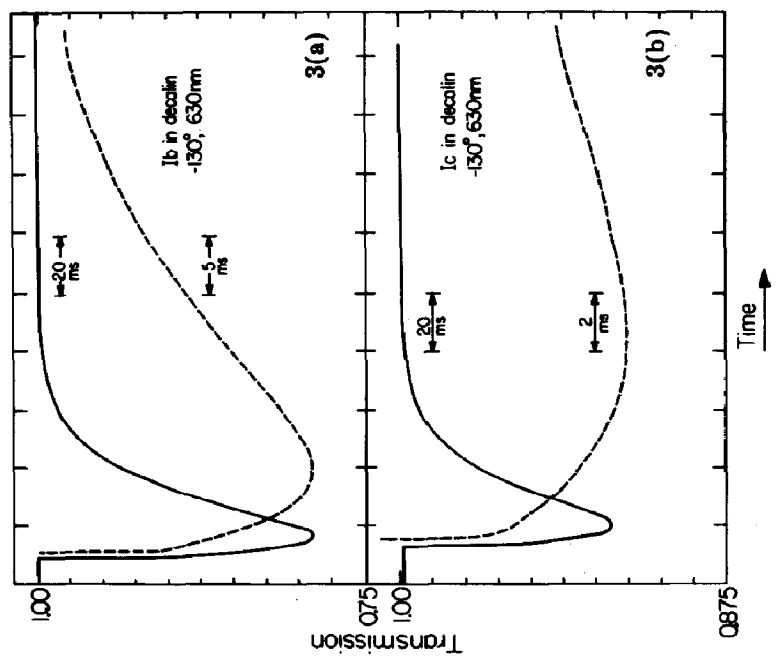


Fig. 4. Decay curves of triplet transients, showing fast initial stage anomaly. Full and broken curves depict the decay on a slow and fast time scale respectively, as indicated. The dotted parts describe the estimated early part of the slow-scale curve in the absence of the fast initial stage anomaly, and the estimated later part of the fast-scale curve in the absence of the slow-decay component. These parts are given only for clarification of the general idea in our working hypothesis. Approximate half-lives of the first stage are 0.5 ms in (a) and 0.06 ms in (b); those of the second stage are 16 ms and 0.8 ms respectively.

and with sensitizers, we wish to report briefly our 1984 results regarding photoisomerization since the triplet state may be involved. Solutions of compounds I - III (trans isomers) in methylcyclohexane (MCH) without and with biacetyl as triplet sensitizer, in decalin and in bromobenzene were irradiated at -20°C (to allow flushing with argon) with filtered light from a 125 W mercury lamp at 254, 313, 366 and 405 nm (direct photoisomerization) or 436 nm (sensitized photoisomerization). After attainment of the photostationary state, iodine was added and the solution irradiated at 546 nm. The atomic iodine thus created causes thermal equilibration of the isomers, *i.e.* almost complete reversion to the trans isomer. The extent of this reversion indicates which part of the observed decrease in absorbance (350 - 400 nm triple peak) is due to photoisomerization. In the results summarized in Table 3, the observed decreases were at least 80% reversible and may therefore be assumed to be mainly due to trans \rightarrow cis photoisomerization, and not to irreversible decomposition. Figure 5 describes two examples. Since we do not know the spectrum of the cis isomer, the spectral changes caused by irradiation allow us to estimate only a lower limit for the photoconversion, by assuming that the cis isomer does not absorb at the peaks of the trans isomer. This is obviously too extreme an assumption (*cf.* footnote a in Table 3). Irradiation at 254 nm causes more extensive isomerization, but also some decomposition, and its results are therefore not included in Table 3. The most extensive conversion of trans into cis was obtained at 405 nm: with III the cis content at the photostationary state amounts to at least 40%! (see also the caption to Fig. 5 regarding the extrapolated spectra). The present observations indicate substantial conversion into the cis isomers, except for Ia, in particular in the "heavy-atom" solvent bromobenzene which enhances intersystem crossing, thus opening or widening the triplet path of trans \rightarrow cis photoisomerization. In view of the large values reported [11] for the quantum yields cis \rightarrow trans in Ia (exceeding unity!), the trans \rightarrow cis quantum yield is obviously not negligible, although its exact determination requires knowledge of the spectra of the respective cis isomers. At -130°C in decalin solutions, no photoisomerization takes place with 405 nm light in either direction. 366 nm irradiation of the cis plus trans mixture (obtained by 405 nm irradiation at -20°C) at -130°C causes a very inefficient cis \rightarrow trans conversion, accompanied by formation of a coloured product with peaks at 422 and 444 nm, erasable with light above 430 nm, and also disappearing on heating. This is probably the photocyclization product, an analogue of 4a,4b-dihydrophenanthrene [15 - 17], as shown in the scheme above. (The DHP may also be derived from the second rotamer of cis, not shown.)

The trans \rightarrow cis quantum yields may increase with increasing temperature much more than those of the reverse reaction, as observed by us with the naphthyl analogues of stilbene [15]. If so, trans \rightarrow cis photoisomerization should be more efficient at, say, $+100^{\circ}\text{C}$. However, we found that at this temperature substantial photodecomposition occurs, making it impossible to determine the extent of photoisomerization.

TABLE 3

Minimal *cis* isomer content^a in argon-flushed solutions of compounds irradiated at -20°C at the wavelengths indicated until attainment of the photostationary state (for solvents see text)

Compound	Solvent	Irradiation wavelength (nm)	Per cent <i>cis</i> ^a at photostationary state	Compound state	Solvent	Irradiation wavelength (nm)	Per cent <i>cis</i> ^a at photostationary state
Ia	MCH	366	<3	Ic	Decalin	366	b
		313	<3			405	6
Ia	BB	436 ^c	5	Ic	BB	366	14
		366	5			313	6
Ia	Decalin	313	3	III	MCH	366	10
II	MCH	405	5			313	10
		366	6	436 ^c	15 ^d		
II	BB	313	6	III	Decalin	366	14
		436 ^c	12			405	29
II	Decalin	366	20	III	BB	313	18
		313	10			334	28
a		366	10	III	BB	366	20
		313	10			405	40

BB, bromobenzene.

^aThe *cis* content at the photostationary state for Ia - Ic was calculated assuming that at the triple peak, in the range 340 - 400 nm, *cis* does not absorb. Actually we can estimate the absorption spectrum of *cis*-Ib using a sample of Ib containing some *cis* isomer. By employing preferential dissolution in "poor" solvents we could obtain *cis*-rich solutions of Ib. Accordingly, at the three peaks the absorption of *cis*-Ib is about 60% that of *trans*-Ib. One may assume roughly the same for Ia and Ic, and conclude that the actual *cis* content at the photostationary state in Ia - Ic is two to three times the values given in this table.

^bSome photodecomposition occurs.

^cIn the presence of biacetyl.

^dBiacetyl is used up in this case.

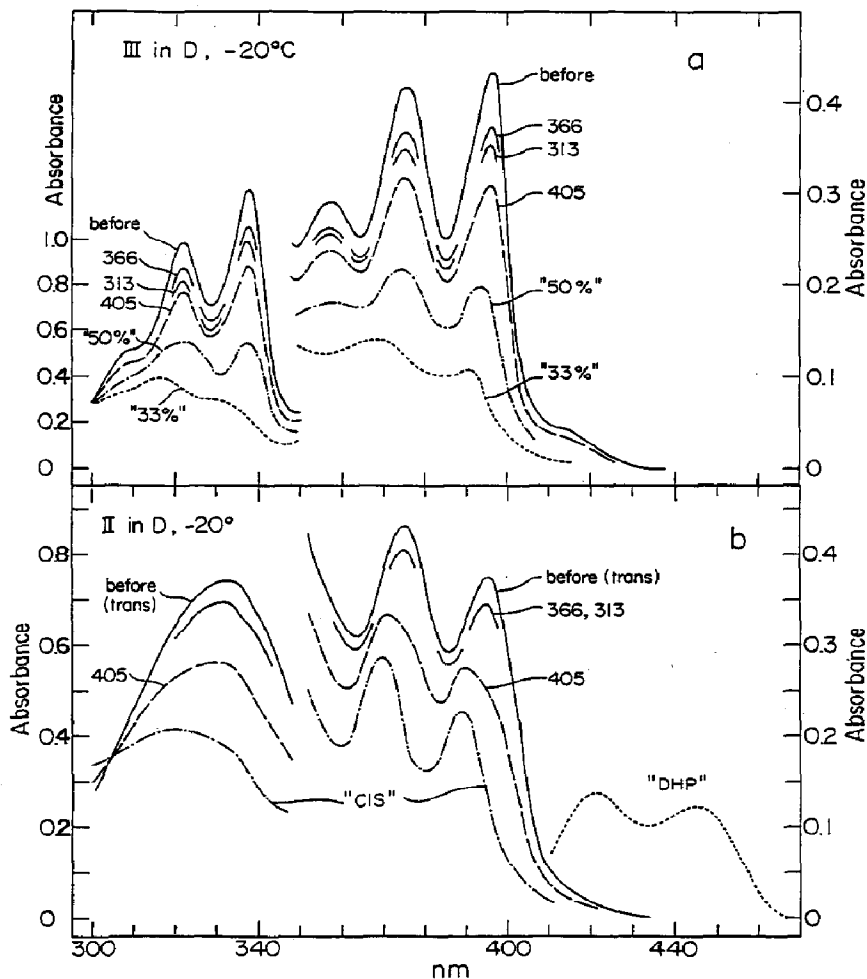


Fig. 5. Absorption spectra of II and III before (—) and after (---) irradiation "to completion" at 405 nm (the photostationary state). The photostationary state spectra at other wavelengths are indicated. Solutions in decalin at -20°C . - · - represents the estimated 100% cis spectrum, obtained by extrapolation with the arbitrary assumption that the 405 nm curve represents a mixture of 50% cis and 50% trans, while · · · · represents the curve estimated for a 33% cis content in the 405 nm curve (III only). This is just to give an idea of the possible shape of the cis spectrum (for extrapolation see ref. 14). The right-hand scale refers to the right-side portion of the spectrum. The spectrum in the range 400 - 460 nm (·····) was taken at a sensitivity five times higher than the right-hand scale, and represents the portion of the 4a,4b-dihydrophenanthrene spectrum in the visible region.

4. Discussion

4.1. Triplet spectra and decay behaviour

The large variation in the T-T absorption spectra with temperature and the various anomalies of the decay behaviour indicate that the 2-styryl-anthracenes exist in the triplet state in at least two different interconvertible

modifications, 3A and 3B . Henceforth this will be our working hypothesis. We propose that these modifications interconvert at rates increasing sharply with increasing temperature. The equilibrium constant $K = [{}^3A]/[{}^3B]$ also varies with temperature, and so do the rates of decay to the ground state(s). As long as equilibration is fast relative to the decay, we expect the photoexcitation to be followed by an initial fast stage of equilibration, followed by a second slower stage of decay to the ground state. The ground state may be either one modification X or a mixture A + B: 1, ${}^3A \rightarrow {}^3B$; 2, $({}^3A \rightleftharpoons {}^3B) \rightarrow A + B$ or X. The observable change in absorbance during stage 1 will be positive, negative or zero, depending on the relative absorption coefficients ϵ of 3A and 3B at each wavelength. Thus, if ${}^3A \rightarrow {}^3B$ during equilibration, and $\epsilon_{\lambda_1}({}^3A) < \epsilon_{\lambda_1}({}^3B)$, growing-in will be found at λ_1 , while for $\epsilon_{\lambda_2}({}^3A) > \epsilon_{\lambda_2}({}^3B)$ a fast initial decay is to be expected at λ_2 . This may serve as a tentative explanation of the growing-in decay anomaly observed in the spectral region characterizing 3B , e.g. 630 and 570 nm, and the fast initial stage decay anomaly at around 670 nm (3A), as well as the time-dependent T-T spectra at appropriate wavelengths and temperatures peculiar to each solvent. The modification 3A in the above scheme is thus identical with that characterized by the long wavelength peak at around 670 nm. K varies with temperature to different extents in different compounds, as expressed in the ratio between the peaks at 670 nm and those at shorter wavelengths, and in its variation with temperature. For compound III in decalin (Fig. 2(b)) some 3A is still observable even at -60°C , while, for example, for Ic 3A does not contribute to the equilibrium at all even at -120°C (Fig. 1(a)).

When the rates of equilibration are no longer drastically faster than the decay rates, again at appropriate temperatures, non-monoexponential disappearance of the transient and variation of disappearance rates with the wavelength may appear. The absence of the long wavelength peak above about -50°C could then be due to the too fast conversion of 3A into 3B . The observation [10] of a similar transient at room temperature, with a half-life of some 80 ns, points in this direction, although this transient was not found with the other compounds [10] and is not reported by Tokumaru and coworkers [11]. At the other extreme, *i.e.* low temperatures and high viscosities, interconversion ${}^3A \rightleftharpoons {}^3B$ becomes much slower than decay to the ground state, and no decay anomalies are observed.

Although a detailed analysis of the situation is difficult, we suggest that the interplay of the various factors mentioned, in particular the temperature variation of the various rate constants and of the equilibrium constant, may provide at least a qualitative explanation of the present observations. The finding that the T-T spectra at room temperature vary somewhat with the wavelength range of the excitation light indicates that two modifications may also exist in the ground state, $A \rightleftharpoons B$, giving rise to photoselective excitation.

Since the phenomena are qualitatively common to all five compounds investigated, and probably to many more, a reasonable explanation would

be to assign the two postulated modifications to rotational conformers, described earlier on the basis of emission anomalies [2, 9]. If so, similar anomalies should not be expected with 1-styrylanthracene and 9-styrylanthracene which do not show the emission anomalies ascribed to rotamers. Indeed, these two do not show the anomalies. Obviously this does not constitute a proof for this hypothesis, and other structure assignments to the two or more different triplet modifications may eventually pop up. However, at present the rotamer hypothesis may serve as one way of explaining, at least in a general way, the complex observations reported here. We hope to be able to check the possible correlation between our earlier quite clear-cut emission findings and the present triplet results under identical conditions. In this context it should be mentioned that the barrier to interconversion between rotamers in the singlet excited state of trans-stilbene-like molecules is much higher than in the ground state [18] so that, within the short lifetime of the singlet excited state, rotamer interconversion can be ignored [1]. No relevant calculations are available as yet for the triplet state, but it appears reasonable that in it the barrier may be somewhere in between (6 - 20 kcal mol⁻¹), in addition to the viscosity barrier which is important at low temperatures [4, 23]. Within the much longer lifetimes of the triplet state interconversion may be expected to take place.

4.2. *Trans* → *cis* photoisomerization and photocyclization

The present results show that the 2-anthrylanalogues of *trans*-stilbene undergo photoisomerization essentially similarly to stilbene and other analogues, *i.e.* a different photostationary state is established at different wavelengths of irradiation, in accordance with the usual rules for reversible photointerconversions [19]. The main difference is that some photodecomposition accompanies the photoisomerization, and that the ratio between the *trans* → *cis* and the *cis* → *trans* quantum yields is much smaller even at -20 °C, as in stilbene and its naphthyl analogues at low temperatures [15]. Ia is the most extreme case in this respect, with only some 5% *cis* at the photostationary state attained by irradiation at 405 nm. Among the five compounds studied in this context, II undergoes the most extensive photoisomerization at -20 °C, with an estimated *cis* content of 50% at the photostationary state at 405 nm, without sensitizers or a heavy-atom solvent (Fig. 5). Unlike all stilbene analogues studied hitherto [15, 16] photoisomerization in both directions stops completely at -130 °C with light at 405 nm, and is sharply attenuated at 366 nm in decalin. Under these conditions irradiation of the *cis* isomer, formed previously at -20 °C, probably causes photocyclization to an analogue of 4*a*,4*b*-dihydrophenanthrene (see scheme above). This is the first case of such a reaction with anthryl analogues of stilbene.

Finally, the enhanced *trans* → *cis* photoisomerization in bromobenzene and the photosensitized photoisomerization show that the triplet pathway of photoisomerization is feasible. This is what makes the T-T transient results relevant to the photoisomerization observations.

5. General conclusions

Anthryl analogues of stilbene attract special attention because of the low singlet and triplet energies of these molecules (probably not very different from those of anthracene), compared with stilbene proper, its naphthyl and even its phenanthryl analogues investigated by us earlier [15, 16, 20]. The idea of "energy trapping" in two- or three-membered ring systems in such stilbene analogues was advanced earlier [21] on the basis of an initial report that the emission spectra of *trans*- and *cis*-2-styrylnaphthalene were identical. However, this was later found to be erroneous [22] and the original conclusion does not hold, at least not to the extent forwarded. Although we believe that basically the idea that the energy is concentrated in one part of a large conjugated system is an overstatement, there is perhaps a chance that it applies to some extent to the anthryl analogues. Our relevant emission results are as yet inconclusive, but the above photoisomerization results indicate that photoisomerization takes place in the usual fashion in both directions, although possibly with much lower *trans* → *cis* quantum yields, be it in the singlet or triplet manifold, probably involving even higher energy barriers on the path from the singlet-excited *trans* isomer to the *cis* isomer, than observed with the naphthyl derivatives. It may be concluded that the excited-state behaviour of the anthryl analogues differs from other "stilbenes" quantitatively but not qualitatively. This also holds for the triplets formed by direct flash excitation of the anthryl analogues in substantial yields, which differ from the corresponding naphthyl analogues mainly in their long lifetime even at room temperature. The concept of "one-way isomerization" [11] is thus probably exaggerated, as far as 2-styrylanthracenes are concerned.

The photocyclization reported here for the first time is also not exceptional, but could be observed only thanks to the fact that the *cis* → *trans* quantum yield is attenuated on cooling more sharply than the *cis* → 4*a*-4*b*-dihydrophenanthrene quantum yield.

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Note added in proof

In a recent private communication the authors of ref. 18 calculated the barrier for rotamer interconversion in the triplet state to be 15 - 20 kcal mol⁻¹.