Temperature Dependence of Photoisomerization. Part 9.[1] Electronic Spectra and Excited-state Behaviour of Helicene-forming Diarylethylenes and their Photocyclization Products, and Properties of the Latter

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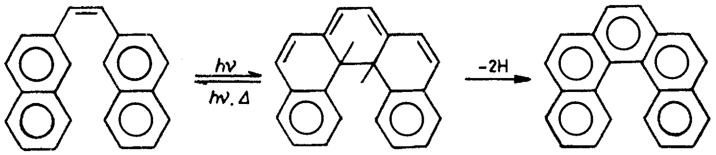
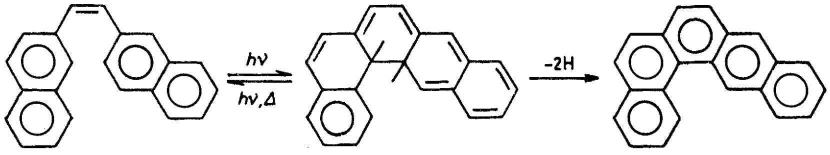
trans $\rightleftharpoons$ *cis* Photointerconversion, photocyclization, *cis* ⟶ DHP (= 4a,4b-dihydrophenanthrene derivatives), photoinduced ring opening DHP ⟶ *cis*, and photocyclodehydrogenation *cis* ⟶ P of solutions of the title compounds were investigated in the temperature range +25 to −180° with static and flash photolytic methods, and quantum yields were determined. Absorption and emission spectra of both isomers of all compounds, and absorption spectra of most cyclization products were measured over the same temperature range. A pronounced variation of the fluorescence spectra of several *trans*-compounds with the temperature and the excitation wavelength was observed, and may be due to conformer equilibria. The *cis* isomers exist as equilibrium mixtures of two to four possible conformers, A, B, B', and C. Of these, short-lived cyclization products of the A and B conformers, $\mathrm{DHP_A}$, and $\mathrm{DHP_B}$, were observed at room temperature in most cases. At reduced temperatures $\mathrm{DHP_B}$ is the predominant product; it was also observed for three compounds with static methods. Quantum yields of all photoreactions are attenuated on cooling, while fluorescence yields increase concurrently, the calculated corresponding critical increments amounting to 1—4 kcal $\mathrm{mol^{-1}}$. This indicates the existence of potential barriers on the path from excited starting molecules to final products. The rate of the thermal reversion DHP ⟶ *cis* increases on heating, with calculated critical increments of 8—18 kcal $\mathrm{mol^{-1}}$.

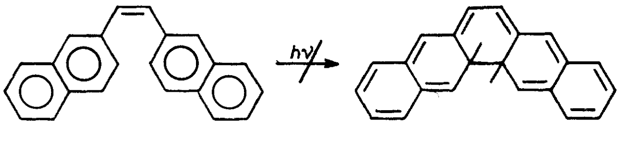
IN earlier publications we described in detail the reversible photoisomerization, *trans* $\rightleftharpoons$ *cis*, and photocyclization, *cis* $\rightleftharpoons$ 4a,4b-dihydrophenanthrene derivative (DHP), for a wide range of temperatures, for stilbene and several derivatives[2] and for the various naphthyl homologues of stilbene.[1] Particular attention was drawn to the primary photocyclization products of the several conformers of 1-phenyl- and 1-naphthyl-2-(2-naphthyl)ethylenes.[1] Specifically, DHPs formed from two of the three possible conformers of *cis*-1,2-di-(2-naphthyl)ethylene [(IA) and (IB)] were observed and identified by oxidation to the corresponding phenanthrene derivatives (IIIA and B). Compound (IIIA) is the simplest member in the helicene series,[3] 'pentahelicene.' Compound (IC) does not photocyclize. Isomers (IIA and B) were found to differ considerably in the conditions of their photoformation and in their spontaneous reactions.



(IA) (IIA) (IIIA)

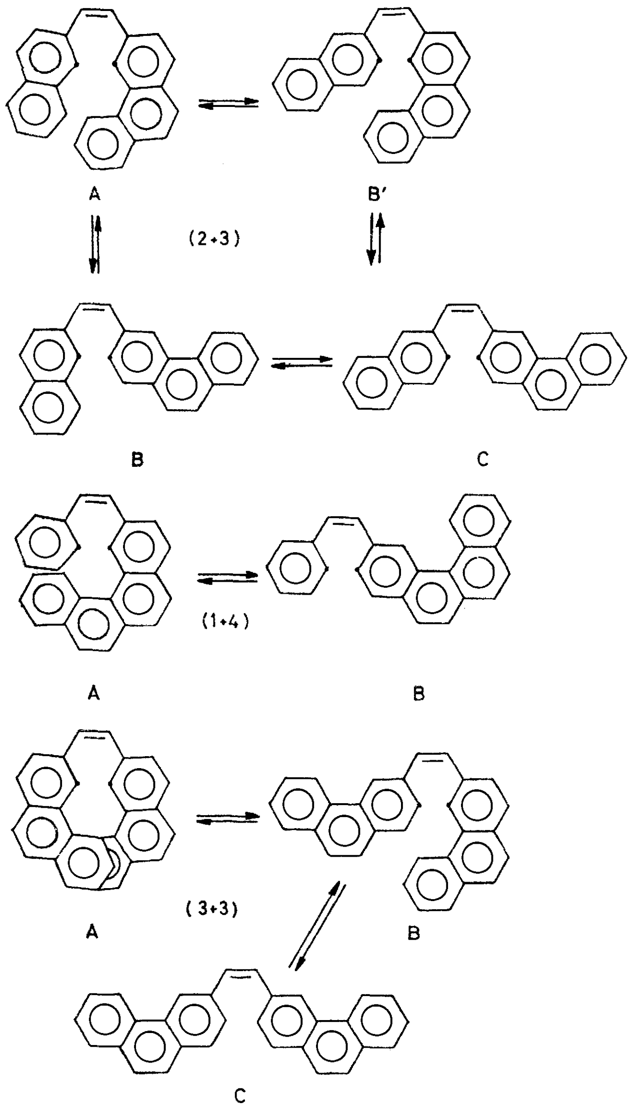


(IB) (IIB) (IIIB)



(IC) (IIC)

We now describe the photochemistry of six higher members in the series of diarylethylenes characterized by their possible photocyclodehydrogenation to the corresponding helicenes. All six are 1,2-diarylethylenes where at least one aryl group is either 3-phenanthryl or 2-benzo[*c*]phenanthryl (Schemes 1 and 2). Martin's notation[4] will be used, according to which each compound is described by two numbers denoting the number of benzene rings in each of the two aryl groups in ArCH=CHAr': 1 is phenyl, 2 is 2-naphthyl, 3 is 3-phenanthryl, 4 is 2-benzo[*c*]phenanthryl. Thus compound (I) is denoted (2 + 2), *etc.* The compounds studied were (1 + 4), (2 + 4), (3 + 4), (4 + 4), (2 + 3), and (3 + 3). All are capable of existing, in their *cis*-form, in two, three, or four conformers, A, B, B′, and C,



SCHEME 1

as depicted in the Schemes. Their photocyclodehydrogenation at room temperature in the presence of iodine has been described by Martin,[4] in connection with the helicenes, except for (2 + 3) which was studied by Laarhoven.[5] According to these authors, polycyclic products derived from conformers A, *i.e.* helicenes, were obtained with all six compounds, while B-type products were observed only with (2 + 3) and (2 + 4), where the reported ratios A : B were 22 : 50 [5,6] and 20 : 65 [4] respectively. No C-type products were obtained in any case. According to semiempirical calculations,[5] the ΣF_r^* values are <1 for all products C (predicting absence of photocyclization), but >1 for all products B and B′ except for (1 + 4), so that the possibility of their observation existed, despite the above results [*] (*cf.* Discussion section). In the course of this investigation the following reactions were studied over the temperature range +25 to −180°: *trans* $\rightleftharpoons$ *cis* photoisomerization, *cis* $\longrightarrow$ *trans* isomerization with atomic iodine, photocyclization of type A and B conformers of the *cis*-isomers to the corresponding DHP derivatives and the reverse reaction, dehydrogenation of the DHPs by atomic iodine to the corresponding phenanthrene derivatives P, and finally the direct photocyclodehydrogenation with iodine as described,[4,5] but also at reduced temperatures. Where possible, quantum yields were determined. Emission spectra and yields of all the *trans*- and the *cis*-isomers were also measured. Conventional static and flash spectrophotometric methods were employed.

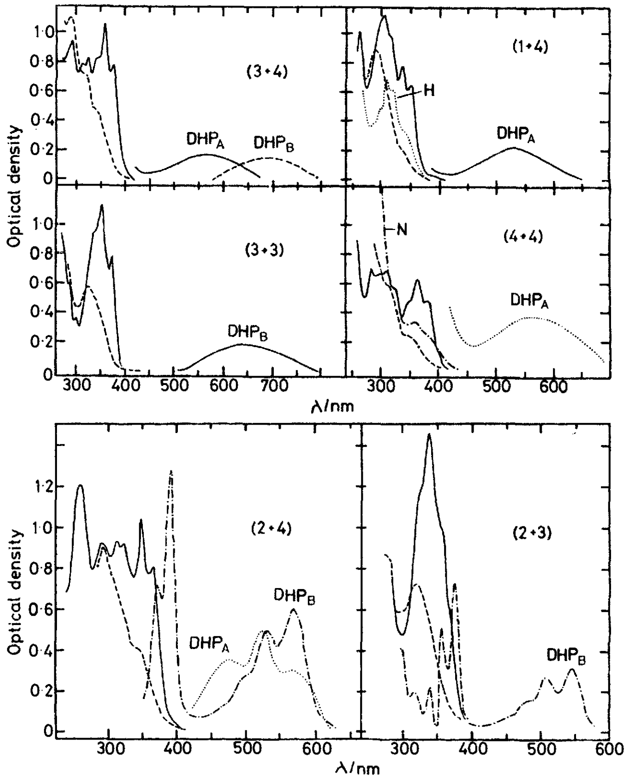


FIGURE 1 Absorption spectra of solutions in MCH–IH (2 : 1) at room temperature, of the compounds indicated. Concentrations were in the range 1.6×10^{-5}—2.9×10^{-5}M. Full curves, *trans*-isomers; dashed curves, *cis*-isomers, DHP curves as indicated. Curves H for (1 + 4) and N for (4 + 4) denote hexahelicene and nonahelicene, respectively. The DHP_B spectra of (2 + 3) and (2 + 4) were obtained by static spectrophotometry, all other DHP spectra were plotted from flash photolysis data

RESULTS

cis–trans *Isomers and Isomerization.*—The *cis*-isomers were usually obtained by u.v. irradiation of the respective *trans*-

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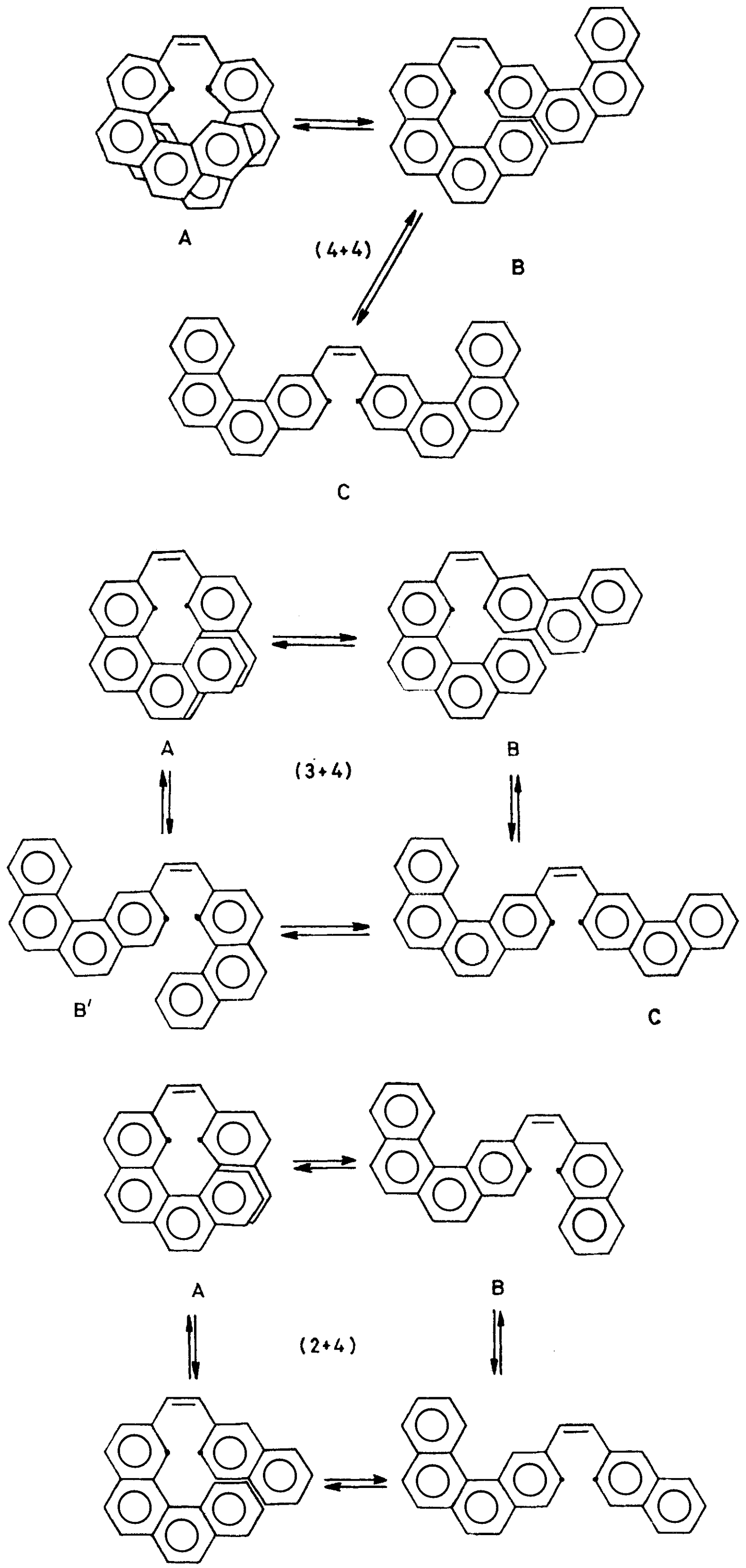
[*] In Part 8[1] we cited evidence from earlier literature that in (2 + 2) (IIIA) is the only photo-oxidation product, and tried to reconcile this fact with our observation of (IIIB). Since then Professor Martin informed us that in his laboratory (IIB) was actually found to constitute a major product of photo-oxidation. This result was confirmed by us, and we are at a loss to explain the absence of (IIIB) reported by earlier authors.



Scheme 2

isomers, and separated by t.l.c., except with (3 + 3), where the photoconversion *trans* → *cis* is very inefficient. Complete *cis* → *trans* conversion could be achieved in all six compounds by atomic iodine, as described earlier,[1,7] The room temperature spectra of the *cis*- and *trans*-isomers are shown in Figure 1, while the absorption and emission spectra at $-170°$ are presented in Figure 2. The spectra of all the *trans*-derivatives show vibrational structure similar to that observed in stilbene and in $(2 + 2)$. The variation of the absorption (and emission) spectra of the *trans*-isomers with the temperature is very pronounced, as seen from a comparison of the absorption spectra in Figures 1 and 2. No structure was observed in the spectra of the *cis*-isomers. [The *cis*-isomers of $(2 + 4)$, $(3 + 4)$, $(4 + 4)$ may contain an impurity which we could not get rid of, and which may be responsible for the absorption peaks at *ca*. 300 nm.] In all cases the *trans*-absorption spectrum is shifted to longer wavelengths, relatively to that of the corresponding *cis*-isomer, and therefore irradiation of *trans* at 366 nm brings about maximal conversion into *cis*, while for the reverse reaction, *cis* ⟶ *trans*, 313 nm was usually the optimal wavelength of irradiation. The *cis* $\rightleftharpoons$ *trans* quantum yields, $Q(trans \longrightarrow cis) \equiv Q_t$ and $Q(cis \longrightarrow trans) \equiv Q_c$, were measured as a function of temperature in the range $+20$ to $-180°$ either in a 2 : 1 mixture of methylcyclohexane (MCH) and isohexane (IH) or in 2-methyltetrahydrofuran (MTHF). The results are summarized in Figure 3.

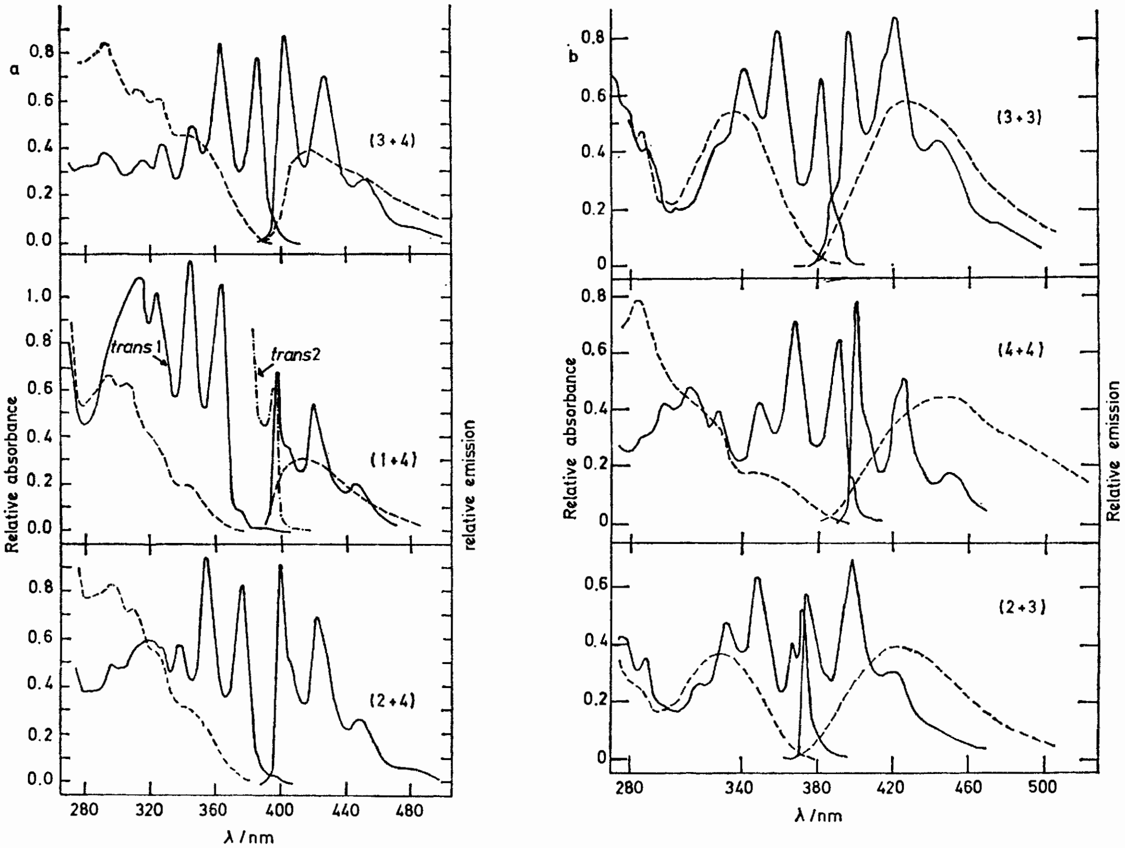


FIGURE 2 Absorption and emission spectra of solutions in MCH–IH at -170 to $-180°$. Full curves, *trans*; dashed curves, *cis*; left side, absorption; right side, emission. For $(1 + 4)$ the absorption spectrum of the *trans*-isomer was also taken at a 50-fold higher concentration, (*trans* 2). The concentrations of *cis* and *trans* are identical

The pronounced temperature dependence of Q_t observed for stilbenes[8] is exhibited by the present compounds from $-120°$ downwards. Compounds $(2 + 3)$ and $(3 + 4)$ show in addition a plateau at intermediate temperatures followed by another sharp decline at still lower temperatures. A similar situation prevails in the naphthyl derivatives described earlier.[1] In $(3 + 3)$ the photoisomerization *trans* ⟶ *cis* is so inefficient that Q_t could not be measured. Q_t is also quite small in $(2 + 3)$ and $(3 + 4)$. Accordingly the fluorescence yield, to be described later, is 0.7—0.8 at room temperature, compared with 0.06 in stilbene. The emission is thus the main deactivation path of the excited *trans*-isomer in these cases even at room temperature. Q_c of most compounds in MTHF solutions, as well as Q_t where measured, remain constant on cooling, and start falling off only at rather low temperatures ($-140°$), as already observed in *cis*-stilbene. Some MCH solutions show different behaviour: Q_c of $(3 + 3)$ falls off on cooling from room temperature, while in $(1 + 4)$ and $(3 + 4)$ Q_c at room temperature is very small and can be measured only at low temperatures. The probable reason is the existence of competing reactions which are cut out at low temperatures. In $(2 + 4)$ Q_c could be measured only at $-180°$: $Q_c = 0.002$ (!), a unique case so far.

A plot of log Q_t and log Q_c against T^{-1} shows roughly an Arrhenius-type relationship, with different slopes in the high and low temperature ranges. The activation energies E_a for the photoisomerization reactions in nonpolar solvents calculated in this way are summarized in Table 1. The values for stilbene are included for comparison. Values in the low-temperature range probably include viscosity effects.

Fluorescence Spectra and Yields.—The emission and absorption spectra, measured in MCH–IH solutions at −170 to −180°, are shown in Figures 2a and b. The spectra of the *trans*-isomers are rather similar to that of *trans*-stilbene, with vibrational structure which becomes more pronounced at low temperatures.[1,8] In several *trans*-compounds the emission spectra vary markedly on cooling and also with the wavelength of excitation, suggesting a variation in the ratio between two modifications.[9]

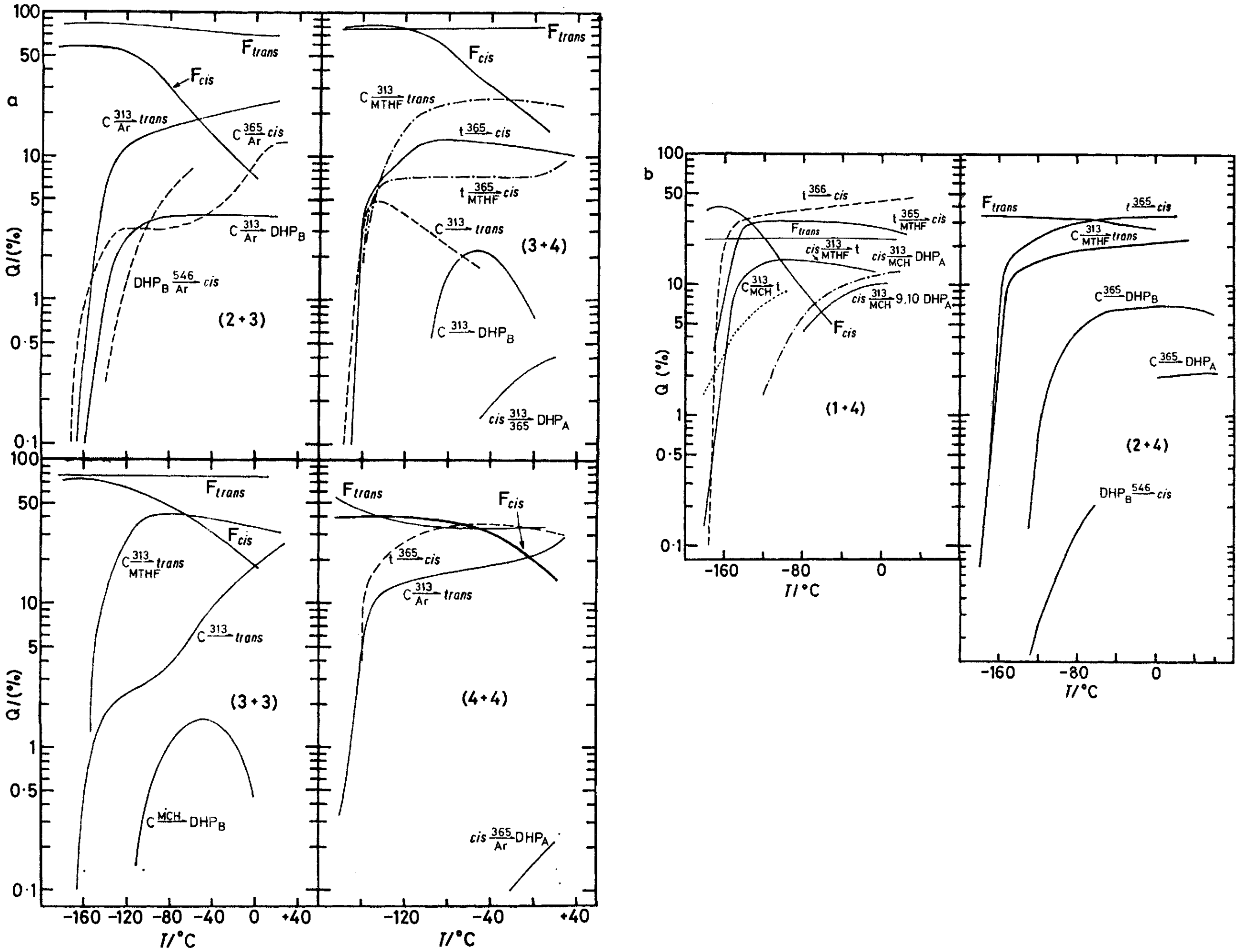


FIGURE 3 Quantum yields of photoisomerization, photocyclization, photoinduced ring opening, and fluorescence. in the temperature range +25 to −180°. Solvent MCH–IH unless denoted MTHF or MCH

TABLE 1

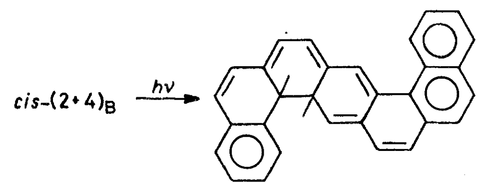
Activation energies E_a, calculated from Arrhenius-type plots of Q_t and Q_c against T^{-1} measured in a MCH–IH mixture

Compound	Reaction	E_a/ kcal mol^{-1}
(2 + 3)	*trans* → *cis* (high T)	3.0
(2 + 3)	*trans* → *cis* (low T)	1.3
(2 + 3)	*cis* → *trans* (low T)	3.3
(2 + 4)	*trans* → *cis* (low T)	1.7
(1 + 4)	*cis* → *trans* (low T)	1.1
(1 + 4)	*trans* → *cis* (low T)	4.0
(3 + 3)	*cis* → *trans* (high T)	2.3
(3 + 3)	*cis* → *trans* (low T)	1.9
(3 + 4)	*trans* → *cis* (low T)	3.0
(3 + 4)	*cis* → *trans* (low T)	3.6
(4 + 4)	*trans* → *cis* (high T)	0.7
(4 + 4)	*cis* → *trans* (low T)	2.5
Stilbene	*trans* → *cis*	2
Stilbene	*cis* → *trans* (low T)	1.2

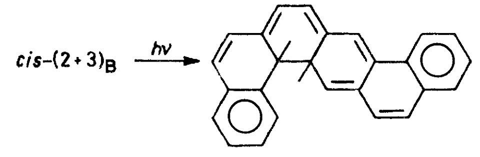
The emission spectra of the *cis*-isomers are structureless, with much larger Stokes' shifts than those observed in the *trans*-isomers, again as reported for stilbene and its derivatives,[10] and for its naphthyl homologues.[11] Like in the latter, the fluorescence quantum yield of the *trans*-isomers, Q_t^F, is appreciable already at room temperature, and increases further on cooling, parallel to the decrease in Q_t. Only in (1 + 4) Q_t^F retains its rather low value even at −180° where $Q_t \longrightarrow 0$. The fluorescence yield of the *cis*-isomers, Q_c^F was negligible at room temperature, so that emission measurements showed only the spectra of the small but unavoidable fraction of the corresponding *trans*-isomers. Only with (4 + 4) some ' real ' *cis*-emission was observed at room temperature, with Q_c^F *ca.* 0.10. Such cases are very rare among the *cis*-diarylethylenes.[12] Q_c^F increases on cooling and in most cases reaches rather high values at −180°, so that the emission due to traces of *trans* no longer interferes. Only with (2 + 4) no *cis*-emission could be established unambiguously even at −180°. On the whole, the variation of Q_c^F with the temperature complements that of Q_c and/or $Q(cis \longrightarrow \text{DHP})$, to be described later. Thus emission takes over when deactivation *via* isomerization and/or cyclization is slowed down.

Photocyclization and Photoinduced Ring-opening. Static Methods.—As mentioned in the introduction, the photocyclodehydrogenation of all six compounds at room temperature yields polycyclic aromatic products derived from the A conformers, and in two cases also products derived from the B conformers. If we follow the accepted assumption that photocyclodehydrogenation is a two-stage process, $cis \xrightarrow{h\nu} \text{DHP} \xrightarrow{-2\text{H}} \text{P}$, it should be possible to observe the DHPs derived from A in all compounds, and those derived from B in some cases, as a result of u.v. irradiation of the *cis*-isomers in the absence of oxidants, *i.e.* in argon-flushed solutions.

No coloured photoproducts, or in fact any photoproducts, were observed under these conditions with any of the compounds at room temperature. At low temperatures extensive photocolouration was found with solutions of (2 + 3) and (2 + 4). The reaction could be reversed with visible light. The absorption of the photoproduct in the visible and its photoerasure with visible light fitted the expected properties of DHPs. They were identified as DHP_Bs by their dehydrogenation with atomic iodine, which led to the polycyclic products expected from the B conformers in both compounds. As described earlier, this procedure also allowed calculation of the extent of phototransformation into DHP_B in each case [60% at −80° with (2 + 4) and 30% at −100° with (2 + 3)].



(2+4) DHP_B



(2+3) DHP_B

The spectra of the pure DHP_Bs of (2 + 3) and (2 + 4) constructed from these results are shown in Figure 1. In common with DHPs described previously, they are characterized by a broad structured band in the visible extending to 600 nm, and another one in the near u.v. region.

The variation of $Q(cis \xrightarrow{313} \text{DHP})$ and $Q(\text{DHP} \xrightarrow{546} cis)$ with temperature was studied with both compounds (Figure 3) (*cf.* also next paragraph). As already reported[1] for DHP_B formed from (2 + 2), the yield of its formation is fairly constant down to *ca.* −60°, (2 + 4), or −120°, (2 + 3), and then falls off sharply at lower temperatures. The photoreversion, $\text{DHP}_\text{B} \longrightarrow cis$, with light at 546 nm, could be measured only in the temperature range of the DHP_Bs thermal stability. Its yield was found to drop on cooling. An Arrhenius-type plot yielded activation energies, for the respective *Q*s, of 2.3 for (2 + 4) and 1.7 kcal mol^{-1} for (2 + 3).

In (1 + 4) a very slight photocolouration was observed at −40 to −80°, and ascribed to DHP_A. In view of its unique photochemistry this compound is described separately.[13]

Photocyclization. Flash Methods.—A flash photolytic study in the temperature range from +25 to −100° revealed the existence of coloured transients in all six compounds (Figure 1) including of course the two mentioned in the preceding paragraph. All of them decayed at rates depending on the temperature. The decay could be speeded up by employing intense monitoring light. These transients thus exhibit three of the properties characterizing DHPs, absorption in the visible range, erasure with visible light, and thermal reversion to the corresponding *cis* isomers. Another major property, dehydrogenation to the corresponding polycyclic hydrocarbons, could be demonstrated only qualitatively and indirectly because of the thermal instability of the transients. With (2 + 3) and (2 + 4) the DHP_Bs were identified by their spectra, which are similar to those observed 'statically' at low temperatures, as described in the preceding paragraph. The identification of the other DHPs described in Figure 1 was indirect, by means of the photocyclodehydrogenation yields and products in a range of temperatures described in the following paragraph and its comparison with the temperature dependence of the relative yield of formation of the transients (measured by absorbance created per flash). No DHP_As were observed in (2 + 3) and (3 + 3), despite the fact that the respective P_As are formed by photodehydrogenation at room temperature. Similarly, no DHP_B was observed with (4 + 4), although P_B was the sole product of photo-oxidation with iodine at −40°. The quantum yields $Q(cis \longrightarrow \text{DHP})$ in Figure 3 were calculated from the relative yields at various temperatures, and the absolute yield of photocyclodehydrogenation $Q(cis \longrightarrow \text{P})$ at one suitable temperature, assuming the two *Q*s to be identical at that temperature. [More correctly, $Q(cis \longrightarrow \text{DHP}) \geqslant Q(cis \longrightarrow \text{P})$]. The quantum yields of cyclization $Q(cis \longrightarrow \text{DHP}_\text{A})$ at room temperature were low, except for (1 + 4): (1 + 4) 0.12, (2 + 4) 0.02, (3 + 4) 0.004, (4 + 4) 0.002. As shown in Figure 3, these yields drop on cooling, with no DHP_A being observable below *ca.* −30°. DHP_B formation is also slowed down on cooling, but at much lower temperatures, with no DHP_B observable below *ca.* −120°. The cyclization yields decrease with increasing size of the ring system.

The absorption spectra of the DHP_Bs were in most cases shifted to longer wavelengths, in comparison with the corresponding DHP_As. (2 + 4) is an exception. Fortunately the thermal decay of the DHP_Bs above *ca.* 0° was much faster than that of the DHP_As, and this fact aided in the differentiation between DHP_A and DHP_B in the flash experiments. As seen in Figure 1, the absorption of the DHP_Bs of (3 + 3) and (3 + 4) extends to almost 800 nm; and that of the DHP_As is peaked at *ca.* 550 nm, compared with 450 nm in stilbene (1 + 1).

From measurements of the decay rate of these DHPs in a wide temperature range we calculated the activation energies for thermal ring fission, $\text{DHP} \longrightarrow cis$. The results are given in Table 2. Some representative half-life times of thermal decay of various DHPs were as follows: $(1 + 4)_\text{A}$ 6 s at 20°, $(2 + 3)_\text{B}$ 0.6 s at 20°, $(2 + 4)_\text{A}$ 30s at 20°, $(2 + 4)_\text{B}$ 1.7 s at 20°, $(3 + 3)_\text{B}$ 1.3 ms at −40°, $(3 + 4)_\text{A}$ 0.4 s at 20°, $(3 + 4)_\text{B}$ 4.4 ms at −50°, $(4 + 4)_\text{A}$ 1.4 s at 20°. The

DHP_As are thus characterized by much slower decay rates. This conforms with our earlier observations [1] in (2 + 2).

Photocyclodehydrogenations (*PCDH*) *with Iodine over a Wide Range of Temperatures*.—As mentioned in the Introduction, these reactions have been studied extensively at room temperature by the groups of Martin [3,4,6] and Laarhoven.[5] P_As were observed in all six compounds, while P_Bs were found only with (2 + 3) and (2 + 4). In view of our observation of DHP_Bs of several additional compounds by low temperature flash photolysis it seemed appropriate to look for P_Bs in the rest of the compounds, by carrying out the PCDH, *cis* $\xrightarrow{h\nu}$ DHP $\xrightarrow{-2H}$ P, at reduced temperatures too, in addition to measuring quantum yields of the photoformation of P_As and P_Bs in a wide temperature range.

TABLE 2

Activation energies E_a/kcal mol^{-1} for the thermal fission, calculated from kinetic flash results in the temperature ranges indicated

	DHP_A (T/°C)	DHP_B (T/°C)
(2 + 3)		22 (+20 to −20)
(3 + 3)		12 (−20 to −80)
(2 + 4)	13 (+25 — +65)	17 (+25 — +65)
(1 + 4)	12 (+15 to −10)	
(3 + 4)	9 (+20 to −30)	8 (−40 to −70)
(4 + 4)	8 (+20 to −40)	

Since only spectrophotometric methods were used for analysis, it was much easier to detect P_Bs, characterized by rather sharp absorption peaks, than P_As, *i.e.* helicenes, with their rather smeared-out absorption spectra (Figure 1). We could observe photoformation of P_Bs in all compounds except (1 + 4) by u.v. irradiation of the *cis*-isomers in the presence of iodine at reduced temperatures. As the temperature is lowered, P_Bs gradually turn to be the sole products because, as we saw, the formation of DHP_As is slowed down sharply on cooling, while that of DHP_B is attenuated only at much lower temperatures (Figure 3). The quantum yields of the reaction are low (>0.01) even at room temperature for all but (1 + 4). Some typical values for P_A formation are 0.004 with (3 + 4) and 0.0025 with (4 + 4). The reaction virtually stops at −40 and −20°, respectively. The spectra of the P_Bs of (3 + 4), (4 + 4), and of (3 + 3) are shown in Figure 4, since they have not been reported hitherto. Those of (2 + 3) and (2 + 4) have been described.[4,5] With (3 + 3), the P_B formed in the first stage undergoes further PCDH to the eight-ring system E. The second stage does not take place at −80°, and P_B is the final product. It was prepared in this way and purified by t.l.c. (*cf.* the spectrum in Figure 4). Its irradiation at 366 nm and 25° in the presence of iodine yielded E with a quantum yield of 0.013. E is also not described in the literature. Its absorption spectrum in the visible range shows peaks at 405 and 430 nm.

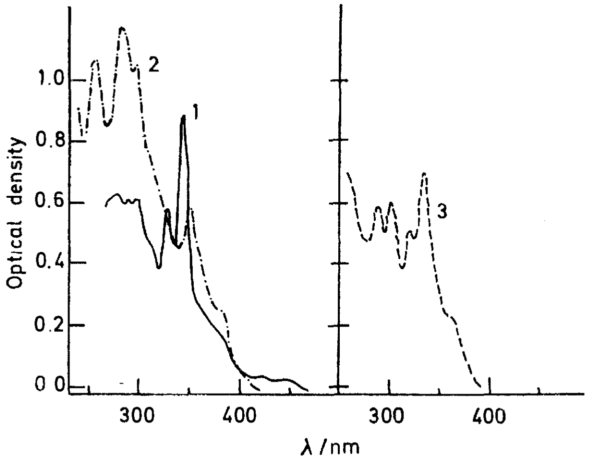
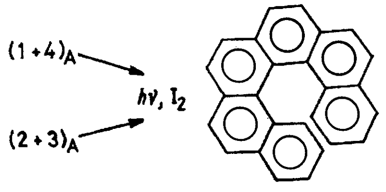
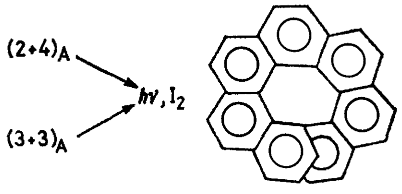


FIGURE 4 Absorption spectra of photocyclodehydrogenation products formed by u.v. irradiation in the presence of excess of iodine at reduced temperatures. Curve 1, assumed P_B-(3 + 4), *ca.* 10^{-5}M in MCH, formed from *cis*-(3 + 4) at −30°. Curve 2, assumed P_B-(4 + 4), obtained from *cis*-(4 + 4) at −40°, followed by t.l.c., *ca.* 2 × 10^{-5}M. Curve 3, assumed P_B-(3 + 3), obtained from *cis*-(3 + 3) at −80°, *ca.* 1.7 × 10^{-5}M



hexahelicene



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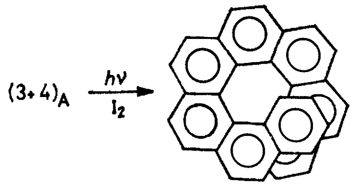

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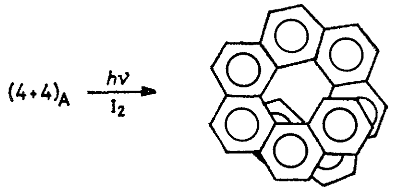

nonahelicene

The P_Bs of (3 + 3), (3 + 4), and (4 + 4), as well as E, were not prepared in larger quantities. They were identified indirectly by means of their absorption spectra, as follows. For (3 + 3), the spectrum of the compound expected from the PCDH of *cis*$_U$ is described by Clar,[14] and differs from the spectrum observed and ascribed to P_B. The second stage, PCDH to E, also fits this assumption. E has an absorption spectrum closely similar to that of the polycyclic benzo[*ghi*]perylene,[14] which is the second stage product of PCDH of (2 + 2). For (3 + 4), P_B and $P_{B'}$ could be formed. $P_{B'}$ would be expected to undergo a second-stage PCDH, similar to that seen with (3 + 3). The absence of such a second stage indicates that P_B is indeed the product obtained by us. For (4 + 4), the spectrum tentatively assigned to P_B differs from that of the known product expected from PCDH of cis_C. Hopefully the spectra of unequivocal samples of the above P_Bs and of E will eventually be available for comparison.

DISCUSSION

Cyclization.—According to Laarhoven,[5] ring closure in the excited state of *cis*-stilbene-like molecules to 4a,4b-DHP-like molecules is expected to take place only if the sum of the ' free valence numbers ' ΣF_r^* exceeds unity. If several cyclization routes are ' allowed,' they will take place roughly in the order of decreasing ΣF_r^*. In Table 3 we cite the ΣF_r^* values reported by Laarhoven [5] for the present compounds.

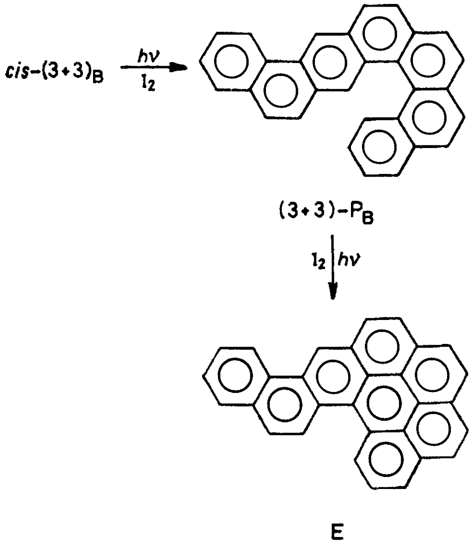

TABLE 3

Sums of free valence numbers in the excited state of various diarylethylenes according to Laarhoven,[5] and DHPs and Ps observed (*cf.* text and formulae)

Compound	Conformer	ΣF_r^*	DHP	P
(1 + 4)	A	1.12	+	+
	B	0.95	−	−
(2 + 3)	A	1.19	−	+
	B	1.08	+	+
	B′	1.02	−	−
	C	0.92	−	−
(2 + 4)	A	1.22	+	+
	B	1.08	+	+
	B′	1.05	−	−
	C	0.91	−	−
(3 + 3)	A	1.13	−	+
	B	1.03	+	+
	C	0.93	−	−
(3 + 4)	A	1.15	+	+
	B	1.05	+	+
	B′	1.02	−	−
	C	0.92	−	−
(4 + 4)	A	1.18	+	+
	B	1.05	−	+
	C	0.92	−	−

Our PCDH results show that the expected P_As and P_Bs are indeed observed in all cases. The $P_{B'}$s also expected in three cases are not formed, but may have escaped detection because of their small contribution to the overall product. No P_Cs were observed at any temperature. Our results thus fully conform to the qualitative expectations of the calculations. Regarding the ratio between P_A and P_B, P_B is the preferred product in (2 + 3) and (2 + 4) despite the lower corresponding ΣF_r^* values. This correlates with the fact that only in these cases the P_Bs can be almost coplanar. In the other P_Bs, and of course in the P_As, steric repulsions prevent coplanarity. This may be a secondary factor in determining the relative contributions of several allowed cyclization paths. Technical factors, such as too low concentrations or too short lifetimes, may be responsible for the fact that three DHPs expected according to the observed Ps were not detected. The quantum yields of PCDH decrease as we move to higher homologues in the diarylethylenes series: $(4 + 4) < (3 + 4) < (3 + 3)$, and therefore the possibility of flash-photolytic detection of DHPs derived from higher members, *e.g.* (4 + 5), (5 + 5), is small.

On the whole, the control of DHP formation by the conformational equilibrium in the ground state, $cis(\mathrm{A}) \rightleftharpoons cis(\mathrm{B}) \rightleftharpoons cis(\mathrm{C})$ first reported [1] for (2 + 2) seems to exist also in the present compounds. Steric factors *i.e.* molecular overcrowding, are seen to decrease the photocyclization yields in the higher members. This may be due to a real decrease in $Q(cis_A \longrightarrow \mathrm{DHP_A})$ or to shifts in the conformeric equilibria in favour of the less hindered *cis*(B) and *cis*(C) conformers. However, the main deviation from coplanarity already exists in *cis*-stilbene, and fusing on additional benzene rings in any position makes little difference.[10,15]

The relationship between the properties of $\mathrm{DHP_A}$s and $\mathrm{DHP_B}$s described above roughly parallels that reported [1] for (2 + 2): $\mathrm{DHP_B}$s absorb at longer wavelengths in the visible region, decay faster at room temperature, and are still formed at much lower temperatures. It would have been of particular interest to compare the properties of those pairs of $\mathrm{DHP_A}$s which on dehydrogenation yield the same helicene, *i.e.* DHPs which differ only in the position of the single bond: (2 + 2) and (1 + 3), (2 + 3) and (1 + 4), (2 + 4) and (3 + 3). Unfortunately (1 + 3) was not available at the time, while no $\mathrm{DHP_A}$s of (2 + 3) and (3 + 3) were detected.

The pronounced variation of the cyclization quantum yields with the temperature observed in (2 + 2) and related compounds [1] was also found in the present series, indicating again the existence of substantial energy barriers on the path from singlet-excited *cis* to $\mathrm{DHP_A}$, and to a smaller extent $\mathrm{DHP_B}$. Again it is plausible to blame steric factors.

Spectra.—Figures 2a and b show all *trans*-absorption and -emission spectra to be rather similar, with almost complete overlap of the longest absorption and shortest emission bands. The former is rather weak in most cases, and in particular in (1 + 4). We may conclude that the geometry in the ground and the excited states of the *trans*-molecules is similar, and that these are almost coplanar.[10,15] The observed variation of the emission spectra of several *trans*-compounds with the temperature and the excitation wavelength may be ascribed to the existence, in solution, of an equilibrium mixture of two or more modifications. These could be either conformers, as postulated earlier,[9,11,16] for (1 + 2) and (2 + 2), or association products.[17] Some of the overlap of absorption and emission spectra may be due to the fact that both are actually superpositions of several spectra.

In the *cis*-isomers large Stokes' shifts were observed, indicating extensive relaxation processes immediately following excitation, and again following emission. As described before,[10] these relaxations result from the fact that the equilibrium angles of twist around the central quasi-double bonds in the *cis*-isomers are determined mainly by the bond order and by the usual tendency towards coplanarity, opposed by the repulsion between the protons and carbon atoms in the *ortho*-positions of the two rings. The bond orders and therefore the angles of twist vary greatly between the ground and the excited states.

EXPERIMENTAL

Techniques of photochemistry, absorption and emission spectrophotometry, and flash photolysis, all over a wide range of temperatures, were essentially as described.[1] The copper block technique [18] was used throughout. Flash cells were made of reactangular cross section quartz tubing (4 × 16 mm) or Pyrex tubing (3 × 12 mm) with light paths of 20—70 mm.[18]

All compounds except (2 + 4) were kindly furnished by Professor R. H. Martin, Brussels; (2 + 4) was a gift from Professor W. H. Laarhoven, Nijmegen. When necessary, *cis*-isomers were prepared by u.v. irradiation. The compounds were purified by t.l.c. (alumina).

Methylcyclohexane (spectrograde) and isohexane were passed through columns of Woelm basic alumina to remove traces of water and aromatic compounds. 2-Methyltetrahydrofuran was passed through a similar column to remove water and peroxides and then distilled *in vacuo* into the cells, which were fused off. Solutions in open, long-necked cells were flushed continuously by argon containing <5 p.p.m. oxygen. The argon was initially passed through the solution and later above it, to prevent air from seeping in. Argon flushing also served to mix the solutions when required.

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