

THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF PENTAHelicene

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Summary

Pentahelicene(II) undergoes photocyclodehydrogenation (PCDH) to benzoperylene(IV) when irradiated with UV in the presence of iodine at temperatures as low as -100°C . The quantum yield varies with the concentration of iodine, reaching a maximum of about 0.15 at $[\text{I}_2] = (2 - 3) \times 10^{-4}$ M. Flash studies in the microsecond and nanosecond ranges failed to provide evidence for the existence of the postulated primary photocyclization product III in the ground state. Two transients were observed: the first was identified as triplet pentahelicene ($^3\text{II}^*$), while the second, which was formed from the first, was tentatively assigned to the triplet state of dihydrobenzoperylene(III), *i.e.* the cyclization is postulated to take place at the triplet level. The sequence $^1\text{II} \rightarrow ^1\text{II}^* \rightarrow ^3\text{II}^* \rightarrow ^3\text{III}^* \rightarrow$ "products" was investigated in the temperature range 70 to -180°C . In the presence of iodine $^3\text{II}^*$ is partially quenched to ^1II , while $^3\text{III}^*$ is dehydrogenated. The competition between these two opposing effects of iodine is responsible for the observed variation of the quantum yield with $[\text{I}_2]$. With benzopentahelicene(V) which does not undergo PCDH, only one transient, triplet V, was observed.

1. Introduction

The reversible photocyclization of *cis*-1,2-diarylethylenes, $\text{Ar}-\text{CH}=\text{CH}-\text{Ar}'$, to derivatives of 4a,4b-dihydrophenanthrene (DHP) (Fig. 1) and the dehydrogenation of the latter to phenanthrene derivatives have been studied extensively [1]. A prominent property of the diarylethylenes is their flexibility because of the rotation about the two quasi-single bonds

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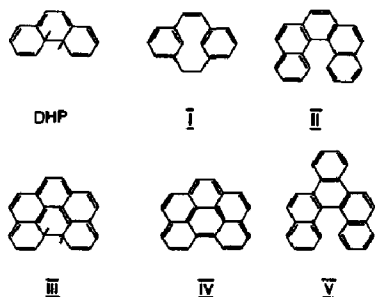


Fig. 1. The compounds investigated.

(with the exception of metacyclophane-ene(I) in which photocyclization is particularly facile [2]). It was therefore of particular interest to investigate in a wide range of temperatures the photocyclization and photocyclodehydrogenation (PCDH) of the rather rigid pentahelicene II the lowest member in the helicene series [3] of which the optical antipodes have been separated [4].

Pentahelicene, and many of its benzoderivatives, when irradiated in the UV at room temperature in the presence of iodine, undergo [5] facile PCDH to benzo[g,h,i]perylene(IV) and its benzoderivatives, in accordance with calculations of reactivity indices [5].

Comparable irradiation in the absence of oxidants has no effect, while in the presence of oxygen an inefficient production of unidentified compounds (but not IV) takes place. The only exception is benzopentahelicene (V) which should not, and indeed does not, undergo any photoreaction in the presence of iodine (see Section 3). In accordance with similar reactions, the primary photoproduct is expected to be the dihydrobenzoperylene III.

2. Results

2.1. Static experiments[†]

The absorption spectra of pentahelicene(II) and its oxidation product IV are shown in Fig. 2. The weak absorption band of II at the long wavelength edge is shown in Fig. 3, together with the corresponding fluorescence and phosphorescence spectra. The sharp absorption bands of IV in the 350 - 400 nm range served to estimate the extent of PCDH. We observed no variation of the quantum yield Q_{PC} of PCDH with the intensity of the photoactive light.

2.1.1. Variation of quantum yield Q_{PC} of PCDH with the concentration of iodine

As shown in Fig. 9, the yield passes through a maximum of about 0.15 at iodine concentrations of $(2 - 3) \times 10^{-4}$ M. This fact is of major importance since it indicates that no direct photodehydrogenation of excited II takes place (see Discussion).

[†]These measurements were carried out in Rehovot.

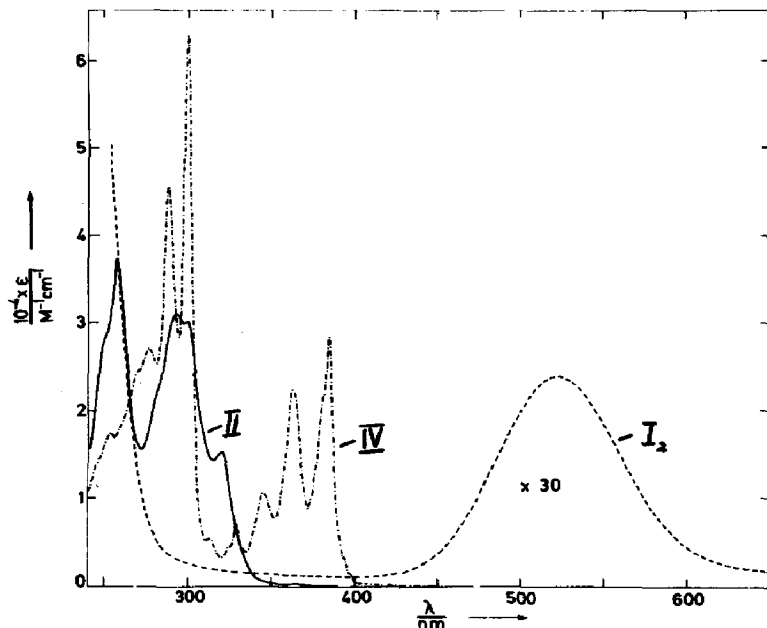


Fig. 2. Absorption spectra of pentahelicene(II), benzo[g,h,i]perylene(IV) and iodine in MCH at room temperature.

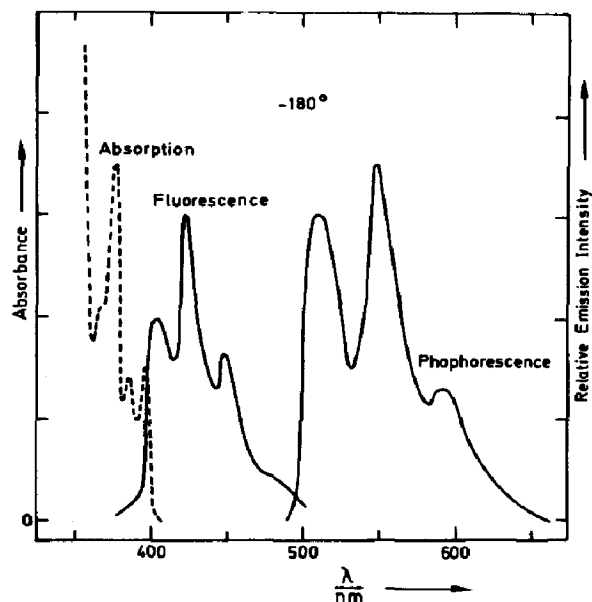


Fig. 3. Absorption, fluorescence (uncorrected) and phosphorescence (uncorrected) spectra of pentahelicene(II) in MCH-IH (2:1) at -180°C . For the absorbance $[II] \approx 5 \times 10^{-4}\text{ M}$.

2.1.2. Variation of Q_{PC} with the temperature

Qualitatively, PCDH was observed even at -100°C at the optimal iodine concentration described above. However, during irradiation below -50°C a

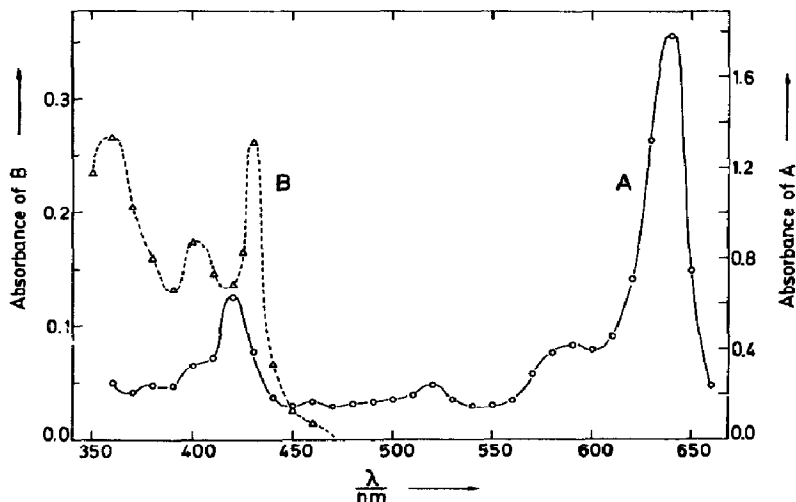


Fig. 4. Transient absorption spectra observed with a 7×10^{-5} M solution of penta-helicene(II) in MCH-IH (2:1). Transient A: measured at -180°C with the microsecond flash apparatus. (At higher temperatures the absorption bands become broader, but λ_{max} does not shift.) Transient B: measured at 20°C with the nitrogen laser. The absorbances of A and B cannot be compared in this figure.

complex X absorbing strongly in a broad range between 320 and 520 nm was formed which made a spectral determination of IV impossible without warming up the solutions. X has been observed during the low temperature oxidation of many 4a,4b-dihydrophenanthrenes with iodine [1] but its formation during this reaction with II is the most marked observation so far. X gradually disappears, even at -100°C and faster at higher temperatures, decomposing into IV and iodine. It is not formed when II and iodine are irradiated in the visible region, where only iodine absorbs. Formation of the dehydrogenation product IV seems to be essential. Indeed, UV irradiation of IV at -100°C in the presence of iodine also produces X, while the sharp peaks of IV decline. When a 2×10^{-5} M solution of II was UV irradiated at -100°C in the presence of only an equivalent concentration of iodine, partial dehydrogenation to IV took place, while X was formed at the same time with a peak absorbance of 0.2. In this case the spectra of IV and X are superimposed. At higher iodine concentrations the absorption of X predominates. X could be the product of a complex formed from excited IV and iodine, decomposing immediately at -100°C . Another possible explanation would be the reversible formation of a complex containing only iodine, photocatalysed by excited IV or other aromatic hydrocarbons. Since most experiments with iodine were done at higher temperatures, we do not postulate any role for X in the PCDH mechanism.

In the range 25 to -50°C Q_{PC} varies as shown in Table 1. An Arrhenius plot of these values yields an activation energy of $17 \pm 1 \text{ kJ mol}^{-1}$. Measure-

TABLE 1

Variation of Q_{PC} with the temperature

T (°C)	25	0	-10	-30	-50
Q_{PC}	0.155	0.07	0.06	0.027	0.020

[II] = 2×10^{-5} M in a mixture of MCH and IH. $[I_2] = 2 \times 10^{-4}$ M. Irradiation was at 313 nm.

ments in the temperature range 25 to 90 °C, with iodine concentrations varying from 2.5×10^{-5} to 5×10^{-4} M, showed that Q_{PC} is virtually constant.

2.1.3. Fluorescence spectrum, yield and lifetimes

The fluorescence spectrum of II is shown in Fig. 3. As expected for a rather rigid molecule, the overlap between the longest absorption and the shortest emission bands is extensive. An impurity emitting strongly at about 380 nm was removed laboriously by very careful thin layer chromatography (TLC). The fluorescence quantum yield in a mixture of methylcyclohexane (MCH) and 2-methylpentane, 3-methylpentane ("isohexane" (IH)) was observed to be practically constant between 25 °C and -185 °C at 0.070 ± 0.005 . The fluorescence was quenched by oxygen and by iodine to a similar extent, as seen in Table 2.

The estimated lifetime according to Berlman's approximation method [6] was 25 ns at 25 °C. The natural lifetime is therefore of the order of 350 ns, in accordance with the very weak longest absorption band (compare the actual τ_F measurements in Section 2.2).

2.1.4. Phosphorescence spectrum, yield and lifetime

The phosphorescence spectrum observed at -180 °C is shown in Fig. 3, its estimated yield being 0.15 ± 0.03 . However, the actual intersystem crossing yield is probably very high (above 0.80) as already reported [7] for a series of helicenes.

2.1.5. Preliminary time-resolved measurements

Flash photolysis with argon-flushed solutions of II in MCH-IH at -180 °C indicated the existence of a transient which possessed an absorption peak at 630 nm and decayed with a lifetime τ of 2 - 3 s. A similar lifetime

TABLE 2

Relative fluorescence quantum yields Q_F^{rel} as a function of oxygen or iodine concentration

$10^4 \times [O_2]$ (M)	0	0.4	2.2	5.5	11	22	55		
$10^4 \times [I_2]$ (M)	0	1.1	4.6	12					
Q_F^{rel}	1	1	0.81	0.74	0.75	0.64	0.61	0.40	0.26

10^{-5} M solution of II in MCH at 25 °C.

was observed for the phosphorescence described earlier and also for the decay of a light-induced electron spin resonance signal at 1530 G, *i.e.* the range characteristic for triplet signals. We therefore conclude that the transient is indeed a triplet state. At $-100\text{ }^{\circ}\text{C}$ τ is down to about $90\text{ }\mu\text{s}$ (flash experiments). An Arrhenius plot of the lifetimes yields an activation energy of $16.8 \pm 0.8\text{ kJ mol}^{-1}$ in the temperature range -180 to $-100\text{ }^{\circ}\text{C}$. No evidence for the existence of the postulated intermediate III was provided by any of the experiments described in this part.

2.2. Time-resolved measurements[†]

Experiments were carried out with nitrogen-flushed or degassed solutions of pentahelicene in MCH ($+70$ to $-50\text{ }^{\circ}\text{C}$) or in a 2:1 mixture of MCH and IH, using two instruments capable of measuring the optical absorption of short-lived transients. In the temperature range $+70$ to $-50\text{ }^{\circ}\text{C}$ a set-up based on a nitrogen laser was employed, with a time resolution of about 5 ns [8]. In the temperature range -80 to $-180\text{ }^{\circ}\text{C}$ we used a conventional microsecond flash apparatus with a time resolution of about $10\text{ }\mu\text{s}$ [9].

2.2.1. Results at room temperature

Two transient absorption spectra were observed. The first (A) with a decay time of about $310 \pm 20\text{ ns}$ was spectrally identical with that observed at $-100\text{ }^{\circ}\text{C}$ and lower temperatures (*cf.* Section 2.1.5) and the second (B) with a decay time of $810 \pm 30\text{ ns}$, characterized by peaks at 428 and 360 nm. Both spectra are shown in Fig. 4. Typical time-resolved curves are recorded in Fig. 5 and they show quite clearly that the fluorescence decay curve and the growth curve of transient A, *i.e.* ${}^3\text{II}^*$, are similar, indicating that this is indeed the intersystem crossing reaction ${}^1\text{II} \rightarrow {}^3\text{II}^*$. Moreover, a quantitative analysis of experiments similar to that described in Fig. 5, taking into account

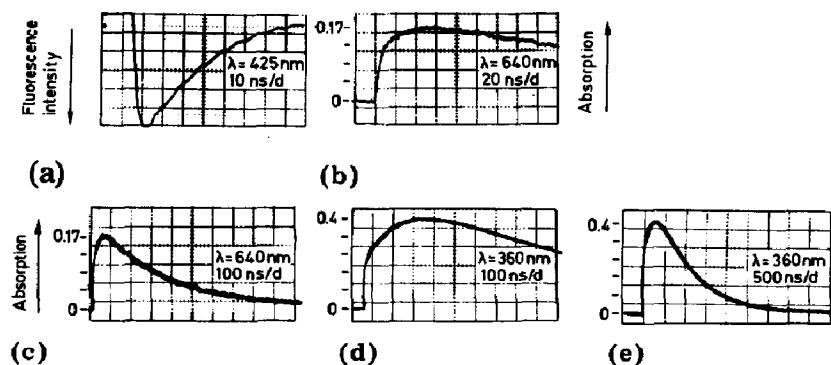
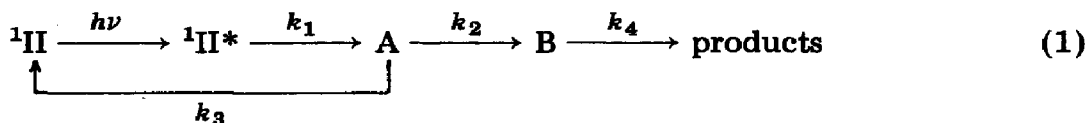


Fig. 5. About 10^{-4} M pentahelicene in MCH-3 methylpentane at $20\text{ }^{\circ}\text{C}$. Oscillograms of fluorescence intensity and of absorption (=1-transmission) vs. time, monitored at the wavelengths and on the time scales indicated (nanosecond per large division): (a), fluorescence decay (vertical scale, fluorescence intensity in arbitrary units); (b) and (c), formation and decay of A; (d) and (e), formation of B from A and decay of B.

[†]These measurements were carried out in Göttingen.

the overlap of the spectra of A and B (Fig. 4), showed that B is formed from A, *i.e.* the sequence of events is given by



The much longer lifetime of B at higher temperatures makes it possible to observe its build-up prior to its decay.

A transient absorbing at 465 nm, which appeared after repeated flashing, was found to be due to traces of the dehydrogenation product IV.

2.2.2. The variation of the decay rates of A and B with the temperature

The kinetics of the decay of A and of the formation and decay of B were measured in the laser apparatus in the range +70 to -50 °C and found to be first order throughout. The rate constants are summarized in Table 3, as are the absorbances of A at "time zero", *i.e.* extrapolated to the time of the flash. The decay rate k_4 of B was found to be virtually constant in the range +70 to +10 °C while that of A ($k_A = k_2 + k_3$) increased sharply with the temperature. The corresponding Arrhenius plot for k_A (Fig. 6, upper part) yields $E_a = 26.8 \text{ kJ mol}^{-1}$, $A = 2 \times 10^{11} \text{ s}^{-1}$. At 70 °C the decay of A is more than ten times faster than the decay of B (*cf.* Table 3) while at -10 °C the

TABLE 3

Decay rate constants of A (k_A) and of B (k_4) and D_0^{600} and D_{max}^{360} at various temperatures (see text)

T (°C)	k_A^a (s^{-1})	D_0^{600}	$10^{-6} \times k_4$ (s^{-1})	t_{max} (μs)	$D_{\text{max}}^{360}{}^b$
70	1.6×10^7	0.15	1.27	0.17	0.10
60	1.3	0.20	1.28	0.20	0.11
50	9.6×10^6	0.26	1.28	0.24	0.17
40	6.6	0.25	1.32	0.30	0.20
30	4.4	0.26	1.31	0.39	0.22
20	3.0	0.26	1.24	0.50	0.29
10	2.2	0.26	1.24	0.70	0.25
0	1.4	0.23	1.0	0.85	0.23
-10	8.5×10^5	0.23	0.7	1.20	0.22
-20	5.4	0.22	0.8	1.50	0.20
-30	3.3	0.21	0.6	1.80	0.22
-50	1.2	0.19	0.4	3.80	0.13
-80	9.2×10^3	0.24	—	—	—
-100	2.5	0.18	—	—	—
-120	1.2	0.32	—	—	—
-140	2.4×10^2	0.27	—	—	—
-160	2.0×10^1	0.24	—	—	—
-180	7.0×10^{-1}	0.35	—	—	—

^a $k_A = k_2 + k_3$ in sequence (1).

^bCorrected for spectral overlap of A and B at 360 nm.

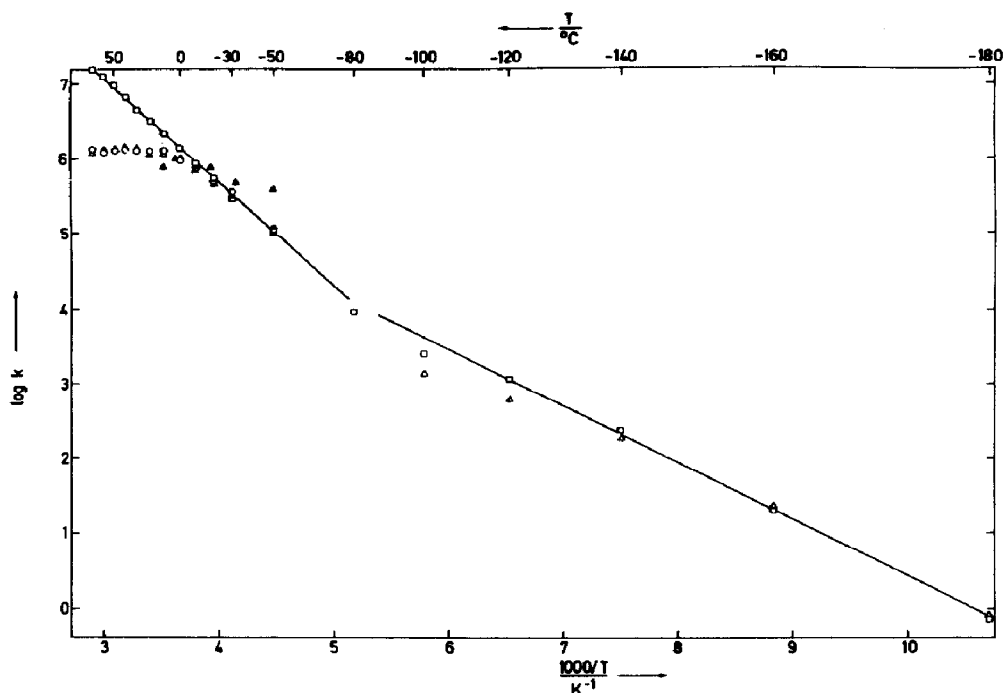


Fig. 6. 3.3×10^{-4} M pentahelicene in MCH (70 to -50 °C) and 7.2×10^{-5} M in MCH-IH (2:1) (-80 to -180 °C). Arrhenius diagram of decay rate constants k_A and k_4 of transients A and B, respectively. Decay of B monitored at 430 nm (Δ), (\blacktriangle). Full triangles are values calculated from growth curves (*cf.* Figs. 8(b) and 8(c)). Decay of A monitored at 600 nm (\square).

TABLE 4

Decay kinetics of the various transients observed in a degassed 6.8×10^{-5} M solution of II in MCH at room temperature, in the presence of varying concentrations of iodine

$10^4 \times [I_2]$ (M)	Species	$^3II^*$ (= A)		$^3III^*$ (= B)	IV
	$^1II^*$ λ_{meas} (nm)	600	D_0^{600}	430	385
	$\frac{425}{10^{-7} \times k_F^a}$ (s^{-1})	$\frac{10^{-6} \times k_A}{(s^{-1})}$		$\frac{10^{-6} \times k_4}{(s^{-1})}$	$\frac{D_{385}^b}{(s^{-1})}$
0	3.3	3.4	0.14	1.2	—
0.21	3.4	4.0	0.13	1.4	0.011
0.81	3.4	4.9	0.14	1.6	0.014
1.6	3.3	5.9	0.14	2.0	0.019
3.1	3.2	7.7	0.18	3.2	0.022
8.0	3.9	13.0	0.11	5.8	0.016
17.0	4.5	23.0	0.07	8.0	0.008

^a Observed fluorescence decay rate constant.

^b Measured after the decay of B.

decay curves at 600 nm and at 360 nm are virtually identical, apart from the initial part at 360 nm. The formation and the decay of B according to sequence (1) is given by

$$[B](t) = [A_0] \frac{k_2}{k_4 - k_A} \{ \exp(-k_A t) - \exp(-k_4 t) \} \quad (2)$$

$[A_0]$ is the concentration of A at "time zero", *i.e.* immediately after the exciting light pulse which is much shorter than the decay time of A. At high temperatures (70 - 30 °C) eqn. (2) reduces as a first approximation to

$$[B](t) \approx [A_0] \frac{k_2}{k_A} \exp(-k_4 t) \quad (2a)$$

because $k_A > k_4$ (*cf.* Figs. 6, 7(a) and 7(b)). k_4 can be estimated in this temperature range from the decay curves monitored at 360 nm (*e.g.* Fig. 7(b)), disregarding the initial parts. In order to evaluate k_4 at temperatures below 30 °C the build-up of B has to be analysed using eqn. (2). To do this the decay of A has to be taken into account, because both intermediates absorb at 360 nm (*cf.* Fig. 4). For this purpose, the initial parts of decay curves at 360 nm such as that given in Fig. 7(e) were recorded at expanded time scales (Fig. 7(c)). We observe a fast rise at the very beginning of the trace because of the optical absorption of A, and a slower build-up and decay caused by the formation of B and the decay of both A and B. The decay of A can be measured independently at 600 nm (*cf.* Fig. 7(d)) and its contribution at 360 nm can be taken into account (*cf.* Fig. 8(a)). The resulting curves for the variation with time of the absorbance D_B^{360} of B at 360 nm are shown in Figs. 8(b) and 8(c).

The time t_{\max} at which [B] reaches its maximum value at each temperature can be evaluated by taking $d[B]/dt = 0$ and solving for t . The resulting eqn. (3) shows that for $k_4 \approx \text{constant}$ and $k_A < k_4$, with k_A decreasing on cooling, t_{\max} should increase on cooling. This is indeed the case, as seen in Figs. 8(b) and 8(c).

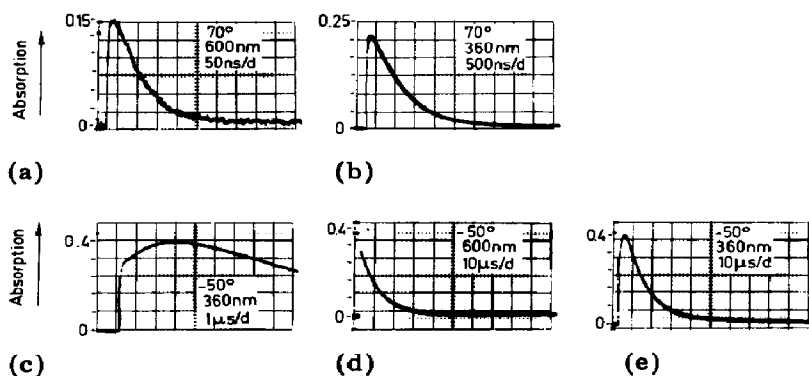


Fig. 7. 3.3×10^{-4} M pentahelicene in MCH. Oscilloscope traces of the decay of A (monitored at 600 nm) and of B (monitored at 360 nm) at 70 °C and -50 °C.

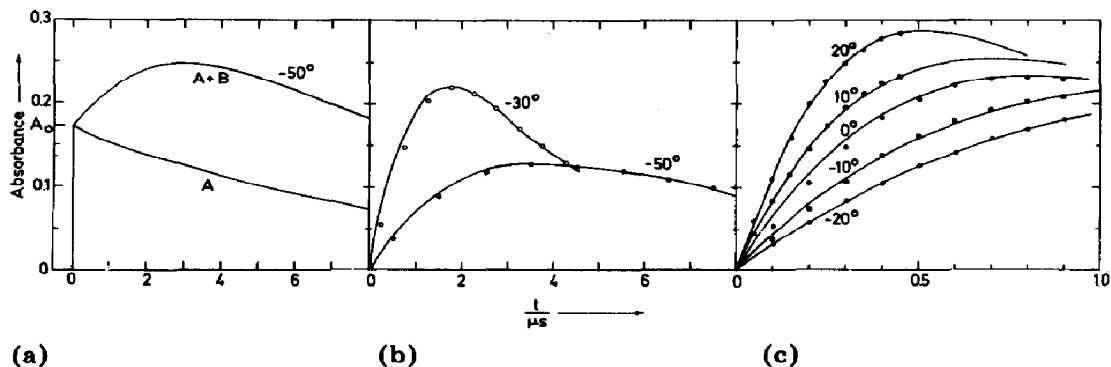
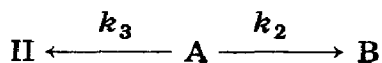


Fig. 8. Build-up of B absorbance at 360 nm and various temperatures. In (a) curve A + B was obtained from oscillogram 7(c) by converting absorption into absorbance. Curve A shows the decay of absorbance due to A (both A and B absorb at 360 nm), calculated from the decay oscillogram 7(d) at 600 nm, where only A absorbs. The differences between curves A + B and A in each case represent the absorbance due to B. The points in Fig. 8(b) and 8(c) describe such differences, taken from the curves of Fig. 8(a) and similar ones at other temperatures. The solid lines were calculated using eqn. (2).

$$t_{\max} = \frac{1}{k_4 - k_A} \ln \frac{k_4}{k_A} \quad (3)$$

From t_{\max} and k_A we can calculate k_4 in eqn. (3) and hence [B] in eqn. (2) as a function of time. The solid lines in Figs. 8(b) and 8(c) were obtained accordingly, introducing an arbitrary factor F to correlate [B] and D_B^{360} : $D_B^{360} = F[B]$ at t_{\max} . Regarding the maximal absorbance D_{\max}^{360} at time t_{\max} , its value according to sequence (1) should increase monotonically with the temperature (provided $k_3 \ll k_2$) and approach a limiting value at high temperatures, when $k_4 \ll k_A$. At this limit $[A_0] = [B_{\max}]$. As seen in the last column in Table 3, D_{\max}^{360} actually passes through a shallow maximum between -30°C and $+20^\circ\text{C}$ and declines sharply in the range $20 - 70^\circ\text{C}$. This indicates the existence of a competing deactivation process of A with an unexpectedly high activation energy, whose rate k_3 in



decreases on cooling much more than k_2 , so that only below about 10°C is $k_3 \ll k_2$, as assumed above.

During measurements with the microsecond flash apparatus at temperatures below -80°C growth of B (at 360 nm) could no longer be observed, obviously because $k_A \ll k_4$. An Arrhenius plot based on the observed decay rates at all three wavelengths (600, 430 and 360 nm) in the temperature range -80 to -180°C yields $E_a = 14.7 \pm 0.8 \text{ kJ mol}^{-1}$ and $A = (3.5 \pm 0.5) \times 10^8 \text{ s}^{-1}$. This activation energy is thus much smaller than the 26.8 kJ mol^{-1} observed in the high temperature region.

2.2.3. The effect of oxygen on the transients

In aerated solutions of II at room temperature the fluorescence decay time is almost halved, from 24.4 to 13.7 ns. This corresponds to a quenching constant k_q of $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

The effect of air on the decay of A and B at room temperature was as follows:

$$\tau_A (\text{nitrogen}) = 291 \text{ ns}$$

$$\tau_A (\text{air}) = 218 \text{ ns}$$

$$\tau_B (\text{nitrogen}) = 820 \text{ ns}$$

$$\tau_B (\text{air}) = 293 \text{ ns}$$

The quenching rate constants k_q by oxygen were 5.7×10^8 and $11 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for A and B, respectively, assuming an oxygen concentration of $2 \times 10^{-3} \text{ M}$ in air-saturated MCH. It was this pronounced quenching of B by oxygen which led us to the working hypothesis that B, like A, is a triplet molecule. We recall that UV irradiation of II in the presence of air does not lead to IV, as it does with iodine. Instead, some ill-defined products are formed with a low yield, so that the quenching of B by O_2 cannot be due to oxidation. We therefore postulate that B is actually the excited triplet state of the elusive dihydrobenzoperylene(III) so that the cyclization takes place in the triplet manifold, the reaction $A \rightarrow B$ being in effect ${}^3\text{II}^* \rightarrow {}^3\text{III}^*$. Since no product is formed, we assume that oxygen quenching of ${}^3\text{III}^*$ results ultimately in the re-formation of II, possibly via III in its ground state. However, no transients apart from A and B were observed under any conditions, and thus we still lack direct evidence for the existence of III.

2.2.4. The effect of iodine on the transients and the formation of IV at room temperature

So far we have not shown any connection between transients A and B and the PCDH with iodine described in Section 2.1. A series of room temperature experiments were therefore performed using the laser flash apparatus in which a degassed solution of II in MCH was flashed in the presence of varying concentrations of iodine, below and above the optimal concentration described in Section 2.1. The changes in absorption were followed at 600 nm (A), 430 nm (B) and 385 nm (characterizing the oxidation product IV). In addition the fluorescence decay at 425 nm was also determined. At the iodine concentrations used, its absorption was negligible at the wavelengths given or else could easily be taken into account. In view of the build-up of IV, only very few flashes could be applied to each cell. The results are summarized in Table 4, together with those obtained in the absence of iodine. The table also shows the values of D_0^{600} (indicating the relative maximal quantities of A formed as a result of the flash) and of D^{385} , *i.e.* the change in absorbance at 385 nm within about $10 \mu\text{s}$. The kinetics of the growth of the absorbance at 385 nm could unfortunately not be analysed because the extinction coefficients of B between 400 and 350 nm are larger than those of IV (*cf.* Figs. 2 and 4). The results of these experiments with iodine may be summarized as follows. (1) Fluorescence decay is enhanced only at higher iodine concentra-

tions. This agrees with the fluorescence quenching results with oxygen and iodine reported in Section 2.1.3. (2) The enhancement of the decay of A and B by iodine follows Stern–Volmer-type equations $\tau_A^0/\tau_A = 1 + (k_q^A/k_A)[I_2]$ and $\tau_B^0/\tau_B = 1 + (k_q^B/k_B)[I_2]$, with quenching rate constants $k_q^A = (13 \pm 1) \times 10^9$, $k_q^B = (5 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which are considerably larger than those observed for oxygen, *cf.* Section 2.2.3. (3) The absorbance at 385 nm passes through a maximum at an iodine concentration of about $2 \times 10^{-4} \text{ M}$, in excellent agreement with the results reported in Section 2.1.1, *cf.* Fig. 9.

2.2.5. Benzopentahelicene, V

Flash experiments with this compound, which does not undergo PCDH with iodine, indicated the existence of a single transient which is quenchable with oxygen and most probably represents the triplet state of this molecule. Its main absorption peaks were at 420 and 605 nm (see Fig. 10), while the lifetimes at room temperature and at 70°C were 120 and $30 \mu\text{s}$, respectively. Within a narrow wavelength range, around 500 nm, another transient was observed which had the same lifetime (26 ns) as the fluorescence. We assign this transient therefore to an $S_1 \rightarrow S_n$ transition.

3. Discussion

The fact that the PCDH quantum yield Q_{PC} reaches an optimal value at a certain iodine concentration already made it evident that any direct dehydro-

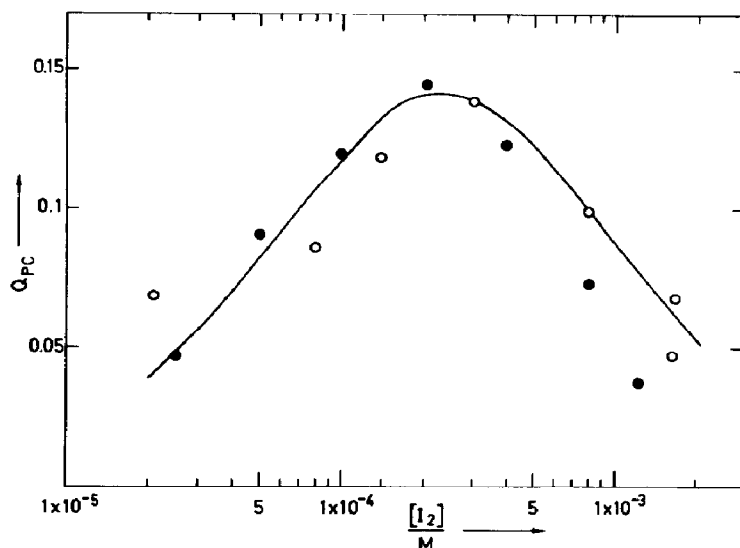


Fig. 9. The photoformation of IV from II in MCH at room temperature as a function of iodine concentration: ●, absolute quantum yields Q_{PC} from static experiments; ○, D^{385} values from flash experiments (*cf.* Table 4) normalized to the calculated curve at $[I_2] = 3.1 \times 10^{-4} \text{ M}$. Solid line: quantum yields calculated from kinetic data using eqn. (5) with $Q_F = 0.07$, $k_2 = 1.9 \times 10^6 \text{ s}^{-1}$, $k_3 = 1.1 \times 10^6 \text{ s}^{-1}$, $k_4 = 1.24 \times 10^6 \text{ s}^{-1}$, $k_6 = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_7 = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

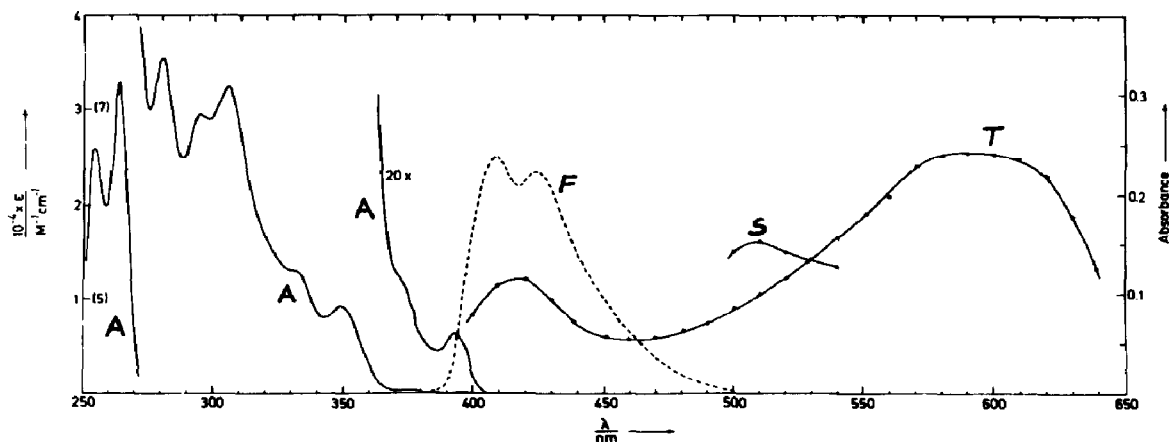
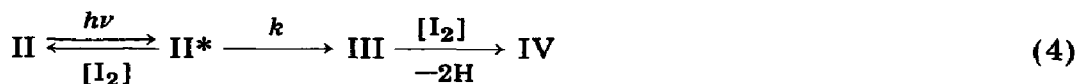


Fig. 10. Benzopentahelicene(V) in MCH: A, absorption spectrum (left-hand scale); F, fluorescence spectrum (arbitrary units). The absorption spectra of the transients were observed in nanosecond flash experiments using degassed solutions (right-hand scale, 4 cm optical path length). T, $T \rightarrow T_n$ absorption; S, $S_1 \rightarrow S_n$ absorption.

generation of excited II is excluded since any such mechanism should result in a monotonic increase of Q_{PC} with $[I_2]$, approaching a limiting value. A mechanism involving competing steps, with the rate of at least one step independent of $[I_2]$, was called for. In its simplest form this would be as follows:



where the cyclization rate k_3 is not affected by iodine, while both the quenching of II^* and the dehydrogenation of III are enhanced by it. The detailed time-resolved results indicate that the actual sequence is more complex, involving two different oxygen-quenchable states which we tend to assign to $^3II^*$ and $^3III^*$. The postulated complete scheme, including the effect of iodine, is presented in Fig. 11.

Steps accelerated by iodine are indicated by $[I_2]$. The actual cyclization k_2 is assumed to take place adiabatically, in the triplet manifold. We have already reported two similar cases: photocyclization of diphenylamines to carbazoles [10] and formation of the photochromic modification of dianthrone derivatives [11]. The observation that the quantity of $^3III^*$ formed

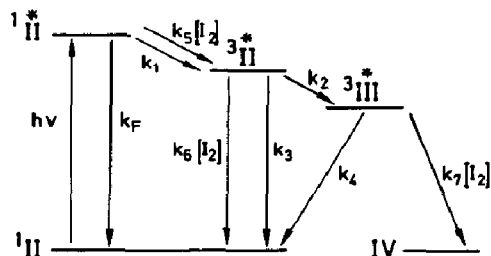
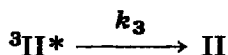
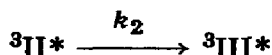


Fig. 11. The reaction scheme.

per flash in the temperature range 70 - 20 °C decreases sharply with increasing temperature indicates the existence of a strongly temperature-dependent reaction of $^3\text{II}^*$ competing with the formation of $^3\text{III}^*$, probably the radiationless transition



If so, the high activation energy of 26.8 kJ mol⁻¹ observed for k_A , *cf.* Section 2.2.2, reflects mainly the variation with the temperature of *this* transition. At lower temperatures the rate of the latter falls off below that of the cyclization



and in the range -80 to -180 °C the observed activation energy of 15.9 kJ mol⁻¹ reflects the variation of the cyclization rate with temperature. In terms of sequence (1) this would mean that in the temperature range 70 - 20 °C

$$k_3 = k_3^0 \exp\{-(26\,800 \text{ J mol}^{-1}/RT)\}$$

and $k_3 \gg k_2$, while in the range -80 to -180 °C

$$k_2 = k_2^0 \exp\{-(15\,900 \text{ J mol}^{-1}/RT)\}$$

and $k_3 \ll k_2$. No information is available regarding the variation with temperature of k_2 and k_3 outside these temperature ranges.

Regarding III in the ground state, if it is formed after all, our failure to detect it could result either from a very fast conversion into II or from absorption in a spectral region outside that covered in our experiments.

In the absence of evidence for ground state III we assume that the dehydrogenation takes place only in its triplet state $^3\text{III}^*$. According to Scheme 1 (Fig. 11) the overall quantum yield of IV as a function of the concentration of iodine can be expressed by

$$Q_{\text{PC}} = \left(1 - \frac{Q_{\text{F}}k_{\text{F}}^0}{k_{\text{F}}}\right) \frac{k_2}{k_2 + k_3 + k_6 [\text{I}_2]} \frac{k_7 [\text{I}_2]}{k_4 + k_7 [\text{I}_2]} \quad (5)$$

where k_{F}^0 and k_{F} are the fluorescence decay rates in the absence and in the presence of iodine at the respective concentration. The fluorescence quantum yield Q_{F} and all rate constants except k_3 are known from the experiments described. The resulting plot of Q_{PC} versus $[\text{I}_2]$ indeed passes through a maximum at about $[\text{I}_2] = 2.5 \times 10^{-4} \text{ M}$, in good agreement with the observations described above, *cf.* Fig. 9. The absolute value of Q_{PC} depends on k_3 . For $k_3 = 0$ we get $Q_{\text{PC}}^{\text{max}} = 0.27$, while the observed value is about 0.15, *cf.* Section 2.1. In order to obtain the latter we have to assume $k_3 = 0.58k_2$. The intersystem crossing yield is probably very high, as indicated by the low Q_{F} , and in analogy with other helicenes [7]. The enhancement $k_5 [\text{I}_2]$ of this yield by iodine is therefore negligible in any case. The quenching $k_6 [\text{I}_2]$ of $^3\text{II}^*$ to II by iodine is quite efficient, while that of $^3\text{III}^*$ is less so and may

actually consist mainly or solely of the dehydrogenation of $^3\text{III}^*$ to IV at the rate $k_7 [\text{I}_2]$.

It is tempting to assume that the observed activation energy of about 17 kJ mol^{-1} for Q_{PC} (cf. Section 2.1.2) is due to the similar activation energy reported for k_A in Section 2.2.2. However, this may be a coincidence, and the attenuation of Q_{PC} on cooling in the range 20 to -50°C may also be due to a diffusion-controlled reaction between iodine and $^3\text{III}^*$. In the absence of a method to determine the extent of $^3\text{III}^*$ formation below about 20°C , the temperature dependence of k_2 at lower temperatures (down to 77 K) remains doubtful. In view of the steric hindrance in II which should actually "encourage" cyclization we would expect that the quantum yield of formation of III does not decrease substantially on cooling, just as observed directly [2] with compound I. In this context it should be mentioned that the increase in internal energy accompanying the formation of III from II in the ground state has been estimated [12] to be about 100 kJ mol^{-1} , so that III cannot serve as an intermediate [4] in the racemization of II.

The obvious weakness of the above reasoning is the absence of *direct* evidence for the involvement of $^3\text{III}^*$ in the formation of IV and for the existence of III in the ground state. However, we feel that the indirect evidence, in particular the variation of Q_{PC} and of D^{385} with the concentration of iodine, suffice to make the suggested mechanism plausible. This conclusion is supported by the fact that in V, which does not undergo PCDH presumably because it does not photocyclize, no second transient, similar to B above, was observed.

4. Experimental

4.1. Materials

Compound II was synthesized from 1,2-di(2-naphthyl)ethylene [1]. Samples were also obtained from Professors Stegemeyer and Laarhoven. In all cases laborious TLC was required to get rid of a tiny amount of impurity emitting at 380 nm. Eventually it was the absence of this emission which served as a criterion of purity. Compound V was kindly supplied by Professor Laarhoven. The solvents used, MCH, 2-methylpentane, 3-methylpentane or a mixture of both (IH) were spectral quality solvents further purified by passage through Woelm activated alumina columns (Rehovot) or by accurate fractional distillation (Göttingen).

4.2. Methods

Removal of dissolved oxygen from the solutions was achieved either by flushing with argon containing less than 5 ppm O_2 (Rehovot), or by the usual freeze-evacuate-thaw method (Göttingen).

In the experiments involving iodine in evacuated cells (Section 2.2.4) the technique used was as follows. Six quartz cells suitable for laser excitation were filled with a solution of pentahelicene in MCH and various amounts

of an iodine stock solution were added. After degassing the cells were sealed off from the vacuum line and the accurate $[I_2]$ was determined from the optical density at 520 nm, assuming an extinction coefficient ϵ_{520} of $850 \text{ M}^{-1} \text{ cm}^{-1}$ for iodine in MCH.

For experiments involving varying concentrations of oxygen, the required mixtures of oxygen and nitrogen were prepared [13] in commercial gas bottles and used for flushing the solutions at temperatures sufficiently low to avoid solvent evaporation.

Cooling and heating of the cells was achieved in all experimental set-ups by means of the copper block technique [14]. In both the flash set-ups cells made of rectangular cross section Suprasil tubing were used [15].

The microsecond flash photolysis apparatus [9] and the nanosecond flash equipment [8] have been described. The latter employs a nitrogen laser providing pulses of 3 ns halfwidth and an energy of 0.3 mJ per pulse. The laser beam and the measuring beam are focussed so as to excite a horizontal layer of thickness 1 mm inside the measuring cell. The cell had a horizontal cross section of 4 mm \times 20 mm with the laser and the monitoring beams traversing the 4 mm and the 20 mm light paths, respectively. The time resolution of the detection system was about 5 ns.

Emission spectra were measured either in a home-made instrument [1] or with a MPF-2A Hitachi Perkin-Elmer instrument. Emission lifetimes were determined on the nanosecond flash apparatus.

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