Temperature Dependence of Photoisomerization. Part VIII.[1] Excited-state Behaviour of 1-Naphthyl-2-phenyl- and 1,2-Dinaphthyl-ethylenes and their Photocyclisation Products, and Properties of the Latter

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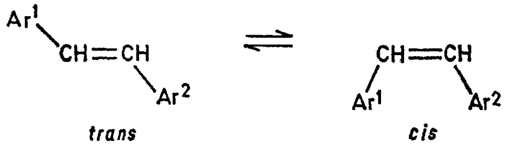
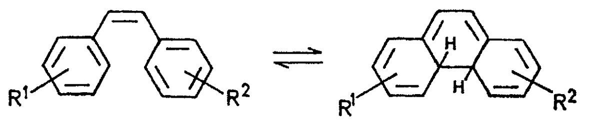
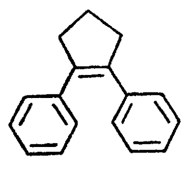
The main deactivation pathways of excited *trans*-isomers of the title compounds in dilute solutions are fluorescence and *trans* ⟶ *cis* conversion, those of excited *cis*-isomers are *cis* ⟶ *trans* and *cis* ⟶ DHP conversion (DHP = 4a,4b-dihydrophenanthrene derivative, the photocyclisation product) and fluorescence, while those of excited DHP are DHP ⟶ *cis* conversion and, in some cases, fluorescence. The quantum yields of fluorescence and of the photoconversions were measured as a function of temperature, in alicyclic and aliphatic hydrocarbon solvents. The relative contributions of these deactivation paths vary sharply with the temperature and the compound, in the above series. In all compounds *trans* ⟶ *cis*, *cis* ⟶ *trans* (with one exception), and *cis* ⟶ DHP photoconversions are slowed down sharply at low temperatures, while DHP ⟶ *cis* is attenuated on cooling only in the 2-naphthyl derivatives. Only in these three compounds was DHP fluorescence observed. The critical increments calculated by an 'Arrhenius treatment' of the variation of these quantum yields with temperature amount to 2—10 kcal mol^{-1}, and may indicate the existence of potential barriers on the way from the excited starting molecules to the final product. In the three 2-naphthyl derivatives, the ratio [*trans*]/[DHP] resulting from the reactions *trans* ⟵ *cis** ⟶ DHP was found to vary sharply with the wavelength of the exciting light (313, 334, and 366 nm). This effect is explained as being due to selective excitation of the various more or less isoenergetic conformers of these compounds which exist in solution. Some of these conformers were observed to give rise to hitherto unknown types of DHPs and their oxidation products, again as a function of the wavelength of the exciting light. The structure of all DHPs formed *via* photocyclisation of the *cis*-isomers was proved, and their complete u.v. and visible absorption spectra determined, by dehydrogenation with atomic iodine to the corresponding benzo- or dibenzo-phenanthrenes. The proton n.m.r. spectrum of the DHPs derived from two dinaphthyl derivatives was determined, and signals were assigned to 4a-and 4b-H. Photodehydrogenation of DHPs involving excited DHP and ground-state oxygen or iodine was also observed. The thermal ring opening reaction DHP ⟶ *cis* was measured over a wide temperature range. The critical increments calculated therefrom were in the range 13—27 kcal mol^{-1}.

DIARYLETHYLENES of the type Ar^{1}CH=CHAr^2 undergo two main types of reversible photoconversions when irradiated in dilute solutions: *cis* ⇌ *trans* isomerisation, and cyclisation of the *cis*-isomer to 4a,4b-dihydrophenanthrene (DHP) and its derivatives. (In this paper DHP will be used to denote both the parent compound and its derivatives.) Earlier publications from this and other groups [2,3] have dealt extensively with these reactions in substituted stilbenes, including two derivatives in which the *cis*-configuration is frozen-in, diphenylcyclopentene (I) [3,4] and 1,2-didehydro-[2.2]metacyclophane (II),[5] where cyclisation is the only reversible photoreaction observed.

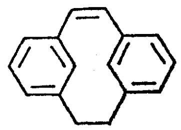




cis DHP



(I)



(II)

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[1] Part VII (erroneously numbered VIII), M. Kaganowitch, G. Fischer, and E. Fischer, *Z. Phys. Chem.*, 1971, **76**, 79.

[2] F. B. Mallory and C. W. Mallory, *J. Amer. Chem. Soc.*, 1972, **94**, 6041 and previous papers listed therein.

[3] (*a*) K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662; (*b*) A. Bromberg, K. A. Muszkat, and E. Fischer, *Israel J. Chem.*, 1972, **10**, 765; (*c*) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 3907; (*d*) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc.* (*B*), 1968, 1156.

[4] A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, 1965, **4**, 259.

[5] (*a*) C. E. Ramey and V. Bokelheide, *J. Amer. Chem. Soc.*, 1970, **92**, 3681; (*b*) R. Naef and E. Fischer, forthcoming publication.

The photobehaviour of five naphthyl analogues [PhCH=CH-1N (Ph-1N), Ph-2N, 1N-1N, 1N-2N, and 2N-2N, where 1N and 2N are 1- and 2-naphthyl, respectively] of stilbene has been described to some extent. This includes *cis* $\rightleftharpoons$ *trans* isomerisation[1,6] and emission[6] properties of Ph-2N and of all five naphthyl analogues,[7] cyclisation of some of the respective *cis*-isomers to the corresponding DHPs,[8-10] and auto- or photo-oxidation of the latter to the corresponding phenanthrene derivatives.[9,10] The direct photocyclodehydrogenation of the three dinaphthyl derivatives has been studied in considerable detail,[11] including the structure of the oxidation products.

In this paper we describe in detail the photobehaviour of the five naphthyl compounds and their photocyclisation products. This includes the absorption and emission spectra, the quantum yields of emission and of all photoreversible processes, as well as the oxidation, the structure, and other relevant properties.

RESULTS

Quantum Yields.—These were measured as a function of the temperature in the range +90 to −190°, in methylcyclohexane (MCH)-2-methylpentane(2-MP) (2 : 1) for the following photoreactions: *trans* → *cis*, *cis* → *trans*, *cis* → DHP, DHP → *cis*. In addition, fluorescence spectra and quantum yields were determined as a function of temperature for all ten *cis*- and *trans*-isomers, as well as for the three DHPs in which fluorescence could be detected (see later).

cis–trans-*Isomers and Isomerisation.*—In all cases the *cis*-isomers were either synthesized directly, or prepared photochemically from the respective *trans*-isomers and separated by t.l.c. Figure 1 shows the absorption spectra of the pairs of isomers for each compound. For all compounds the *cis*-isomer was converted into the *trans* by atomic iodine, formed by irradiation at 546 or 578 nm in the presence of iodine,[3d] which was then removed with copper foil. The absorption and emission spectra of all five pairs of isomers at low temperatures have been briefly mentioned previously,[7] and will be described in detail elsewhere.[12] Only the absorption spectra of *trans*-Ph-2N and *trans*-2N-2N show pronounced vibrational structure, similar to that of stilbene itself (Figure 1C). No such structure was observed with any of the three 1-naphthyl derivatives, including 1N-2N, even at 77 K. The same holds for all the *cis*-isomers.

The *cis* $\rightleftharpoons$ *trans* quantum yields Q in both directions are summarised in Figure 2 (full lines) over a wide range of temperature. The data for stilbene[3a,13] are included (Figure 2C) for the sake of comparison. It is seen that the pronounced temperature dependence of Q(*trans* → *cis*) observed for stilbene[13] at low temperatures is exhibited by the naphthyl analogues of stilbene from +100° downwards. The 1-naphthyl derivatives show in addition a plateau in the range −20 to −100°, followed by another sharp decline at still lower temperatures. Thus at room temperature all Q(*trans* → *cis*) are only *ca.* 0·1, as against 0·5 for *trans*-stilbene. Accordingly the fluorescence yields, to be described later, are *ca.* 0·7 at room temperature, compared with 0·07 in stilbene. Q(*cis* → *trans*) at first remains constant on cooling, and starts falling off only at rather low temperatures, as already observed in *cis*-stilbene. Only 1N-1N behaves differently in this respect.

A plot of log Q against T^{-1} shows an Arrhenius-type relationship. The activation energies E_a calculated in this way are summarised in Table 1, including those for stilbene. The values of E_a calculated for the fluorescence yields of the *cis*-isomers are also given, but only for those cases in which *cis* → *trans* isomerisation is the major photoreaction of *cis*.

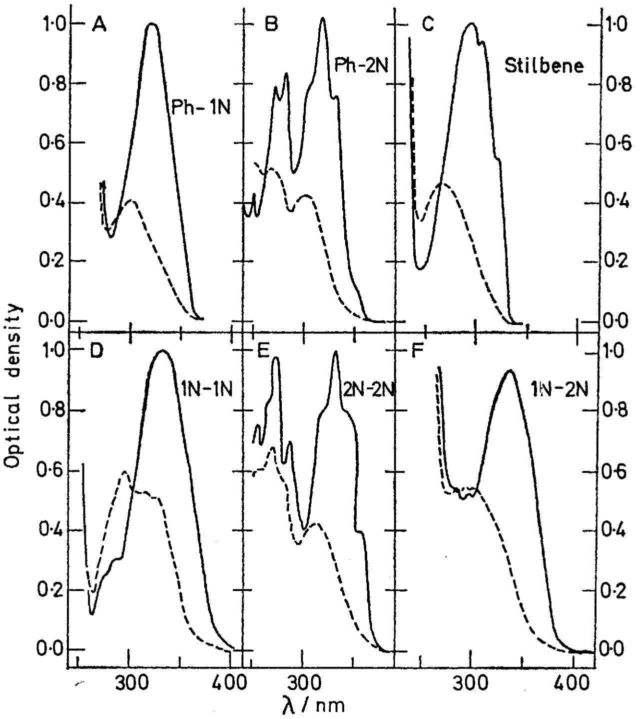

FIGURE 1 Absorption spectra of *trans* and *cis*-isomers, at the same concentration, in MCH at room temperature. Approximate concentrations were as follows: A, $4·35 \times 10^{-5}$; B, $1·8 \times 10^{-5}$; C, 4×10^{-5}; D, 5×10^{-5}; E, $2·7 \times 10^{-5}$; F, $4·35 \times 10^{-5}$M

The results show that the fluorescence yields of the *cis*-isomers attain appreciable values only when the yields of the photoreactions *cis* → *trans* and *cis* → DHP start falling off on cooling. It is only then that fluorescence becomes the main deactivation path of excited *cis*-molecules. Q^F_{cis} is thus complementary to either Q(*cis* → *trans*) or Q(*cis* → DHP), whichever is larger. For the *trans*-isomers, since fluorescence and *trans* → *cis* isomerisation are the only deactivation paths of the excited molecule, the quantum yields of these two processes are complementary (Figure 2). Again the situation is similar

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[6] G. S. Hammond, C. Shin, and S. P. Van, *Mol. Photochem.*, 1969, **1**, 89.

[7] J. Klueger, G. Fischer, E. Fischer, Ch. Goedicke, and H. Stegemeyer, *Chem. Phys. Letters*, 1971, **8**, 279.

[8] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163.

[9] T. Knittel, G. Fischer, and E. Fischer, *J.C.S. Chem. Comm.*, 1972, 84.

[10] T. Knittel-Wismonski, G. Fischer, and E. Fischer, *Tetrahedron Letters*, 1972, 2853.

[11] Ch. Goedicke and H. Stegemeyer, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 782.

[12] Ch. Goedicke, H. Stegemeyer, G. Fischer, and E. Fischer, in preparation.

[13] S. Malkin and E. Fischer, *J. Phys. Chem.*, 1964, **66**, 1153.

to that observed previously for stilbene[13] (Figure 2C) but shifted to higher temperatures.

Photocyclisation and Photochemical Ring-opening: cis $\rightleftharpoons$ *DHP*.—All five *cis*-naphthyl derivatives undergo extensive photocyclisation to isomeric forms derived from DHP proper and related compounds described earlier.[3,4] It should be emphasised again that DHPs can be formed *only via* the excited state of the corresponding *cis*-isomers. *cis*-Conformers not exhibiting pronounced steric hindrance are shown in Scheme 1. Bond formation can take place in principle between the carbons marked by points (see later for structure of DHPs). Photoreversal with visible light to the starting *cis*-isomer is the single most important tool for the characterization of DHPs.

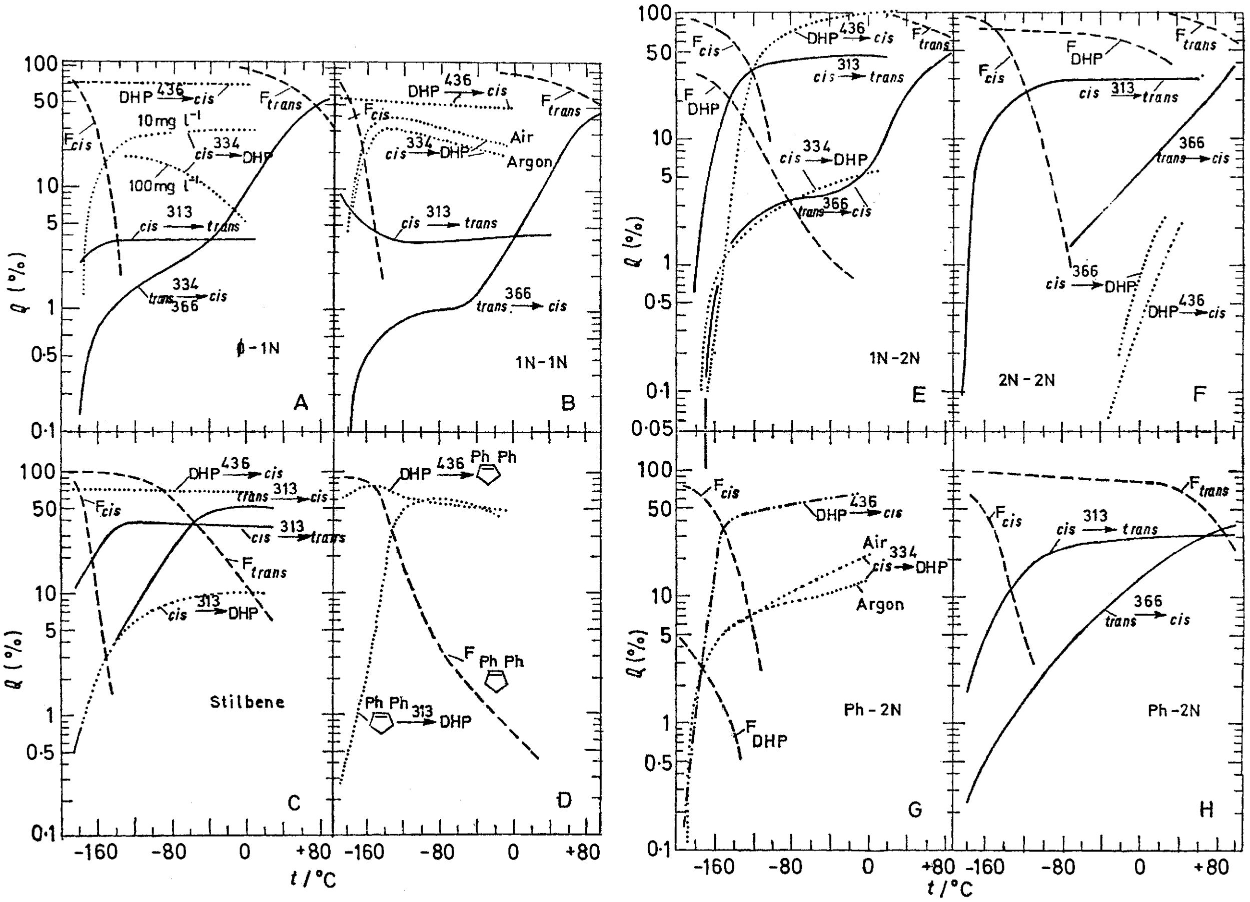

FIGURE 2 Variation with temperature of the quantum yields Q of the photoreactions *trans* $\rightleftharpoons$ *cis*, (full lines), *cis* $\rightleftharpoons$ DHP, (dotted lines), and of the flourescence quantum yields of the *trans*- *cis*-, and DHP forms (dashed lines) measured in MCH–2-MP (2 : 1), except for measurements in the range +20 to +90°, where MCH served as solvent. Note logarithmic scale of Q. Compounds and wavelengths of exciting light were as indicated. See text regarding effect of concentration (Figure 2A) and of dissolved oxygen (2B and G)

The spectra of the *cis*-isomers and of the corresponding DHPs are presented in Figure 3. Since the reaction is photoreversible, complete photoconversion into DHP cannot be achieved with light absorbed by both the DHP and the corresponding *cis*-isomer. The spectra of the pure DHPs were therefore extrapolated from the experimental ones, as detailed later. They are characterised by bands at *ca.* 410, 300, and 250 nm, separated by minima at *ca.* 320 and 280 nm. The band at *ca.* 300 nm is structured in all cases, while the one at *ca.* 410 nm shows vibrational structure only in the three 2-naphthyl derivatives. Ph-1N and 1N-1N do not show any structure even at −180°.

The cyclisation is both thermally (see later) and photochemically reversible. The maximal photoconversion into DHP for each compound, in the absence of thermal ring opening, is determined by the ratios $R_1 = Q(cis \longrightarrow \text{DHP}) : Q(\text{DHP} \longrightarrow cis)$, $R_2 = Q(cis \longrightarrow \text{DHP}) : Q(cis \longrightarrow trans)$, and $R_3 = Q(cis \longrightarrow trans) : Q(trans \longrightarrow cis)$, at the wavelength of the exciting light. [In compounds such as (I) and (II), in which no *cis* $\longrightarrow$ *trans* isomerisation is possible, the maximal conversion is determined solely by R_1.] The *initial* proportion [DHP]/[*trans*] during u.v. irradiation is of course determined by R_2.

The variation with temperature of the quantum yields of DHP formation and decomposition is summarised by the dotted lines in Figure 2. For comparison the results for stilbene and for (I) are also presented * (Figures 2C and D).

The results show that all photocyclisation quantum yields fall off at very low temperatures, as observed[3a,b] in

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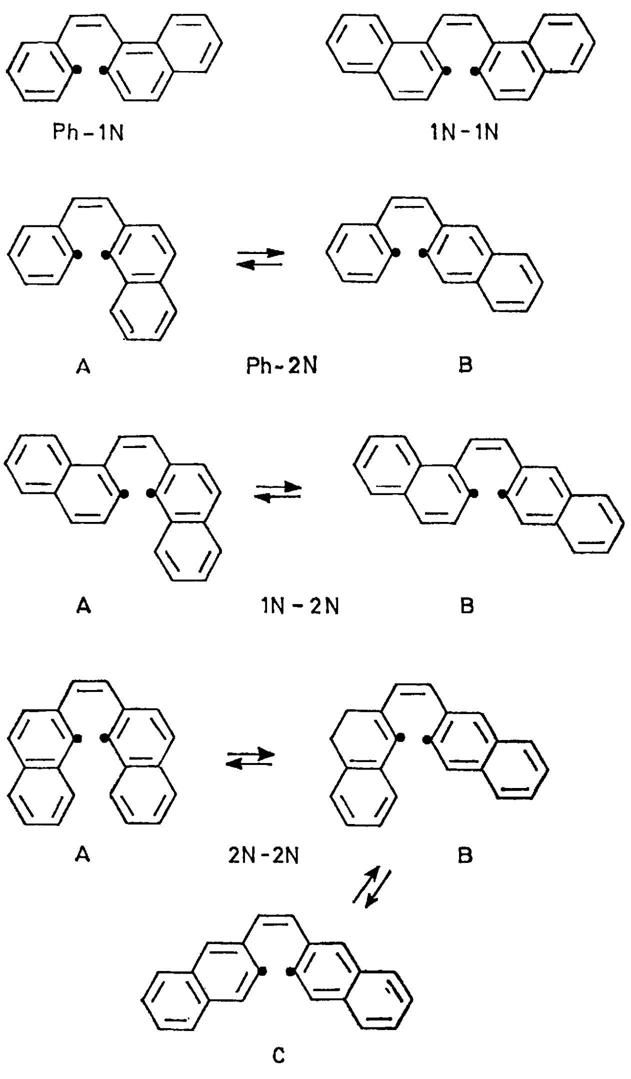
* In our previous paper[3a] the limiting value of the fluorescence yield of (I) at low temperatures was erroneously given as only *ca.* 0·5, while our present more exact measurements gave a value of *ca.* 0·9.

TABLE 1

Activation energies E_a calculated from Arrhenius-type plots of Q(*trans* → *cis*), Q(*cis* → *trans*), and the fluorescence yield Q^{F}_{cis} against T^{-1}

Compound	Reaction	E_a/kcal mol^{-1}	E_a(fluorescence)/ kcal mol^{-1}
Ph-1N	*trans* → *cis* (high T)	4	
Ph-1N	*trans* → *cis* (low T)	3	
1N-1N	*trans* → *cis* (high T)	4	
1N-1N	*trans* → *cis* (low T)	10	
1N-2N	*trans* → *cis* (high T)	6·5	
1N-2N	*trans* → *cis* (very low T)	7	
1N-2N	*cis* → *trans*	2	4
Ph-2N	*trans* → *cis* (high T)	2	
Ph-2N	*trans* → *cis* (low T)	1	
Ph-2N	*cis* → *trans*	1	2·5
2N-2N	*trans* → *cis*	2·5	
2N-2N	*cis* → *trans*	6	4·5
Stilbene	*trans* → *cis* (low T)	2	2·5
Stilbene	*cis* → *trans*	1·2	3

simple stilbene derivatives and in (I), although there are quantitative differences. In fact, the only case in which we have not observed such an attenuation of Q(*cis* → DHP) on cooling is for compound (II), which is 'forced' to cyclise in the excited state, even at −190°.[5b] In those cases in which Q(*cis* → *trans*) ⩽ Q(*cis* → DHP), the curves show that *cis** → DHP and the fluorescence of the *cis*-form are complementary reactions, and as the quantum yield Q(*cis* → DHP) is lowered on cooling, $Q_{cis}{}^{\mathrm{F}}$ increases. A rough quantitative indication of the extent of this variation in the Q values with temperature is provided by E_a calculated from Q–T^{-1} plots. These values are summarised in Table 2.



SCHEME 1

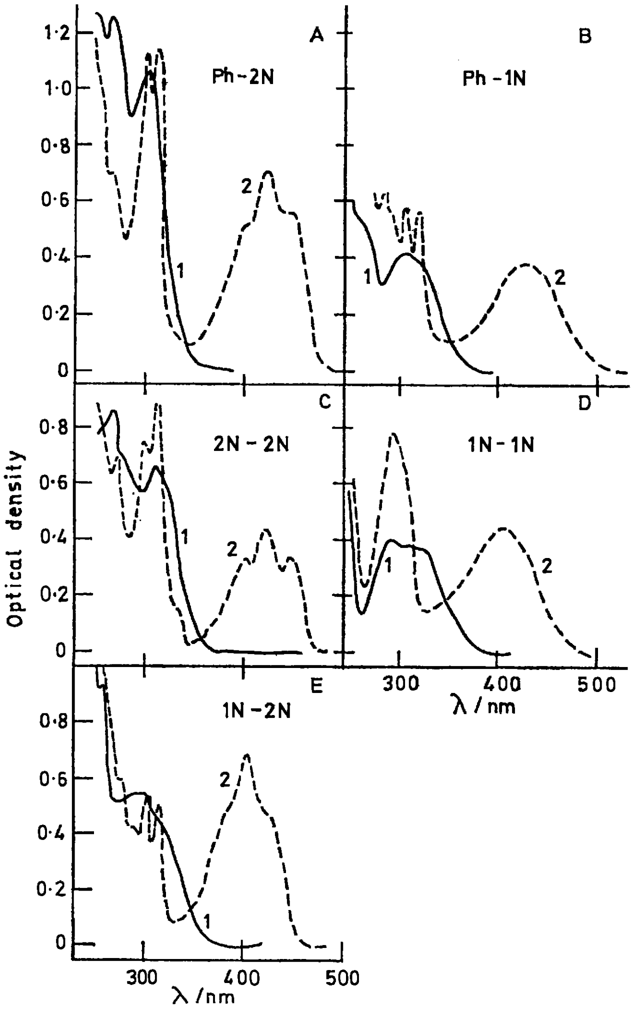


FIGURE 3 Absorption spectra of *cis*-isomers and of the corresponding photocyclisation products (DHPs) determined by extrapolation as described in the text. Spectra at room temperature for 2N-2N, 1N-1N, and 1N-2N, and at 0° for Ph-1N and Ph-2N

A very interesting feature shown in Figure 2 is that the quantum yield of the ring-opening reaction, Q(DHP → *cis*), of stilbene, (I), and the 1-naphthyl derivatives is not attenuated even at the lowest temperatures, while this yield falls off sharply on cooling solutions of the three 2-naphthyl derivatives. Moreover, for the latter group, as in stilbene and its derivatives studied earlier, Q(*cis* → *trans*) ⩾ Q(*cis* → DHP), while in Ph-1N and 1N-1N the reverse holds. In this context it is worth noting the unusual behaviour of 1N-2N (Figure 2E). Owing to the fact that Q(DHP → *cis*), though much higher than

Q($cis \longrightarrow$ DHP), falls off faster at low temperature, optimal conversion into the corresponding DHP is achieved at −160°.

In view of the sharp decline of Q(DHP $\longrightarrow cis$) with temperature for the 2-naphthyl compounds one may expect to observe DHP fluorescence at lower temperatures. This was indeed the case (see later). Again the quantum yields of DHP $\longrightarrow$ *cis* and of DHP fluorescence are complementary, with one increasing while the other decreases upon varying the temperature. While this is qualitatively true also for Ph-2N, Figure 2G shows that below −170° the combined yields of DHP fluorescence and decomposition account for <10% of the fate of excited DHP molecules. An extraordinary feature is the very low value of Q(DHP $\longrightarrow cis$) in the case of 2N-2N (Figure 2F) even at room temperature, and the correspondingly high $Q^{\mathrm{F}}{}_{\mathrm{DHP}}$. Equally remarkable is the pronounced temperature dependence of Q(DHP $\longrightarrow cis$) in the range +30° to −30°.

TABLE 2

Activation energies E_a calculated from Arrhenius-type plots of Q($cis \longrightarrow$ DHP), Q(DHP $\longrightarrow cis$), and $Q_{cis}{}^{\mathrm{F}}$ against T^{-1} in the low-temperature region

Compound	Reaction	E_a/kcal mol^{-1}	E_a(*cis* fluorescence)/ kcal mol^{-1}
Ph-1N	*cis* $\longrightarrow$ DHP	5·5	3·5
1N-1N	*cis* $\longrightarrow$ DHP	2·5	3·5
Ph-2N	*cis* $\longrightarrow$ DHP	4·5	3
Ph-2N	DHP $\longrightarrow$ *cis*	3	
1N-2N	*cis* $\longrightarrow$ DHP	2·5	
1N-2N	DHP $\longrightarrow$ *cis*	4	
2N-2N	*cis* $\longrightarrow$ DHP	10	
2N-2N	DHP $\longrightarrow$ *cis*	6·5	
Stilbene	*cis* $\longrightarrow$ DHP	1·2	
(I)	*cis* $\longrightarrow$ DHP	2·5	2·5

Another pecularity is the decline of Q($cis \longrightarrow$ DHP) with increasing concentration of starting material. This effect was most pronounced in Ph-1N and 2N-2N. Figure 4 presents the results obtained with 2N-2N in three solvents, MCH, benzene, and paraffin oil. The results with the highly viscous paraffin indicate that the effect is mainly one of diffusion, and as such should be intimately connected with the detailed mechanism of DHP formation. The diffusional nature of the phenomena is supported by the observation (Figure 2A) that as the temperature is lowered, Q($cis \longrightarrow$ DHP) at higher concentrations gradually approaches that at lower concentrations. Thus for Ph-1N at 0°, Q at a concentration of 100 mg l^{-1} is *ca.* 0·2 of Q at 10 mg l^{-1}, while at −120° this ratio increases to 0·72.

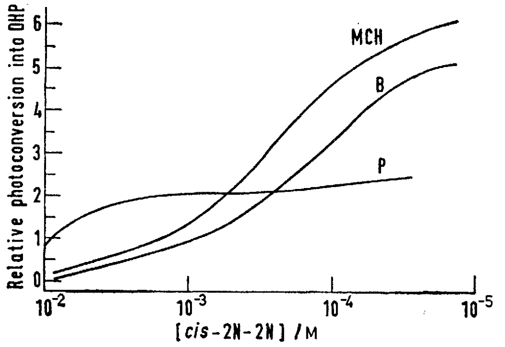


FIGURE 4 Concentration dependence of optimal degree of photocyclisation of *cis*-2N-2N in MCH, benzene (B), and paraffin oil (P). Cells with optical paths from 0·1 mm upwards were used

Finally, oxygen was observed to enhance Q($cis \longrightarrow$ DHP) up to two-fold as shown in Figures 2B and G. Phenomenologically this resembles the very pronounced enhancement of Q($trans \longrightarrow cis$) observed earlier[14,15] in some of these compounds, together with a less pronounced attenuation of Q($cis \longrightarrow trans$). No difference was observed between the spectra of DHP formed in the presence or absence of oxygen.

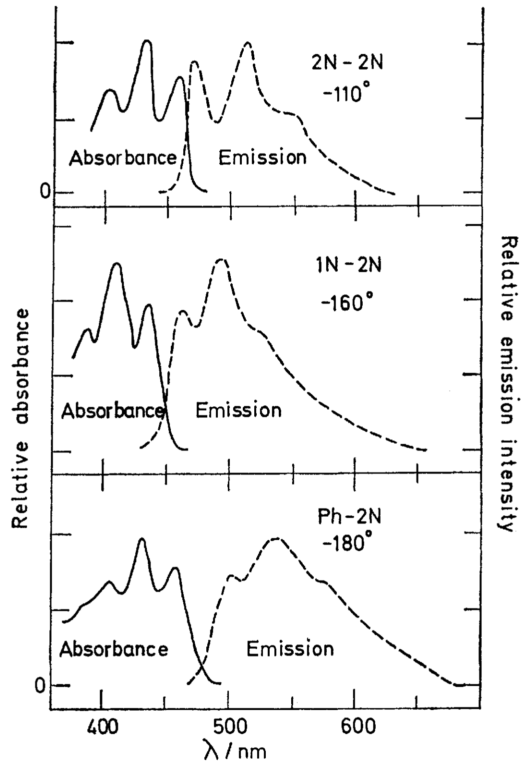


FIGURE 5 Absorption and corrected emission spectra of DHPs, dissolved in MCH–2-MP (2 : 1)

Fluorescence Spectra.—Those of the five pairs of *cis*- and *trans*-isomers will be reported in detail elsewhere.[12] We therefore confine ourselves to the emission spectra of the DHPs derived from the three 2-naphthyl derivatives Ph-2N, 1N-2N, and 2N-2N (Figure 5). The overlap of absorption and emission spectra is normal, as expected for molecules having a rather rigid structure. The long tail of the emission spectra towards long wavelengths is noteworthy, and so is the fact that the emission of the phenyl derivative Ph-2N extends to longer wavelengths than that of the two dinaphthyl derivatives. This is probably the result of a combination of opposing effects resulting from the replacement of a phenyl group by a naphthyl group; on the one hand the overall increase in size of the system, and on the other the retention of aromatic character in those parts derived from the naphthyl groups, thereby possibly interfering with the original DHP system.

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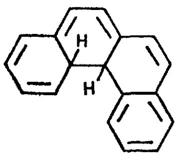
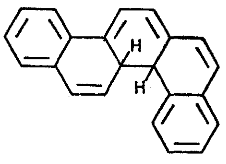
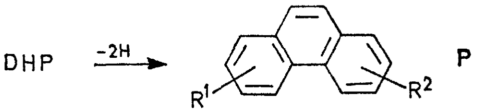
[14] P. Bortolus and G. Galiazzo, *J. Photochem.*, 1974, **2**, 361.

[15] G. Fischer and E. Fischer, *Mol. Photochem.*, forthcoming publication.







Structures and Molar Extinction Coefficients of the DHPs.—The classical method of determining the structures [2,3a,9] of the unstable DHPs and their concentration in solution [3a] is based on their dehydrogenation to the known corresponding phenanthrene derivatives. It is therefore essential to have available a clean method of dehydrogenation. In the simple derivatives of stilbene described earlier,[3a] molecular oxygen acts efficiently in this capacity, but the naphthyl derivatives, and in particular the dinaphthyl derivatives, are oxidized only very slowly by oxygen or molecular iodine. However, atomic iodine brings about a very efficient appearance of the fully aromatic dehydrogenation products,[9] even at −50°. This method was used with all the naphthyl derivatives. Furthermore, since in all cases *cis* → DHP conversion is accompanied by *cis* → *trans* conversion to varying extents, analysis is facilitated by converting all the remaining *cis*-isomer (*i.e.* the fraction which had not undergone cyclisation) into the *trans*-isomer, by photocatalysis with atomic iodine,[3d] and thus arriving at a binary mixture of *trans* and ' oxidation ' product. Incidentally, dehydrogenation by atomic iodine is much faster than *cis* → *trans* isomerisation under similar conditions. A typical example will be described in detail, with the main purpose of establishing the identity and concentration of the product. Two equal volumes of a dilute solution of the *cis*-isomer at a concentration C_0. were irradiated at 366 or 334 nm, to yield equal concentrations of DHP. In cell A the DHP was decomposed by irradiation at 436 nm. To the second cell B a small volume of a solution of iodine was added, corresponding to *ca.* 5 equiv. of the original *cis*-isomer in the cell. Cell B was then briefly irradiated at 546 nm (where only iodine absorbs) until the DHP absorption disappeared. (The absorption spectrum of iodine in MCH has a window in the 400—450 nm range, where DHPs absorb.) Iodine was also added to cell A, and both cells, A and B, were irradiated at 546 nm until no further spectral change was observed. The iodine was then removed by means of copper foil. The resulting solutions should be pure *trans* in cell A, at a concentration C_0, and *trans* + ' oxidation product ' in cell B. If a fraction f of the original *cis*-isomer in cell B was converted into DHP, and then dehydrogenated by atomic iodine to the oxidation product, the concentration of the components after *cis* → *trans* conversion in cell B will be $[trans] = C_0(1-f)$, $[\text{' product '}] = C_0 f$. In order to obtain the spectrum of the pure ' product ', the spectrum of *trans* at a concentration $C_0(1-f)$ has to be deducted from the final spectrum of cell B. A very rough estimate of the concentration of trans, and therefore $(1-f)$, in cell B can be made directly. Difference spectra between cells B and A were therefore taken after diluting A progressively, corresponding to $(1-f)$ values below and above the estimated value. These difference spectra were compared with that of an authentic sample of the expected oxidation product. In all cases a dilution, and therefore a value for f, could be found which gives an excellent fit between the difference spectrum and the spectrum of the polycyclic hydrocarbon expected. In cases such as Ph-2N, 2N-2N, and 1N-2N, where several conformers are expected to exist in solution [11] (*cf.* the paragraph dealing with photocyclisation), only one product was observed, derived from the DHP denoted A in Scheme 1.[11] This method of *thermal* (*i.e.* not involving excited species) dehydrogenation of the respective DHPs is of course much more straightforward than photo-oxidation of the starting *cis*-compound directly to the final polycyclic product,[2,11] *without* first forming and accumulating the DHPs. Figure 6 shows the results obtained with 1N-1N. Table 3 lists the oxidation products obtained in each case.

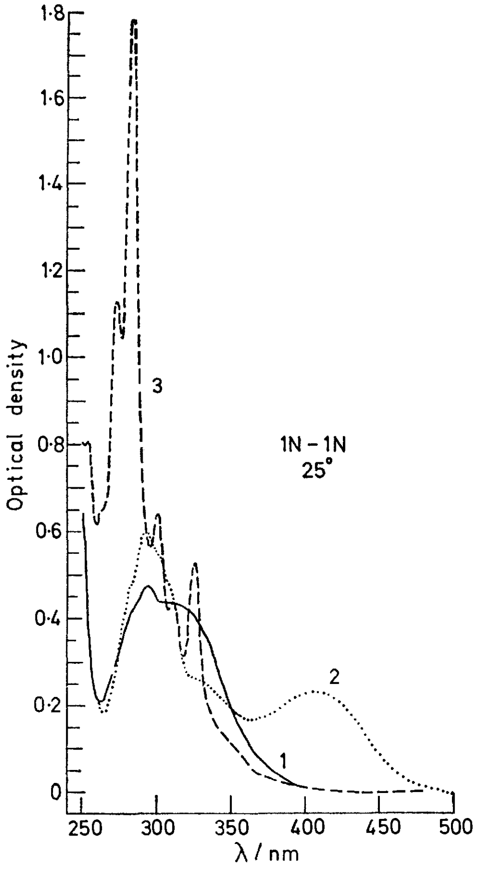


FIGURE 6 Absorption spectra of 4×10^{-5}M-1N-1N in MCH at 25°: 1, *cis*-isomer; 2, same after partial conversion into the corresponding DHP by irradiation at 334 nm; 3, same after oxidation with atomic iodine, to give picene. In this compound *cis* → *trans* isomerisation is much slower than *cis* → DHP (*cf.* Figure 2B) and therefore little *trans*-product is formed

The method leads to a value f for the extent of photoconversion into the respective DHP, and thereby its concentration under the experimental conditions, and it is possible to estimate the molar extinction coefficient of the DHP at its peak, and to construct its complete absorption spectrum. This is done [3a,9] by taking the spectrum of the *cis*-isomer and adding to it the (positive or negative) observed difference in absorbance resulting from decomposition of the DHP, multiplied by f^{-1}. All DHP spectra in Figure 3 were obtained by this extrapolation procedure.

Thermal (*Spontaneous*) *Ring-opening: DHP* ⟶ cis.—The kinetics of the disappearance of the DHPs derived from Ph-1N, Ph-2N, and 2N-2N has been described by Timmons and his co-workers.[8] The following half-lives of DHP disappearance in 10^{-4}M argon-flushed solutions of various DHPs give an idea of their thermal stability at room temperature: Ph-1N, 1 h; Ph-2N, 1 h; 1N-1N, 11 days; 2N-2N, 10 days; 1N-2N, 3 days. First-order kinetics were observed throughout. Application of the Arrhenius relationship to the variation of the rates with the temperature yielded the following values for the activation energy (kcal mol^{-1}): 2N-2N, 27; 1N-1N, 15; 1N-2N, 18·5. For comparison, values reported by Timmons [8] and by us [3a] for various DHPs were: Ph-1N,[8] 12·8; Ph-2N,[8] 14·2; 2N-2N,[8] 23·3; compound (I), 15·5; stilbene, 17·5; 2,2′,4,4′,6,6′-hexamethylstilbene, 22·5. E_a for 2N-2N clearly exceeds those for all other naphthyl compounds.

TABLE 3

Polycyclic products obtained by oxidation with atomic iodine of the DHPs formed by the photocyclisation of 1,2-diarylethylenes

Starting compound	Oxidation product	DHP $\lambda_{max.}$/nm	DHP ε *
ϕ-1N	Chrysene	425	8000
ϕ-2N	Benzo[*c*]phenanthrene	425	11,000
1N-1N	Picene	410	13,000
1N-2N	Benzo[*c*]chrysene	410	13,000
2N-2N	Dibenzo[*c,g*]phenanthrene	425	12,000
2N-2N	Dibenzo[*b,g*]phenanthrene †	575	(10,000)

* The accuracy of the ε values is estimated as ±10%, but is lower for the last compound. † This product is derived from conformer B (Scheme 1). The conditions of its formation are detailed in the text.

In connection with n.m.r. measurements (see later) of the DHPs derived from 1N-1N and 2N-2N, the thermal stability was also checked in 0·05M argon-flushed solutions in benzene. Under these conditions the half-life was reduced to *ca.* 3 days for 2N-2N and 1·5 days for 1N-1N. However, since these measurements were carried out in 0·1 mm cells, the complete absence of traces of air could not be assured, and therefore some DHP might disappear *via* oxidation. It should also be borne in mind that the thermal reaction DHP ⟶ *cis* is strongly exothermic, with an estimated [16] difference in free energy of *ca.* 50 kcal mol^{-1} in the case of 2N-2N. Catalytic effects are therefore quite probable.

Thermal Dehydrogenation of DHPs.—Oxidants used were oxygen, molecular iodine, and atomic iodine. In the present context the criterion for a thermal oxidation, as against a photo-oxidation, is that no electronically excited states of the DHPs are involved.

As mentioned above, the dehydrogenation of the DHPs of the present series by molecular oxygen is much slower than that of the simpler DHPs described earlier.[3a] In air-saturated 10^{-4}M-MCH solutions of DHPs derived from the three 1,2-dinaphthylethylenes the rates of disappearance of DHP were 10—20-fold those found in argon-saturated solutions. Thus the half-life for the DHP from 1N-1N was reduced to *ca.* 13 h and that for the DHP from 2N-2N to *ca.* 1 day. In 0·05M solutions in benzene the enhancement of the rates of disappearance by air is even higher, *ca.* 30—50-fold. Thus the half-life for the DHP from 1N-1N is 1·7 h, and for the DHP from 2N-2N 1 h. For Ph-1N and Ph-2N the enhancement, measured at 0°, is *ca.* 2-fold, in dilute solutions. In all cases the corresponding aromatic dehydrogenation products were observed in aerated solutions.

Molecular iodine, which oxidises the simpler DHPs rapidly even at −30°, was found to react rather slowly with the naphthyl DHPs, in particular those from 1N-1N and 2N-2N, provided that at least some oxygen is present. To check this point further, experiments with 1N-1N were found to be particularly useful, because of the very intense and sharp absorption peaks which characterise the oxidation product, picene. When a small volume of iodine solution was added to an aerated 10^{-5}M-DHP solution at −30°, no reaction took place. If the air was now flushed out by nitrogen or argon, rapid dehydrogenation took place, which could be stopped by flushing with air. This protective effect of oxygen on the dehydrogenation of the DHPs from 1N-1N and 2N-2N with iodine at room temperature was checked at various partial pressures of oxygen. Up to, and including, an oxygen content of 0·4% in the nitrogen used for flushing the solutions, the reaction with iodine was too fast to be measurable with simple techniques. At 2% oxygen, the half-life of the DHP was 10 min, while with air it increased to several hours. It appears that oxygen interferes somewhere along the chain reaction (1) by which dehydrogenation with iodine probably proceeds:

$$I_2 \rightleftharpoons 2I\cdot \qquad (1a)$$

$$I\cdot + PH_2 \longrightarrow HI + HP\cdot \qquad (1b)$$

$$HP\cdot + I_2 \longrightarrow P + HI + I\cdot \qquad (1c)$$

Here PH_2 denotes the DHP analogue, P the oxidation product, and HP· the radical formed after abstraction of one H from PH_2.

When a solution containing DHP and iodine is irradiated at 546 or 578 nm, where only iodine absorbs, the DHP is efficiently dehydrogenated by the atomic iodine produced by photodissociation of I_2. Aerated and deaerated solutions behave similarly, except for the effect described above. Evidently, whatever the reason for the oxygen effect described above, it no longer operates in the presence of relatively high concentrations of atomic iodine. Dehydrogenation with atomic iodine takes place even at −50°, provided that the iodine concentration does not exceed *ca.* 2×10^{-4}M. At higher concentrations a complex between DHP and I_2 is formed, which is not affected by atomic iodine.[17]

Photodehydrogenation of DHPs to Phenanthrene Derivatives.—In line with the definition used for 'thermal' dehydrogenation, we define by 'photodehydrogenation' a dehydrogenation involving electronically excited DHP reacting with a suitable hydrogen acceptor. In all DHPs investigated so far, the quantum yield of photochemical ring opening, DHP ⟶ *cis*, is so high that irradiation of DHP with visible light results in its conversion into the

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[16] K. A. Muszkat, Sh. Sharafi-Ozeri, and T. A. Pakkanen, *J.C.S. Perkin II*, submitted for publication.

[17] H. Stegemeyer, T. Wismonski-Knittel, and E. Fischer, unpublished results. These show, *inter alia*, that the interaction between DHPs and iodine is rather complex.

cis-isomer only. Only in 2N-2N is the yield $Q(\mathrm{DHP} \longrightarrow cis)$ below 0·01 even at 20°, (Figure 2F) and 0·0006 at −30°, providing ample opportunity for excited, fluorescing DHP molecules to react with suitable reagents. We used oxygen and iodine for this purpose. Irradiation at 436 nm of an air-saturated solution of the DHP from 2N-2N at 25° caused decomposition just as fast as in an argon-saturated solution. At −30° the rate of decomposition was *ca.* 40-fold in the air-saturated solution, indicating that $\mathrm{DHP}^* + O_2 \longrightarrow \mathrm{P}\ (+H_2O_2?)$ can now compete successfully with the radiative decay of DHP*, and of course with its conversion into the *cis*-product. Spectral analysis left no doubt that the polycyclic product, dibenzo-[*c, g*]phenanthrene, is indeed formed under these conditions just as during the reaction between this DHP, in its ground state, with atomic iodine. The quantum yield of this photo-oxidation in MCH solutions was 0·005 at −30°, and remained constant down to −120°. The decreased rate of diffusion at −120° is probably compensated by the increased solubility of oxygen at this temperature. (Solubility data of oxygen in MCH at low temperatures are not available, but the general trend of its variation with the temperature is illustrated by data [18] for the concentration of oxygen in air-saturated iso-octane: −30°, 0·004M; −50, 0·0047; −80, 0·0056).

Initial experiments had shown that photo-oxidation takes place even with traces of oxygen. The reaction was therefore measured in solutions kept at −30° and flushed continuously with nitrogen containing varying amounts of oxygen. The results, expressed as relative rates of DHP disappearance by dehydrogenation, were as follows: at 20% O_2, 6; 2%, 3·3; 0·4%, 2·5; 0·03%, 1·1; 0·0005%, <0·02. In order to distinguish between the two reaction paths (2) and (3), quenching of DHP fluorescence was

$$\mathrm{DHP} \xrightarrow{h\nu} \mathrm{DHP}^* \xrightarrow{O_2} \mathrm{P} \qquad (2)$$

$$\mathrm{DHP} + O_2 \longrightarrow [\mathrm{DHP} \cdots O_2] \xrightarrow{h\nu} \mathrm{P} \qquad (3)$$

measured at various oxygen concentrations. No quenching was observed with nitrogen containing 2% oxygen, while the fluorescence yield was reduced to 90% in air- and to 60% in oxygen-saturated solutions of DHP at −30°, relatively to an argon-saturated solution. In view of the pronounced photo-oxidation observed already with nitrogen containing 2% oxygen, this result favours mechanism (2), *i.e.* diffusional interaction between DHP* and dissolved oxygen.

A similar photo-oxidation was observed with molecular iodine: $\mathrm{DHP} \xrightarrow{h\nu} \mathrm{DHP}^* \xrightarrow{I_2} \mathrm{P}$. Fortunately iodine absorbs very little light at 405 nm, while one of the peaks of the DHP from 2N-2N is at this wavelength, and the reaction between ground-state DHP and photocreated I· can therefore be excluded. Small volumes of a concentrated solution of iodine in MCH were added to $1{\cdot}5 \times 10^{-5}$M solutions of the DHP from 2N-2N in the same solvent at −30°, to give iodine concentrations of 6—20 × 10^{-5}M. Irradiation at 405 nm resulted in rapid oxidation of the DHP.

A rough estimate of the quantum yield Q at 405 nm, at various concentrations of iodine, shows that Q passes through a maximum of *ca.* 3 at an iodine concentration of *ca.* 8 × 10^{-5}M. Q falls off rapidly at lower iodine concentrations, and more slowly at higher ones. Iodine in large excess protects the DHP by forming a light-stable complex.[17] Quantum yields exceeding unity are probably due to a chain reaction: $\mathrm{DHP}^* + I_2 \longrightarrow \mathrm{HP}\cdot + \mathrm{HI} + \mathrm{I}\cdot$ followed by reactions (1b) and (1c) *etc.*

The common method employed for the photocyclodehydrogenation of stilbene derivatives to phenanthrene derivatives involves u.v. irradiation in the presence of air and iodine.[19] In view of the present results it appears plausible that under these conditions the DHPs produced primarily are dehydrogenated by a combination of three processes: spontaneous oxidation with molecular oxygen and iodine, oxidation with atomic iodine, and oxidation involving electronically excited DHP. It is unlikely that singlet oxygen is also involved, in view of the absence of reports on similar dehydrogenation reactions.

DHPs derived from Various Conformers of 2N-2N.—Each of the three *cis*-2-naphthyl derivatives may be expected to exist in solution as a mixture of two or three more or less isoenergetic conformers A—C, in dynamic equilibrium with each other (Scheme 1). Nevertheless the polycyclic hydrocarbons formed during photocyclodehydrogenation of these *cis*-compounds are reported to be derived solely from conformer A.[11,20] Calculations have shown [21,22] that this is indeed to be expected, because the ' reactivity measure ' of the two carbon atoms between which a bond is to be formed in the excited state is higher in these conformers. An exception is conformer B of 2N-2N, for which *e.g.* the electronic overlap population, serving as a reactivity criterion, is almost as large as in conformer A.[16] Nevertheless, no indication for photo-oxidation products derived from B has been found hitherto.[11] Preliminary results [23] of a flash-photolytic investigation of *cis*-2N-2N showed, among other unexpected phenomena, that another much less thermally stable product was formed. From the temperature dependence of its decay it appeared possible to stabilize this product at sufficiently low temperatures. 303 + 313 nm irradiation at −140° indeed resulted in a stable product, absorbing at much longer wavelengths than the ' regular ' DHP, derived from conformer A, and completely photoreversible with light beyond 400 nm. The approximate spectrum of this product X is shown in Figure 7. The main peaks are at 572, 530, and 495 and at 382, 365, and 346 nm. Spectrum B in Figure 7 was obtained by assuming an experimental photoconversion $cis \longrightarrow \mathrm{X}$ of 33% and extrapolating accordingly. X was characterized by means of its photoreversion to *cis* with light beyond 400 nm. Fortunately, the *trans*-isomer, which is formed extensively (Figure 2F) concurrently with X, precipitates under these conditions,[24] so that after u.v. irradiation the solution contains mainly X and *cis*. No DHP derived from conformer A is formed below −40° (Figure 2F). The new form X is thermally unstable even at −140°, with a half-life of *ca.* 1 h, and disappears rapidly at *ca.* −120°. At these low temperatures no oxidation with molecular oxygen can be expected.

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[18] A. Bromberg, K. A. Muszkat, E. Fischer, and F. Klein, *J.C.S. Perkin II*, 1972, 588.

[19] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

[20] E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.

[21] K. A. Muszkat and Sh. Sharafi-Ozeri, *Chem. Phys. Letters*, 1973, **20**, 397.

[22] W. H. Laarhoven, T. Cuppen, and R. Nivard, *Rec. Trav. chim.*, 1968, **87**, 687.

[23] T. Berocovici, T. Wismonski-Knittel, and E. Fischer, *J.C.S. Chem. Comm.*, 1974, 716.

[24] E. Fischer, *J. Phys. Chem.*, 1973, **77**, 859.

Since it is imperative to dehydrogenate X in order to establish its identity, oxidation with atomic iodine was attempted by adding a small volume of concentrated iodine solution to a solution of X, and irradiating with light at 436 nm, where X does not absorb. Since iodine solutions in MCH turn translucent at −140°, this photoreaction could not be followed at −140°. However, after warming, the absorption spectrum provided clear evidence for the formation of dibenzo[*b,g*]phenanthrene, *i.e.* the expected oxidation product of the DHP derived from conformer B (Table 3). It follows that X is identical with this DHP.

Flash experiments at room temperature with light at various wavelengths [23] showed that the ratio between the quantities of the regular DHP and X formed from cis^* *via* X $\longleftarrow \mathit{cis}^* \longrightarrow$ DHP depends strongly on the wavelength of the photoactive light, with X being preferred at 334 nm and shorter wavelengths, and regular DHP at 366 nm. At −40°, when no regular DHP is formed by any irradiation, the preferred formation of X at shorter wavelengths expresses itself in higher yields than at longer wavelengths.

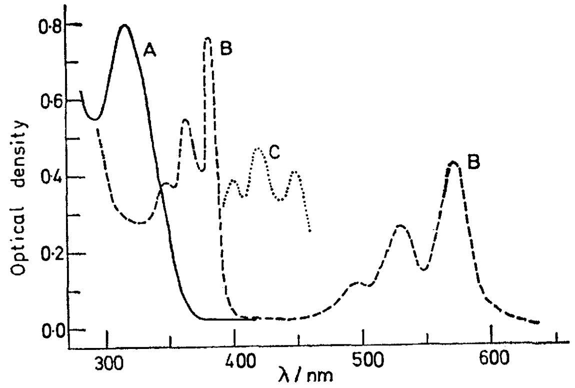

FIGURE 7 Low-temperature irradiation results for *cis*-2N-2N. A *ca.* 3×10^{-5}M solution in MCH–2-MP at −140° was irradiated at 303 + 313 nm and yielded a spectrum b (both spectra are not shown). This latter solution was irradiated at 546 + 578 nm and yielded spectrum A. Spectrum B was obtained by extrapolation from the difference 'b' − A, assuming that b is the spectrum of 2/3 A and 1/3 B. For comparison, the long wavelength part of the spectrum of the regular DHP is shown in curve C (*cf.* Figure 3C)

Wavelength Dependence of the Ratio [trans] : [*DHP*] *in* trans $\longleftarrow$ cis* $\longrightarrow$ *DHP*.—An inspection of the quantum yields $Q(\mathit{cis} \longrightarrow \mathrm{DHP})$ and $Q(\mathit{cis} \longrightarrow \mathit{trans})$ at room temperature for 1N-2N and 2N-2N (Figures 2E and F) shows that formation of *trans* is greatly preferred, by a factor of 10 or more. Nevertheless, the fact remains that considerable conversion into DHP can be attained,[9] *ca.* 30% for 2N-2N at 20°, and *ca.* 60% for 1N-2N at −160°. This inconsistency was resolved when the *initial* ratio [*trans*] : [DHP] was measured as a function of the wavelength of the light used for photoconversion. It is important to measure the initial ratio, because only in the early stages of the photoconversion '$\mathit{cis}^* \longrightarrow$ products' can one ignore the photochemical back reactions, $\mathit{trans}^* \longrightarrow \mathit{cis} \longleftarrow \mathrm{DHP}^*$. Optical cells of 8 cm light path were used with 2N-2N at 20° in order to observe small increases in the concentrations of DHP and *trans*. During experiments with 1N-2N at −160° use was made of the 0–0·1 optical density accessory of the Cary 14 spectrophotometer. Some typical results are presented in Table 4.

TABLE 4

The ratio [*trans*] : [DHP] as a function of exciting wavelength for solutions of 2N-2N and 1N-2N in MCH at room temperature, Ph-2N in MCH at −10°, and 1N-2N in MCH–2-MP at −160°. Solutions were saturated with either argon, air, or oxygen

Compound (*t*/°C)	Wavelength/nm	[*trans*]:[DHP]		
		Argon	Air	Oxygen
2N-2N (25)	366	1·4		0·8
2N-2N (25)	334	18		18
2N-2N (25)	313		38	
1N-2N (25)	366	1	1	
1N-2N (25)	334	4	4	
1N-2N (25)	313	4	7	
1N-2N (−160)	366	0·5		
1N-2N (−160)	334	3		
1N-2N (−160)	313	5		
Ph-2N (−10)	366	1·2		
Ph-2N (−10)	334	1·5		
Ph-2N (−10)	313	4·3		

For 2N-2N the wavelength effect is particularly pronounced, with the ratio [*trans*] : [DHP] increasing 13-fold when going from 366 to 334 nm in argon, and 22-fold in oxygen. In view of the proximity of these two wavelengths, and their position within the first absorption band of *cis*-2N-2N, it seems unlikely that excitation to different excited electronic levels, or different vibrational levels of the first excited electronic state, can cause the effect. At present the most reasonable explanation seems to be preferential light absorption by the various conformers. Steric factors make conformer A slightly less stable than the others and therefore their fraction in the dynamic conformer equilibrium should be smaller than that of the others. (The two-dimensional structural formulae greatly overemphasise [16] these steric repulsions which make A less stable than B and C. Nevertheless, it is interesting to note that in the crystalline state *cis*-2N-2N exists in the C form.[25]) During photoexcitation, a large fraction of the light is absorbed by those conformers B and C which do not undergo photocyclisation to DHPs which can be observed at room temperature with 'slow' techniques. This partly accounts for the low $Q(\mathit{cis} \longrightarrow \mathrm{DHP})$ values. The various conformers may be expected to have similar absorption spectra. However, this does not exclude possibly large differences in absorption at the long wavelength tail of the bands, and we suggest that such differences enable preferential light absorption by one of the conformers. Thus for *cis*-2N-2N at room temperature, we assume that 366 nm light is absorbed predominantly by conformer A, which undergoes $\mathit{cis}^* \longrightarrow \mathit{trans}$ and $\mathit{cis}^* \longrightarrow \mathrm{DHP}$ to about an equal extent. At 334, and even more so at 313 nm, light is absorbed predominantly by conformers B and C. To summarize, we propose the reactions (4)—(6).

$$\mathit{trans} \longleftarrow \mathrm{A}^* \longrightarrow (\mathrm{DHP})_{\mathrm{A}} \tag{4}$$

$$\mathit{trans} \longleftarrow \mathrm{B}^* \longrightarrow (\mathrm{DHP})_{\mathrm{B}} \tag{5}$$

$$\mathit{trans} \longleftarrow \mathrm{C}^* \not\longrightarrow (\mathrm{DHP})_{\mathrm{C}} \tag{6}$$

In principle, the conformer equilibrium may change during the lifetime of the excited state. However, two

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[25] Z. Shaked and D. Rabinovich, unpublished results.

considerations make this unlikely. First, a very short lifetime is indicated by the absence of fluorescence at room temperature, and secondly, the bond order of those essentially single bonds which are responsible for the existence of conformers in the ground state is much higher in the excited state.[26]

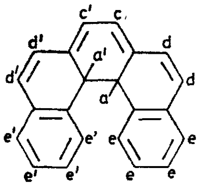
N.m.r. Spectra of DHPs.—Ever since the discovery of DHPs it seemed desirable to characterise 4a- and 4b-H by means of their n.m.r. signals. The major practical difficulties were due to the fact that photoconversion into DHP cannot in principle be complete, and that it is very difficult to separate the DHP from its parent *cis*-compound. However, for identification and assignment it is not at all essential to work with a pure DHP solution, and the criterion of photoreversal with visible light suffices to assign signals to the DHP. A more serious difficulty stems from the thermal decomposition and auto-oxidation of many DHPs. In this respect the DHPs derived from 2N-2N and 1N-1N are much better candidates for n.m.r. measurements, as described in previous paragraphs. The DHP from 2N-2N has the further advantage of lower sensitivity to stray visible light [low $Q(\text{DHP} \longrightarrow \textit{cis})$]. The only remaining technical difficulty derives from the pronounced drop of the yield of DHP at higher concentrations of the *cis*-compounds. The technique eventually applied for the preparation of samples was as follows. *cis*-2N-2N or 1N-1N (5 mg) dissolved in MCH (500 ml) were irradiated at room temperature until an optimal concentration of DHP was obtained. This solution, containing *cis*- and *trans*-ethylene derivatives, and DHP, was evaporated to dryness under argon at 0° and the residue dissolved in CS_2 or CCl_4. The n.m.r. spectrum of this solution, flushed with argon, was measured (Bruker 90 MHz) immediately, and also after irradiation *in situ* with visible light to reconvert the DHP into the *cis*-isomer. All signals disappearing as a result of visible irradiation were assigned to the respective DHP. Table 5 shows the results for the DHP from 2N-2N.

TABLE 5

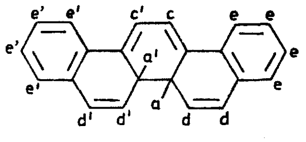
^{1}H N.m.r. signals of DHP derived from 2N-2N

δ *	Assignment
4·0 (2H, s)	a, a′
5·9 (2H, s)	c, c′
6·4 (4H, $J_{d,d'}$ 10 Hz)	d, d′
7·0 (8H, m)	e, e′

* For CS_2 solutions containing 1% hexamethyldisilane as standard.



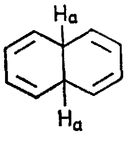
DHP from 2N-2N



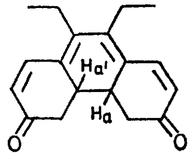
DHP from 1N-1N

The results for the DHP from 1N-1N were more difficult to obtain, and a c.a.t. had to be used. The suggested assignments are δ 3·3 (2H, a-, a′-H), 6·0 (2H, c-, c′-H) and 6·4 and 6·6 (4H, d-, d′-H). Signals due to e-H could not be identified.

The signals assigned to the a-H, at δ 3·3 and 4·0 in the two cases, may be compared, for lack of more suitable examples, to those assigned to the bridgehead protons in 4a,8a-dihydronaphthalene (III)[27] (δ 2·8 and 3·25 for the *trans*- and *cis*-isomers, respectively) and to a-H in the phenanthrenedione derivative (IV)[28] (δ 2·3). The upfield shift of the a-H signal in the 1N-1N derivative, compared with that for the DHP from 2N-2N, may be due to the diamagnetic shielding by the neighbouring aromatic rings.



(III)



(IV)

DISCUSSION

Regarding the mechanisms of the reactions described here, we wrote[3a] previously, ' The photochemical ring-formation and ring-opening reactions are probably reactions of the first excited singlet level of the reacting molecules and do not involve triplet states.' Essentially the conclusion that photocyclisation is a concerted process taking place in the singlet-excited state remains unchallenged, though a DHP-like precursor Y may be involved in some cases.[23] Involvement of singlet-excited product molecules during photocyclisation, $\textit{cis}^* \longrightarrow \text{DHP}^* \longrightarrow \text{DHP}$, is energetically feasible in the simpler stilbene derivatives described earlier, but not in the dinaphthyl derivatives.[16] No evidence for such involvement has been found so far. The reverse reaction, involvement of singlet-excited *cis*-isomers, $\text{DHP}^* \longrightarrow \textit{cis}^* \longrightarrow \textit{cis}$, is ruled out by the observation that no *trans*-compound is formed during photodecomposition of DHPs.

The photocyclisation behaviour of the *cis*-2-naphthyl derivatives is strongly affected by the existence of several conformers with similar energies. The existence of a second, hitherto unknown DHP derived from conformer B of *cis*-2N-2N was proven, and shows that the so-called reactivity indices governing photocyclisations have a more limited validity than expected. The pronounced wavelength variation of the quantum yields of formation of the two DHPs in this case can be ascribed to differences in absorption spectra. The small degree of photocyclisation of $\textit{cis}\text{-(2N-2N)}_A$ to the corresponding $(\text{DHP})_A$ and its strong attenuation on cooling may well be due in part to the conformer equilibrium $A \rightleftharpoons B \rightleftharpoons C$ and its variation with temperature (see Results section).

As regards $\textit{cis} \rightleftharpoons \textit{trans}$ photoconversions, the controversy[29,30] regarding triplet involvement in direct stilbene isomerisation probably applies here too, except

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[26] A. Bromberg and K. A. Muszkat, *Tetrahedron*, 1972, **28**, 1265.

[27] E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, 1967, **89**, 151.

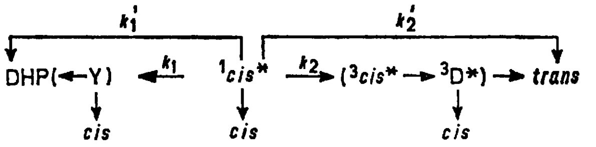
[28] T. D. Doyle, N. Filipescu, W. R. Benson, and D. Banes, *J. Amer. Chem. Soc.*, 1970, **92**, 6371.

[29] E. Fischer, *Mol. Photochem.*, 1973, **5**, 227.

[30] J. Saltiel, *Mol. Photochem.*, 1973, **5**, 231.

that in all naphthyl derivatives, as distinct from stilbene, fluorescence is the main deactivation path of the singlet-excited *trans*-isomer. The pronounced enhancement of *trans* ⟶ *cis* photoconversion by oxygen [14,15] and by solvents containing heavy atoms [15] is reasonably explained by oxygen- or heavy-atom-enhanced intersystem crossing. Moreover, photosensitised *cis* ⇌ *trans* isomerisation has been reported [6] for Ph-2N, and observed by us in several other cases, so the least one can say is that triplets *may* be involved.

In view of the available evidence, the fate of the excited *cis*-molecules may thus be described by Scheme 2.



SCHEME 2

Here $^3cis^*$ denotes triplet *cis*, and ^{3}D* represents the distorted triplet ethylene from which both *cis*- and *trans*-products are formed. Both Y and triplet *cis* may function as transients in only some of the photoconversions described. The ratio of the rates k_1 and k_2 is a function of the compound, the conformer distribution, the temperature, and possibly the solvent and the viscosity. (The last two points have not been investigated in detail as yet.)

The pronounced temperature dependence of *Q*(*trans* ⟶ *cis*), as distinct from *Q*(*cis* ⟶ *trans*), in stilbene and some of its derivative has been described in detail earlier.[1,3c,d] It was explained as indicating the existence of energy barriers between electronic excited states of reactants and products, or between such states of the reactant and the ground-state products.[3c] The present results with naphthyl derivatives are basically similar, though more complex, and critical increments of up to 10 kcal mol^{-1} are observed. The situation regarding the fate of excited *cis* and DHP molecules is somewhat similar: the cyclisation yields drop sharply on cooling in all cases, while the yields of ring-opened products are either not affected at all by cooling, or else drop only at rather low temperatures. Again 2N-2N is an extreme example, in particular its DHP, and will therefore be treated separately in more detail.[16] Critical increments of up to 10 kcal mol^{-1} were observed, and indicate the existence of energy barriers on the path leading from excited *cis* or DHP to the respective product. A deeper understanding of the situation necessitates a detailed knowledge of the potential energy as a function of the distance between the two carbon atoms between which a bond is either formed or broken, and of course of other molecular parameters which change at the same time. No such potential curves are as yet available, and one can only deduce from the observations that energy barriers are indeed situated somewhere along these curves.

EXPERIMENTAL

Low and High Temperature Photochemical and Spectrophotometric Techniques.—These were essentially as described,[3c] except that our copper block technique [31] was used throughout in absorption, emission, and flash photolytic measurements. Quantum yields of photoreversible reactions were estimated from initial concentration changes, because the accurate method [32] based on attainment of photostationary states could not be applied in most cases. The reasons are (a) irreversible photoreactions also take place, with efficiencies not small enough to be ignored, and (b) the existence of three, instead of the usual two, components in the photoreversible system, *trans* ⇌ *cis* ⇌ DHP. Fluorescence yields were determined by comparison with standards taken from Berlman's compilation.[33] The DHP fluorescence was compared with that of fluorescein.[34] Whenever possible, a medium pressure 125 W mercury arc (Mazda) was used, since high-pressure mercury arcs have a much higher background continuum, and monochromaticity is more difficult to attain. Also, high light intensities tend to cause local heating in the immediate vicinity of the absorbing molecules, irrespective of the temperature measured macroscopically in the solution.[35]

Materials.—*trans*-1N-1N was a commercial sample (Columbia Organic Chemicals). All the other *trans*-naphthylethylenes, as well as cis-1N-2N, *cis*-2N-2N, and *cis*-Ph-1N, were synthesised according to literature methods. Small quantities of all *cis*-isomers were prepared by u.v. irradiation of the *trans*-isomers, followed by separation *via* t.l.c. Solvents [MCH (spectrograde) and 2-MP] were freed from traces of water and aromatic impurities by passage through Woelm basic alumina columns. Solutions in the cells were flushed continuously with either argon containing <5 p.p.m. oxygen, or with the desired nitrogen–oxygen mixture. At temperatures below 0° no solvent was lost by evaporation. At higher temperatures the gas was first saturated with solvent vapour to prevent such losses. On reaching temperatures where the viscosity is high, the gas was passed above, instead of through, the solutions. Nitrogen–oxygen mixtures were prepared by introducing the two gases into empty commercial gas cylinders at the required pressures.

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