PHOTOISOMERIZATION AND PHOTOCYCLIZATION OF STYRYLPHENANTHRENES, AS COMPARED WITH DINAPHTHYLETHYLENES, YIELDING IDENTICAL PHOTO-OXIDATION PRODUCTS[†]

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Summary

The trans → cis photointerconversion, the absorption and emission spectra of both isomers and the photocyclization of 1-, 2- and 3-styryl-phenanthrene were studied at temperatures from 90 to −170 °C. The trans → cis and the cis → 4a,4b-dihydrophenanthrene (DHP) photoconversions take place down to −170 °C, unlike with the dinaphthylethylenes, yielding identical photocyclodehydrogenation products. The DHPs derived from the styrylphenanthrenes are thermally much less stable than those derived from dinaphthylethylenes, probably because of their higher energy content. The respective absorption spectra are also quite different, and so is the variation, with the temperature, in the quantum yields of the photointer-conversions cis ⇌ DHP.

1. Introduction

In a series of papers [2 - 4] the Rehovot group has described the photoisomerization and photocyclization of diarylethylenes Ar—CH=CH—Ar′ (with the aryl groups being phenyl, naphthyl, phenanthryl and benzophenanthryl) for a wide range of temperatures, solvents and viscosities, while the Nijmegen group has reported on the synthetic usefulness of photocyclodehydrogenation of these compounds at ambient temperature (for a review, see ref. 5).

Of particular interest were the photocyclization reactions of the cis isomers to derivatives of 4a,4b-dihydrophenanthrene (DHP) [6]. These labile compounds are unobtainable by other methods, and revert both


[†]For a preliminary report of parts of this investigation see ref. 1.

thermally and photochemically to the corresponding cis compounds. They also undergo facile dehydrogenation with iodine and other oxidants to derivatives of phenanthrene (P). In one case only have we so far observed [3, 7] both a spontaneous and a photoinduced intramolecular hydrogen shift in a DHP (Scheme 1): (1 + 4) → "DHP" → $6a,16d$-dihydrohexahelicene (DHH).

cis   DHP   P   BP

"1+4"   DHP -[6]   6a, 16d - DHH
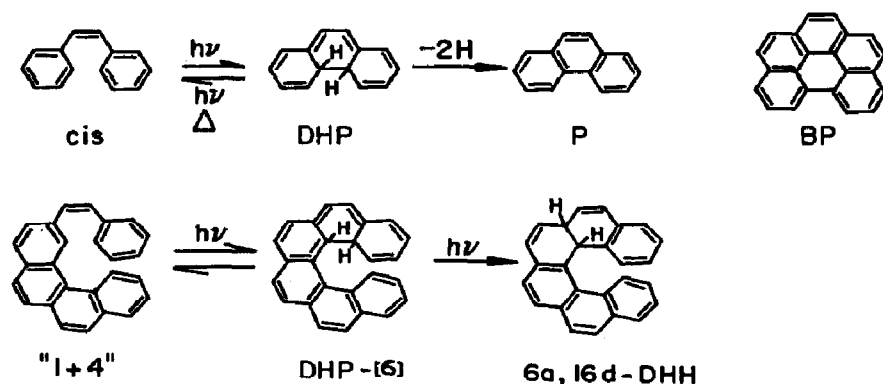
Scheme 1.

The major aim of the present investigation is to compare the DHPs derived from the dinaphthylethylenes [2] with those derivable, in principle, from the 1-, 2- and 3-styrylphenanthrenes 1 - 3 (Scheme 2). As shown in Fig. 1, each of the three cis-styrylphenanthrenes B_1 - B_3 should yield a DHP (D_1 - D_3) which is isoskeletal with a DHP (C_1 - C_3) derived from one of the dinaphthylethylenes A_1 - A_3 and is dehydrogenated to a common dibenzo-phenanthrene (P_1 - P_3) (picene, P_1; benzo[a]chrysene, P_2; pentahelicene, P_3). The DHPs C_1 - C_3 have been investigated previously [2], while for the styrylphenanthrenes only the photocyclodehydrogenation products have been isolated [5]. One may infer from their existence that D_1 - D_3 serve as
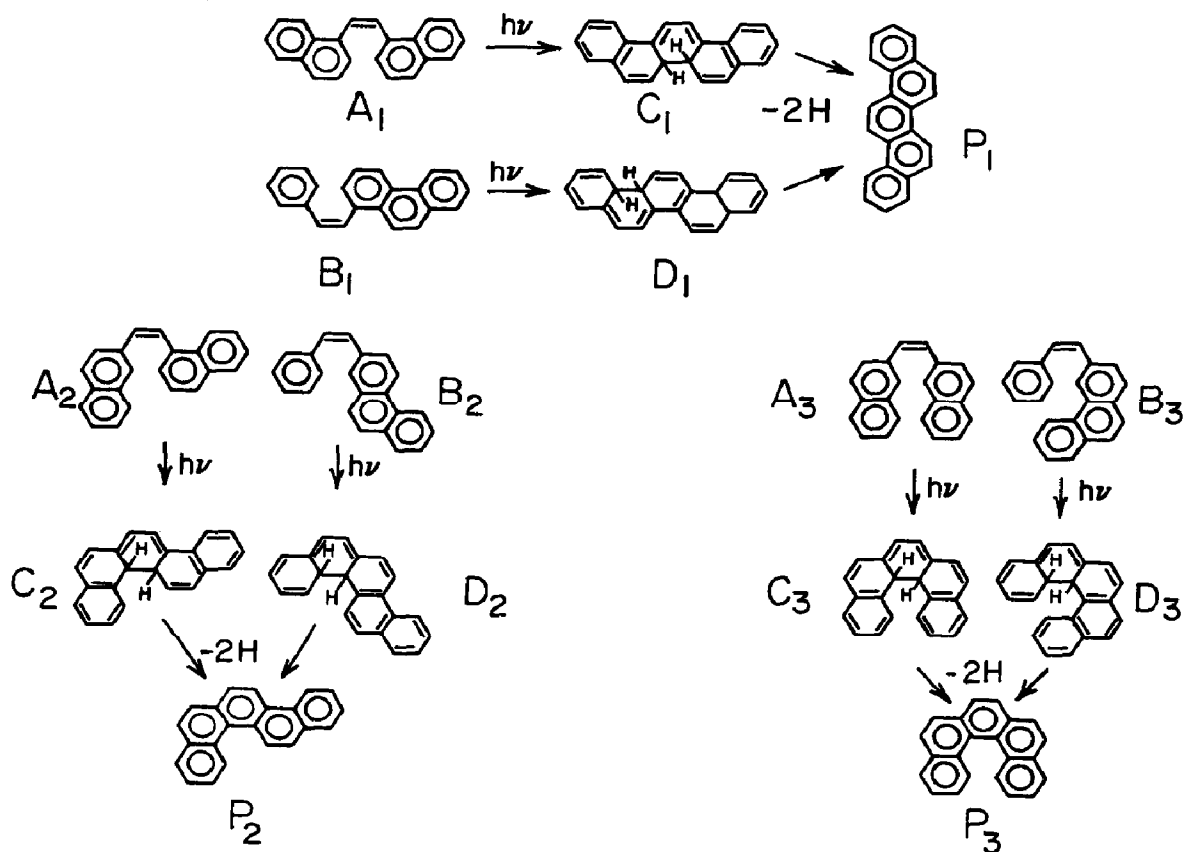

A

B

1   2   3
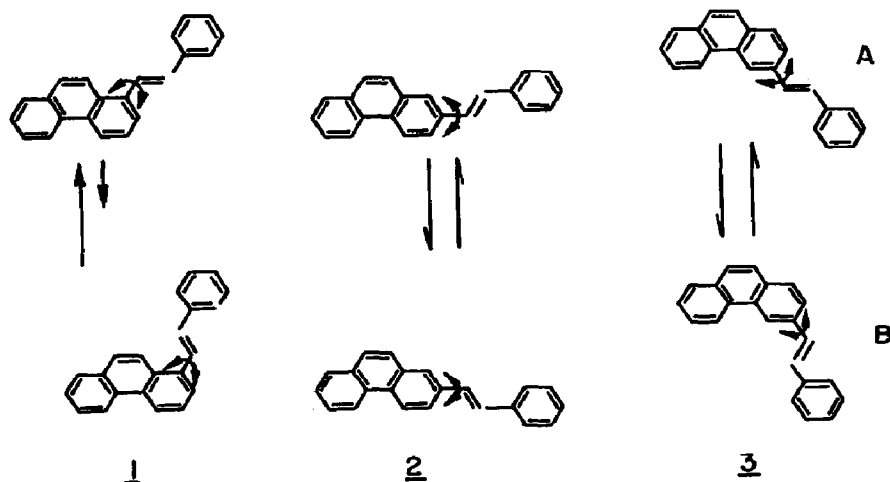
Scheme 2.

Fig. 1. Cyclizations of the Z isomers of the dinaphthylethylenes A_1, A_2 and A_3 and of the Z isomers of the styrylphenanthrenes B_1, B_2 and B_3, into the same end products P_1, P_2 and P_3.

intermediates in the primary photocyclization reaction. In each of the three pairs C_1–D_1, C_2–D_2 and C_3–D_3 the DHPs are isoskeletal, differing in the position of the two aliphatic carbons. We have now prepared D_1 - D_3 and can thus compare their properties with those of C_1 - C_3. As in our earlier studies, we have also investigated the trans $\rightleftharpoons$ cis photointerconversion of 1 - 3 and their emission properties and we have looked for possible hydrogen shifts in the primary photoproducts D_1 - D_3.

2. Results

2.1. General results

All solutions were (2×10^{-6}) - 10^{-5} M in argon-flushed 2:1 mixtures of methylcyclohexane (MCH) and 2- or 3-methylpentane (2-MP or 3-MP), unless stated otherwise. Since our main purpose was a comparison between primary photocyclization products, we did not determine absolute quantum

yields of photoisomerization, photocyclization and fluorescence, as we did in previous work [2, 4].

The three styrylphenanthrenes were synthesized by Wittig reactions upon bromination of the corresponding methylphenanthrenes. To avoid the formation of isomeric compounds, the synthesis of 2-methylphenanthrene was achieved by the photocyclization of 1-bromo-2-methylstilbene. Details are given in Section 4 (Scheme 5).

2.2. Cis—trans isomers and isomerization

cis-B_1 and cis-B_2 were isolated, but in most experiments with cis isomers we started with a trans solution, this being converted to at least 90% cis by irradiation at 366 nm, just as observed for the naphthyl compounds A_1 - A_3. Irradiation, in the visible region, of cis solutions containing molecular iodine results in complete reversion to the trans isomers, caused by the atomic iodine that is produced. The absorption spectra of the three pairs of trans and cis isomers are shown in Fig. 2. The small peak at around 370 nm characterizes the trans isomers, and this is more prominent at low temperatures. Unlike our observations for naphthyl compounds, e.g. A_1 - A_3, the quantum
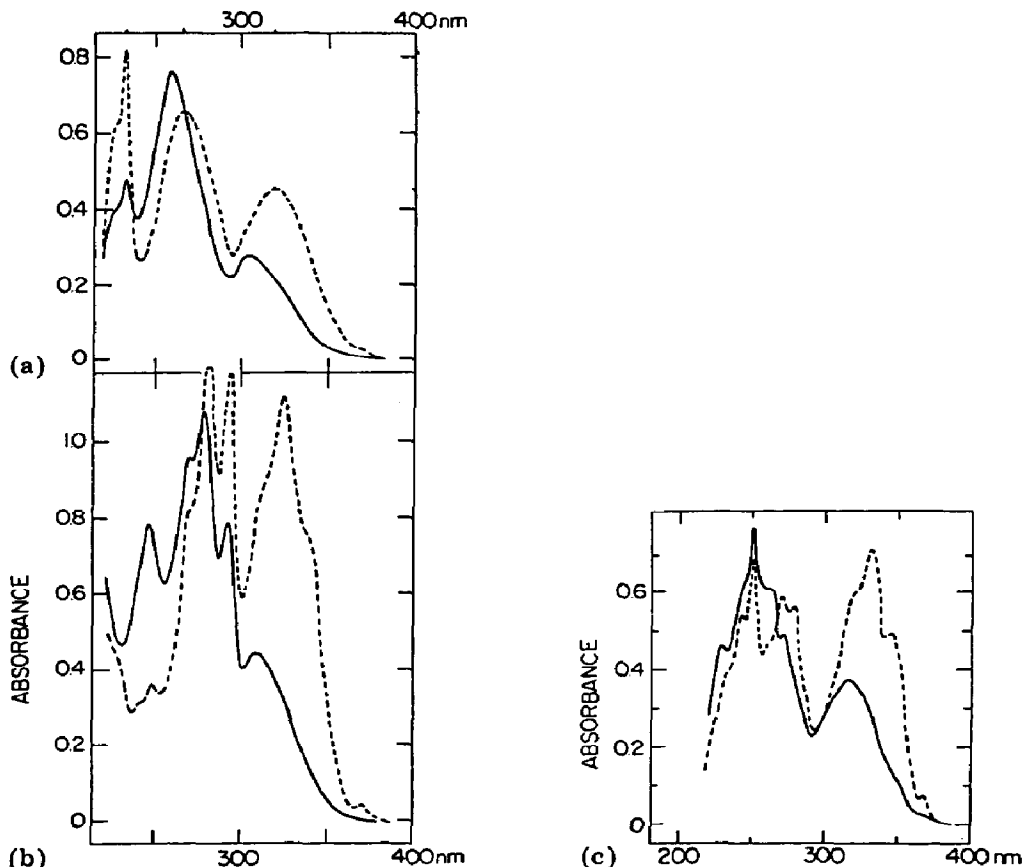

Fig. 2. Absorption spectra of the trans (broken lines) and about 90% cis isomers (full lines) of B_1 - B_3 in MCH: (a) B_1 at 20 °C; (b) B_2 at 25 °C; (c) B_3 at 25 °C.

yields of trans → cis photoconversions are little affected by cooling the system down to −170 °C. Irradiation at 313 nm, at which both isomers absorb, creates a photostationary trans–cis mixture, in addition to the photocyclization products described below. Representative spectral data for *trans-* and *cis*-3 at −120 °C are as follows. Trans peaks are at 367, 350, 335, 319, 280, 270, 249 and 241 nm, cis peaks are at 318, 264, 250 and 226 nm and isosbestic points are at 313 and 269 nm. For 2, 313 nm irradiation rapidly creates a photostationary cis–trans mixture, which is then gradually converted into D_2 (see below). Irradiation of D_2 with visible light converts it into the cis isomer (*i.e.* B_2), so that the overall result of irradiation of trans isomers with UV and visible light is extensive conversion into cis isomers.

2.3. Photocyclodehydrogenation

At ambient temperature, UV irradiation of solutions of 1 - 3 in the presence of iodine leads to the formation of polynuclear products, as reported previously [5]. In all three cases, P_1 - P_3 shown in Fig. 1 are practically the sole final products. Special attention was given to the possible formation of 5-phenylacephenanthrylene from B_1 (Scheme 3); this might be expected theoretically, and indeed this compound was observed as a product of the irradiation of 1-(9-phenanthryl)-1-phenylethylene [8]. The absence of the characteristic peaks of 5-phenylacephenanthrylene in the UV and nuclear magnetic resonance (NMR) spectra demonstrated that this compound was not present.

Also, the possible formation of dibenzo[*a,j*]anthracene from B_2 (Scheme 3) was carefully examined, because of contradictory reports in the literature. (On irradiation of *m*-distyrylbenzene P_2 was observed and no dibenzo[*a, j*]anthracene (DBA) [9, 10], while Morgan [11] reported the formation of the latter compound from *m*-distyrylbenzene. Irradiation of 3-styrylphenanthrene did not give a DBA as a photoproduct [12], whereas on photocyclodehydrogenation of 3-(*p*-methylstyryl)-phenanthrene 1% of methyldibenzo[*a, h*]anthracene could be isolated in addition to the main product, methylbenzochrysene [13].) However, when formed it was only present in much less than 0.5% yield. From B_3, the primarily formed pentahelicene (P_3) is further photocyclodehydrogenated, in the presence of iodine, to benzoperylene (BP) (see below for a discussion of its low temperature behaviour). In the absence of iodine, with oxygen as the sole oxidant, the formation of P_1 - P_3 is observed to be slow. For B_3, unlike the situation encountered in the presence of iodine, photodehydrogenation stops at P_3, and no BP is formed. However, parallel to the appearance of P_3, we observed the formation of a new product X, its UV spectrum differing from that of P_3 or BP (Fig. 3) and characterized by sharp absorption peaks at 285 nm and 297 nm (room temperature). X is formed down to −100 °C. High resolution ^{1}H NMR measurements indicate the presence of methine protons at 3.4 ppm and 4.6 ppm and vinyl protons at 6 - 7 ppm, the methine protons being mutually coupled ($J = 18$ Hz). The methine
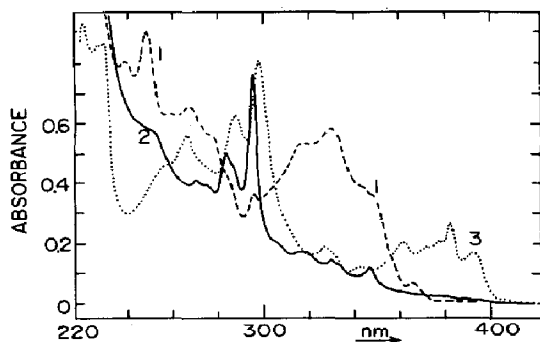
302

B 1   5-phenyl phenanthrylene

B 2   dibenzo [a,j] anthracene

B 3   DHPH
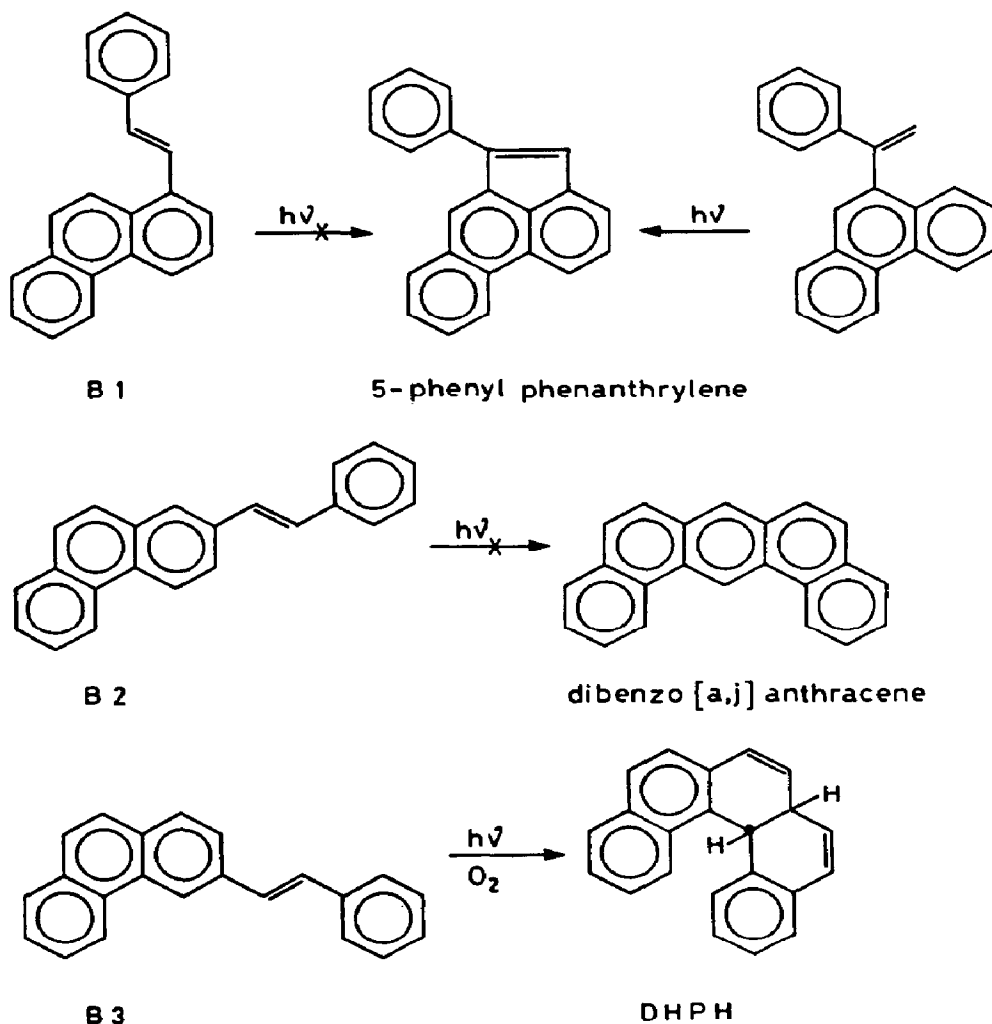
Scheme 3.

Fig. 3. Photoproducts of B$_3$ at -20 °C: curve 1, solution of *cis-3—trans-3* (photostationary state at 313 nm); curve 3, same solution after complete photocyclodehydrogenation with iodine (313 nm irradiation to completion in the presence of iodine, followed by removal of iodine; this is almost pure BP); curve 2, solution of B$_3$ after irradiation at 313 nm in the presence of oxygen (this curve represents a mixture of P$_3$ and the new product DHPH).

proton at higher field was also coupled with four vinyl protons with equal coupling constants (J = 2.5 Hz), thus forming double quintets. The pattern is very similar to that observed in the spectrum of 6a,16d-DHH, the product of the 1,5-hydrogen shift following the primary photocyclization in compound (1 + 4), mentioned in Section 1 (Scheme 1). In the latter case the low field methine proton absorbs at 5.3 ppm owing to the larger deshielding by the opposite rings. We therefore suppose X to be 6a,14c-dihydropentahelicene (2a,10c-dihydrodibenzo[c,g]phenanthrene) (DHPH) (Scheme 3). This supposed structure was affirmed by the very similar behaviour of the two compounds. Compound X decomposes slowly on standing in solution or during chromatography to give P_3. DHPH could not be detected when the irradiation was carried out in methanol as the solvent. Contrary, however, to the formation of 6a,16d-DHH, DHPH is only formed in the presence of oxygen; this is a unique case so far. The following scheme summarizes the results:
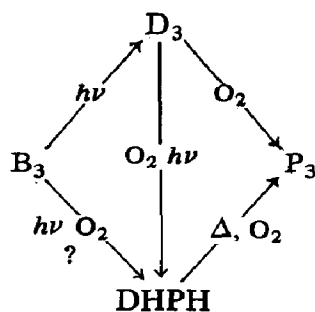
Attempts to observe the formation of a DHPH from A_3, by several methods, were not successful.

2.4. Emission spectra

All three trans compounds fluoresce even at room temperature with yields estimated to be above 0.1, and the fluorescence increases as the temperature is lowered. The emission spectra sharpen on cooling, as do the absorption spectra. The emission spectra of 2 and 3 vary with the excitation wavelength ("rotamer effect") as reported for many diarylethylenes derived from 2-styrylnaphthalene [14 - 16]. The effect is more pronounced at lower temperatures (sharper spectra allow better photoselection) and for trans-3. The following two sets of emission peaks, presumably characterizing the two rotamers 3A and 3B (Scheme 2), were observed at −170 °C: A — 369, 392.5 and 415 nm; B — 375, 400 and 423 nm. No rotamer effect was found for trans-1, as has already been reported for 1-styrylnaphthalene [14]. However, at very high viscosities a viscosity-dependent variation of emission spectra with excitation wavelength was observed as described recently [17]. In order to check for possible emission of the cis isomers, we employed our usual method for mixtures of weakly emitting cis isomers and small unavoidable quantities of the respective strongly emitting trans isomers [18]. Making use of the fact that at long excitation wavelengths trans

absorbs much more than cis while at short excitation wavelengths both isomers absorb to a similar extent (Fig. 2), we compare emission spectra excited at both wavelengths, *e.g.* 370 nm and 300 - 320 nm. As long as the emission is due only to the trans isomers, the spectra excited at the two wavelengths are identical. As the temperature is lowered and the viscosity increases, true cis emission builds up, and the two emission spectra start to differ, to a degree depending on the relative fluorescence quantum yields of the isomers. In cases where the trans isomers can assume almost coplanar configurations, the spectra of the isomers differ considerably [18], and the spectrum of the pure cis isomer can be estimated by subtraction. For all three cis isomers the quantum yields of fluorescence are very low, and one has to cool the solutions to $-180\,°C$ to obtain reasonable cis spectra. For *cis*-2 even this temperature seems to be too high. The emission of *cis*-1 and *cis*-3 consists of broad bands centred at about 430 nm, with estimated quantum yields of less than 0.01 even at $-180\,°C$.

### 2.5. Photocyclization to coloured 4a,4b-dihydrophenanthrene derivatives

All three cis isomers $B_1 - B_3$ form coloured products on irradiation at 313 nm (Fig. 4), which are decomposed by visible irradiation as well as thermally and undergo oxidation with iodine even at $-50\,°C$. Since the detailed behaviour is different for each of the three compounds, they will be described separately.
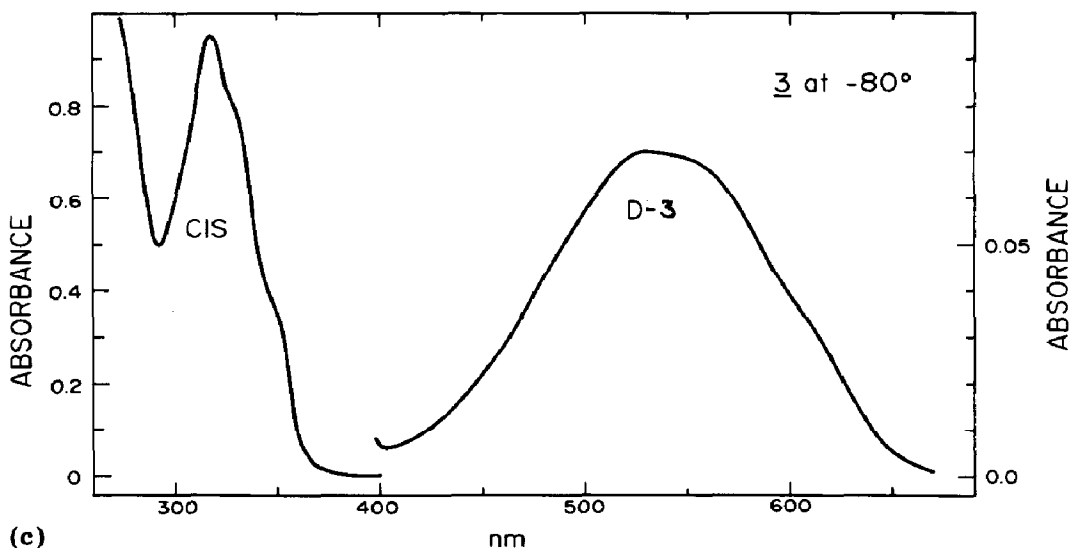
2.5.1. 2-Styrylphenanthrene (2)

This is the least complicated case. At all temperatures down to $-170\,°C$, irradiation at 366 nm or at 313 nm results in rapid trans–cis photoequilibration, followed by formation of a coloured product (Fig. 4(b)), with peaks at 470 nm, 445 nm and 420 nm and a half-life of about 0.5 h at room

(a)
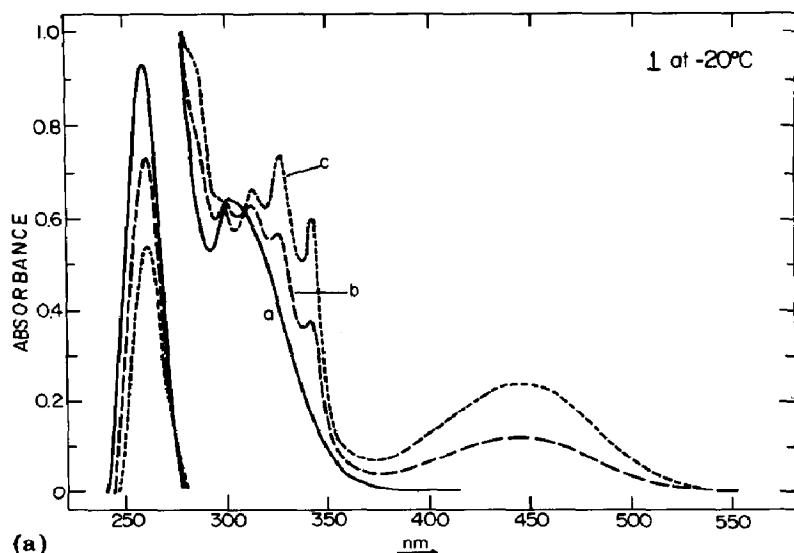
Fig. 4 *(continued)*.
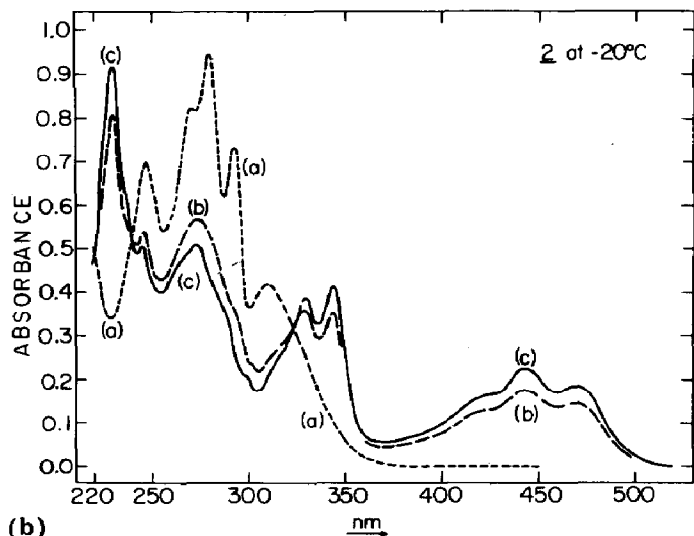
Fig. 4. Absorption spectra of B_1 - B_3 and their coloured photocyclization products D_1 - D_3. (a) and (b): curves a, cis isomers before irradiation; curves b, photostationary state attained by irradiation at 313 nm, representing a mixture of cis and D_1 or D_2; curves c, extrapolated spectra of pure D_1 or D_2, assuming 50% conversion into D_1 and 80% conversion into D_2 in curves b. (c): curve CIS, B_3; curve D-3, photostationary state attained by 313 nm irradiation. The extent of conversion into D_3 is estimated to be less than 10% and therefore no attempt was made to determine the pure D_3 spectrum by extrapolation.

temperature. Facile decolouration takes place with visible light. When a solution of *trans*-2 is irradiated at, say, −160 °C for a prolonged period, and the coloured product is erased with visible light, the resulting solution contains about 95% *cis*-2 and 5% *trans*-2. Oxidation of the coloured product with iodine yields a spectrum identical with that of P_2. We conclude that

the coloured product is D_2. This reaction was used to estimate the extent of the photoconversion cis-2 → D_2 and thereby the absorption spectrum of pure D_2, as follows. An argon-flushed solution of cis-2 (Fig. 4(b), curve a) was irradiated at −120 °C with 313 nm light "to completion", warmed to −20 °C (Fig. 4(b), curve b), dehydrogenated with iodine which was then removed by copper foil, and the solution was recooled to −120 °C. Its spectrum will be denoted "A". Iodine was then added again and the solution was irradiated to completion at 313 nm and −20 °C to achieve *complete* photocyclodehydrogenation. The iodine was removed and the spectrum was taken at −120 °C (spectrum "B"). (DHP is formed more extensively at −120 °C, but iodine can be added, and the latter reacts best with D_2 at −20 °C.) Comparison of spectra "A" and "B" showed that the substance yielding spectrum "A" contains about 80% of the product described by spectrum "B", *i.e.* P_2. Accordingly, Fig. 4(b), curve b, describes a mixture of 80% D_2 and 20% B_2 (ignoring traces of *trans*-2). Extrapolation to 100% conversion yields Fig. 4(b), curve c, for the estimated pure D_2. The estimated extinction coefficient of D_2 at the double peak in the region 330 - 340 nm is seen to be about equal to that of the starting cis isomer B_2, at 310 nm. In Table 1 we compare the properties of all three DHPs derived from A_1 - A_3 with those derived from B_1 - B_3.

TABLE 1

Comparison of properties of DHPs (C_1 - C_3) derived from dinaphthylethylenes and those (D_1 - D_3) derived from styrylphenanthrenes

	C_1	D_1	C_2	D_2	C_3	D_3
λ_{max} (nm)	305, 410	310 - 350, 445	300, 305, 400	330, 340, 420 - 470	300 - 310, 410	?, 530
$\tau_{1/2}$	12 d	320 min	3 d	30 min	10 d	0.1 min
E_a (kcal mol^{-1})	15	10(18)	18.5	(20)	27	12 - 15.5
F	—	+	—	+	—	+
E	—	+	—	+	—	+

λ_{max}, longest absorption bands; $\tau_{1/2}$, half-life of spontaneous disappearance at room temperature in argon-flushed solutions; E_a, activation energy calculated from Arrhenius curves for spontaneous disappearance (values in parentheses were obtained by flash photolysis); F, photoformation at −120 °C; E, photoerasure at −120 °C.

2.5.2. 1-Styrylphenanthrene (1)

Irradiation of solutions of cis-1 (B_1) at 366 nm does not cause colouration, but at shorter wavelengths (313 nm and 303 nm) a strongly coloured product is formed, as shown in Fig. 4(a), curve b. Addition of iodine rapidly dehydrogenates this product to picene (P_1) and we therefore assign to it the structure D_1. D_1 reverts to B_1 by irradiation at 366 nm and in the visible

region. As described above, UV irradiation of B_1 in the presence of iodine converts it completely into P_1. By employing a method similar to that described for 2 in Section 2.5.1, the extent of photoconversion of 1 into D_1 was estimated, and the absorption curve of pure D_1 was obtained by extrapolation (Fig. 4(a), curve c). D_1 is almost stable at room temperature in an argon atmosphere, having a half-life of 320 min at 30 °C. There is no evidence for the existence of more than one coloured product. The shape of the spectrum in the visible and near UV does not change during progressive formation or erasure of the coloured product, nor during its spontaneous thermal disappearance. The thermal decay of D_1 was measured by static methods in the range 20 - 40 °C, under argon, and by flash photolysis in decalin solutions in the range 80 - 140 °C. In the static experiments the decay was first order, while in the flash experiments an initial fast decay of about 10% of the total D_1 was followed by a first-order decay. An Arrhenius plot of the results gives a rather wide spread about a straight line, with activation energies of 10 ± 2 kcal mol^{-1} for the static experiments and 18 ± 2 kcal mol^{-1} for the flash experiments. While the photoerasure of D_1 leads to the starting compound B_1, this no longer holds for the products of *thermal* decay which include, besides B_1, either P_1 or a spectrally similar product, with absorption peaks at 320, 309, 300, 280, 271 and 253 nm. This was confirmed in a cumulative experiment in which D_1 was formed and then left to decay at room temperature four times in succession. The same results were obtained with argon-flushed decalin solutions at 100 °C in the flash photolysis apparatus. The product is not affected by iodine, even with irradiation in the visible to create atomic iodine. Possible explanations are dehydrogenation by unknown oxidants, spontaneous splitting-off of hydrogen, or hydrogen shifts in D_1 to form products which are spectrally similar to P_1. D_1 is slowly oxidized by molecular oxygen in a temperature-dependent reaction, with a half-life of 25 min at 5 °C, the activation energy being 5 kcal mol^{-1} for temperatures from 5 to -40 °C. The large discrepancy between the activation energies for D_1 disappearance under argon observed at low and high temperatures and the deviations of the Arrhenius plots from linearity are probably connected with the type of products formed during the spontaneous decomposition of D_1. The properties of D_1 and C_1 are compared in Table 1.

2.5.3. 3-Styrylphenanthrene (3)

At -50 °C and below, down to -170 °C, 313 nm irradiation results in the formation of a coloured product (curve D-3 in Fig. 4(c)) but to a very slight extent. Thus with a solution of B_3 having an absorbance of 3 at the 318 nm peak, the absorbance of the product at 530 nm was only 0.04. Assuming $\epsilon = 5 \times 10^4$ mm^2 mol^{-1} for B_3 and $\epsilon = 10^4$ mm^2 mol^{-1} for D_3 (in rough analogy with other DHPs), this means about 7% conversion into DHP in the photostationary state. The coloured product is erasable with visible light and also disappears on reacting with iodine. However, in view of the very low conversion, we could not prove directly that P_3 is the product

of this reaction. For the same reason, we could not apply the method of oxidation, used for 1 and 2, to estimate the extent of the photoconversion $B_3 \rightarrow D_3$. The fact that P_3 and its photocyclodehydrogenation product BP are the sole products of UV irradiation in the presence of iodine thus constitutes the only, albeit indirect, justification for assigning structure D_3 to the coloured photoproduct of B_3. Above $-30\,°C$, D_3 is too unstable thermally (probably reverting to B_3) to allow its detection by static methods. Flash photolysis was therefore applied in the temperature range up to $90\,°C$. The transient observed (in 70 mm cells, because of the low extent of photoconversion) had a spectrum identical with that shown in Fig. 4(c). D_3 is thus the sole primary coloured photoproduct (on the 10 μs scale) in the temperature range $-170 - 90\,°C$. The rate of D_3 decay in the flash experiments was a function of the intensity of the measuring light, down to fairly low intensities. This is due to photoerasure of D_3 by the measuring light, which has to be avoided by employing a sufficiently weak and monochromatic analysing light beam. The kinetics of D_3 thermal disappearance was followed both by flash photolysis ($10 - 90\,°C$) and in the Cary spectrophotometer (from -50 to $-28\,°C$). In the latter the kinetics was first order, except for a tiny initial fast step. The Arrhenius plot yields an activation energy of about 12 ± 2 kcal mol^{-1}. In the flash experiments a first fast stage definitely exists. The Arrhenius plot of the main stage leads to an activation energy of 15.5 ± 2 kcal mol^{-1}. Typical half-lives for D_3 disappearance were 0.023 s at $84\,°C$ and 1.2 s at $30\,°C$. The decay kinetics in the flash experiments were measured at 490, 530 and 570 nm, in the hope of finding evidence for the existence of more than one coloured photoproduct, differing in their absorption spectra and decay kinetics. Within the rather large experimental uncertainty (even in 70 mm cells the absorbance of the transient was only 0.05 at the 530 nm peak!) no such evidence was provided by the results. However, the fast initial stage of DHP decay indicates the possible existence of a short-lived precursor of D_3, which is difficult to catch because of the experimental limitations. The properties of C_3 and D_3 are compared in Table 1.

2.6. Comparison of pairs of dihydrophenanthrenes which are dehydrogenated to the same dibenzophenanthrenes

The most prominent differences concern the absorption spectra, the conditions of photoformation and photoerasure of the DHPs, their rate of thermal decomposition and their activation energy of thermal decomposition. Compounds $C_1 - C_3$ have been described previously [2] and their properties are compared in Table 1 with those of $D_1 - D_3$ reported in this paper. The major differences are as follows.

(a) Both the visible and the long UV peaks of $D_1 - D_3$ are shifted to longer wavelengths by 35 - 110 nm.

(b) The thermal decay of $D_1 - D_3$ is much faster.

(c) The photocyclization $B \rightarrow D$ takes place down to $-170\,°C$, while $A \rightarrow C$ is strongly attenuated on cooling even to, say, $-50\,°C$.

(d) The same holds for photoerasure D → B as against C → A.

(e) The activation energy E_a for the thermal decomposition of D_3 is much lower than that of C_3. Regarding the two other cases there is no such regularity.

(f) Thermal decomposition of C_1 - C_3 yields A_1 - A_3 in a clean first-order reaction, while that of D_1 and D_2 seems to be complex. (The products of D_3 decomposition are not amenable to analysis because of the very low photoconversion into D_3.)


3. Discussion

3.1. Photoisomerization and iodine-catalysed cis ⇌ trans isomerization

On the whole, UV irradiation results in the establishment of photostationary states whose composition varies with the wavelength of irradiation according to the relative absorption of the two isomers, modified by the parallel cis → DHP photocyclization. Unlike the naphthyl and dinaphthyl analogues of stilbene [2], but similarly to phenanthryl and benzophenanthryl analogues [4], the trans → cis photoconversion yield does not drop on cooling down the system to at least −160 °C in MCH–2-MP mixtures. Thus the energy barriers on the path from singlet-excited trans to final cis, which we encountered with stilbene and many of its derivatives, whether or not involving the triplet manifold, are too low in the present case to make themselves felt.

Atomic iodine is an excellent catalyst for the establishment of the cis–trans equilibrium and it has been used extensively by us [2, 19] for this purpose. However, this holds only for those derivatives or analogues without steric interference around the central double bond. Thus, α,α'-dimethylstilbene and 2,4,6,2',4',6'-hexamethylstilbene do not undergo this reaction [19], while with α-methylstilbene, 2,4,6-trimethylstilbene, 2-bromostilbene and even 1-styrylnaphthalene the reaction is inefficient, probably for steric reasons which affect the reversible iodination of the double bond. The same working hypothesis explains our present results of efficient catalysis of cis-2 → trans-2 and cis-3 → trans-3, but inefficient cis-1 → trans-1. As in stilbene proper [19] and its naphthyl analogues [2], the thermal equilibrium greatly favours the trans isomer: no spectral changes were observed when irradiating solutions of the three trans isomers with visible light in the presence of iodine.

3.2. Photocyclization

Both the trans and the cis isomers of B_1 - B_3 can exist in solution as a mixture of two rotational conformers, as illustrated in Scheme 2 for the trans isomers. Each of the corresponding pairs of cis rotamers could in principle yield two different photocyclization products. Thus for B_3 one might expect the two primary products D_3 from B_3 (Fig. 1) and D_3' from B_3' (Scheme 4). However, calculations of the sum ΣF^* of the free valence
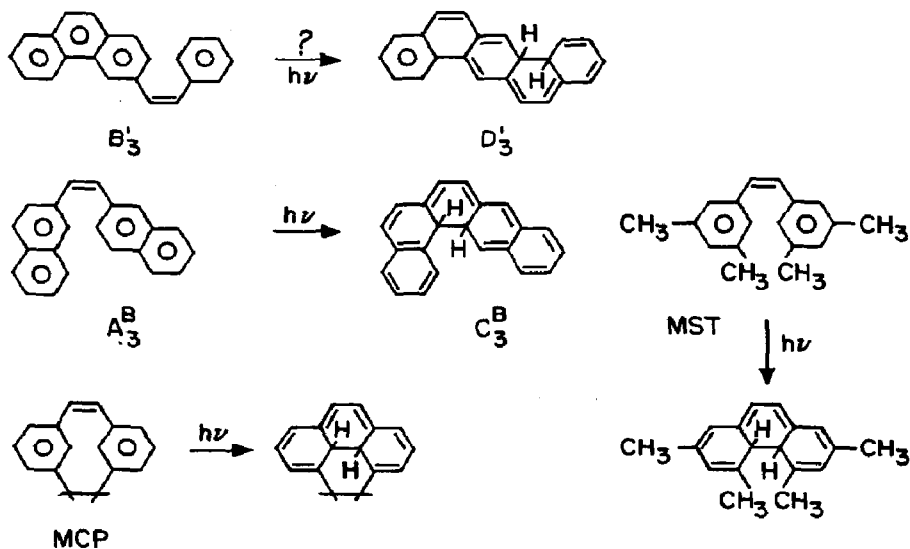
Scheme 4.

numbers of the atoms concerned in the cyclization show [5, 13] that this sum exceeds unity for only $B_1 \to D_1$, $B_2 \to D_2$ and $B_3 \to D_3$, and not for $B_2' \to D_2'$ and $B_3' \to D_3'$. The actual values of ΣF^* are as follows: B_1, 1.024; B_2, 1.14; B_2', 0.992; B_3, 1.071; B_3', 0.963. In accordance with the empirical rule that photocyclization takes place only when $\Sigma F^* \geqslant 1$ [13], one therefore expects $D_1 - D_3$ to be the sole products of photocyclization and $P_1 - P_3$ the sole photocyclodehydrogenation products. Indeed we now find no evidence for the formation of more than one DHP in each case. Moreover, the photocyclodehydrogenation experiments described above showed that if any of the potential oxidation products $P_1 - P_3$ are formed, they amount to less than 1% of the total products.

Unlike our observations for the DHPs $C_1 - C_3$ formed from the dinaphthylethylenes, the rates of photocyclization of $B_1 \to D_1$, $B_2 \to D_2$ and $B_3 \to D_3$ are not slowed down on cooling down to about $-170\,^\circ C$ where viscosity effects may start to be involved. This means that the potential barriers of 1 - 5 kcal mol^{-1} reported by us [6] hitherto to exist somewhere on the path from singlet-excited-cis to ground-state DHP do not exist, or are much smaller, in the styrylphenanthrenes. Our original explanation of these barriers was by way of the steric repulsion between the two CH groups involved in the photocyclization, and this also helped to understand why no such barrier was found for the photocyclization of metacyclophenes (MCP in Scheme 4) [20]. However, both the present and some previous results obtained with B-type rotamers of A_2 and A_3, e.g. A_3^B [2], and with 3,5,3',5'-tetramethylstilbene [21], indicate that this naive reasoning is insufficient, and a better one is required, necessitating improved information about the potential surfaces involved.

The half-lives of $D_1 - D_3$ at ambient temperature are much longer than those observed for $C_1 - C_3$. This may be explained qualitatively by assuming

that the energy difference between each cis isomer and the corresponding DHP is much larger for the D–B pairs than for the A–C pairs. This is supported by two sets of calculations: thermochemical calculations by Mallory (see Appendix A) and force field calculations (carried out using the MCA–QCPE–PI program package by A. Warshel and M. Levitt, QCPE 247, Indiana University, 1974, on an IBM 370/158 computer at the Nijmegen Computer Centre), which gave the results shown in Table 2 regarding the potential energy differences.

TABLE 2

Potential energy differences between each cis isomer (A_1 - A_3 and B_1 - B_3) and its cyclization product (C_1 - C_3 and D_1 - D_3)

Photocyclo-dehydrogenation product	$\Delta(C - A)$ (kcal mol^{-1})	$\Delta(D - B)$ (kcal mol^{-1})	$\Delta\Delta$ (kcal mol^{-1})
P_1	18.3	32.3	14.0
P_2	22.5	37.8	15.3
P_3	20.3[a]	38.5	18.2[a]
	27.3[b]		11.2[b]

[a]Conformation "a" for C_3.
[b]Conformation "b" for C_3.

For C_3, two conformations were calculated, as shown in Fig. 5. These may be similar to those described by one of us previously [22]. The energy difference of 11 - 15 kcal mol^{-1} calculated in this way probably reflects the difference in resonance energy between the two sets of DHPs, as also shown in Mallory's thermochemical calculation. Qualitatively this explains
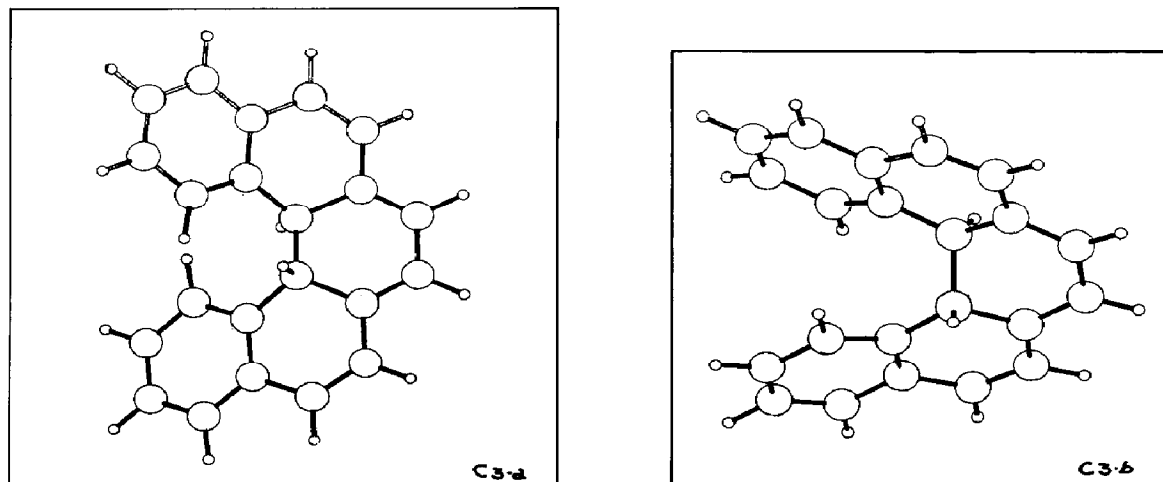

Fig. 5. Structures of C_3 in two conformations a and b as calculated by a force field method (see text).

the much lower thermal stability of D_1 - D_3, as compared with C_1 - C_3, reflected in their half-lives at room temperature. Quantitatively, the observed order of thermal stability at room temperature within each of the series C_1 - C_3 and D_1 - D_3 is also in accordance with the order of the corresponding values of Δ (using the more stable "a" conformation for C_3).

Unfortunately, no similar clear-cut correlation exists between the observed activation energies E_a for the thermal disappearance of C_1 - C_3 and D_1 - D_3 (Table 1) and the above values of Δ. The situation is of course complicated by the wide spread of the E_a and the uncertainty regarding the products of decomposition of D_1 - D_3.

Finally, the much higher energy differences $\Delta(D - B)$ *versus* $\Delta(C - A)$ obviously do not affect the ease of photocyclization: D_1 - D_3 are formed down to rather low temperatures while C_1 - C_3 are not. The height of the energy barriers on the path from singlet-excited cis to DHP is thus independent of $\Delta(DHP - cis)$.

The electronic overlap population method [6] has been applied in the past to a variety of photocyclizations and has proved itself to be of wider applicability than the ΣF^* method in predicting ring closures in larger analogues of stilbene. We do not know whether it could be extended to explain the energy barriers observed in the photocyclization of A_1 - A_3 and not observed for C_1 - C_3, and the other cases mentioned above.

3.3. Dehydrogenation

This is generally assumed [6] to be a secondary step (not involving electronically excited molecules in most cases) following the primary photocyclization. As shown by Mallory [23] and others in many cases, iodine is a much more efficient oxidant than oxygen. For B_3 the difference between oxygen and iodine is particularly large regarding the second step $P_3 \xrightarrow{-2H} DBP$; photocyclodehydrogenation of B_3 with oxygen virtually stops at the P_3 level. Even with iodine the two steps $B_3 \rightarrow P_3 \rightarrow DBP$ can be separated to a large extent owing to a pronounced attenuation of the second step at low temperatures.

3.4. Photoinduced hydrogen shift in dihydrophenanthrenes in the presence of molecular oxygen

Hydrogen shifts in DHPs are rare. One case we have described previously [3, 7] takes place in an inert atmosphere in hydrocarbon solvents, both thermally and photochemically (see Section 1). The shift described in this work, presumably $D_3 \rightarrow DHPH$, is unique in so far that it takes place only in the presence of oxygen and not in alcoholic solvents. We cannot as yet suggest an explanation. Previously we observed that irradiation of diarylethylenes in the presence of very small amounts of iodine (below 2 mol.%) under an argon atmosphere leads to dihydro aromatics [24]. Also, irradiation of stilbenes in primary amines as solvents leads to dihydrophenanthrenes, partly by a dehydrogenation–hydrogenation reaction, but also by a direct hydrogen transfer via the amine [25].

3.5. Electronic absorption spectra of dihydrophenanthrenes

In Muszkat's review of DHPs [6], the effect of annelation of benzene rings to DHP proper on the absorption spectrum is discussed as follows. Benzoannelation across a double bond in DHP substitutes a bond with half double-bond character for a double bond, thereby decreasing both the length of the interacting system and the strength of the interaction (exciton model) and causing a hypsochromic shift. Annelation of two benzene rings results in an even larger shift to shorter absorption wavelengths. In D_1 - D_3, only one double bond in DHP is annelated in this way, while in C_1 - C_3 two double bonds are annelated. This provides a qualitative explanation for the observation that the longest absorption peaks of D_1 - D_3 are at considerably longer wavelengths than in C_1 - C_3, but it does not suffice to explain the 530 nm peak of D_3, far beyond that of DHP proper at 450 nm. Clearly the overall size of the system also plays a role.

4. Experimental details

4.1. Variable temperature photochemical and spectrophotometric techniques (Rehovot)

The copper block technique [26] was used throughout for cooling and heating in absorption, emission and flash photolysis measurements. The instruments employed were a Varian 2200 absorption spectrophotometer with irradiation facilities *in situ* (125 W medium pressure mercury arc with light filters), a Perkin–Elmer MPF-44 spectrofluorometer, and a home-assembled flash apparatus limited to decay times beyond 40 μs and provided with interference filters between the measuring light and the thermostatted cell (light path, 20 - 70 mm).

4.2. Other techniques (Nijmegen)

Mass spectra were taken with a VG-70-70 instrument, IR spectra with a Perkin–Elmer 397 instrument and UV spectra with a Cary 15 or a Perkin–Elmer 555 spectrophotometer. NMR spectra were measured with Hitachi–Perkin–Elmer R24B or Bruker WH-90 apparatus, using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Melting points were determined using a Leitz melting point instrument and are uncorrected.

4.3. Solvents (Rehovot)

MCH was Kodak Spectrograde and 2- and 3-MP were Fluka products. All were dried before use by passing through columns of Woelm basic activated alumina which also served to remove traces of aromatic impurities.

4.4. Synthesis (Nijmegen)

4.4.1. 1-Styrylphenanthrene (1)

1-Methylphenanthrene was prepared by irradiation of 2-methylstilbene [27]. Bromination with *N*-bromosuccinimide (NBS) gave 2-bromomethylphenanthrene in 70% yield [27]. After reacting the bromide with

triphenylphosphine, a Wittig reaction of the resulting phosphonium salt was performed with benzaldehyde in dimethyl fluoride (DMF) as the solvent and sodium methoxide as the base. This gave a mixture of *trans-* and *cis-*1. The pure trans isomer was crystallized from ethyl acetate (melting point, 173 - 174 °C (literature value [28], 173 - 174 °C)). Peaks and ϵ (cm^2 mol^{-1}) values in the UV for a solution in methanol were as follows: 370 nm (1460); 319 (25 100); 264 (35 300); 230 (49 600); 224 (45 800).

4.4.2. 2-Styrylphenanthrene (2)

This substance was synthesized as shown in Scheme 5. 2,6-Dimethyl-bromobenzene [29] (10.0 g) was brominated with NBS in carbon tetra-chloride, giving a mixture of the monobromide and the dibromide. The 2,6-bis(bromomethyl)bromobenzene (0.3 g; melting point, 102 °C) crystallized from the solution. Distillation of the residue gave 2-methyl-6-bromomethylbromobenzene (boiling point, 130 °C, 15 mm Hg) in a yield of 10.1 g. Reaction of 10 g of the monobromomethyl derivative with 10 g triphenylphosphine in xylene yielded 18.5 g of the corresponding phosphonium salt, which melted at 274 - 275 °C. The Wittig reaction of this phosphonium salt
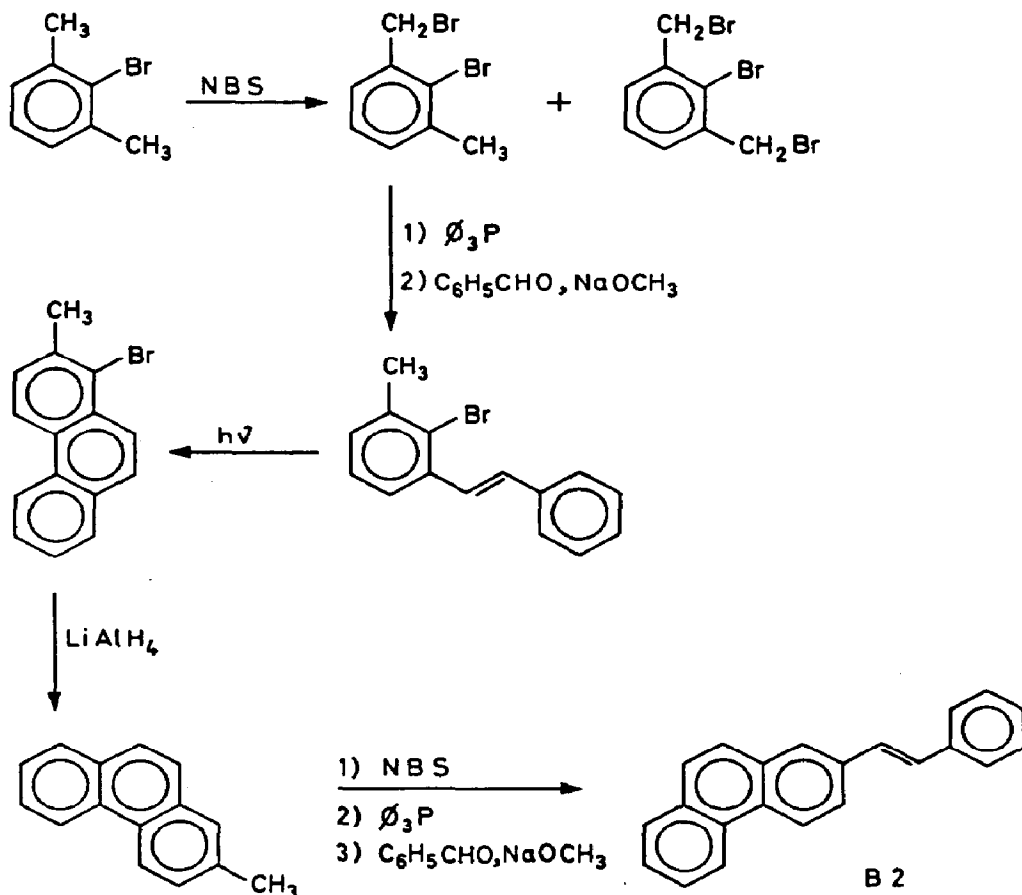
Scheme 5.

with benzaldehyde in DMF as the solvent and sodium methoxide as the base gave a mixture of *cis-* and *trans*-2-bromo-3-methylstilbene. Photo-cyclodehydrogenation at 300 nm in hexane as the solvent and with iodine as the oxidant formed 1-bromo-2-methylphenanthrene (melting point, 151 - 152 °C) in 50% yield after crystallization from ethyl acetate. Re-fluxing an ether solution of this phenanthrene and LiAlH$_4$ in fivefold excess overnight gave 2-methylphenanthrene in 90% yield (melting point, 56 - 57 °C (literature value [30], 56.5 - 57.5 °C)). Bromination with NBS of this compound yielded 2-bromomethylphenanthrene in 80% yield (melting point, 113 - 114 °C (literature value [13], 113 - 114 °C)). After treatment with triphenylphosphine, a Wittig reaction of the phosphonium salt with benzaldehyde in DMF gave a mixture of *cis-* and *trans*-2-styrylphenanthrene in 80% yield. The pure trans isomer melted at 211 - 212 °C (literature value [12], 210 - 211 °C). The peaks and ϵ values in the UV for a methanolic solution were 370 (1130), 338 (30 900 sh), 324 (42 300), 311 (32 800), 293 (45 100), 280 (47 450), 271 (32 750 sh), 247 (16 950), 238 (35 000 sh) and 220 (27 100). These data differ from those reported previously (*cf.* ref. 28). We believe that the latter refer to the cis isomer or to a cis–trans mixture. All data agree well with those reported for solutions in dioxane [12].

4.4.3. 3-Styrylphenanthrene (3)

4-Methylstilbene was photodehydrocyclized [31] to obtain 3-methyl-phenanthrene. Bromination with NBS yielded the 3-bromomethyl derivative, which was converted into its phosphonium salt by reaction with triphenyl-phosphine. In a Wittig reaction of the salt and benzaldehyde in DMF as the solvent and with sodium methoxide as the base, a mixture of *cis-* and *trans*-3-styrylphenanthrene was formed. Purification by chromatography gave the pure trans isomer (melting point, 150 - 152 °C (literature value [32], 151 - 152 °C)). The peaks and ϵ values in the UV for a methanolic solution were 367 (3700), 343 (25 000), 330 (33 300), 320 (27 000 sh), 287 (13 500 sh), 278 (25 000), 270 (25 300), 260 (20 250 sh), 249 (30 500) and 241 (23 800).

4.5. Preparative irradiations (Nijmegen)

These were carried out in a Rayonet photochemical reactor fitted with 254, 300 or 350 nm lamps, in 0.5 - 1.5 l Pyrex or quartz tubes filled with (2×10^{-3}) - 10^{-4} M solutions of the styrylphenanthrenes in hexane or methanol with or without added iodine and with or without previous deaeration with argon. At several time intervals samples were taken from the solutions and examined by UV spectroscopy and thin-layer chromato-graphy (TLC) for product formation. After completion of the photoreac-tion the solvent was distilled off and the residue carefully chromatographed over silica with hexane as the eluent. Each fraction was analysed by TLC and by UV and NMR spectroscopy. From the irradiation experiments of 1-styrylphenanthrene, only P$_1$ could be detected as a photocyclization

product, and from 2-styrylphenanthrene only P_2 could be detected. Irradiation of 3-styrylphenanthrene under completely anaerobic conditions resulted only in photoisomerization. Irradiation in the presence of air for 1.5 h led to the formation of compound X, as shown by its characteristic UV spectrum. However, by working up the solution by chromatography (TLC or column) only the presence of P_3 as a photoproduct could be demonstrated. By carefully distilling the solvent off *in vacuo* at room temperature and crystallizing the residue from deaerated (argon) ethyl acetate, it was possible to obtain a crystalline fraction which contained X contaminated with about 10% of P_3. Irradiation in the presence of air for longer periods resulted in the formation of P_3 and small fractions of more polar products. From the latter a red substance could be isolated by chromatography, constituting less than 1% of the starting amount. In the UV–visible spectrum a broad band centred at 500 nm was present and in its mass spectrum the parent peak was at 312, indicating two oxygens more than the starting compound. The IR spectrum showed absorptions at 1720 cm^{-1} and at 1660 cm^{-1}. Irradiation of B_3 in the presence of iodine resulted in the formation of BP (80%). The remainder consisted of more polar unidentified products.

Acknowledgments

References

1 N. Castel, E. Fischer and W. H. Laarhoven, *Proc. Xth IUPAC Symp. on Photochemistry, Interlaken, 1984*, p. 73.
2 T. Wismontski-Knittel, G. Fischer and E. Fischer, *J. Chem. Soc., Perkin Trans. II*, (1974) 1930.
3 T. Wismontski-Knittel and E. Fischer, *Mol. Photochem.*, 9 (1978/9) 67.
4 T. Wismontsky-Knittel and E. Fischer, *J. Chem. Soc., Perkin Trans. II*, (1979) 449.
5 W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas, 102* (1983) 185, 241.
6 K. A. Muszkat, *Top. Curr. Chem., 88* (1980) 91.
7 W. H. Laarhoven, Th. J. H. M. Cuppen and H. H. K. Brinkhof, *Tetrahedron, 38* (1982) 3179.
8 W. H. Laarhoven and Th. J. H. M. Cuppen, *Recl. Trav. Chim. Pays-Bas, 95* (1976) 165.
9 F. Dietz and M. Scholz, *Tetrahedron, 24* (1968) 6845.
10 W. H. Laarhoven, Th. J. H. M. Cuppen and R. J. F. Nivard, *Tetrahedron, 26* (1970) 1096.
11 D. D. Morgan, S. W. Morgan and M. Orchin, *Tetrahedron Lett.*, (1972) 1789.
12 G. Snatzke and K. Kunde, *Chem. Ber., 106* (1973) 1341.
13 W. H. Laarhoven, Th. J. H. M. Cuppen and R. J. F. Nivard, *Tetrahedron, 26* (1970) 4865.
14 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem., 82* (1978) 1638.
15 E. Fischer, *J. Phys. Chem., 84* (1980) 403.

16 E. Fischer, *J. Photochem.*, *17* (1981) 331.
17 N. Castel, E. Fischer, U. Mazzucato, G. Bartocci and F. Masetti, *J. Chem. Soc., Perkin Trans. II,* in the press.
18 J. Klueger, G. Fischer and E. Fischer, *Chem. Phys. Lett., 8* (1971) 279.
    Ch. Goedicke, H. Stegemeyer, G. Fischer and E. Fischer, *Z. Phys. Chem., N.F., 101* (1976) 181.
19 G. Fischer, K. A. Muszkat and E. Fischer, *J. Chem. Soc. B,* (1969) 156.
20 R. Naef and E. Fischer, *Helv. Chim. Acta, 57* (1974) 2224.
21 A. Bromberg, K. A. Muszkat and E. Fischer, *Isr. J. Chem., 10* (1972) 765.
22 T. Wismontski-Knittel, M. Kaganowich, G. Seger and E. Fischer, *Recl. Trav. Chim. Pays-Bas, 98* (1979) 114.
23 F. B. Mallory and C. W. Mallory, *J. Am. Chem. Soc., 94* (1972) 6041.
24 J. H. Borkent, J. W. Diesveld and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas, 100* (1984) 114.
25 J. B. M. Somers, J. A. Couture, A. Lablache Combien and W. H. Laarhoven, *J. Am. Chem. Soc., 107* (1985) 1387.
    W. H. Laarhoven, *Pure Appl. Chem., 56* (1984) 1225.
26 E. Fischer, *Mol. Photochem., 2* (1970) 99.
27 M. Sindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc., 100* (1978) 3813.
28 R. H. Hayward and C. C. Leznoff, *Tetrahedron, 27* (1971) 5115.
29 J. Coops, W. Th. Nauta, M. J. E. Ernsting and A. C. Faber, *Recl. Trav. Chim. Pays-Bas, 59* (1940) 1109.
30 W. E. Bachmann and A. G. Anderson, Jr., *J. Org. Chem., 13* (1948) 297.
31 C. S. Wood and F. B. Mallory, *J. Org. Chem., 29* (1964) 3373.
32 S. Akiyama, N. Nakasuji and M. Nakagawa, *Bull. Chem. Soc. Jpn., 44* (1971) 2231.

Appendix A[†]

The various thermal ring-opening reactions are drawn out in Scheme A1. It seems that one can account for the observations that the D → B ring openings are faster than the corresponding C → A ring openings by a simple and approximate argument based on the following assumptions. (1) A useful and self-consistent group of values for aromatic resonance energies (in kilocalories per mole) is 36 for benzene, 61 for naphthalene and 92 for phenanthrene. (2) The resonance energy associated with each conjugation between two double bonds or between one double bond and an aromatic ring has some small and reasonably constant value, designated a (a specific value is not assigned to a because in this analysis it ultimately cancels out). (3) Isomers such as C_1 and D_1 (see Scheme A1) will not differ appreciably in energy *on the basis of CC and CH bond energies* because each isomer has the same number of each type of bond (*e.g.* 10 sp^2–sp^2 CC "double" bonds, 11 sp^2–sp^2 CC "single" bonds, 4 sp^2–sp^3 CC bonds, 1 sp^3–sp^3 CC bond, 14 sp^2 CH bonds and 2 sp^3 CH bonds). (4) Similarly, isomers such as A_1 and B_1 will not differ appreciably in energy *on the basis of bond*

[†]Comments on the comparison of the decay rates of DHPs derived from dinaphthyl-ethylenes and styrylphenanthrenes, by Frank B. Mallory, Department of Chemistry, Bryn Mawr College, Bryn Mawr, PE 19010.
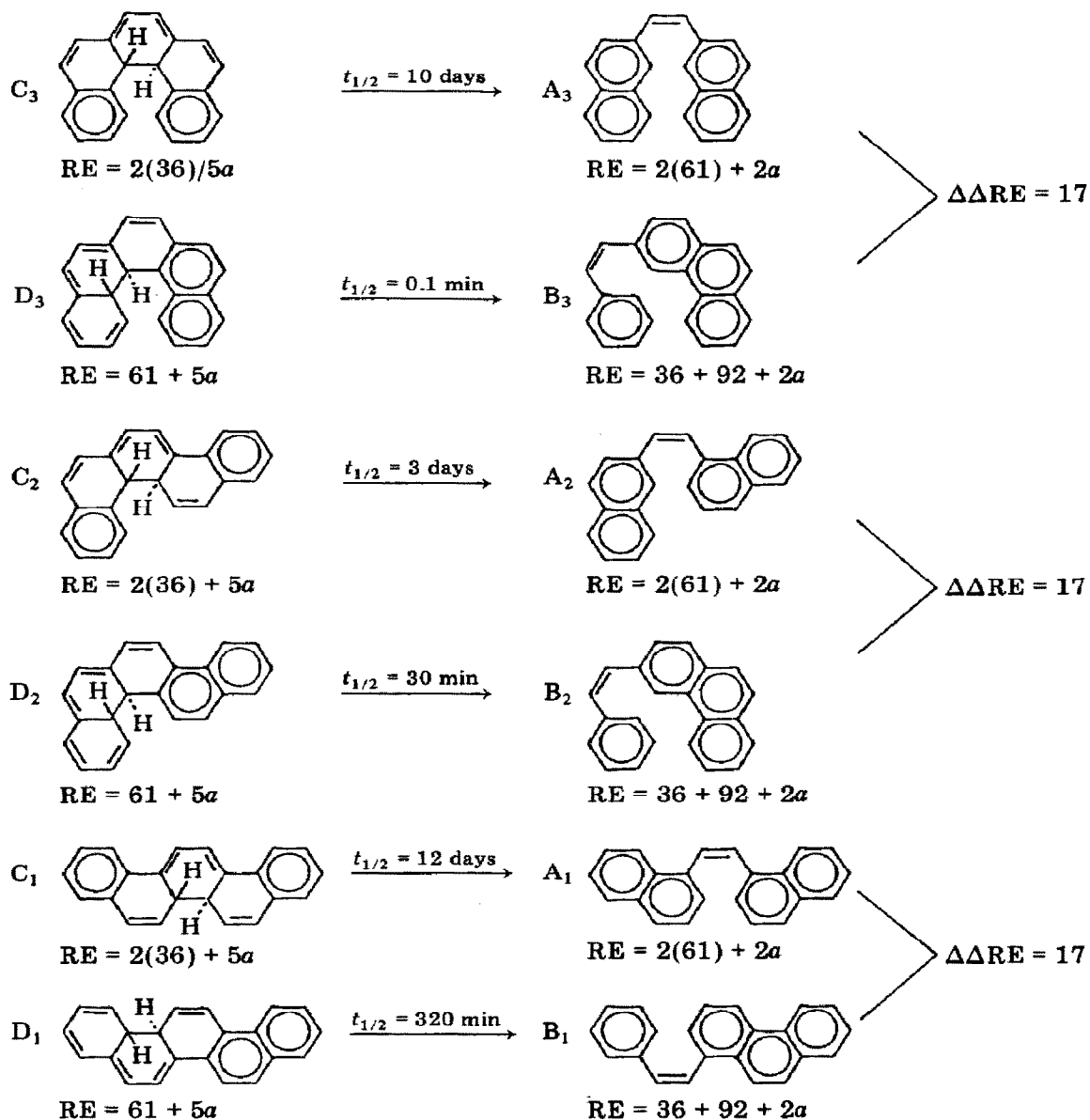
Scheme A1.

energies. (5) The destabilizing strain energies of isoskeletal isomers such as C_1 and D_1 are essentially equal.

With the assumptions listed above, one can estimate that $D_1 \rightarrow B_1$ should be more exothermic than $C_1 \rightarrow A_1$ by about 17 kcal mol^{-1}. Thus the following resonance energies (in kilocalories per mole) can be estimated: $72 + 5a$ for C_1, $122 + 2a$ for A_1, $61 + 5a$ for D_1 and $128 + 2a$ for B_1. From these values, the increase in resonance stabilization (in kilocalories per mole) for the $C_1 \rightarrow A_1$ reaction is $50 - 3a$, and that for the $D_1 \rightarrow B_1$ reaction is $67 - 3a$. (Note that these are only the resonance energy contributions to the overall exothermicities, not the exothermicities themselves. But with

the assumptions that bond energy contributions and strain energy contributions cancel out, the *difference* in the overall exothermicities for the two reactions will be given by just the difference in the resonance energy contributions.) Therefore the $D_1 \rightarrow B_1$ reaction is estimated to be more exothermic than the $C_1 \rightarrow A_1$ reaction by $(67 - 3a) - (50 - 3a) = 17$ kcal mol^{-1}. At this approximate level of analysis, this same value of 17 kcal mol^{-1} is found for the difference in exothermicity for $C_2 \rightarrow A_2$ *versus* $D_2 \rightarrow B_2$ and also for $C_3 \rightarrow A_3$ *versus* $D_3 \rightarrow B_3$ as indicated in Scheme A1.

For comparisons within each isoskeletal pair, the resonance energy factor of 17 kcal mol^{-1} accounts for the observation that the $D \rightarrow B$ ring opening is much faster than the $C \rightarrow A$ ring opening. That is, there is an additional driving force of about 17 kcal mol^{-1} for each $D \rightarrow B$ reaction compared with the corresponding $C \rightarrow A$ reaction, and one may expect that the transition states for these two types of reaction will differ in energy by some fraction of this overall exothermicity difference. As a first approximation, one can ignore the differences in the relief of strain energy on ring opening for these pair-wise comparisons. These strain energy considerations *should* play a role, however, in comparisons of one system with another. The relief of strain on ring opening should be largest in series 3 and smallest in series 1 of the three systems studied. This concept successfully accounts for the observation that the $D \rightarrow B$ ring openings increase in rate from series 1 ($t_{1/2} = 320$ min) to series 2 ($t_{1/2} = 30$ min) to series 3 ($t_{1/2} = 0.1$ min). On the basis of this strain-relief argument, one would expect the $C \rightarrow A$ reactions to increase in rate in a similar sequence. In fact, however, the observed rate for $C_3 \rightarrow A_3$ ($t_{1/2} = 10$ days) seems anomalously slow compared with the rates for $C_2 \rightarrow A_2$ ($t_{1/2} = 3$ days) and $C_1 \rightarrow A_1$ ($t_{1/2} = 12$ days). It appears that previous experimental studies of C_3 provide more direct evidence that C_3 is a special case with regard to its anomalously slow ring opening. Another way of using the rate data to reveal this apparent anomaly is to note that the ratio of the $D \rightarrow B$ rate to the $C \rightarrow A$ rate is similar for both the 2 series and the 1 series (a rate ratio of about 10^2), whereas it is markedly different for the 3 series (a rate ratio of about 10^5).

The preceding analysis of these ring-opening reactions has focused on rates (as expressed by $t_{1/2}$ values) rather than activation energies because the experimental values for E_a seem quite puzzling. There does not appear to be an obvious way to reconcile the $t_{1/2}$ and E_a results.