The Role of Conformers in the Reversible Photocyclisation of *cis*-1,2-Diarylethylenes. A Flash-photolytic Study

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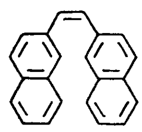
Summary Flash-photolytic experiments showed that the photocyclisation of 1,2-di(2-naphthyl)ethylene, (I^a), results in the formation of two isomeric 4a,4b-dihydrophenanthrenes derived from two of the possible three conformers of (I^a), and differing in thermal stability by a factor of 10^{10}.

In solution, *cis*-1,2-di(2-naphthyl)ethylene, (I^a), is assumed to exist as an equilibrium mixture of the three almost isoenergetic conformers (I^a_A) $\rightleftharpoons$ (I^a_B) $\rightleftharpoons$ (I^a_C). (Subscripts A, B, C refer to the various conformers, and superscripts a, b, c denote the *cis*-ethylene, the corresponding dihydrophenanthrene analogue, and its oxidation product, respectively). Nevertheless, at room temperature, photocyclisation to the corresponding 4a,4b-dihydrophenanthrene (DHP) derivative, and photocyclodehydrogenation to the corresponding dibenzophenanthrene, give exclusively (I^b_A)[1–4] and (I^c_A),[5,6] respectively, derived from conformer (I^a_A). A similar situation exists[4,6] with the related compounds (II) and (III), each of which is assumed to exist in solution as a mixture of two conformers: (II^a_A) $\rightleftharpoons$ (II^a_B), (III^a_A) $\rightleftharpoons$ (III^a_B). MO theory predicts[5–9] that (II^b_A) should be formed exclusively, while (I^b_B) and (III^b_B) should be formed to some extent,[8,9] though (I^b_A) and (III^b_A) should be the major products of photocyclisation.

Flash photolysis[10] of (I^a) in methylcyclohexane at room temperature was shown to give, in addition to the stable (I^b_A), a transient X with a half-life of the order of 10^{-4} seconds, and characterised by peaks at around 570, 530 and 500 nm. From studies of the decay rate of X in a wide temperature range, we calculated an Arrhenius critical increment of 12 k cal mol^{-1} for X $\rightarrow$ (I^a). The photoformation of (I^b_A) is sharply temperature-dependent[2,4] and stops completely below −30°. In contrast, X is formed even at −140°, and thus remains the sole unstable photoproduct below −30°. Oxidation of X with iodine irradiated at 546 + 576 nm ("atomic iodine")[2,3] at −100° yielded (I^c_B), i.e. the oxidation product expected from (I^b_B). We therefore feel justified to identify X as (I^b_B), as distinct from (I^b_A). The thermal instability of (I^b_B) makes its quantitative oxidation impossible. (I^b_B) is completely photoerasable with light in the visible region, down to at least −180°. Its main absorption peaks in the visible are red-shifted by about 150 nm in comparison with (I_A^b). Above −30°, when both DHP's are formed, the ratio $R = [\mathrm{I}_B^b]/[\mathrm{I}_A^b]$ per light-flash varies sharply with the wavelength of the active light. Thus at 20° R is *ca.* 1·3 at >340 nm, and *ca.* 4·2 at 300—340 nm. We suggest that this results largely from preferential absorption of light at longer wavelengths by (I_A^a), thereby increasing the apparent yield of (I_A^b) at such wavelengths. We estimate the apparent quantum yield of the photoformation of (I_B^b) as about 0·05 at 313 nm and 20°. For (I_A^b) at 366 nm we found 0·03.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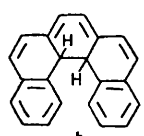
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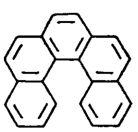
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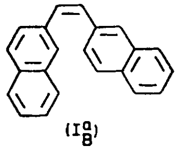
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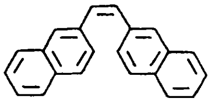
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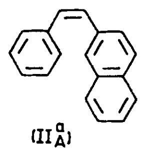
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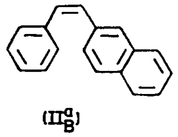
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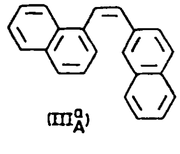
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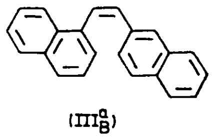
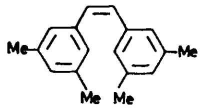
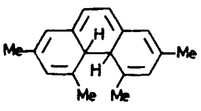

(III_B^a)



(IV)



(V)

An activation energy of 12 ± 0·5 kcal mol⁻¹ was found for $(\mathrm{I}_B^b) \rightarrow (\mathrm{I}_B^a)$, as compared with 27 ± 1 kcal mol⁻¹ for $(\mathrm{I}_A^b) \rightarrow (\mathrm{I}_A^a)$. As a result, the former process is about 10^{10} times faster than the latter. This explains the failure to produce (I_B^c) during photocyclodehydrogenation of (I) at room temperature.[5,6]

With compound (III) a short-lived transient similar to X was observed (peaks at 603, 570, and 540 nm) and identified as (III_B^c) by oxidation to (III_B^a). However, in this case both (III_A^b) and (III_B^b) are formed down to −180°, with (III_A^b) predominating. Here too (III_B^b) is formed preferentially at short wavelengths. At 20° the approximate quantum yields of photoformation were 0·003 for (III_B^b) at 313 nm and 0·06 for (III_A^b) at 334 nm. Combined u.v. and visible flash photolysis proved that (III_B^b) is photoerasable with visible light. From the temperature dependence $(\mathrm{III}_B^b) \rightarrow (\mathrm{III}_B^a)$ a critical increment of 11·5 kcal mol⁻¹ was calculated. For $(\mathrm{III}_A^b) \rightarrow (\mathrm{III}_A^a)$ the value is 18·5. In this context it should be mentioned that for the strongly-hindered cyclisation product[11] (V) of (IV) we found[12] an activation energy of only 7 kcal mol⁻¹ for (V) → (IV), the lowest value observed so far[1,4,13] for this type of reaction.

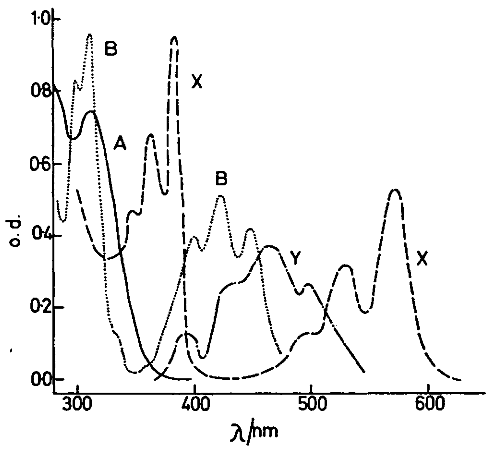


FIGURE. Compound (I) in MCH, *ca.* 3 × 10⁻⁵M. Absorption spectra of (I)-curve A, (I_A^b)-curve B, (I_B^b)-curve X, and Y. The three latter curves were extrapolated from experimental ones, assuming reasonable extents of photoconversion. For orientation only, the molar extinction coefficient of $(\mathrm{I}^{\mathrm{A}})$ at 425 nm is about 12,000.

Finally, flash experiments showed that (I_A^b) is formed from (I_A^a) *via* a transient Y with a half-life of about 10 s at 20°. Its absorption spectrum is somewhat red-shifted relative to (I_A^b). From the temperature dependence of Y → (I_A^b) we calculated an activation energy of 15 ± 0·5 kcal mol⁻¹. Oxygen has no effect on Y. In the absence of other evidence for its structure, we suggest that Y is an unstable steric isomer of (I_A^b). This appears plausible in view of the pronounced steric interactions in (I_A^b).[9]

The absorption spectra of (I) are summarized in the Figure.

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