nyl)-1-phenylethylene is proposed based on product analysis, fluorescence measurements, and transient species detected by flash photolysis experiments.

The rate of photocyclization from the singlet state is 100 times faster than the apparent cyclization rate constant from the triplet state. This can be accounted for in the following manner.

(1) The intermediate X, being a ground-state singlet species, can be formed more easily from an excited state of the same multiplicity and probably via an electrocyclic ring-closure route.

(2) The energetic factors can be important. If one assumes the existence of a common transition state from the excited singlet and triplet states to produce X, it would follow that the activation energy would be smaller for reaction from the singlet state than from the triplet state. Hence photocyclization from the singlet state would be favored kinetically.

(3) It is more likely, according to the results described in part 1,[2] that the mechanisms of formation of X via the singlet and triplet state would be different, since the twisting of the double bond will differ in these two states affecting the spatial arrangement of the atoms to be linked.[10]

Further experiments will be carried out with other diarylethylenes.

References and Notes

(1) Equipe de Recherche Associée au CNRS no. 167.
(2) See part 1: Lapouyade, R.; Koussini, R.; Fornier de Violet, P. *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) Horgan, S. W.; Morgan D. D.; Orchin, M. *J. Org. Chem.*, **1973**, 38, 3801–3803.
(4) Laarhoven, W. H.; Cuppen, Th. J. H. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2074–2079.
(5) Lapouyade, R.; Koussini, R.; Rayez, J. C. *J. Chem. Soc., Chem. Commun.*, **1975**, 675–676.
(6) Ware, W. R.; Doemeney, L. J.; Nemzek, T. L. *J. Phys. Chem.*, **1973**, 77, 2038–2048.
(7) Fornier de Violet, P.; Bonneau R.; Joussot-Dubien, *J. Chem. Phys. Lett.*, **1974**, 28, 569–572.
(8) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press: New York, N.Y., 1955; p 92.
(9) At this wavelength, which is on the steeply rising side of the absorption band of P_2, the slits of the monochromator are around 0.5 mm, giving a resolution of 3 mm. It follows that $\epsilon_{315nm} = 1800 \pm 350$ M^{-1} cm^{-1}.
(10) The values of the rate constants k_{TX} and k_{nr_3} have been evaluated by assuming that the triplet state observed by flash spectroscopy is the cyclizing species. On account of its lifetime, this triplet should be a "planar" state, the ethylenic CH$_2$ still being in the molecular plane. On the contrary, if the cyclization of the triplet occurs after rotation of the double bond, on one hand, the lifetime of the observed triplet would give the rate of rotation of the double bond and not that of cyclization; on the other hand, the rate of cyclization of the "twisted" triplet should be much larger than the 3.3 × 10^5 s value reported above, since its lifetime must be much shorter than 1.75 μs.

π,π-Biradicaloid Hydrocarbons. The Pleiadene Family. 4.[1] Involvement of Upper and/or Hot Excited Singlet and Triplet States in a Photochemical Conversion of a Polycyclic Cyclobutene to a Butadiene

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Abstract: The mechanism of the photochemical electrocyclic transformation of the cyclobutene **2** to pleiadene **1** in a rigid glass (77 K) with long-wavelength light involves successive absorption of two photons, with triplet **2** as the intermediate state. At shorter wavelengths, the reaction proceeds by the ordinary one-photon mechanism. It is concluded that thermalized S_1 and T_1 states are unreactive and that the reaction occurs in upper and/or hot excited states with quantum yields of the order of 1%. It is pointed out that the common practice of ignoring such possible upper and/or hot excited state contributions to unimolecular photochemical reactivity of organic molecules in solution is questionable.

The photochemical preparation of pleiadene (**1**) by irradiation of the cyclobutene precursor **2** in rigid organic glasses has been reported.[3,4] Alkyl derivatives[5,6] as well as more highly condensed polycyclic analogues[4,7] are similarly accessible. We now wish to report in detail our mechanistic investigation of this photochemical cyclobutene → butadiene conversion. Its unusual nature has already been briefly described[4,7–9] and the theoretical implications were discussed.[10–12]

Results

Excited States of 1 and 2. The absorption spectrum of **1** and seven of its alkyl derivatives was reported and analyzed previously.[5,6] The energies, polarizations, and relative intensities of the first six transitions were in excellent agreement with π-electron calculations, which led to an assignment of the second excited singlet state as doubly excited. The first transition is short-axis polarized and lies in the near-IR region (0–0 band at 11 700 cm^{-1}); no fluorescence was observed. The lowest triplet is calculated to lie only about 3000 cm^{-1} above the singlet ground state and no experimental evidence for it has been obtained. In a rigid glass at 77 K, **1** is stable for many hours, both in the dark and under UV irradiation.

The absorption and uncorrected fluorescence and phosphorescence spectra of **2** are shown in Figure 1 and correspond well to expectations for noninteracting acenaphthene and benzocyclobutene chromophores. The absorption reveals the expected presence of the three low-energy transitions of the naphthalene chromophore (N1 = ^1L_b, N2 = ^1L_a, N3 = ^1B_b) and of the lowest benzene transition (B1 = ^1L_b). Polarization measurements on these transitions[13] by the stretched polymer method are in perfect agreement with expectations, given the C_s symmetry and the 115° dihedral angle between the plane
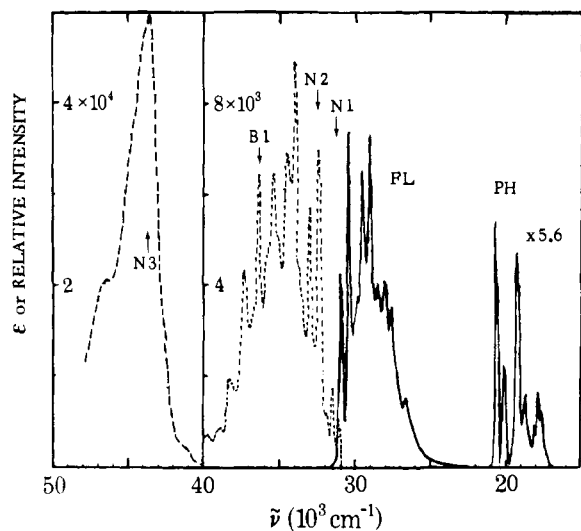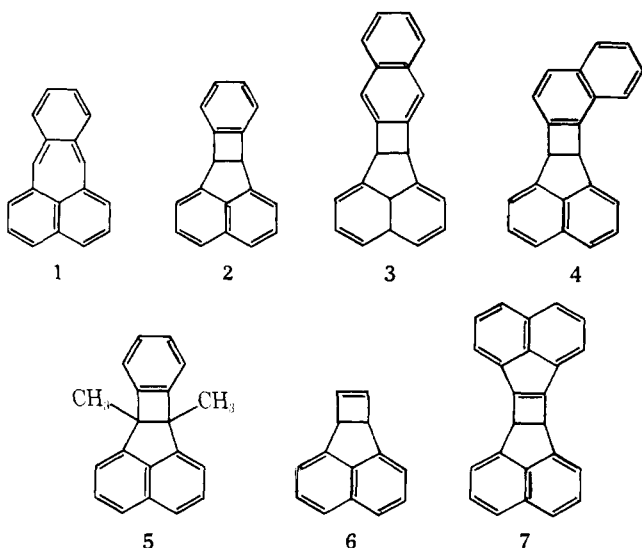
Figure 1. Absorption (- - -) and uncorrected fluorescence (FL) and phosphorescence (PH) spectra of **2** (3-MP, 77 K).

Figure 2. Concentration of **1** as a function of time (arbitrary units) for different light intensities I. Points represent experimental data; the 1 $h\nu$ and 2 $h\nu$ lines represent theoretical expectations for the rate of an I- and I^2-dependent reaction, respectively, as I is reduced below 100% (3-MP, 77 K).

of the naphthalene and the benzene moieties determined by X-ray crystallography:[14] N1 and N3 are polarized perpendicular to the plane of symmetry, and N2 and B1 are polarized in the plane of symmetry and lie in the naphthalene and benzene planes, respectively.

Both emissions are those expected for the naphthalene chromophore. In 3-methylpentane (3-MP) at 77 K, ν_{0-0} (FL) = 31 200 cm^{-1}, ϕ (FL) = 0.41 ± 0.02, ν_{0-0} (PH) = 20 800 cm^{-1}, ϕ (PH) = 0.041 ± 0.002; τ (PH) = 3.0 ± 0.1 s. The corrected excitation spectra of both emissions are identical with the absorption spectrum within an experimental error (a few percent). The ratio of fluorescence to phosphorescence intensity is independent of excitation wavelength at least down to 214 nm.

Single-Beam Photochemistry of 2. Broad-band irradiation of a rigid glass containing **2** with a 1-kW xenon arc filtered to remove wavelengths below 300 nm rapidly produces **1**. The initial rate of product formation, followed by UV-visible absorption spectroscopy, is proportional to the second power of light intensity (I^2). The reaction can also be effected with monochromatic radiation. With 303-nm light, the initial rate of formation of **1** is proportional to I^2, but at 229 and 214 nm, it is proportional to I (Figure 2). With 254-nm light, the reaction proceeds extremely slowly. The quantum yields of the one-photon processes were determined by uranyl oxalate and
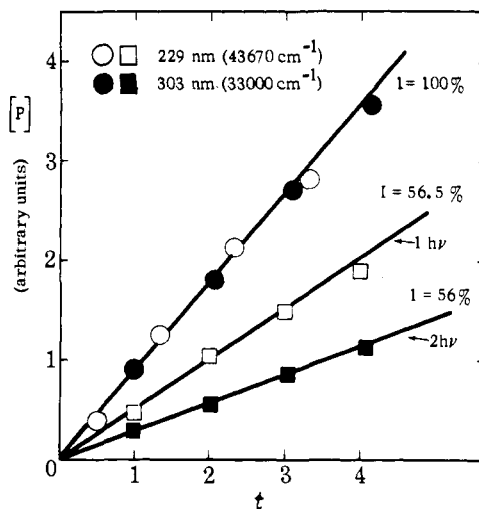
ferrioxalate actinometry; ϕ (214) = 0.009, ϕ (229) = 0.006, ϕ (254) < 0.0003 (zero within experimental error).

Double-Beam Photochemistry of 2. Since efficient simultaneous absorption of two photons (or even a $S_1 + h\nu \rightarrow S_n$ process) are out of the question considering the intensities available from our light sources, the square dependence on light intensity in the case of long-wavelength irradiation demands the presence of a relatively long-lived intermediate which absorbs the second photon. This conclusion was confirmed by an experiment using two directly opposed beams impinging on the sample. One of these was a weak monochromatic beam of 303-nm light, which caused only a very slow reaction. The other was an intense broad band beam filtered by a band-pass filter (330-410 nm) chosen so as to guarantee that the beam was not absorbed by the starting material **2** in its ground state. The second beam caused no photoreaction in the absence of the first beam. If both beams were turned on, **1** was formed at least an order of magnitude faster than with the first beam alone. The initial rate of the transformation **2** → **1** was proportional to the intensity of the second beam (Figure 3).

The nature of the intermediate was inferred from the action spectrum of the second photon. For this experiment, the intensity of the second beam was maximized and it passed through a circular wedge interference filter before impinging on the sample. The initial rate of the phototransformation was measured as a function of the wavelength of the second beam and was normalized to unit intensity of the second beam. The resulting action spectrum is shown in Figure 4, which also indicates a typical transmission curve for the wedge filter. Because of its relatively large half-width, no fine structure can be expected in the measured action spectrum. The reported[15] triplet-triplet absorption spectrum of naphthalene is shown on logarithmic scale, and the great similarity between the action spectrum for the intermediate and the T-T absorption spectrum of the naphthalene chromophore is obvious.

In order to identify the intermediate state as the lowest triplet T_1 of **2** more firmly, its lifetime was estimated. In this experiment, the first beam was replaced by a 1.5-μs xenon flashlamp and the second beam was again filtered with a band-pass filter (330-410 nm) so that it was not absorbed by the ground state of the starting material **2.** The second beam was blocked, the flashlamp was fired to populate the intermediate state, and after a delay of Δt seconds the second beam was turned on. After all phosphorescence disappeared ($\sim$20
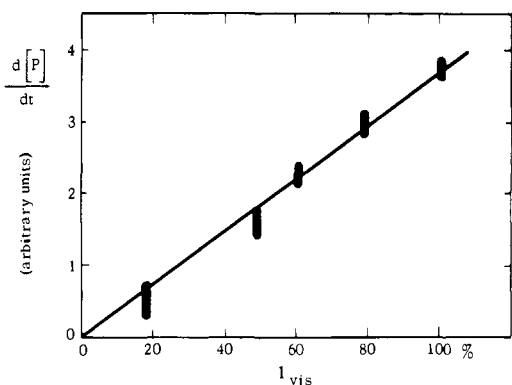
Figure 3. Initial rate of formation of **1** (3-MP, 77 K) in a two-beam experiment as a function of the intensity of the second beam (330 < λ < 410 nm).

Figure 4. Action spectrum of the second beam in the process **2** → **1** (3-MP, 77 K). An example of the transmission curve of the circular wedge interference filter used is shown in the lower right as a dashed line. The solid curve shows log ε for the triplet-triplet absorption spectrum of naphthalene.[15]

s), the flashlamp was fired again and the procedure was continued for about 2 h. The rate of product formation in this mode of operation was extrapolated to zero time. The experiment was then repeated using the same flash frequency but a different delay Δt. A plot of the logarithm of the initial rate against Δt yielded a straight line with a negative slope of 2.4 ± 0.5 s, in good agreement with the phosphorescence lifetime of **2**. An exact agreement cannot be expected, not only because of experimental uncertainties, but also because the lifetime cannot be exactly the same in the presence and in the absence of the second beam (an attempt to measure the lifetime shortening directly failed since the shortening was within the experimental error for the light intensities available).

Since these results leave little doubt that the intermediate is the naphthalene-like T_1 triplet state of **2**, one can assume that its average decadic molar extinction coefficient in the 330-410-nm region is of the order of $\epsilon_{TT} = 10^4$ L/mol·cm.[15,16] This assumption, along with the expression derived by Keller and Hadley[16] for the triplet optical density in a sample irradiated with light of known intensity, permitted an actinometric determination of the quantum yield of the second step in the process **2** → **1** as 0.005 (ϕ_{isc} was taken to be 0.59 since S_1 is photochemically inactive as discussed below, and otherwise quite similar to S_1 of naphthalene). While this number is subject to considerable uncertainty, particularly owing to the lack of accurate information on the average value of ϵ_{TT} of **2**, the order of magnitude is undoubtedly correct. Our attempts to observe the triplet-triplet absorption spectrum of **2** directly upon continuous UV irradiation failed since the conversion to **1** was too rapid when sufficient light intensities were used. Accurate values of ϵ_{TT} may become available from flash measurements in the future, and would then allow a more accurate reevaluation of the presently reported quantum yield.

Photochemical Transformation of Analogues and Derivatives of 2. We have performed qualitative mechanistic tests on related condensed cyclobutenes **3**, **4**, and **5** whose photochemical conversion to the corresponding pleiadenes has already been reported.[4,5] All behaved similarly to **2** and, in particular, showed a great increase in the rate of the photochemical ring opening when irradiated by a second beam of light (330-410 nm) not absorbed by the starting molecules in their ground states. Similar behavior has been reported for **6**.[17,18]

Discussion

The spectral data show that the photophysical properties of **2** are comparable to those of other simple naphthalene derivatives. Excitation to higher vibrational levels of S_1 or to the higher singlets S_n leads to production of thermally equilibrated S_1 in approximately 100% yield. Significant intersystem
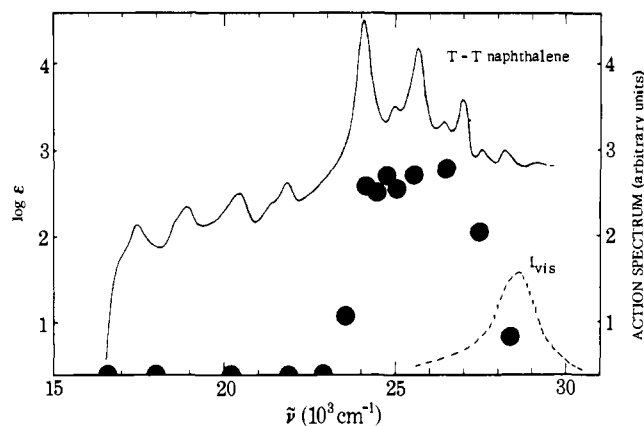
crossing to the triplet manifold occurs, but only after this initial internal conversion and thermalization in S_1. However, the photochemical results show that the initial conversion to thermalized S_1 cannot be fully 100% efficient, since **1** is formed upon absorption of a single photon. The quantum yield of the conversion **2** → **1** is a function of the energy of the photon. It decreases from about 1% at 214 nm to essentially zero (<0.03%) at 254 nm. Since the two-photon mechanism prevails at longer wavelengths a direct measurement of the one-photon quantum yield could not be performed for λ >254 nm, but it clearly must be at least an order of magnitude smaller at 303 nm than the ca. 0.5% quantum yield of the second step of the two-step mechanism in order to account for the perfect I^2 dependence of the initial reaction rate. Indeed, there is no evidence that the thermally equilibrated S_1 state and the triplet states reached from thermalized S_1 by intersystem crossing are reactive at all. The wavelength dependence of the one-photon quantum yield is presumably complementary to the wavelength dependence of the quantum yields of the emissions of **2** and thus should be reflected in a deviation of the excitation spectra from the absorption curve. Unfortunately, the expected magnitude of the deviation is well within our experimental error, so that this independent confirmation of the wavelength dependence is not available.

We conclude that the photochemical process **2** → **1** occurs from higher vibrational and/or higher excited singlet and triplet states of **2** but occurs either very much more slowly or not at all from less highly excited singlet and triplet **2** (E < ca. 40 000 cm^{-1}).

While there is no evidence that the thermalized S_1 or T_1 states of **2** are converted to **1** spontaneously, the results clearly show that T_1 of **2** is converted to **1** upon absorption of a second photon, which takes the molecule to an upper excited triplet state. This is the main pathway for product formation under conditions of broad-band irradiation or long-wavelength monochromatic irradiation. The wavelengths efficient in the **2** (T_1) + $h\nu$ → **1** process are those for which the extinction coefficient ϵ_{TT} is large; the observed inefficiency of longer wavelength photons (Figure 4) may be due to low values of ϵ_{TT} in this region and/or to lack of reactivity of the triplet states reached. Thus, it is presently impossible to determine the limiting energy above which the triplet states become reactive, but it is clear that while **2** is unreactive in T_1, it rearranges to **1** in triplet states located at 45 000-50 000 cm^{-1}. The efficiency of the process **2** (T_n) → **1** is of the order of 0.5%, comparable with the efficiency of the process **2** (S_n) → **1**.

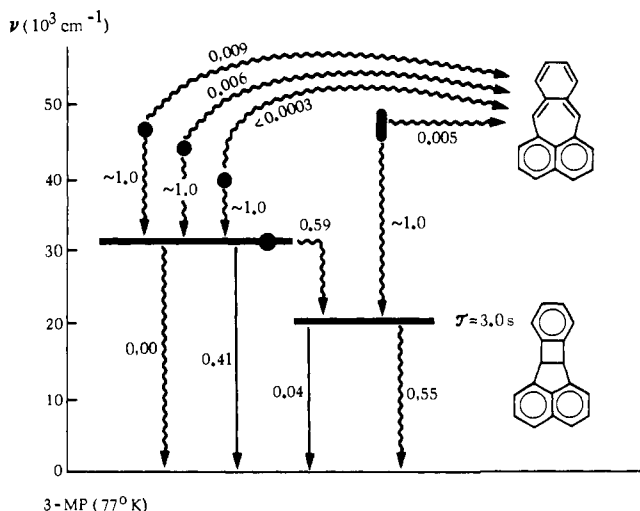The mechanism deduced from our experimental data is

Figure 5. A summary of the photophysics and photochemistry of **2**. The numbers given are quantum yields of processes starting at levels indicated by black dots.

summarized in Figure 5. The numbers given are quantum yields of various photophysical and photochemical processes starting at the points indicated by dots. Initially, a large part of the "excess" energy of the excited molecule above S_1 or T_1 is of electronic nature, and it is quite possible that the photochemical reactions occur in higher electronic excited states. It is also possible that the actual chemical transformation is preceded by internal conversion from the initially reached higher electronic states to one of the lower states, possibly even S_1 or T_1, and that the vibrationally hot molecule thus produced then undergoes a chemical transformation before it loses its excess energy to the solvent. The distinction between these two possibilities is clear-cut only within the Born–Oppenheimer approximation. Since we have no experimental basis for distinguishing whether the extra energy is electronic or vibrational when the rearrangement to **1** occurs, we prefer to refer to the reacting states as "higher and/or hot" excited states.

The data suggest quite strongly that the conversions **2** (S_n) → **1** and **2** (T_n) → **1** follow two different pathways, i.e., that S_n and T_n do not interconvert rapidly. The reaction path **2** (S_n) → **2** (T_n) → **1** can be excluded since the efficiency of the S_n → T_n process at 214 nm can be at best a percent or so [the ratio ϕ (FL)/ϕ (PH) is wavelength independent within experimental error down to 214 nm] so that the efficiency of the **2** (T_n) → **1** process would have to be nearly 100% rather than the observed 1% in order to account for the observed one-photon quantum yield. While the T_n state initially reached in the S_n → T_n intersystem crossing could well be different from the roughly isoenergetic T_n state reached in T_1 → T_n absorption, it would be unreasonable to postulate a very rapid isoenergetic S_n-T_n interconversion and at the same time a much slower interconversion between isoenergetic states within the T_n manifold. The reaction path **2** (T_n) → **2** (S_n) → **1** is also highly unlikely. In chromophores such as naphthalene, attempts to observe the T_n → S_n process show that it is very inefficient[19] and we see no reason why the same should not hold in **2**. With efficiencies of the order of a percent or less, it again becomes impossible to account for the observed quantum yield of the process **2** (T_n) → **1** without postulating an efficiency near 100% for the **2** (S_n) → **1** process; yet, the directly measured efficiency of the latter is of the order of 1%.

Thus, it appears likely that the singlet as well as triplet reactions of **2** are separate processes of types already well accepted for other electrocyclic cyclobutene → butadiene ring openings. We propose that excited singlet **2** produces

ground-state singlet **1**, with the return from the excited to the ground potential energy hypersurface presumably occurring at the antiaromatic geometry halfway through the disrotatory reaction path, via the pericyclic minimum resulting from an avoided crossing characteristic of a ground-state "orbital symmetry forbidden" reaction coordinate, as discussed for cyclobutene itself by van der Lugt and Oosterhoff.[20] We propose that triplet **2** produces triplet **1** along a similar disrotatory path, and the low-energy triplet of **1** is then rapidly converted to singlet ground state **1**. We have no direct evidence for the formation of triplet **1** in the triplet photochemical process, nor would observable phosphorescence be expected, but such direct evidence is available in the triplet state opening of a related cyclobutene constrained to open in a disrotatory fashion, 1,4-Dewar naphthalene.[21] Of course, in most instances of triplet state cyclobutene ring openings the equilibrium geometry of the product diene triplet is twisted rather than planar (e.g., for butadiene itself), and we expect the ring opening to take a nonconcerted "semirotatory" reaction path in which only one of the termini of the doubly allylic bond rotates,[12,22] but for constrained "dienes" such as **1** or naphthalene planarity or near planarity of the triplet, and thus a concerted reaction path, appears reasonable.

What sets the "photochemically allowed" disrotatory electrocyclic cyclobutene to butadiene conversion **2** → **1** and related conversions of **3-6** apart from most known "allowed" photochemical cyclobutene ring opening reactions is the absence of reaction from thermalized S_1 and T_1 states and the requirement for extra energy to be available to the molecule before the transformation can occur. Other types of photophysical and photochemical processes have been reported to proceed by the S_0 → S_1 → T_1 → T_n → product and S_0 → S_n → product processes, with S_1 and T_1 being unreactive, and in some of these the need for extra energy is obvious, e.g., in some photoionizations where this sequence of events was established already a long time ago.[23] In the photodissociation of the benzylic C–H bond of methylated aromatics[24] and in the presently discussed class of disrotatory cyclobutene ring-opening reactions the need for extra energy does not simply follow from overall energetics, certainly not for reactions from the S_1 state. Dewar[25] and Dougherty[26] proposed that the need for extra energy in the case of **2** arises from its bichromophoric nature: it is the benzene rather than the naphthalene chromophore which is situated properly with respect to the cyclobutene ring and which thus needs to be excited. This proposal does not explain why 254-nm excitation, which is absorbed by both chromophores, is without effect. Moreover, **3** and **4** behave like **2**, although in these molecules excitation at essentially any wavelength excites both chromophores present. After all, although **2** formally is bichromophoric, the reacting bond is in benzylic position with respect to both chromophores. As soon as motion along the reaction coordinate starts, the two chromophores are in conjugation and their excitations inseparable. Finally, it is worth noting that a photochemical cleavage of the doubly benzylic bond in a strained derivative of acenaphthene upon excitation of the naphthalene chromophore has been reported recently.[27]

In terms of potential energy hypersurfaces, the lack of reactivity of the thermalized S_1 and T_1 states of **2** implies that these emissive states correspond to fairly deep local minima in the S_1 and T_1 surfaces, separated by sizable barriers from regions of geometries where the surfaces slope downhill toward the product geometry (T_1) or toward the presumably present pericyclic minimum which allows efficient return to the ground-state surface followed by motion toward the product geometry (S_1). Extra energy is then needed to move over these barriers: either vibrational energy if the nuclear motions are controlled by the S_1 or T_1 hypersurfaces, or possibly electronic energy, permitting the required nuclear motions to occur in a

higher electronic state in whose hypersurface the barriers are absent. The low quantum yields suggest that the extra energy is not utilized very efficiently; i.e., most of the energy loss (cooling) is vertical and only a small fraction of the molecules manage to move to the other side of the barrier before losing too much energy to the environment.

As pointed out soon after the discovery of the need for extra energy in these reactions[10] and discussed in detail elsewhere,[11,12] the presence of barriers in the S_1 and T_1 surfaces in the reaction **2** → **1** and in similar reactions of **3-6** and their absence in disrotatory opening of most simple cyclobutenes follow readily from orbital and state correlation diagrams. These barriers then are of the same origin as those in photochemically "forbidden" pericyclic processes and show that the original Woodward-Hoffmann rules,[28] which provide the same prediction for all cyclobutenes, need to be modified if they are to be applied to complicated chromophores: not every disrotatory cyclobutene to butadiene ring opening is photochemically "allowed" in the S_1 and T_1 states. The nature of the state correlation diagram is readily deduced from orbital correlation diagrams.[11,12] The barriers found in **2** and related molecules result from "abnormal orbital crossover" (the bonding orbital ψ_1 and the antibonding orbital ψ_2 which cross along the reaction coordinate are not the HOMO and the LUMO of the system, respectively, so that the frontier orbital approximation is inappropriate). The occurrence of abnormal orbital crossover can be usually predicted by inspection of the size and sign of the coefficients in Hückel molecular orbitals of the π systems with respect to which the bonds to be broken or made are benzylic. Some ambiguity results from the requirement of sufficiently large coefficients at the proper positions,[11,12] since it is not always clear just how large they need to be. Thus, we originally expected only a small barrier to the opening of the cyclobutene **7** but in reality the barrier appears to be sizable.[7]

In summary, the physical basis for the need for extra energy in the reactions of type **2** → **1** appears to be qualitatively well understood and predictions for other molecules are possible. It has become clear that for systems of this degree of complication the original simple formulations of the Woodward-Hoffmann[28] or van der Lugt-Oosterhoff[20] photochemical rules are not applicable (note that the presence of the pericyclic minimum in itself does not make the reaction allowed; one also needs the lowest excited state of the starting material to correlate with a low-lying excited state of the product). Clearly, however, the underlying physical principles remain valid. A more detailed discussion is available in ref 29.

A final comment on the likely generality of the phenomena described here for the cyclobutene **2** is in place. There is no reason to believe that the rates of the photophysical processes in **2**, such as internal conversion, are anything but normal. The order of magnitude of 1% may thus be a usual reaction efficiency for higher and/or hot excited singlet and triplet states of other photoreactive organic molecules, too (cf. ref 30). Consequently, hot and/or upper state contributions may be quite common in monomolecular organic photochemical reactions initiated from any excited level above the thermalized S_1 (or T_1) state. It is common practice to ignore these types of contributions in mechanistic schemes. How good an approximation this is will clearly depend on the quantum yield with which the reaction proceeds from the thermalized S_1 (or T_1) state. If this is quite low, the standard practice is questionable. Certainly, when the thermalized quantum yield is zero within experimental error, as is the case for **2**, the "hot contribution" is the only contribution and it becomes difficult indeed to justify its neglect. Although wavelength dependence in organic photochemistry can occur for a variety of reasons, it is likely that some of the recent findings of such dependence are related to the phenomena studied here (cf. ref 9 and 30).

Experimental Section

The preparation and purification of samples have been described.[4,6] All measurements were done at the temperature of liquid nitrogen in a rigid 3-MP glass. The purification of the solvent followed the procedure of ref 4. All concentrations given in the text refer to room temperature volumes and are not corrected for shrinkage upon cooling to 77 K. However, such corrections (a factor of 1.28) were incorporated in all calculations which required knowledge of extinction coefficients. Samples were degassed by freeze-pump-thaw cycles using a 10^{-6} Torr vacuum line; only one-photon photochemical quantum yields were measured on undegassed samples. The Suprasil sample cells and liquid nitrogen Dewars were as in ref 4. Absorption spectra were measured on a Cary 17 spectrophotometer; emissions were measured in the front-surface excitation mode on a homemade instrument described elsewhere.[31]

The light sources for photochemistry were low-pressure metal vapor lamps (Zn, 214 nm; Cd, 229 nm; Hg, 254 nm), medium-pressure and high-pressure mercury lamps (303 nm), and a high-pressure Xe lamp (>300 nm) with either appropriate interference and glass filters or a 0.25-m monochromator isolating the desired lines. Neutral density filters were used to vary light intensity. All measurements were repeated at least three to four times, except for the quantum yield for the second photon, which was measured twice.

Fluorescence and Phosphorescence. The emission spectra were not corrected; the excitation spectra were corrected in the region 245-320 nm by comparison with the absorption and emission spectra of naphthalene measured under the same conditions, assuming a wavelength-independent quantum yield for naphthalene. Below 245 nm the intensity of the xenon light source was too low. Down to 245 nm, the excitation spectra of fluorescence and of phosphorescence are identical. The ratio of fluorescence to phosphorescence intensity was also measured using other monochromatic light sources and found to be the same within ±5% at 214, 229, 254, and 287.5 nm. The quantum yields were determined using naphthalene as standard. The angle between the incident and emitted beams was ~55° in order to avoid complications due to photoselection.[32] The measurements were performed by adjusting the position of a cell with a ~2 × 10^{-4} M solution of **2** in the Dewar to maximize signal intensity, recording the emission, replacing the cell by a cell with naphthalene solution (~4 × 10^{-4} M) of the same optical density at the exciting wavelength (287.5 nm), maximizing signal intensity, recording the emission, replacing the cell by the one with the solution of **2**, etc. The process was repeated five times for each sample and the results were very reproducible. The quantum yields were evaluated by measurement of areas under the emission curves, using the value 0.31 for the fluorescence quantum yield and 0.033 for the phosphorescence quantum yield of naphthalene.[33] The lifetime of the phosphorescence of **2** was measured by exciting a 8 × 10^{-5} M solution at 287.5 nm and monitoring the decay of the emission at 513 nm, digitizing the data and finding the best exponential fit on a PDP-11/10 minicomputer.

Photochemistry. The photochemical conversion **2** → **1** was monitored as a function of time by absorption at 433 nm, where **1** has an intense peak (ϵ 15 000)[4-6] while **2** does not absorb. All conversions were less than 10%. The quantum yields at 214 and 229 nm (metal lamp plus a 220-nm broad-band interference reflection filter) were measured using the uranyl oxalate actinometer described by Pitts et al.[34] (1 × 10^{-3} to 5 × 10^{-3} M, quantum yield of photodecomposition 0.51 at 214 nm and 0.575 at 229 nm[35]). The concentration used at 214 nm was 4 × 10^{-4} M; the concentrations used at 229 nm were varied between 2 × 10^{-3} and 8 × 10^{-5} M with no effect on the result. The quantum yield at 254 nm (low-pressure Hg lamp, 260-nm broad-band interference reflection filter) was measured using the ferrioxalate actinometer.[36] The concentration of **2** was 4 × 10^{-4} M.

The intensities of the two light beams needed for the determination of the quantum yield of the second step in the two-photon process were determined by ferrioxalate actinometry. The sample absorbed the UV beam completely; the triplet-triplet optical density was calculated according to ref 16 assuming ϵ_{TT} = 10^4 L/mol·cm. The first beam was obtained from a 200-W high-pressure mercury lamp and passed through a water filter, a 310-nm broad-band interference reflection filter, and a 310-nm narrow-band interference filter. The second beam was obtained from a 1000-W high-pressure xenon lamp and passed through a water filter, and Schott WG2, WG7, and WG280 and Corning 7-39 glass filters (350 < λ < 410 nm).

In the measurement of the action spectrum, the second beam was

obtained from a 1-kW Xe arc by passing through a water filter and a Barr and Stroud circular wedge filter (UGS in the UV, CGS in the visible). Its intensity as a function of wavelength was measured by an Eppley thermopile calibrated by actinometry. The measured reaction rate was corrected for the independently determined small amount of reaction due to the first beam alone.

In the determination of the lifetime of the intermediate, light from a 1-kW Xe arc was passed through a water filter, Schott WG4 and GG18 filters, and converged on the sample through an ~120° open sector in a slowly rotating large disk. The disk also contained a trigger located at an adjustable angle before the open sector. The trigger fired a Xenon Corp. water-cooled Xe flash lamp (Micropulser, 7000 V) located behind the sample. The total irradiation time was 2 h for each delay setting.

References and Notes

(1) Part 3: R. P. Steiner and J. Michl, *J. Am. Chem. Soc.*, **100**, 6413 (1978).
(2) NATO Postdoctoral Fellow, 1975-76.
(3) J. Kolc and J. Michl, *J. Am. Chem. Soc.*, **92**, 4147-4148 (1970).
(4) J. Kolc and J. Michl, *J. Am. Chem. Soc.*, **95**, 7391-7401 (1973).
(5) J. Downing, V. Dvořák, J. Kolc, A. Manzara, and J. Michl, *Chem. Phys. Lett.*, **17**, 70-73 (1972).
(6) J. Kolc, J. W. Downing, A. P. Manzara, and J. Michl, *J. Am. Chem. Soc.*, **98**, 930-937 (1976).
(7) J. M. Labrum, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **96**, 2636-2637 (1974).
(8) J. Michl and J. Kolc, *J. Am. Chem. Soc.*, **92**, 4148-4150 (1970).
(9) J. Michl, A. Castellan, M. A. Souto, and J. Kolc in "Excited States in Organic Chemistry and Biochemistry", B. Pullman and N. Goldblum, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1977, pp 361-371.
(10) J. Michl, *J. Am. Chem. Soc.*, **93**, 523-524 (1971).
(11) J. Michl, *Mol. Photochem.*, **4**, 287-314 (1972).
(12) J. Michl in "Chemical Reactivity and Reaction Paths", G. Klopman, Ed., Wiley, New York, N.Y., 1974, Chapter 8.
(13) J. Michl and E. W. Thulstrup, *Spectrosc. Lett.*, **10**, 401-415 (1977).
(14) A. C. Hazell and R. G. Hazell, *Acta Crystallogr., Sect. B*, **33**, 360-365 (1977).
(15) Y. H. Meyer, R. Astier, and J. M. Leclercq, *J. Chem. Phys.*, **56**, 801-815 (1972).
(16) R. A. Keller and S. G. Hadley, *J. Chem. Phys.*, **42**, 2382-2387 (1965).
(17) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Am. Chem. Soc.*, **92**, 7604-7606 (1970).
(18) N. J. Turro, V. Ramamurthy, R. M. Pagni, and J. A. Butcher, Jr., *J. Org. Chem.*, **42**, 92-96 (1977).
(19) R. A. Keller, *Chem. Phys. Lett.*, **3**, 27-29 (1969).
(20) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042-6049 (1969).
(21) R. V. Carr, B. Kim, J. K. McVey, N. C. Yang, W. Gerhartz, and J. Michl, *Chem. Phys. Lett.*, **39**, 57-60 (1976).
(22) J. Michl, *Mol. Photochem.*, **4**, 257-286 (1972).
(23) For a review, see R. Lesclaux and J. Joussot-Dubien in "Organic Molecular Photophysics", Vol. 1, J. B. Birks, Ed., Wiley, New York, N.Y., 1973, pp 457-487.
(24) F. P. Schwarz and A. C. Albrecht, *J. Phys. Chem.*, **77**, 2411-2417, 2808-2822 (1973), and references cited therein.
(25) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761-776 (1971).
(26) R. C. Dougherty, *J. Am. Chem. Soc.*, **93**, 7187-7201 (1971).
(27) J.-F. Muller, D. Muller, H. J. Dewey, and J. Michl, *J. Am. Chem. Soc.*, **100**, 1629-1630 (1978).
(28) For a review, see R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781-852 (1969).
(29) J. Michl, *Top. Curr. Chem.*, **46**, 1-59 (1974).
(30) M. A. Souto, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, following paper in this issue.
(31) J. Kolc, E. W. Thulstrup, and J. Michl, *J. Am. Chem. Soc.*, **96**, 7188-7202 (1974).
(32) A. H. Kalantar, *J. Chem. Phys.*, **48**, 4992-4996 (1968).
(33) R. Li and E. C. Lim, *J. Chem. Phys.*, **57**, 605-612 (1972), report $\phi_F = 0.37$ and $\phi_{PH} = 0.04$ in EPA at 77 K, using a nondegassed solution of 9,10-diphenylanthracene as a standard with $\phi_F = 1.0$. These values must be multiplied by 0.83: G. Heinrich, S. Schoof, and H. Gusten, *J. Photochem.*, **3**, 315-320 (1974-1975); cf. K. Salisbury, *Spec. Period. Rep.: Photochem.*, **8**, 60-104 (1977). V. L. Ermolaev, *Sov. Phys. Usp.* **6**, 333-358 (1963), gives $\phi_F = 0.29$.
(34) J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor, and W. Brim, *J. Am. Chem. Soc.*, **77**, 5499-5501 (1955).
(35) G. S. Forbes and L. J. Heidt, *J. Am. Chem. Soc.*, **56**, 2363-2365 (1934); the value taken for 229 nm is the average of values reported for 214 (0.51) and 254 nm (0.64).
(36) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518-536 (1956).

Upper and/or Hot Excited States in Organic Photochemistry in Dense Media. A Cycloreversion in a Polycyclic Cyclobutene†1

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Abstract: The mechanism of the photochemical cycloreversion reaction of the condensed cyclobutene **1** to phenanthrene in a rigid glass at 77 K with long-wavelength light involves successive absorption of two photons, with triplet **1** as the intermediate state. At short wavelengths, the reaction proceeds by the ordinary one-photon mechanism. It is concluded that thermalized S_1 and T_1 states of **1** are unreactive and that the reaction occurs with significant quantum yields in upper and/or hot singlet and triplet excited states. The results reinforce existing doubts concerning the general validity of the usual assumption of exclusive role of cool S_1 and T_1 states in organic photoreactions in dense media.

In photochemical reactions of organic molecules in fluid or rigid solutions, and even in gas phase at moderate to high pressures, it is commonly assumed without question that both internal conversion to the lowest excited electronic state of the initially reached multiplicity and thermal equilibration of vibrational motion with the surrounding medium occur much more rapidly than any chemical transformations. Mechanistic schemes proposed for reactions initiated by direct irradiation

in dense media then typically start with a thermally equilibrated ("cool") lowest excited singlet state S_1 even if the original excitation is to a higher vibronic level, or, exceptionally, with a cool lowest triplet state T_1 if the molecule contains special structural features[2] which greatly enhance the intersystem crossing rate. Similarly, mechanistic schemes for sensitized reactions typically start with a cool T_1 species. Acknowledged exceptions to the general rule that organic photochemical reactions in dense media occur only from cool S_1 and T_1 states are provided, first, by molecules in which S_2 or

† Dedicated to Professor Egbert Havinga on the occasion of his 70th birthday.