36. Photoisomerization Pathways of 8,16-Methano[2.2]metacyclophane-1,9-diene. A Model Case for Adiabatic Electrocyclic Ring Closure in the Excited Singlet State

by **Jakob Wirz***, **Gabriele Persy** and **Erika Rommel**

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and **Ichiro Murata** and **Kazuhiro Nakasuji**

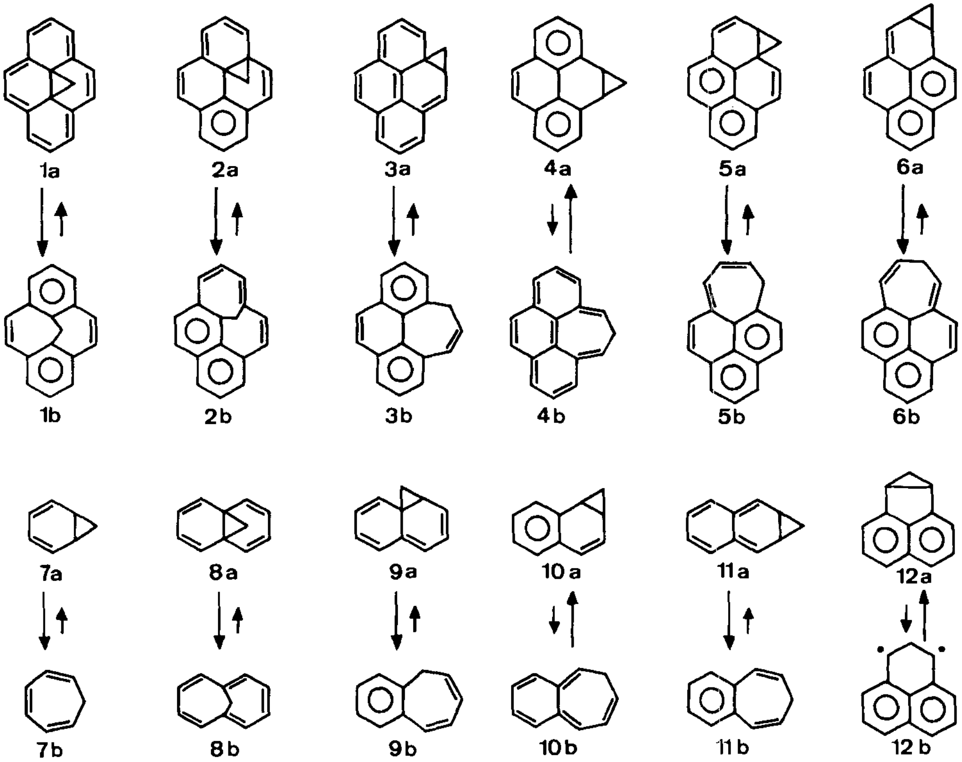
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(9.XI.83)

Summary

The title compound **1b** ideally meets the theoretical requirements for the occurrence of an adiabatic photoisomerization in the lowest excited singlet state (^{1}**1b***) and, indeed, the predominant primary photoreaction observed is the conversion to its fluorescent valence isomer 10b,10c-methano-*cis*-10b,10c-dihydropyrene (^{1}**1a***). The mechanism for the formation of the previously observed photoproduct 8b,9a-dihydro-9*H*-cyclopropa[*e*]pyrene (**4a**) has been analyzed in some detail *(Scheme)*. Below −30°C the reaction path consists of a three quantum process (two di-π-methane rearrangements and a photochemical 1,7-H shift) involving two thermally stable, but light-sensitive isomers, 8,11b-methanocyclodeca[*cde*]naphthalene (**2b**) and 9*H*-cyclohepta[*def*]-phenanthrene (**3b**). At room temperature the rearrangement **2b**→**4a** proceeds with a single excitation step bypassing the ground state intermediate **3b**. Finally, upon prolonged irradiation of **4a**, the methylene group is lost to yield pyrene. Compound **2b** completes the series of all possible adducts of methylene to a C=C bond of pyrene.

Introduction. – The homologization of aromatic hydrocarbons by the replacement of one or more C=C subunits by cyclopropane rings has been a rich source of exciting new compounds. The addition of methylene to pyrene is formally possible at six nonequivalent C=C bonds giving rise to six constitutionally isomeric cyclopropa-dihydropyrenes (**1a** to **6a**). Each of these is associated with a ring-opened valence tautomer (**1b** to **6b**) in analogy to the well-known norcaradiene (**7a**) – cycloheptatriene (**7b**) pair. In practice, the above reaction yields the single isomer 8b,9a-dihydro-9*H*-cyclopropa[*e*]pyrene (**4a**) [1]. Four other isomers, 9*H*-cyclohepta[*def*]phenanthrene (**3b**) [2], 8,16-methano[2.2]metacyclophane-1,9-diene (**1b**) [3] and a mixture of 6*H*-cyclohepta[*cd*]phenalene (**5b**) and 7*H*-cyclohepta[*cd*]phenalene (**6b**) [4] have been synthesized by different methods. The preparative photolysis of **1b** has yielded the isomer **4a** in near quantitative yield; the valence isomer 10b,10c-methano-*cis*-10b,10c-dihydropyrene (**1a**) was proposed as a plausible intermediate [3]. The radical anion of **1** has been observed by ESR spectroscopy, but an unambiguous identification of its structure (**a** or **b**) has not been possible; it converts readily to the radical anion of pyrene [5a, b].

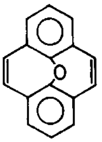


The **a**$\rightleftharpoons$**b** type valence isomerization is an extremely facile, *Woodward-Hoffmann*-allowed process in the ground state [6]. Direct kinetic measurements of the reaction **7a**$\to$**7b** have recently been performed at low temperatures by *Rubin* who obtained a free energy of activation, $\Delta G^{\neq}$ (100 K) = 26 kJ/mol, and an extrapolated room temperature rate constant of $1 \cdot 10^7$ s^{-1} for this process [7]. Thus, depending on the equilibrium constant of a given **a**/**b** pair, only one of the valence isomers (or an equilibrium mixture) is isolable at room temperature as is known from many derivatives of norcaradiene (**7a**) [7] as well as of 1,6-methano[10]annulene (**8b**) [8] and its isomers **9** to **11** [9] [10]. Naphthocyclopropane (**12a**) represents an unusual case, since its open-chain valence isomer **12b** is a biradical with a triplet ground state which is stable at 77 K due to the spin barrier [11].

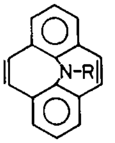
Interconversions between constitutional isomers of cyclopropa-dihydroarenes are known to occur thermally (usually at elevated temperatures), photochemically, and *via* the formation of radical ions. Reactions of the type **a**$\to$(**a'**$\rightleftharpoons$**b'**) have been coined *walk*-rearrangements or *Berson-Willcott* rearrangements and their stereochemical course has been studied in detail on derivatives of norcaradiene (**7a**) [12] and benzonorcaradiene (**10a**) [9]. Reactions of the type **b**$\to$(**a'**$\rightleftharpoons$**b'**) can be formulated either as *di-π-methane* rearrangements [13] or as 1,7-group migrations. The latter mechanism was found to prevail in the photoreactions of the benzotropilidenes **9b** and **11b** [10]. Facile *walk*-rearrangements of radical anions (**8b**$^{\overline{\cdot}}$, **9b**$^{\overline{\cdot}}$, and derivatives) have been reported by *Gerson et al.* [5b,c].

Heteroatom-bridged analogues of **1b** (**13b** and **14b**) and open-chain analogues of **1a** (**15a** and **16a**) have been synthesized by *Boekelheide et al.* [14]. Some derivatives of **1b**, *e.g.* 5,13-dimethoxy-4,6,12,14-tetramethyl-

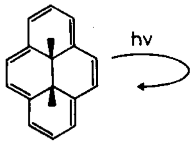
8,16-methano[2.2]metacyclophane-1,9-diene **17b** have also been investigated [15][1]. Evidence for a photochemical or thermal **a**$\rightleftarrows$**b** type valence isomerization was obtained only for the *trans*-configurated 10b,10c-dihydropyrenes (**16a**) [16]. Note that the orbital symmetry conservation rules are inverted for the *trans*-isomers, *i.e.* the valence isomerization **16a**$\rightleftarrows$**16b** is a ground-state-forbidden, excited-state-allowed process. In fact, the photoreaction does proceed in both directions, but the forbidden thermal reaction **16b**$\rightarrow$**16a** is also observed with remarkably low activation energies in the range of $\Delta G^{\neq} = 94 \pm 10$ kJ/mol for various derivatives [16b,c].



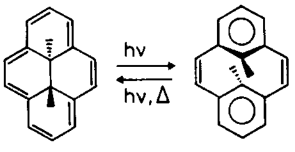
13b



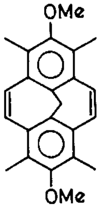
14b



15a

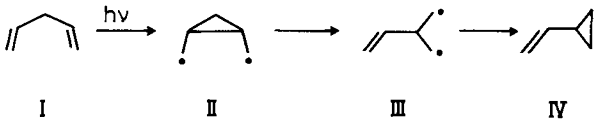


16a **16b**



17b

The photoreaction of the title compound, **1b**$\rightarrow$**4a** [3], has attracted our attention for two reasons. *First,* the remote relationship between **1b** and **4a** immediately raises questions about the reaction mechanism. The high yield of **4a** in dilute solution excludes a methylene expulsion-bimolecular readdition. Does the methylene group then 'bicycle' across three bonds in a single stride? In terms of conventional reactions one might envisage a sequence of three photochemical di-π-methane rearrangements *via* the ground state intermediates **2a**$\rightleftarrows$**2b** and **3a**$\rightleftarrows$**3b**. *Second,* we were interested to study the rôle of the unstable valence isomer **1a** which had been suggested to be an intermediate in this reaction [3]. Indeed, the reaction **1b** $\xrightarrow{h\nu}$ **1a** would correspond to the first step, **I** $\xrightarrow{h\nu}$ **II**, of a di-π-methane rearrangement, **1b**$\rightarrow$**2a**, as expressed by *Zimmerman*'s general scheme [13] shown below.

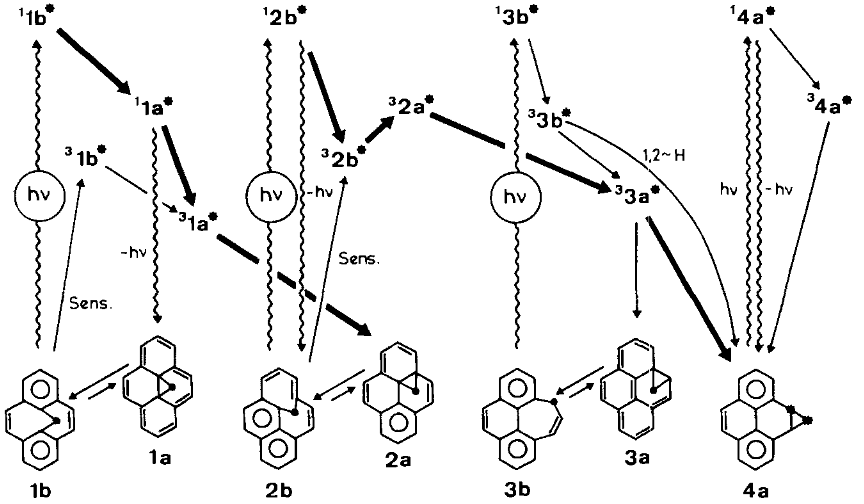


However, two problems arise here. *i*) The same process **1b** $\xrightarrow{h\nu}$ **1a** is forbidden by the *Woodward-Hoffmann* rules since it is allowed in the ground state. *ii*) It is hard to imagine that the subsequent transformation **II**$\rightarrow$**IV**, corresponding in this case to the ground state reaction **1a**$\rightarrow$**2a**, should compete effectively with the facile cycloreversion **1a**$\rightarrow$**1b**. The present work provides detailed insight into the complex mechanism of the unusual photoreaction **1b**$\rightarrow$**4a**. It will be shown that the primary photoprocess

---

[1] In the patent literature [15b, c] these derivatives are described as blue, sublimable solids. It is likely that the blue colour arose from the presence of impurities, *e.g.* derivatives of **15a** or **16a**.

proceeds adiabatically yielding ^{1}**1a*** (the lowest excited singlet state of the valence isomer **1a**) *because* this process is classified as a forbidden reaction. A major decay pathway from ^{1}**1a*** then leads to the isomer 8,11b-methanocyclodeca[*cde*]naphthalene (**2b**). A second photoreaction yields the isomer **4a** from **2b**. The results are summarized in the *Scheme*.



Scheme. *Mechanistic Proposal for the Photochemical Transformation* **1b→4a**. The suggested positions of the original methano-C-atom (● or two alternative *) have not been established.

Results. – To begin with, the reader should be adverted that the amount of starting material **1b** available for this study was *ca.* 10 mg which posed some limitations on the preparative work. Nevertheless, the new compound **2b** has been unambiguously identified by its fully resolved high-field ^{1}H-NMR spectrum[2]). The reaction mechanism was studied by the combined methods of kinetic and spectrographic laser flash photolysis, continuous monochromatic photolysis with intermittent spectrophotometric analysis, fluorescence measurements, quantum yield determinations, and steady-state quenching analyses. These measurements were done at various temperatures down to 77 K.

The First Photoreaction **1b→2b**. The spectrophotometric monitoring of the conversion of **1b** to **4a** upon 313-nm irradiation and the analysis of these spectra by the method *Mauser* [17] immediately revealed that the reaction proceeded *via* a spectroscopically detectable intermediate. The secondary photolysis of this intermediate was found to be strongly retarded by the admission of oxygen or by lowering the temperature. Irradiation of **1b** in an EPA glass (5 parts diethylether, 5 parts isopentane, 2 parts ethanol) at 77 K thus gave a clean conversion to this intermediate *(Fig. 1)* which was isolated and identified as 8,11b-methanocyclodeca[*cde*]naphthalene (**2b**), a naphtho-derivative of 1,6-methano[10]annulene. Prolonged overirradiation of **2b** at 77 K resulted in the formation of pyrene.

---

[2]) We are most grateful to Prof. *Hans Fritz, Ciba-Geigy SA*, Basel, for providing this spectrum and for valuable assistance in the analysis.

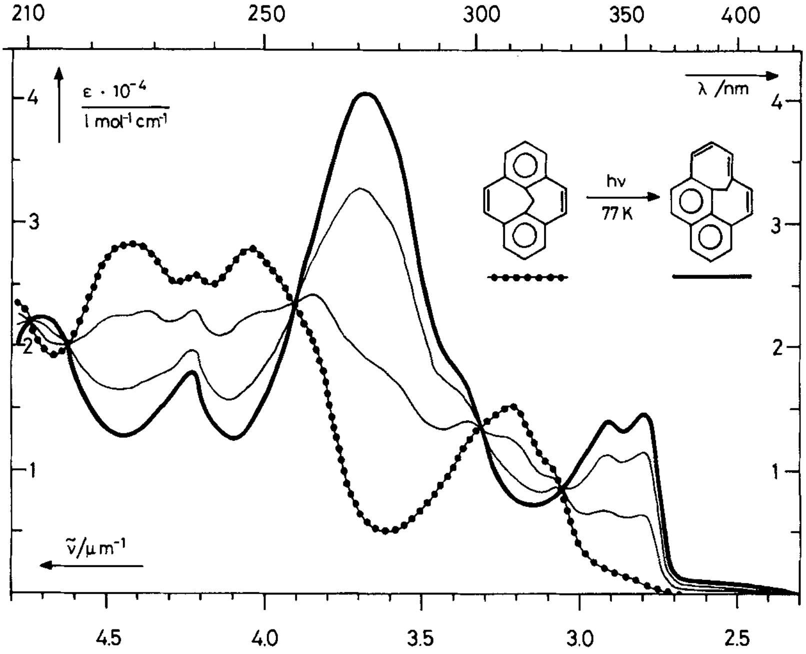


Fig. 1. *Photochemical conversion of* **1b** *to* **2b** *in an EPA glass at 77 K*

Spectrographic laser flash photolysis of **1b** showed that the photoproduct **2b** was formed within ≈ 50 ns and no transient intermediate was detected even at low temperature. *Fig. 2* displays the fluorescence spectrum of **1b** obtained by excitation of a fresh, degassed hexane solution with a single laser pulse at 265 nm. The three components ① to ③ were readily separated due to their widely different lifetimes by choosing different delay times and time windows on the gateable image intensifier of the diode array camera. The weak, structured component ① ($\lambda_{max} = 391$ nm) was very long-lived ($\tau = 450 \pm 30$ ns at ambient temperature), identical with the fluorescence of pyrene. Component ② ($\lambda_{max} = 463$ nm) was short-lived ($\tau \leq 7$ ns) and later found to correspond to the fluorescence of **2b**. The intensity of this component increased rapidly when the same solution was flashed repeatedly. The observation of ① and ② may be attributed to biphotonic processes within the laser pulse, *i.e.* formation of pyrene and **2b** and reexcitation within 20 ns, and/or the presence of these compounds as minor impurities prior to photolysis.

The *red fluorescence emission* ③ ($\lambda_{max} = 595$ nm) had a lifetime τ of (16 ± 2) ns in degassed and ≤ 7 ns in aerated solution. Its quantum yield ϕ_F was determined as 0.04 ± 0.01 *(cf. Experimental)* and its excitation spectrum was in excellent agreement with the absorption spectrum of **1b**. The spectral distribution of the emission did not change with temperature down to −180 °C until a rather sudden colour change from red to yellow-orange ($\lambda_{max} = 563$ nm) was observed on further cooling. Crystals of **1b** also exhibited a bright-yellow structureless fluorescence emission ($\lambda_{max} = 564$ nm). Similar qualitative observations (reddish fluorescence in solution, yellow fluorescence of the solid) have been reported some time ago for the derivative **16b** [15a]. The unusually

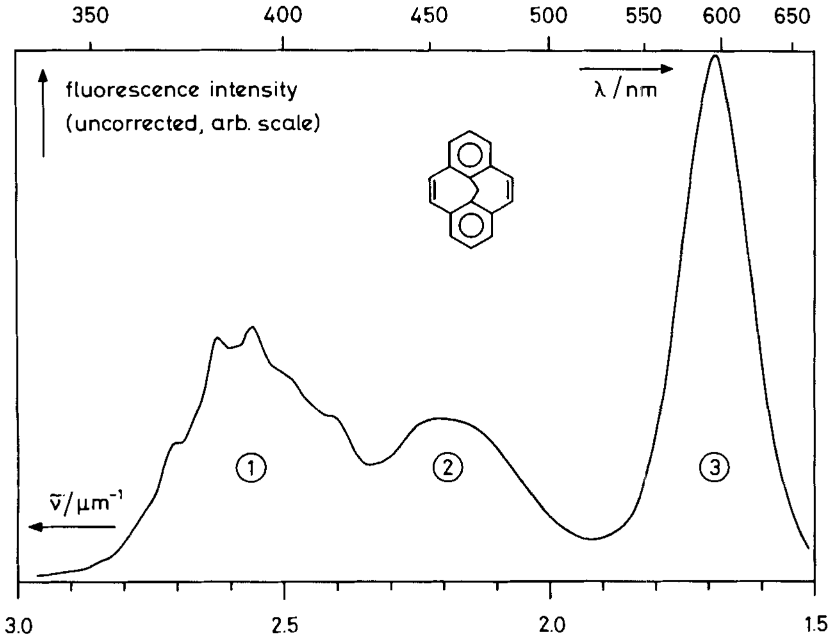


Fig. 2. *Fluorescence emission of* **1b** *in degassed hexane at ambient temperature.* The settings of the image intensifier (time delay and window) were chosen so as to maximize the intensities of components ① and ②.

large *Stokes'* shift (long wavelength absorption onset *ca.* 380 nm, short wavelength emission onset *ca.* 540 nm) and the distinct blue shift associated with the hardening of the EPA glass at −185 °C both clearly show that the emitting species must have a different structure than the absorbing compound **1b**. The blue shift in the solid environments reflects a partial inhibition of this structural change. Note that in the usual case of molecules undergoing minor geometrical changes upon excitation the emission spectrum of their crystalline solids is red-shifted due to exciton interactions.

The assignment of the emitting species to the excited valence isomer ^{1}**1a*** is then near at hand. The first absorption band (^1L_b) of the related hydrocarbon **15a** lies at 602 nm [14c]. For **1a** one would expect to find this band at somewhat shorter wavelengths due to the distortion of the [14]annulene moiety arising from the cyclopropane bridge. This is in perfect agreement with the position of the red emission ③. Since the ^1L_b bands of [4n + 2]annulenes have very low oscillator strengths, $f = 0.001$ to 0.003 (*cf. e.g.* the spectra of **15a** [14c] and **16a** [16b]), the radiative rate constant k_F for fluorescence emission from ^{1}**1a*** should lie in the range of $(1 \text{ to } 3) \cdot 10^6\ s^{-1}$. From the experimental values of ϕ_F and τ we obtain, *via* the relation $\phi_F = \phi_{ad} \cdot k_F \cdot \tau$, a value of $(2.5 \pm 1) \cdot 10^6\ s^{-1}$ for $k_F \cdot \phi_{ad}$. We conclude that ϕ_{ad}, the quantum yield for the adiabatic process ^{1}**1b***→^{1}**1a***, is not far from unity. In fact this process is probably by far the most efficient decay channel for ^{1}**1b***, *i.e.* $\phi_{ad} = 1$, since we have not been able to detect any fluorescence from ^{1}**1b*** above the weak and long-lived background ① from pyrene which was virtually absent in the emission spectrum of crystalline **1b**. Also there was no evidence for a grow-in of the fluorescence of ^{1}**1a*** at the end of the laser pulse (*ca.* 5 ns). The alternative interpretation that the red emission arises from direct excitation of **1a**, which may be present in a small equilibrium concentration with **1b**, is clearly ruled out by the above results (excitation spectrum, quantum yield). We estimate that even trace concentrations of **1a** down to a mole fraction of 10^{-4} would have been readily detected by the sensitive technique of fluorescence excitation. **1a** should exhibit a moderately strong ^1L_a band near 430 nm (log $\varepsilon \approx 4$) while the absorption and excitation spectra of concentrated solutions of **1b** were completely blank above 390 nm.

The quantum yield ϕ_{2b} for the formation of **2b** from **1b** in degassed hexane with 313 nm light was 0.3 ± 0.1. It was not reduced by the addition of *cis*-piperylene (up to 10M, *i.e.* neat) or oxygen (up to 2 atm). In fact, the admission of oxygen resulted in a slight but significant increase of ϕ_{2b} to a value of 0.4 ± 0.1 (the statistical errors of these measurements were, of course, much smaller than the estimated absolute error limits quoted). This rather unusual observation is, by itself, a good indication for the occurrence of a fast adiabatic reaction [18]. On the other hand, the intensity of the fluorescence ③ was quenched by a factor of $(13 \pm 2)^{-1}$ in a solution saturated with 1 atm of oxygen in accordance with the observed reduction of the lifetime τ upon the admission of air. We interpret these results as follows. There are three competitive decay channels for ^{1}**1a***: fluorescence ($\phi_F = 0.04$) and radiationless internal conversion ($\phi_{IC} = 0.6_6$) yielding **1a** in the ground state, and intersystem crossing ($\phi_{ISC} = 0.3$) yielding ^{3}**1a*** which rapidly (≤ 50 ns) forms **2b**. Oxygen quenching of ^{1}**1a*** gives rise to an enhanced yield of ^{3}**1a*** and thus of **2b** *(Scheme).*

The triplet state of benzophenone, observed at 530 nm after 353-nm excitation, was quenched at an approximately diffusion-controlled rate by **1b** (10^{-3}M) in acetonitrile solution. No further transient absorption resulting from the quenching process was detected. TLC analysis of the product mixture after steady-state irradiation of the same solution at 365 nm indicated the formation of **2b** and **4a** from **1b**. Thus it is likely that ^{3}**1b*** is also short-lived due to a rapid adiabatic reaction to ^{3}**1a***. Sensitization experiments were not further pursued due to material restrictions.

In spite of a careful search we have not been able to obtain direct evidence by flash photolysis for the ground state reactions **1a**→**1b** and **2a**→**2b** although, according to our analysis, these intermediates should be formed with a quantum yield of 0.7 and 0.3, respectively. However, this is not surprising in view of the rate of the norcaradiene (**7a**)→cycloheptatriene (**7b**) cycloreversion of 10^7 s^{-1} at room temperature [7]. The disappearance of **1a** and **2a** may be expected to be even faster considering the additional strain energy of these systems. Thus the lifetime of **1a** is probably shorter than that of its excited state precursor ^{1}**1a***. In fact, our experimental evidence that ^{1}**1a*** is produced by an adiabatic reaction is most convincing *because* the photoproduct has no stable ground state and therefore the emission cannot be due to the trivial two quantum process of ground state product formation and subsequent re-excitation under steady-state irradiation [19].

The Second Photoreaction **2b**→**3b** *and/or* **4a**. At room temperature the photoisomerization **2b**→**4a** proceeded smoothly without the intervention of a spectroscopically detectable intermediate (irradiation at 313, 365, or 405 nm of *ca.* 10^{-4}M solutions of **2b** in degassed hexane). A quantum yield ϕ_{4a} close to unity (experimental value 0.7 ± 0.2, 365 nm) was determined under these conditions. As noted above, this reaction was strongly quenched by the admission of oxygen or by lowering the temperature. It was reduced by a factor of $(7 \pm 1)^{-1}$ in oxygen-saturated solution. Lowering the temperature not only reduced the reaction rate but also changed the product distribution. At 77 K the reaction was virtually halted except for the very slow formation of pyrene which was identified by its absorption spectrum, fluorescence spectrum, and fluorescence lifetime3).

At moderately low temperatures (below −30°C) the intervention of yet another photoproduct became apparent, particularly under 405-nm irradiation, by which it was not further photolyzed and accumulated to about 30% of the product balance. The absence of this product in the room temperature photolyses was not due to its thermal instability but to a change in the photochemical reaction mechanism. The new compound could be isolated, though not fully separated from **4a**, by TLC at room temperature and was identified as 9*H*-cyclohepta[*def*]phenanthrene (**3b**) by ^{1}H-NMR spectroscopic comparison with an authentic sample [2].

The fluorescence characteristics of **2b** (spectrum, lifetime) have been already described as those of component ② (*cf. Fig. 2*). Flash photolysis of **2b** in degassed hexane gave rise to a broad transient absorption (λ_{max} 490 nm and 390 nm, *Fig. 3*) with a lifetime of (200 ± 50) ns at room temperature which was reduced to (100 ± 30) ns in air-saturated solution. The lifetime of this transient rapidly increased upon lowering the temperature *(Table)*. Taken together with the dependence of the quantum yield ϕ_{4a} on the same parameters (oxygen concentration and temperature) these data provide convincing evidence for the identification of this transient as $^{3}\mathbf{2b}^{*}$ and as a reactive intermediate of the photoisomerization **2b**→**4a**. The fact that at room temperature this reaction proceeds with a single excitation step suggests that $^{3}\mathbf{2b}^{*}$ is adiabatically converted *via* $^{3}\mathbf{2a}^{*}$ to $^{3}\mathbf{3a}^{*}$, which then proceeds to **4a** at room temperature, but is partly diverted to ($\mathbf{3a} \rightleftharpoons \mathbf{3b}$) at temperatures below −30°C *(Scheme)*. The lifetime data for $^{3}\mathbf{2b}^{*}$ collected in the *Table* do not give a linear *Arrhenius* plot (log *k vs.* $1/T$). The curvature suggests that two processes compete for the deactivation of $^{3}\mathbf{2b}^{*}$, one with a 'normal' preexponential factor $A \cong 10^{13}$ s^{-1} and an activation energy $E_a \cong 40$ kJ/mol dominating at high temperature, and a second process with both a low *A*-factor (*ca.* 10^{4} s^{-1}) and a low activation energy dominating at low temperature. These observations nicely support the suggested mechanism if we associate the first process with the spin-allowed, adiabatic reaction $^{3}\mathbf{2b}^{*} \rightarrow {}^{3}\mathbf{2a}^{*}$ and the second process with a nonradiative decay channel to **2b**.

The Third Photoreaction **3b**→**4a**. This reaction was not investigated in detail. Spectrophotometric monitoring of the reaction indicated a clean conversion of **3b** to **4a** upon 313- or 365-nm irradiation of a 10^{-4}M solution in degassed hexane. In analogy to the results with benzotropilidenes (**9b** and **11b**) [10], the reaction mechanism is more

Table. *Lifetimes* τ *of* $^{3}\mathbf{2b}^{*}$ *in Degassed Petroleum Ether at Various Temperatures*

τ/μs	0.20 ± 0.05	2.0 ± 0.3	8.4 ± 1	25 ± 5
T/K	295	250	225	195

---

3) These data allow for a clearcut distinction between pyrene and its methyl-derivatives [20]. We are grateful to Prof. *R. G. Harvey*, University of Chicago, for a gift of 4-methylpyrene.

likely described as a 1,7-H shift than as a di-π-methane rearrangement. In this case the methylene C-atom of **1b** would migrate to the 8b-position of **4a** in the overall reaction sequence *(Scheme)*.

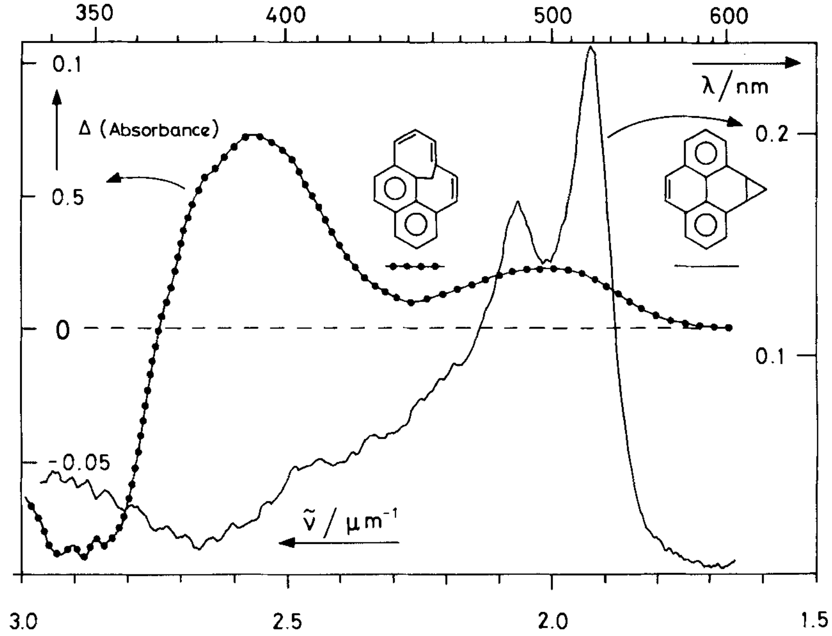


Fig. 3. *Triplet-triplet absorption spectra of* $^{3}\mathbf{2b}^{*}$ *and* $^{3}\mathbf{4a}^{*}$ *in degassed hexane at ambient temperature*

The Fourth Photoreaction **4a**→*Pyrene.* Although **4a** is relatively photostable and was formed in near quantitative yield by preparative photolysis of **1b** at room temperature, prolonged irradiation of **4a** yielded pyrene as a final product in a very slow, but essentially clean photoreaction. Evidence presented above shows that pyrene was also formed as a minor side product in the photolyses of **2b** and probably **1b**. We note in passing that the amino-bridged analogues **14b** ($R{=}NCH_3$) and **14b** ($R{=}N{-}CO_2CH_2CH_3$) have yielded pyrene as a main photoproduct[4]).

The photophysical properties of **4a** were determined as follows. The moderately intense fluorescence (λ_{max} = 390 nm) had a lifetime of (13 ± 1) ns at room temperature and the triplet absorption spectrum *(Fig. 3)*, which is similar to that of phenanthrene [21], was readily observed upon direct excitation. These data are unexceptional for a photo-stable aromatic hydrocarbon. However, the triplet lifetime was only (4 ± 1) µs in degassed solution at ambient temperature, much shorter than the lifetimes of *ca.* 1 ms observed for purely benzenoid hydrocarbons (*e.g.* phenanthrene) in solution. This may well be due to a thermally activated, adiabatic valence isomerization $^{3}\mathbf{4a}^{*} \rightarrow {}^{3}\mathbf{4b}^{*}$, followed by rapid intersystem crossing to **4b** and thermal recyclization to **4a**.

---

[4]) We thank Prof. *V. Boekelheide*, University of Oregon, for samples of these compounds.

Discussion. – We have shown that the photoisomerization of the title compound (**1b**) to 8b,9a-dihydro-9*H*-cyclopropa[*e*]pyrene (**4a**) is a two- or three-quantum process depending on the temperature. At room temperature the main pathway involves two sequential photoreactions with 8,11b-methanocyclodeca[*cde*]naphthalene (**2b**) as a thermally stable ground state intermediate. At temperatures below −30 °C the reaction proceeds in part *via* a second ground state intermediate, 9*H*-cyclohepta-[*def*]phenanthrene (**3b**). The first two reactions, **1b**→**2b** and **2b**→**3b**, may be classified as di-π-methane rearrangements, while the third, **3b**→**4a**, more probably corresponds to a 1,7-H shift. Pyrene is formed as a final product upon prolonged irradiation *(Scheme)*.

The occurrence of sequential photoreactions is probably a common, but often overlooked phenomenon in preparative photolyses. Such cases may be readily detected by intermittent spectrophotometric monitoring of the reaction progress using dilute solutions. The computer-assisted quantitative analysis of these spectra by various numerical methods [17] [22] is advantageous, but qualitative conclusions are often possible on inspection, *e.g.* from the presence or absence of isosbestic points. In favourable cases, such as the present one, the sequential reactions may then be disentangled by a variation of manageable parameters like the irradiation wavelength or dose, the temperature, and the presence or absence of quenchers (oxygen, piperylene) or sensitizers. This certainly helps to elucidate the mechanism of photochemical reactions and may lead to the synthesis of new products of practical interest. The new compound, **2b**, obtained on this work completes the series of all possible adducts of methylene to a C=C bond of pyrene (**1** to **6**).

The experimental data reported for the first photoreaction **1b**→**2b** provide convincing evidence that the primary photochemical process following excitation is an essentially *quantitative adiabatic electrocyclic ring closure in the lowest excited singlet state,* ^{1}**1b***→^{1}**1a***. Notwithstanding, this same reaction is classified as an excited-state-forbidden process in the sense of the *Woodward-Hoffmann* rules: '... and there is in general, corresponding to every ground state reaction, a related excited-state process for which the rule is simply reversed' [6]. The success of this rule in the realm of photochemistry has been a puzzling fact for some years after its enunciation, mainly for two reasons. *First,* the molecular orbital arguments put forward were applicable only to adiabatic photoreactions leading to the photoproduct in an excited state. In many cases, such as the photochemical electrocyclization of butadiene, an adiabatic reaction is impossible on energetic grounds. *Second,* a general derivation of the rule for photoreactions was left as an exercise to the reader. Such a derivation is straightforward only by reference to the lowest doubly excited configurations which do not represent the photoreactive state of most reactants in question. However, it is now realized that the doubly excited configurations gain importance as the molecules begin to explore the S_1 surface in providing 'pericyclic minima' or 'funnels' which favour internal conversion to the ground state at biradicaloid geometries and thus determine the structure of the photoproducts [23]. Hence, the products of excited-state-allowed reactions are usually formed in the ground state, *i.e.* these reactions follow a diabatic pathway. Some exceptions have been reported in recent years, noteably highly exergonic cycloreversion reactions which in part yield excited state products [24] [25].

Due to obvious geometrical constraints the valence isomerization **1b**⇄**1a** is forced to follow a ground-state-allowed, excited-state-forbidden pathway. Note, however, that the orbital symmetry conservation rules do not, in general, predict a symmetry-imposed barrier for an excited state reaction, be it allowed or forbidden. In particular, no barrier is predicted from an orbital correlation diagram for the reaction **1b**⇄**1a** (*Fig. 4,*

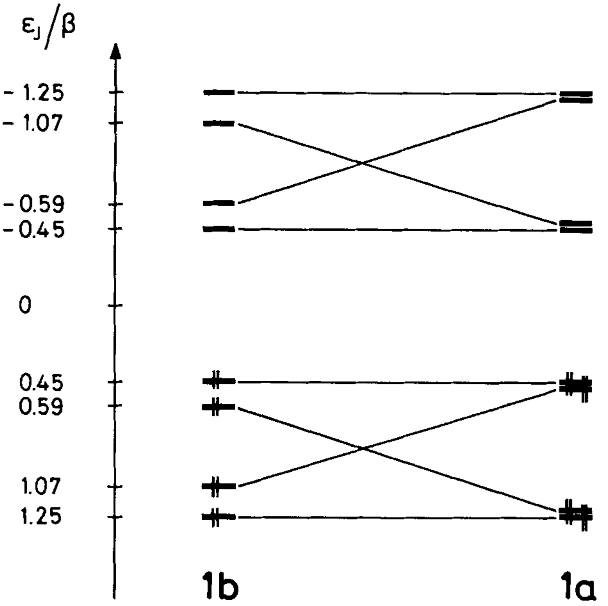


Fig. 4. *Orbital correlation diagram (*Hückel *approximation) for the reaction* **1b**$\rightleftharpoons$**1a**. Only the relevant inner orbitals are shown.

for a more general discussion see [26]). The basic difference lies in the fact that such a reaction pathway avoids biradicaloid molecular geometries where internal conversion to the ground state occurs readily. Thus, if a forbidden excited state reaction is feasible on energetic grounds, and if competitive allowed pathways are barred by some stereochemical bias, the occurrence of an adiabatic reaction should be expected. In essence, these predictions were made many years ago by *Dougherty* [27].

Obviously the title compound ideally meets the requirements defined above. Although the valence isomerization **1b**→**1a** is endergonic by at least 20 kJ/mol in the ground state, corresponding to an equilibrium mole fraction **1a**/(**1a** + **1b**) $\leq 10^{-4}$, this is made up by the large difference of *ca.* 100 kJ/mol in the excitation energies of the stilbene-like **1b** and the bridged [14]annulene **1a**. To our knowledge this is the first example of an adiabatic electrocyclic ring closure in the singlet excited state. The elegant work of *Becker* [28] on the adiabatic singlet state cycloreversion reactions of lepidopterenes has provided a number of examples which also conform to the setting mentioned above, although this has not been explicitly stated.

For reactions in the lowest triplet state, electronic relaxation is forbidden by the spin conservation rule. Thus we may expect that adiabatic reactions in the triplet state occur more frequently, but these will also be more difficult to identify. In fact, the present work has provided circumstantial evidence for several adiabatic triplet state reactions along the reaction sequence **1b**→**4a**, namely ^{3}**1b***→^{3}**1a***, ^{3}**2b***→^{3}**2a***→^{3}**3a***, and ^{3}**4a***→^{3}**4b*** *(Scheme)*.

Experimental. – *Kinetic and Spectrographic Flash Photolysis.* Frequency tripled (353 nm) or quadrupled (265 nm) light pulses of *ca.* 50-mJ energy per pulse and 20-ns duration were used as an excitation source. The detection system allowed for the simultaneous recording of the kinetics (at a given wavelength) and the spectra (at a given time delay after excitation) of the transient absorptions in digital form with ns time resolution. Details of the experimental setup will be given elsewhere [29].

Fluorescence Spectra and Fluorescence Lifetimes. Fluorescence spectra were recorded both on a conventional spectrofluorometer (*Zeiss ZFM 4, PMQII,* equipped with a red-sensitive photomultiplier *EMI 9785 QB*) and, with laser excitation, on a gateable ($\geqslant 5$ ns) diode array camera (*B + M AK 500* with microchannel plate image intensification) and were not corrected for spectral response. All fluorescence spectra exhibited a minor contribution from pyrene fluorescence which was, however, readily identified by its long lifetime (*ca.* 450 ns) and characteristically structured spectrum (λ_{max} 390 nm) and could be largely eliminated by using short gating periods.

For the determination of fluorescence lifetimes the duration of the exciting laser pulse was reduced to *ca.* 5 ns full width at half height using a *JK 2000* pulse chopper. The fluorescence decay signals at a given wavelength were recorded with a *Tektronix AD 7912* digitizer and fitted to a single exponential.

Quantum Yield Determinations. The fluorescence quantum yield of ^{1}**1a*** obtained by 365 nm excitation of **1b** ($5 \cdot 10^{-4}$M degassed hexane solution) was determined using rhodamine 6G as a fluorescence standard (10^{-7}M solution in EtOH, $\phi_F = 0.95$ [30]). Since the emission spectra of ^{1}**1a*** and the standard are similar, only relatively small corrections for the spectral response sensitivity of the instrument were necessary which were done by comparison of the observed emission spectrum of rhodamine 6G with a corrected spectrum [30].

The quantum yields for the photoreactions **1b**→**2b** (313 nm) and **2b**→**4a** (365 nm) were determined by spectrophotometric monitoring of the chemical conversions using *Aberchrome 540* as an actinometer ($\phi_R = 0.20$, $\varepsilon(494) = 8200\text{M}^{-1}\,\text{cm}^{-1}$ [31])^5). To avoid complications by the sequential photoreaction of **2b**, the photoreaction **1b**→**2b** was monitored at conversions of less than 2%; the build-up of **2b** (monitored at 354 nm) was found to be linear with the light dose up to at least 5% conversion.

Photochemical Preparation of 8,11b-Methanocyclodeca[cde]*naphthalene* (**2b**). 8,16-Methano[2.2]metacyclophane-1,9-diene (**1b**, 4 mg) was irradiated for a period of 3 h in an EPA glass (3 ml, immersed in liquid N_2) with 313-nm light filtered from an *Osram HBO* 200-W high-pressure Hg-arc equipped with quartz optics. Every 30 min, the glass was briefly thawed to restore a homogeneous mixture. The conversion of **1b** to **2b** was readily apparent from the change in the visible fluorescence emission from yellow-orange (**1b**) to blue (**2b**). The photoproduct was separated as the first fraction by thin layer chromatography with cyclohexane on silica. Sublimation at 100° under high vacuum yielded **2b** (2 mg) as a pale yellow solid. UV: see *Fig. 1.* ^{1}H-NMR($CDCl_3$, 360 MHz): –0.46 (*dd*, $^2J(11,12) = 9$, $^4J(4,11) = 1.3$, H_{11}); 1.53_5 (br. *d*, $^2J(11,12) = 9$, H_{12}); 6.78 (br. *d*, $^3J(2,3) = 6.8$, H_3); 7.35 (*dd*, $^3J(1,2) = 10.2$, $^3J(2,3) = 6.8$, H_2); 7.45 (*d*, $^3J(4,5) = 10.5$, H_5); 7.61 (br. *d*, $^3J(4,5) = 10.5$, H_4); 7.74 (*d*, $^3J(9,10) = 8.6$, H_9 or H_{10}); 7.83 (*dd*, $^3J(6,7) = {}^3J(7,8) = 7.7$, H_7); 7.89_5 (*d*, $^3J(9,10) = 8.6$, H_{10} or H_9); 7.98 (*d*, $^3J(1,2) = 10.2$, H_1); 8.07 (*d*, $^3J(6,7)$ or $^3J(7,8) = 7.7$, H_6 or H_8); 8.10 ppm (*d*, $^3J(7,8)$ or $^3J(6,7) = 7.7$, H_8 or H_6).

*Photochemical Preparation of 9*H-*Cyclohepta*[def]*phenanthrene* (**3b**). A 3-mg sample of **1b** was photoisomerized to **2b** as described above and subsequently subjected to 405-nm irradiation from the same light source for 2 h at a temperature of *ca.* –78° (dry ice/acetone). Chromatography and sublimation as above yielded *ca.* 1 mg of **3b** (contaminated by **4a**) which was identified by spectroscopic comparison with an authentic sample [2].

This work was performed as part of project No. 2.470-0.82 of the *Swiss National Science Foundation.* Financial support by *Ciba-Geigy SA, F. Hoffmann-La Roche & Cie SA,* and *Sandoz SA,* Basel, is gratefully acknowledged. Thanks are due to Profs. *V. Boekelheide, R.G. Harvey, H.G. Heller,* and *H. Fritz* for their contributions acknowledged in the text and to Prof. *F.-G. Klärner* for valuable comments and suggestions.

REFERENCES

[1] *E. Müller & H. Kessler,* Tetrahedron Lett. *1965,* 2673.

[2] *I. Murata, K. Yamamoto, Y. Kayane & H. Ori,* Tetrahedron Lett. *1975,* 131.

[3] a) *K. Nakasuji, M. Katada & I. Murata,* Angew. Chem. *91,* 1011 (1979); Angew. Chem. Int. Ed. *18,* (1979); b) *I. Murata & K. Nakasuji,* Israel J. Chem. *20,* 244 (1980).

---

[5]) We wish to thank Prof. *H.G. Heller,* University College of Wales, for the gift of a sample of *Aberchrome 540* ((*E*)-α-(2,5-dimethyl-3-furylethylidene) (isopropylidene) succinic anhydride).

[4] *K. Yamamoto, Y. Kayane & I. Murata,* Bull. Chem. Soc. Jpn. *50,* 1964 (1977).

[5] a) *F. Gerson,* Topics Curr. Chem. *115,* 57 (1983); b) *A. Metzger,* Dissertation Universität Basel, 1983; c) *F. Gerson, W. Huber & K. Müllen,* Angew. Chem. *90,* 216 (1978); Angew. Chem. Int. Ed. *17,* 208 (1978); Helv. Chim. Acta *62,* 2109 (1979).

[6] *R.B. Woodward & R. Hoffmann,* Angew. Chem. *81,* 797 (1969); Angew. Chem. Int. Ed. *8,* 781 (1969).

[7] *M.B. Rubin,* J. Am. Chem. Soc. *103,* 7791 (1981).

[8] a) *D. Cremer & B. Dick,* Angew. Chem. *94,* 877 (1982); Angew. Chem. Int. Ed. *21,* 865 (1982); b) *E. Vogel, T. Scholl, J. Lex & G. Hohlneicher,* Angew. Chem. *94,* 878 (1982); Angew. Chem. Int. Ed. *21,* 869 (1982); c) *R. Bianchi, T. Pilati & M. Simonetta,* J. Am. Chem. Soc. *103,* 6426 (1981); d) *H.J. Dewey, H. Deger, W. Frölich, B. Dick, K.A. Klingensmith, G. Hohlneicher, E. Vogel & J. Michl,* J. Am. Chem. Soc. *102,* 6412 (1980); e) *R.K. Hill & C.B. Giberson,* 186th ACS National Meeting, Washington D.C. 1983.

[9] a) *J.S. Swenton, K.A. Burdett, D.A. Madigan, T. Johnson & P.D. Rosso,* J. Am. Chem. Soc. *97,* 3428 (1975); b) *M. Kato, H. Kobayashi, H. Yamamoto, K. Seto, S. Ito & T. Miwa,* Bull. Chem. Soc. Jpn. *55,* 3523 (1982).

[10] a) *J.S. Swenton, K.A. Burdett, D.A. Madigan & P.D. Rosso,* J. Org. Chem. *40,* 1280 (1975); b) *K.A. Burdett, F.L. Shenton, D.H. Yates & J.S. Swenton,* Tetrahedron *30,* 2057 (1974).

[11] a) *M. Gisin, E. Rommel, J. Wirz, M.N. Burnett & R.M. Pagni,* J. Am. Chem. Soc. *101,* 2216 (1979); b) *J.-F. Muller, D. Muller, H.J. Dewey & J. Michl,* J. Am. Chem. Soc. *100,* 1629 (1978); c) *R.M. Pagni, M.N. Burnett & H.M. Hassaneen,* Tetrahedron *38,* 843 (1982); d) *W.R. Roth & K. Enderer,* Justus Liebigs Ann. Chem. *730,* 82 (1969).

[12] a) *J.A. Berson & M.R. Willcott,* J. Am. Chem. Soc. *88,* 2494 (1966); b) *F.-G. Klärner & B. Brassel,* J. Am. Chem. Soc. *102,* 2469 (1980); c) *F.-G. Klärner & S. Yaslak,* Chem. Ber. *112,* 2286 (1979).

[13] *S.S. Hixson, P.S. Mariano & H.E. Zimmerman,* Chem. Rev. *73,* 531 (1973); *H.E. Zimmerman,* in 'Rearrangements in Ground and Excited States', Vol. 3, ed. P. de Mayo, Academic Press, New York, 1980, p. 131.

[14] a) *B.A. Hess, Jr., A.S. Bailey, B. Bartusek & V. Boekelheide,* J. Am. Chem. Soc. *91,* 1665 (1969); b) *B.A. Hess, Jr., & V. Boekelheide,* J. Am. Chem. Soc. *91,* 1672 (1969); c) *R.H. Mitchell & V. Boekelheide,* J. Am. Chem. Soc. *96,* 1547 (1974).

[15] a) *H.B. Renfroe,* J. Am. Chem. Soc. *90,* 2194 (1968); b) *L.A.R. Hall & J.A. Gurney,* US Pat. 3,390,192 (1968); c) *L.A.R. Hall, J.A. Gurney & H.B. Renfroe,* US Pat. 3,557,218 (1971).

[16] a) *H.-R. Blattmann, D. Meuche, E. Heilbronner, R.J. Molyneux & V. Boekelheide,* J. Am. Chem. Soc. *87,* 130 (1965); b) *H.-R. Blattmann & W. Schmidt,* Tetrahedron *26,* 5885 (1970); c) *W. Schmidt,* Helv. Chim. Acta *54,* 862 (1971).

[17] *H. Mauser,* Z. Naturforsch., B. *23,* 1025 (1968).

[18] *R. Haag, J. Wirz & P.J. Wagner,* Helv. Chim. Acta *60,* 2595 (1977).

[19] *A. Zweig, K.R. Hoffmann, J.B. Galliwan, M.K. Orloff & F. Halverson,* J. Am. Chem. Soc. *96,* 1449 (1974).

[20] *G. Förster & J. Wagner,* Z. Phys. Chem. *B37,* 353 (1937).

[21] *G. Porter & M.W. Windsor,* Proc. R. Soc. *A245,* 238 (1958); *T.G. Pavlopoulos,* Chem. Phys. Lett. *27,* 245 (1974).

[22] *H. Gampp, M. Maeder & A.D. Zuberbühler,* Talanta *27,* 1037 (1980).

[23] a) *H.E. Zimmerman,* J. Am. Chem. Soc. *88,* 1566 (1966); b) *W. Th. A.M. van der Lugt & L.Y. Oosterhoff,* J. Am. Chem. Soc. *91,* 6042 (1969); c) *J. Michl,* Mol. Photochem. *4,* 243, 257, and 287 (1972).

[24] *N.J. Turro, J. Mc Vey, V. Ramamurthy & P. Lechtken,* Angew. Chem. 91, 597 (1979); Angew. Chem. Int. Ed. *18,* 572 (1979).

[25] *S. Yamamoto & K.-H. Grellmann,* Chem. Phys. Lett. *92,* 533 (1982); *W.K. Smothers & J. Saltiel,* J. Am. Chem. Soc. *105,* 2794 (1983).

[26] *J. Michl,* in 'Chemical Reactivity and Chemical Paths', ed. G. Klopman, Wiley, New York, 1974; see also [23c].

[27] *R.C. Dougherty,* J. Am. Chem. Soc. *93,* 7187 (1971); *M.J.S. Dewar & R.C. Dougherty,* 'The PMO Theory of Organic Chemistry', Plenum Press, New York, 1975; see also [24].

[28] *H.-D. Becker,* Pure Appl. Chem. *54,* 1589 (1982).

[29] *M.A. Hangarter & J. Wirz,* to be published.

[30] *K.H. Drexhage,* J. Res. N.B.S. *80A,* 421 (1976).

[31] *H.G. Heller & J.R. Langan,* J. Chem. Soc., Perkin Trans. 2 *1981,* 341.