

**122. Energy Profiles for Ring Formation- and Ring Opening-
Processes in the *cis*-Stilbene-4a,4b-Dihydrophenanthrene System.
An Example of the Feasibility of a Process Forbidden¹⁾
by the Rules of Orbital Symmetry Conservation**

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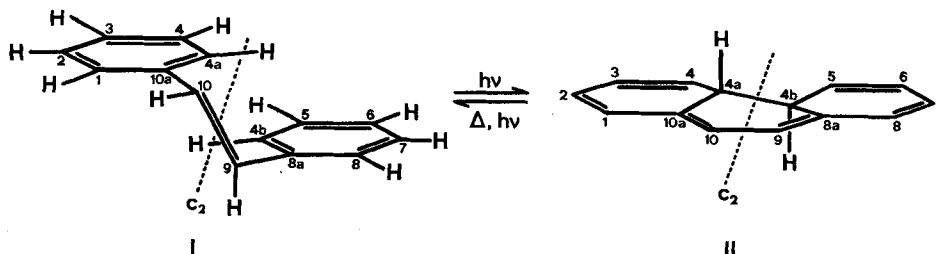
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Summary. An Extended *Hückel* MO treatment of the system *cis*-stilbene (I)-4a,4b-dihydrophenanthrene (II) indicates that the concerted photocyclisation is a conrotatory process of the first excited electronic state. The activation energies for the photocyclisation and for the thermal ring opening and the ground state energy difference between I and II, as predicted by the present calculation, are in good agreement with the experimental findings. The observed effects of substituents on the photocyclisation quantum yields are satisfactorily accounted for by a general qualitative treatment and thus indicate that the photocyclisation takes place in the first excited state.

We have carried out an MO calculation of the energy profiles for the electrocyclic concerted [1] cyclisation and ring opening processes in the *cis*-stilbene (I)-4a,4b-dihydrophenanthrene (II) system³⁾.

Scheme A. *Initial geometries of cis-stilbene and of 4a,4b-dihydrophenanthrene and numbering system*



Our calculations indicate that in the lowest excited electronic state, the conrotatory cyclisation of I and the reverse ring cleavage of II (photocyclisation and photochemical ring opening) are *allowed* processes¹⁾. As expected [2], this behaviour is entirely parallel to that predicted for the excited state processes in the hexatriene (III)-cyclohexadiene (IV) system by the rules of orbital symmetry conservation laid down by *Woodward & Hoffmann* [1]. The similar behaviour in the systems of schemes

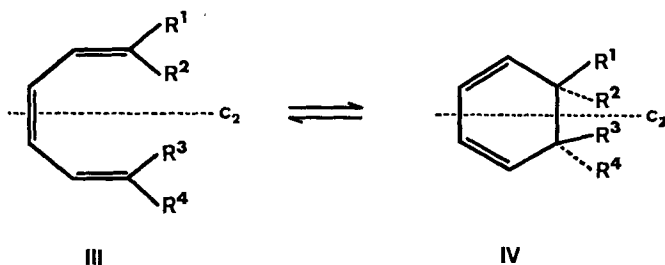
¹⁾ In the present context the terms '*allowed*' and '*forbidden*' refer to the magnitudes of the *Boltzmann* factors for the respective rate constants.

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³⁾ The numbering of the atoms in the present publication is that used in the MO calculation. The standard numbering is given in ref. [2].

A and B is due to equal symmetry properties of the highest occupied and lowest unoccupied MO in I and III, and in II and IV with respect to the C_2 operation.

Scheme B

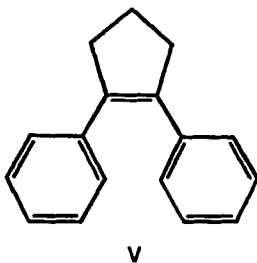


In the electronic ground state, our calculations show that the *conrotatory* ring formation in I is endothermic and therefore very *strongly forbidden*¹⁾. However, the conrotatory ring opening process in II is only *weakly forbidden*.

These theoretical results are in complete agreement with the experimental results for system A, which may be summarised as follows [2] [3].

II is formed by UV. irradiation of I. Sensitisation experiments indicate that the photocyclisation involves only the excited singlet state. That the photocyclisation is a reaction of an excited electronic state of I and not of a vibrationally excited ground state may be deduced from the following observations:

a) The photocyclisation requires ca. 2 kcal/mole of activation energy [2], indicating that a rather long lived state precedes the formation of the transition state. This requirement is incompatible with the short lifetimes of vibrationally excited molecules in solution.

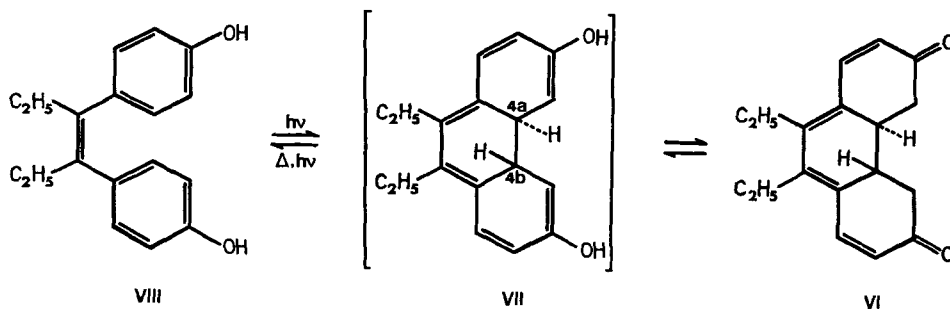


b) In 1,2-diphenylcyclopentene (V), the values of the respective quantum yields, at different temperatures, indicate that cyclisation and fluorescence are competing processes [2].

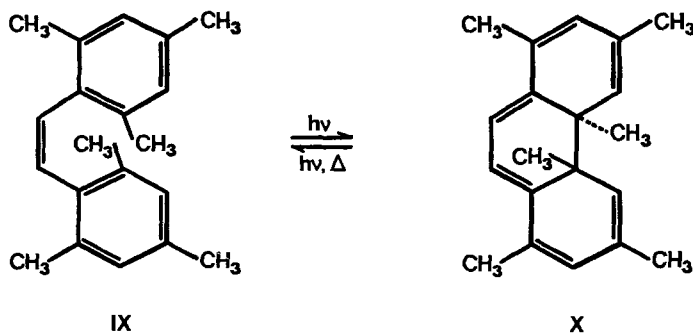
c) The cyclisation quantum yields (Φ_{PC}), in solution, of I and of its derivatives, are independent of the irradiation wavelength [2], and are therefore also independent of the excess of vibrational energy.

d) In the gas phase [4], the Φ_{PC} of I is 30-fold smaller than in solution, and is not influenced by the addition of inert polyatomic gases. As vibrational relaxation is slower in the gas phase than in solution, an increase in the quantum yield would be expected if the reaction takes place in the vibrationally excited ground state.

The kinetics of the reaction of II with molecular oxygen [2] [5], as well as the mass spectrum of VI which is the keto form of VII, and is formed by photocyclisation of VIII [6], indicate that the 4a and 4b hydrogens in the cyclic product are in *trans* position. Therefore the photocyclisation is a *conrotatory process* [1]. This finding definitely establishes that the reacting state in the photocyclisation is the first excited singlet state.



The observation that the hexamethylstilbene IX gives the corresponding 4a,4b-dihydrophenanthrene derivative X by photocyclisation, and the relatively enhanced thermal stability of this product [2] [7] also point to the same conclusion.

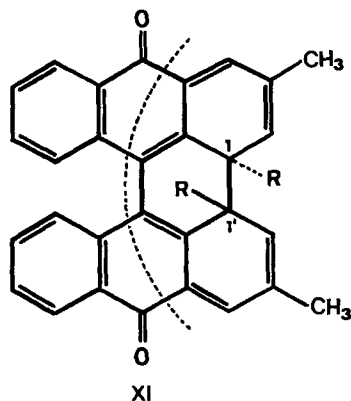


If a product X with a *cis* arrangement of the 4a- and 4b-methyl groups were formed, it would be necessarily less stable towards thermal ring opening than the corresponding hypothetical *cis*-4a,4b-isomer of II. The reduced stability would be due to a very high non-bonded interaction between the two CH₃ groups at the 4a- and 4b-positions.

Empirical estimates indicate that the difference in the ground state energies between II and I amounts to *ca.* 35 kcal/mole [3]. Due to the formation of the keto form however, this difference between VIII and VI is considerably smaller [6].

Thermal cyclisations of *cis*-stilbenes have not been observed, though these processes are supposed to precede the cyclo-dehydrogenation to the corresponding phenanthrene derivatives, which occurs only at higher temperatures [3]. Thus I is completely unreactive at 170°C even in the presence of oxygen [4]. Only at 550°C is the formation of phenanthrene moderately fast [4], notwithstanding the fact that the dehydrocyclisation product is, by far, thermodynamically preferred.

The *thermal ring opening* reaction of 4a,4b-dihydrophenanthrenes, which is *forbidden* in the conrotatory mode [1], is nevertheless a rather fast process even at room temperature [2]. Only X is slightly more stable [2] [7]. Similar thermal behaviour is observed for the C cyclic form (XI, R = CH₃) of 1,1',3,3'-tetramethyl-9,9'-bianthro-



ne, which also contains the 4a,4b-dihydrophenanthrene moiety [8]. The activation energies for the thermal ring opening reactions of 4a,4b-dihydrophenanthrenes fall within the range of 15–23 kcal/mole [2]. Similar activation energies were measured for XI, R = H, and for its 3,3'-dimethyl derivative XI, R = CH₃ [9]. The reason for the apparent discrepancy between the experimental finding and the *forbidden* character for this process according to the rules of orbital symmetry conservation will be discussed subsequently.

The effects of substituents, both at the 2 and 4 (*meta*) positions [10] and at the 3 position (*para*) [2] [11], on Φ_{PC} have been determined experimentally. The results are relative to the Φ_{PC} value of I [2].

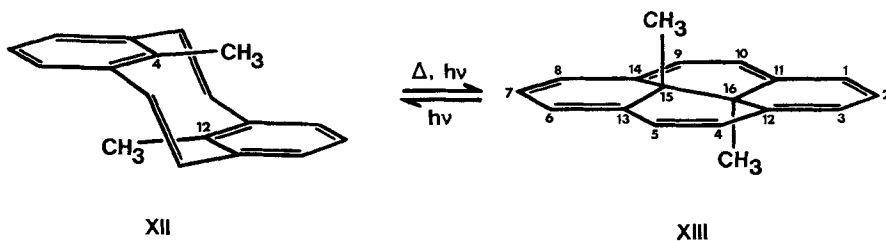
At the *meta*-positions [10], substituents with lone-pairs (–NH₂, –OCH₃) increase the cyclisation quantum yield. Substituents with low lying unoccupied π orbitals (–CN) decrease the quantum yield. Both effects are in agreement with the present MO calculations (see below). Thus we here adopt a point of view contrary to that of *Güsten & Klasinc* [10]. These authors have correlated the quantum yields with small changes in the ground state HMO electronic charges on the *ortho*(4a and 4b)-positions, and have therefore concluded that the photocyclisation takes place in the vibrationally excited ground state. We consider that such an argument would imply that the cyclisation proceeds through an ionic intermediate, and therefore that this correlation [10] is rather fortuitous.

At the *para*-positions, substituents with lone-pair orbitals (–N(CH₃)₂, –OCH₃, –NH₂) lower the Φ_{PC} values by about one order of magnitude [11]. Substituents with low lying empty π orbitals (nitro, acetyl and benzoyl) reduce the quantum yield to practically zero [2] [11]. Other substituents (F, Cl, Br, CH₃) at the *para* positions have only minor effects on Φ_{PC} [2] [11].

Description of the Calculation. We have obtained the energy profiles for the conrotatory cyclisation mode by calculating pointwise the one electron energies and wavefunctions for different geometries of the system represented in scheme A. The

method used was the Extended *Hückel* procedure of *Hoffmann* [12]. The hydrogen 1s exponent was 1.3. This method has recently been applied with success to investigations of electrocyclic processes in the 4,12-dimethyl-[2.2]metacyclophanediene (XII)–*trans*-dimethyldihydropyrene (XIII) system [13], and of the ground and excited state geometrical forms of benzophenone [14].

Scheme C



Molecular Geometries. In the present study the reaction coordinate (R) is the distance between C4a and C4b. Unless the geometry is adequately optimised, very strong non-bonded interactions are likely to arise in the central part of I and of II at short C4a–C4b distances.

The initial geometry of I is derived from the *X*-ray analysis of di-*meta*-xylylene [15] and of 4,12-dimethyl-[2.2]metacyclophane [16]. All C–H bond lengths are 1.080 Å. The H(4a)–H(4b) distance is 3.65 Å. C_2 symmetry is maintained. The H(4)–H(5) distance is 1.75 Å. The C4a–C4b distance (R) is 2.70 Å.

The geometry of II was derived from the *X*-ray study of XIII [17]. The C–H distances are 1.080 Å, except the C4a–H and C4b–H distances. These were set equal to 1.100 Å as C4a and C4b are sp^3 hybridised. Since II is a polyene, alternating single and double bond lengths were assumed.

The geometries of the intermediate conformations along the reaction coordinate were obtained by the following procedure [13a] which will be described at length elsewhere [13b]. For each point along the reaction coordinate R the geometry is varied by means of the six parameters φ , χ , ζ , η , τ and γ . The C_2 axis is defined as in scheme A. φ , χ and ξ are the respective rotation angles about the C_2 axis of C10, C4a and C10a. η is an out of plane bending angle between the plane defined by C10a, C4a and C4 and the plane defined by C1, C10a, C4 and C3. τ is the measure of the hybridisation of C4a, which changes from sp^3 in II to sp^2 in I. Hence τ defines the position of H(4a) and the C4a–H bond length. This bond length was assumed to change linearly over the reaction coordinate (from 1.080 Å in I to 1.100 Å in II). γ defines the amount of bond alternation (no bond length alternation in I, complete bond alternation in II).

The initial and final values of these six parameters were obtained from the geometries of the model compounds. For intermediate geometries these parameters were changed in a linear way. The H(4)–H(5) distance was kept constant (1.75 Å).

These six parameters define the coordinates of C2, C1, C10a, C10, C4a, H(2), H(1), H(10), H(4a) and H(4). The positions of the other atoms are given by symmetry, so that the C_2 symmetry is conserved along the whole reaction coordinate.

The initial (I) and the intermediate geometrical forms for system A obtained by this procedure, are not the true geometries at which the strain and the non-bonded

interaction energies attain their minimum values for a given external constraint R . However, these geometries are expected to approach this limit very closely. An analysis of the non-bonded interactions [18] indicates that this procedure gives geometries with minimal non-bonded interactions, with the exception of the H(4)–H(5) interaction which amounts to 1.5 kcal/mole. Since this distance is kept constant along R , this interaction does not affect our conclusions.

A geometry parameter which changes considerably along the course of the reaction is the torsional angle about the C10a–C10 and C9–C8a bonds. A few representative values of this angle (α) are given in the table.

Torsional angle about the C10a–C10 bond (α), as a function of the reaction coordinate R

R	(Å)	1.533	1.766	2.116	2.467	2.700
α	(deg)	1.0	14.9	30.6	38.7	40.8

Results and Discussion

The calculated configuration correlation diagram for the conrotatory isomerisation $I \rightleftharpoons II$, in the ground and in the first excited singlet states, is given in Fig. 1 (full lines).

In the region of the transition state (of the ground state) configurations of the same symmetry (species A in group C_2) will cross. Consequently, the effective energy is lowered because of configuration interaction. In Fig. 1, the dotted line (**a**) below the curves for the A state represents an estimate of the effect of configuration interaction. For a polyene the depression of the ground state energy due to configuration interaction has been recently estimated at 5 kcal/mole [19].

At $R = 1.95$ Å the electronic configuration of the ground state changes from $(a)^2 \dots (b)^2(a)^2$ to $(a)^2 \dots (b)^2(b)^2$. Curves **b** and **c** (Fig. 1) represent the energy profiles for the two possible doubly excited configurations obtained by changing R beyond the crossing point while retaining the initial electronic configuration of either I or II.

Considering the approximate character of the Extended *Hückel* procedure [12], the results shown in Fig. 1 correspond satisfactorily with the experimental findings as discussed in the previous section.

In the ground states, the calculated energy difference between I and II amounts to 29 kcal/mole.

The calculated energy of activation for the thermal ring opening amounts to 23 kcal/mole if the energy depression in the region of the transition state is neglected. It drops to *ca.* 18.5 kcal/mole however, if configuration interaction is taken into account.

The cyclisation in the excited state is predicted to require no electronic activation energy (Fig. 1, curve for state B). This result is in fair agreement with the experimentally measured activation energy of *ca.* 2 kcal/mole. The slight discrepancy can be attributed to one of the two following factors: (a) the experimental activation energy is due to a viscosity effect [20] [21], *i.e.*, the activation energy of 2 kcal/mole represents the energy required for the formation of a certain free volume cavity in which the geometrical changes take place [20]; (b) the true minimum for the B state is not at $R = 1.85$ Å as calculated, but at $R = 2.10$ Å.

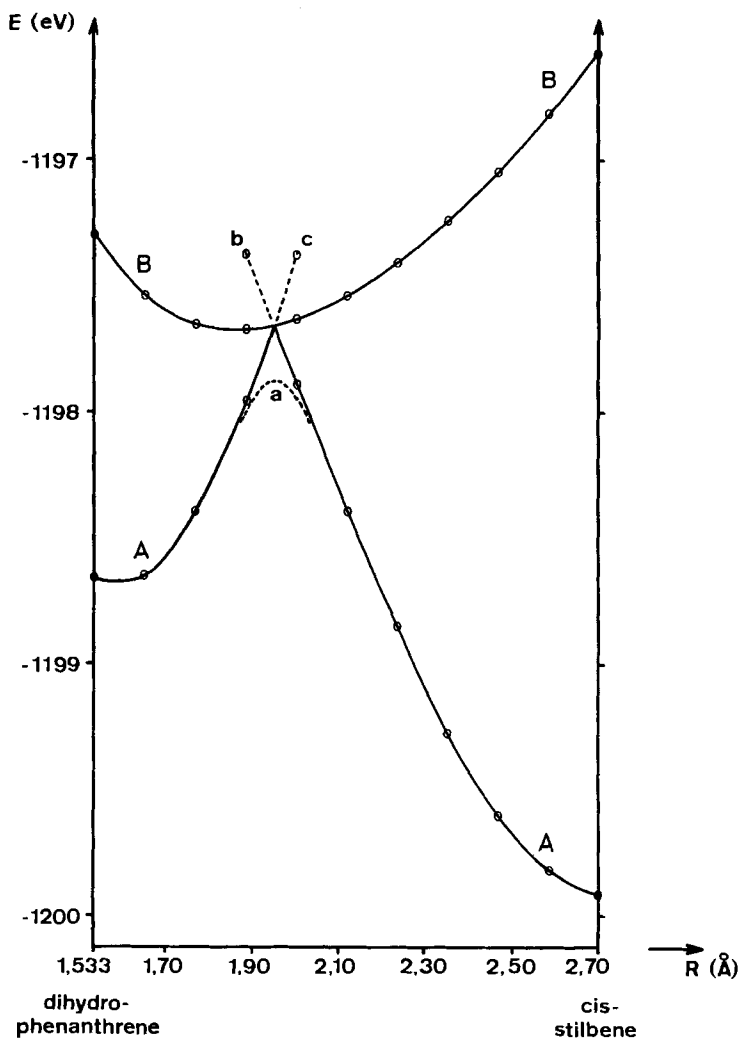


Fig. 1. State correlation diagram for system A

In agreement with the experimental findings, our calculated energy profile shows that there is no activation energy for the ring opening mode in the excited state.

The present calculation predicts an electronic excitation energy (${}^1B \leftarrow {}^1A$) of $27\,200\text{ cm}^{-1}$ for I. This value is in good agreement with the experimental estimate of $29\,700\text{ cm}^{-1}$ [22] for the 0,0 band. For II an electronic excitation energy of $11\,250\text{ cm}^{-1}$ is predicted. In this case the exact position of the 0,0 band is not known, though it is certainly at an energy lower than $17\,500\text{ cm}^{-1}$ [2].

The calculated orbital correlation diagram for the conrotatory mode in system A is represented in Fig. 2. The orbitals are classified with respect to the symmetry elements of point group C_2 . The diagram includes only the π orbitals of I; two of these are converted to $p\sigma$ orbitals as a result of the formation of the C4a–C4b bond in II.

The horizontal dashed line indicates the occupation limit; the highest occupied and the lowest unoccupied orbitals are seen to change symmetry in the region of the transition state, as in the case of linear polyenes.

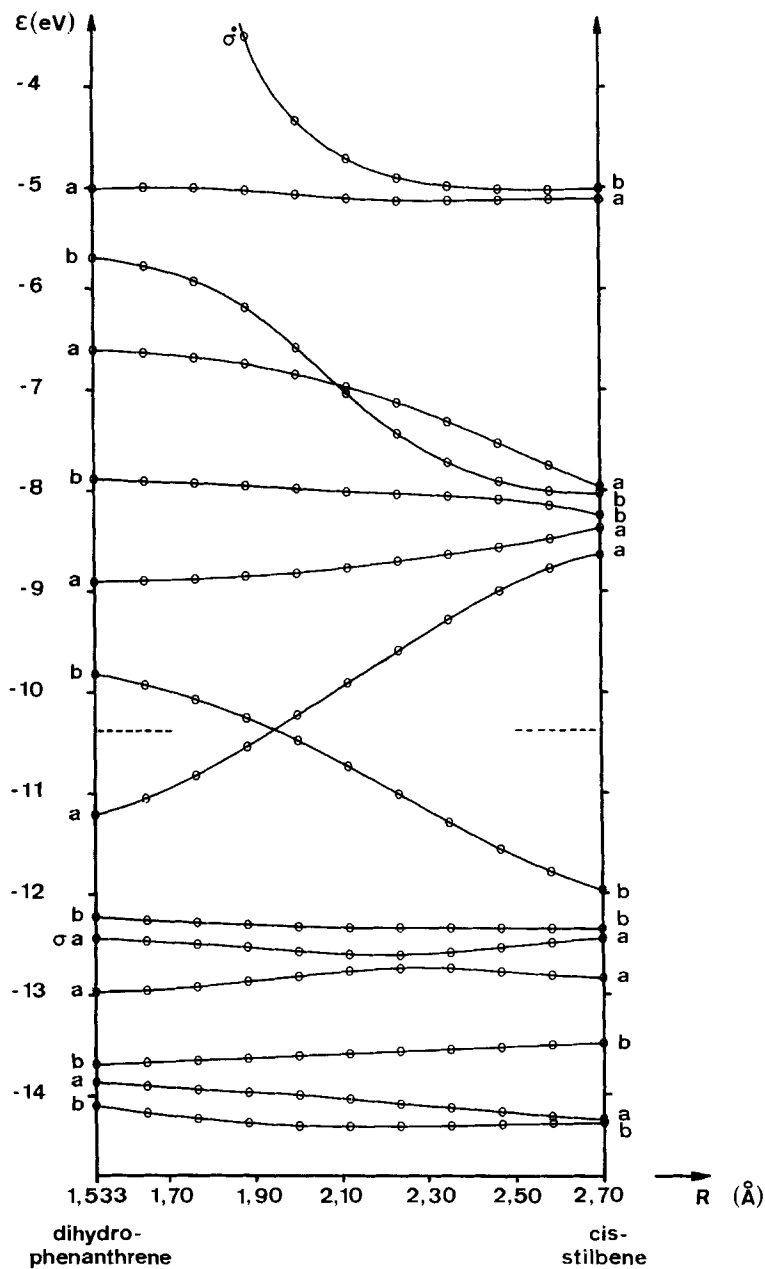


Fig. 2. Orbital correlation diagram for system A

The calculated values of the electronic overlap populations of several representative bonds along the reaction coordinate of system A are given in Fig. 3. As R becomes

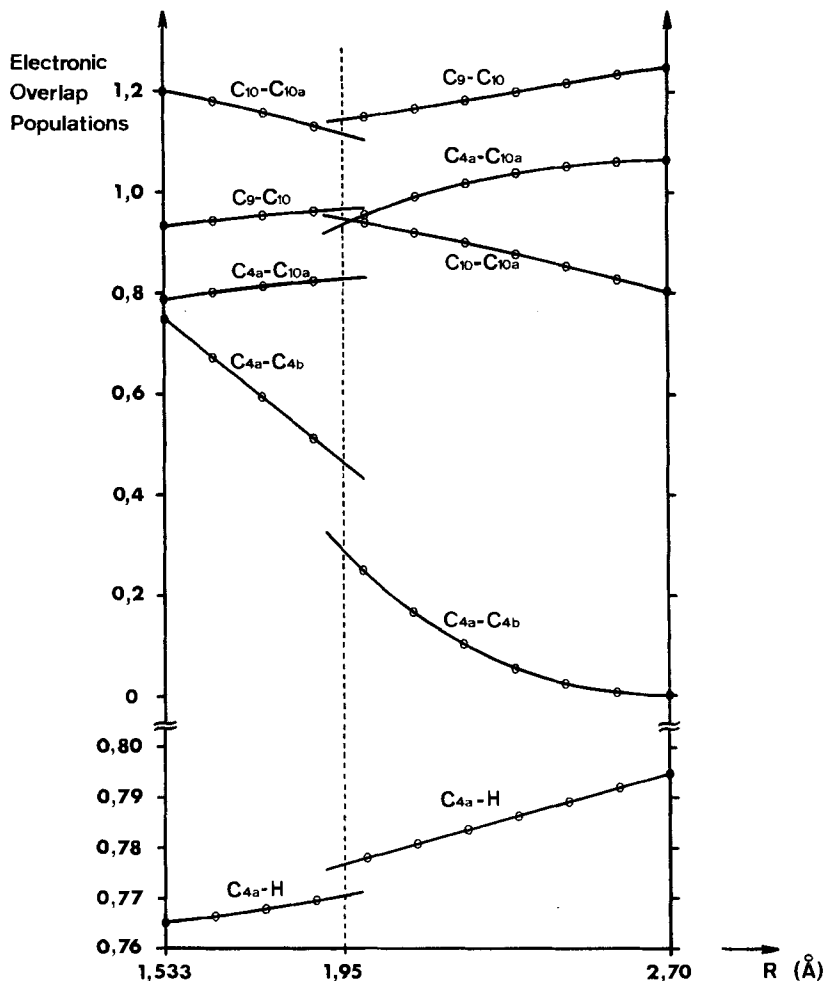


Fig. 3. *Overlap populations as function of reaction coordinate in system A*

shorter, the overlap populations for bonds $C_{4a}-C_{4b}$ and $C_{10}-C_{10a}$ increase, *i. e.*, the new bond $C_{4a}-C_{4b}$ is formed, and bond $C_{10}-C_{10a}$ acquires increased double bond character. At the same time the overlap populations for bonds C_9-C_{10} and $C_{4a}-C_{10a}$ decrease. These two bonds become pure single bonds in II.

The calculated change in the overlap population of the $C_{4a}-H(4a)$ bond during the cyclisation process also shows the behaviour expected on the basis of the kinetics of the thermal reaction of II with oxygen. These indicate that bond $C_{4a}-H(4a)$ is particularly weak [5a]. The electronic overlap population for this bond (Fig. 3) changes from 0.794 (in I) to 0.765 (in II). The overlap populations for other C-H bonds remain practically constant.

The discontinuities in the various electronic overlap population curves, in the region of the crossing point at $R = 1.95 \text{ \AA}$, are due to the neglect of configuration interaction, and are expected to disappear when this factor is taken into consideration.

The value obtained for the energy of activation for the conrotatory ground state ring opening, indicates that processes which are essentially *forbidden* according to the rules of orbital symmetry conservation can nevertheless be observed. The necessary conditions are: (a) the ground state energy of the reactant is sufficiently higher than that of the product, and (b) the energy gap between the orbitals, which cross in the transition state, is small both in I and in II.

The decomposition of *cis*-bicyclo[2.2.0]hexadienes to the corresponding benzenes [23] is, in this respect, similar to the thermal ring cleavage of II.

Effects of substituents on cyclisation quantum yields. We shall base the present discussion on the first and second order perturbation effects of substituents on the energies of the highest occupied and lowest unoccupied molecular orbitals. We have already seen (Fig. 2) that these orbitals cross in the region of the transition state. Among the orbitals experimentally accessible, only these two are affected by a change in reaction coordinate, and as we shall show, by first and second order perturbation effects.

In order to describe the influence of substituents on the photocyclisation quantum yield we shall use a rule which we formulate as follows: *Rates and quantum yields of concerted reactions in excited states are proportional to the value of the slope of the curve of electronic energy vs. reaction coordinate for the ground state nuclear configuration of the reactant.*

This rule is deduced from the following considerations. The photocyclisation competes with fluorescence, intersystem crossing, and with other paths of internal conversion [2] [21]. If the potential curve is steep (in the present case—state *B* at $R = 2.70 \text{ \AA}$ in Fig. 1), the electronic energy of the excited state will be converted efficiently into kinetic energy of the nuclei. This vibrational kinetic energy will be initially concentrated in those normal modes, whose nuclear displacements correspond to the displacements of the atoms along the reaction coordinate, and will favour the photocyclisation process. If, on the other hand, the potential curve is flat, other processes of radiationless deactivation and fluorescence will predominate and the quantum yield of the cyclisation will drop to zero.

The highest occupied (No. 34 in our Extended *Hückel* treatment) and the lowest unoccupied (No. 35) molecular orbitals of I and II are shown in Fig. 4. Substituents with orbitals of appropriate symmetry and energy can interact with these two orbitals and increase, or lower, their energies.

On the basis of Fig. 2, it is evident that the slope of the potential curve of excited I at $R = 2.70 \text{ \AA}$, is proportional to the energy gap between orbitals 35*a* and 34*b* of Fig. 4. Hence we shall use Perturbation Theory to estimate the energy changes of these orbitals due to the substituents. The approach used here will be fully described elsewhere [13 b].

In this context, we limit ourselves to two classes of substituents: (a) Substituents with σ bonds or lone pairs in close proximity to the stilbene π -system—alkyl groups, halogens, $-\text{OCH}_3$, $-\text{NH}_2$ and $-\text{N}(\text{CH}_3)_2$. (b) Substituents with empty π -orbitals which

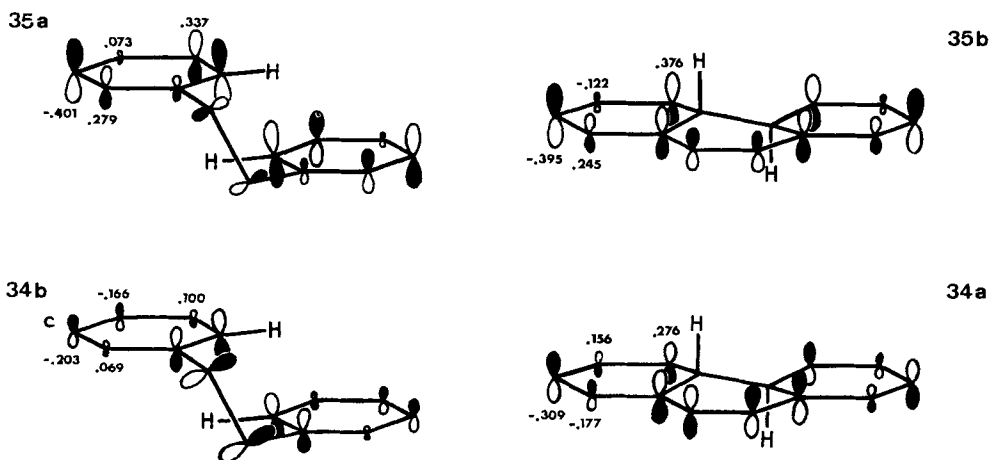


Fig. 4. Highest occupied and lowest unoccupied molecular orbitals in I and in II

may conjugate with the stilbene π -system—nitro, cyano, formyl, acetyl and benzoyl groups.

If the orbitals of the substituent lie at low energies, relative to the highest occupied (34b) or lowest unoccupied (35a) orbitals of I, then the mutual perturbation is of the second order type (eq. 1),

$$\delta\epsilon_i = \frac{C_{ri}^2 C_{sj}^2}{\epsilon_i - \epsilon_j} \beta_{rs}^2 \quad (1)$$

In this equation C_{ri} and C_{sj} are AO coefficients, ϵ_i and ϵ_j the orbital energies, and β_{rs} is the interaction element. The bond is between atom r of the substituent and atom s of I. i and j refer respectively to the MO of the substituent and of I.

In the case of the methyl group, the most important orbitals which enter into the perturbation sum are the e occupied orbitals ($\epsilon_i = -15.52$ eV according to an Extended *Hückel* calculation [13]). The unoccupied orbitals of the methyl group are at high energy (+4.27 eV and above [13]) and do not affect the 34b and the 35a orbitals of I. Therefore the destabilisations, $\delta\epsilon_b$ and $\delta\epsilon_a$, of the orbitals of I are small, and are roughly proportional to the squares of the coefficients at the substitution position. Since in the *meta* positions the coefficients of 35a are larger than those of 34b, the former will be destabilised more than the latter. Therefore the energy gap $A - B$ (Fig. 1) increases as well as the slope at $R = 2.70$ Å of the excited state potential curve, resulting in a slightly higher Φ_{PC} value. In the *para* position the 34b orbital has a coefficient larger than that of 35a, and should thus be destabilised to a larger extent. The initial slope decreases, but the overall effect on Φ_{PC} is expected to be insignificant due to the smallness of the C_{sj} .

Similar arguments apply for the fluoro substituent. Since the lone pair orbital is at a very low energy (-17.42 eV in the Extended *Hückel* treatment [13]), the overall effect should be even smaller than for a methyl group.

In the case of $-\text{OCH}_3$ and of $-\text{NH}_2$, the lone pair orbitals are at higher energies (*i.e.* -13.37 eV for $-\text{NH}_2$). Therefore from eq. 1 we expect that MO 35a will be

destabilised more than MO 34*b* if the substituent is in the *meta* position, and so Φ_{PC} should increase accordingly.

The opposite effect is predicted if $-\text{OCH}_3$ or $-\text{NH}_2$ are introduced at the *para* position, as MO 34*b* will thus be shifted to a higher energy more than is MO 35*a*, and therefore Φ_{PC} should decrease for such substituents.

Substituents of class **b** have low lying unoccupied π -orbitals with high coefficients at atom *r*. The EHT energies of these orbitals, in the isolated fragments, are close to those of MO 35*a* of I $-\varepsilon_1 = -10.6 \text{ eV}(\text{NO}_2)$, $-9.87 \text{ eV}(\text{HC}=\text{O})$, $-9.49 \text{ eV}(\text{CH}_3-\text{C}=\text{O})$ and $-8.23 \text{ eV}(\text{CN})$.

Introduction of any of these substituents at *any* position in I produces a new low lying π^* orbital, which replaces the original MO 35*a*. The energies of these π^* orbitals are essentially equal to the energies of the π^* orbitals of the isolated substituent ($-\text{NO}_2$, $\text{HC}=\text{O}$, $\text{CH}_3-\text{C}=\text{O}$). In the case of the CN group, a slight lowering occurs relative to the isolated substituent. The new unoccupied orbitals (MO 35) have large AO coefficients on the substituent atoms. However, the highest occupied orbital of I remains essentially unaffected.

In terms of Perturbation Theory, class **b** substituents bring about a strong first order energy change $\delta\varepsilon$ in level 35 given by

$$\delta\varepsilon_{35} = C_{r35} C_{sj} \beta_{rs} \quad (2)$$

(the symbols and indices are as in eq.1). The result is a considerable stabilisation of MO 35, the extent of which depends on the magnitude of C_{ri} and is essentially independent of the substitution position, because the π^* orbital of the substituent rotates MO 35*a* of I so as to maximise the interaction. As a consequence of the strong stabilisation of the lowest unoccupied orbital of I, both the energy gap *A*–*B* and the

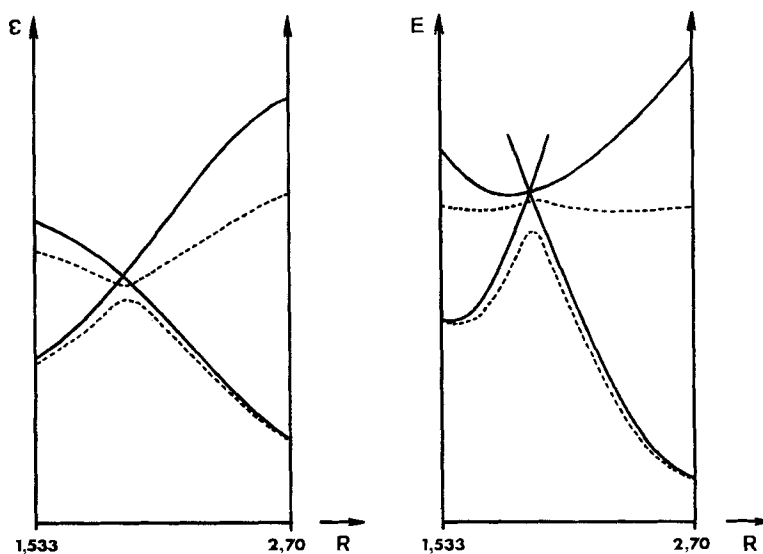


Fig. 5. Schematic correlation diagrams of orbitals (left) and of states (right) for system in scheme A. Full lines – without substituent, dashed line – nitro substitution. Since ring substituents destroy the C_2 symmetry, the 34 and 35 orbitals no longer cross in the transition state region.

initial slope of the excited state profile drop considerably. Therefore the value of Φ_{PC} decreases to a large extent. On the basis of the Extended *Hückel* calculations on the isolated fragments we expect that Φ_{PC} would decrease in the following order: CN, $\text{CH}_3\text{C}=\text{O}$, $\text{HC}=\text{O}$ and NO_2 .

The influence of a nitro group on the orbitals (34 and 35) and on the states (*A* and *B*) is illustrated in a schematic way in the correlation diagrams (Fig. 5). The strong first order mixing between the unoccupied nitro group orbital and the unoccupied hydrocarbon orbital occurs predominantly at $R = 1.533$ and 2.70 \AA . In the intermediate region (especially near the transition state) the interaction is essentially of the second order type and therefore much weaker.

The present rather qualitative treatment of the effects of substituents on Φ_{PC} is based on the assumption that the photocyclisation is a reaction of the first excited electronic state of I. Conversely, the success of the present treatment should be taken as an important indication that this basic presumption is correct⁴).

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⁴) An explicit EHT study of the effects of substituents on system A fully confirms the present qualitative arguments [24].