

Photocyclization of 2-Vinylbiphenyls and Related Compounds under Triplet Sensitization: An Adiabatic Reaction on the Triplet Surface

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Abstract: The mechanism of the cyclization of 2-vinylbiphenyl derivatives under sensitization by the triplet state of xanthone has been studied by laser-flash photolysis. The first step of the mechanism is an adiabatic reaction giving a cyclized polyene in the triplet state which decays to the ground state with a lifetime in the range 550–750 ns. From the effect of oxygen on the yield of formation of the polyene, the rate constant of cyclization of the planar triplet is found to be around $3 \times 10^8 \text{ s}^{-1}$. When a 90° twist of the vinylic double bond is allowed by the molecular structure, the resulting perpendicular triplet gives a nonstereospecific cyclization which occurs, most probably, after distortion of the biphenyl moiety. In some cases, a transient absorption assigned to the triplet state of an unreactive rotamer of the arylethylenic compounds has been observed, and the effect of rotamers on the reaction quantum yield is briefly discussed.

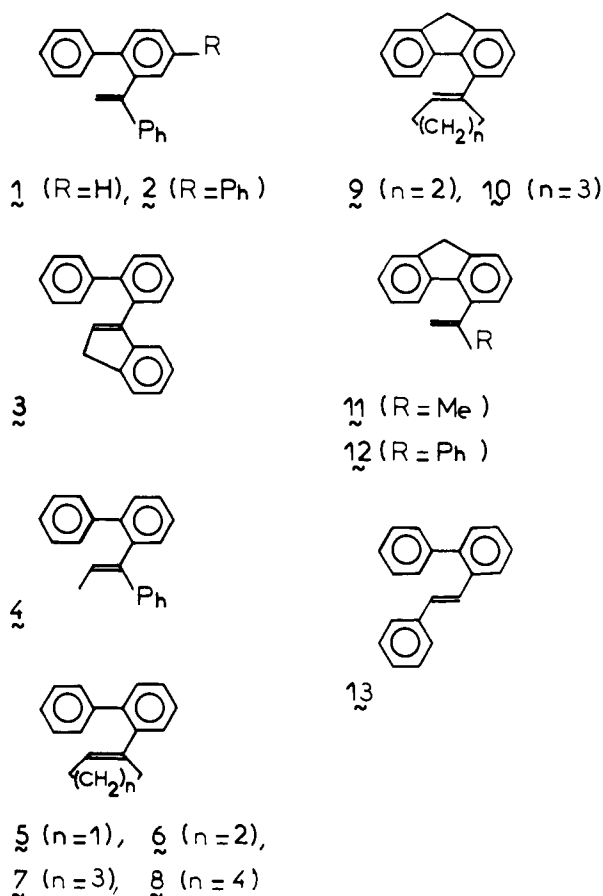
Upon direct excitation, 2-vinylbiphenyls and structurally related compounds undergo a cyclization reaction to give dihydrophenanthrene derivatives in a quantitative chemical yield. This photochemical reaction has been used for the synthesis of several aromatic compounds.¹⁻⁶ A flash-photolysis study revealed that the first step of the photocyclization is the formation of a cyclic polyene.³ This primary photoproduct may then undergo a 1,5 hydrogen shift to give the dihydrophenanthrene derivative or may be dehydrogenated in a substituted phenanthrene by reaction with an oxidizing agent such as iodine. The quantum yield of the reaction greatly depends on the structure of the molecule and can be rather large: for instance $\phi = 0.24$ for **1**, 0.61 for **2**, and 0.33 for **12**.⁷

Unlike the photocyclization of *cis*-stilbene and other related 1,2-diarylethylenes with an hexatrienic subsystem, which is known to occur only from the excited singlet,⁶ the cyclization of many molecules containing the 2-vinylbiphenyl moiety can be triplet sensitized with a large quantum yield:⁷ for instance, $\phi = 0.58$ for **1** and 0.89 for **2**. Similar triplet sensitized photocyclizations have been reported, a long time ago, for 2-biphenyl isocyanates and 2-biphenyl imines,⁸ heteroatomic analogues of the 2-vinylbiphenyls, but with much lower quantum yields.

There are two striking differences between the direct and sensitized photocyclization of 2-vinylbiphenyl derivatives: (a) for some compounds, giving an efficient cyclization under direct excitation, the sensitized reaction is quite inefficient,⁷ for instance, $\phi < 5 \times 10^{-3}$ for **12**; (b) the reaction under direct excitation is stereoselective whereas (in some cases at least) the sensitized reaction is not.⁹

These special features of the sensitized photocyclization have been tentatively explained by assuming that the reactive triplet species is the "perpendicular" triplet (i.e., the triplet biradical given by a 90° twist of the vinylic double bond),^{3,9} but recent studies of the properties of the triplet state of arylethylenic compounds¹⁰

Chart I



lead us to question this interpretation.

We give in this paper a detailed study of the mechanism of the triplet-sensitized cyclization of several 2-vinylbiphenyl (VB) derivatives which reveals that this reaction is an adiabatic reaction giving the cyclic polyene triplet state.

Results

Within the few nanoseconds following the sensitized flash excitation of compounds **1** to **11** (see Chart I) a transient absorption, with a first-order-decay time in the range 500–700 ns, appears between 350 and 450 nm. The species related to this absorption

- (1) Padwa, A.; Doubleday, C.; Mazzu, A. *J. Org. Chem.* **1977**, *42*, 3271.
- (2) Koussini, R.; Lapouyade, R.; Fournier de Violet, P. *J. Am. Chem. Soc.* **1978**, *100*, 6679. Koussini, R. Thèse Univ. de Bordeaux I, 1979.
- (3) Fournier de Violet, P.; Bonneau, R.; Lapouyade, R.; Koussini, R.; Ware, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 6683.
- (4) Kende, A. S.; Curran, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1857.
- (5) McDonald, E.; Martin, R. T. *Tetrahedron Lett.* **1978**, 4723. Veeramani, K.; Paramasivam, K.; Ramakrishnasubramanian, S.; Shanmugam, P. *Synthesis* **1978**, 855.
- (6) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185 and 241.
- (7) Fournier de Violet, P.; Lapouyade, R.; Rayez J. C. *J. Photochem.* **1982**, *19*, 253.
- (8) Swenton, J. S.; Ikeler, T. J.; LeRoy-Smyser, G. *J. Org. Chem.* **1973**, *38*, 1157 (see also: Swenton, J. S. *Tetrahedron Lett.* **1967**, 2855).
- (9) Lapouyade, R.; Koussini, R.; Nourmamode, A.; Courseille, C. *J. Chem. Soc., Chem. Commun.* **1980**, 740.

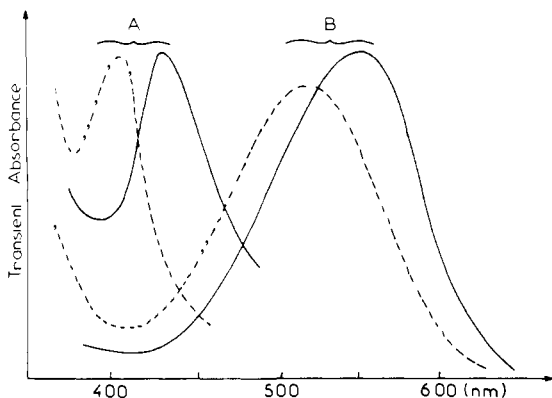


Figure 1. Absorption spectra of the transient species A and B observed upon triplet sensitization of **1** (dashed lines) and **3** (full lines).

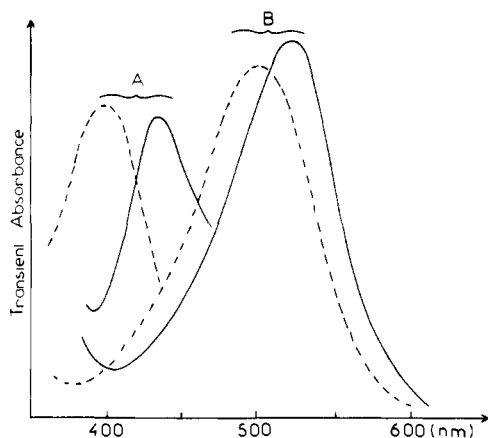


Figure 2. Absorption spectra of the transient species A and B observed upon triplet sensitization of biphenylcycloalkenes **5-8** (dashed lines) and fluorenylcycloalkenes **9-10** (full lines).

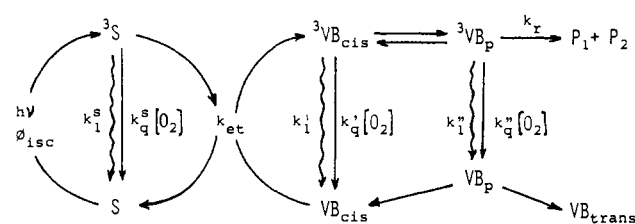
will be called A in the following, and its absorption spectrum is shown on Figures 1 and 2 for several compounds: for biphenyl and fluorene derivatives the absorption band is centered around 400 and 430 nm, respectively.

As A disappears, a second species B, absorbing at longer wavelength, is formed with a rate constant which is equal to the decay rate constant of A. The absorption spectrum of B, shown in Figures 1 and 2, is characterized by a broad band with a maximum in the range 500–550 nm. The species B is easily recognized as being the cyclic polyene (a 8a,9-dihydro-phenanthrene derivative) already observed by direct excitation. Its lifetime, longer than a millisecond, is determined by the rate of the hydrogen shift reaction which leads to the 9,10-dihydro-phenanthrene derivative.

The transient species A is quenched by oxygen, and from the lifetimes measured in solutions saturated with air, N₂, O₂, and a 1/1 mixture of O₂ and N₂, the quenching rate constant is found to be close to $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for each of the studied compounds. As the lifetime of A is decreased by addition of oxygen, the rate of formation of B is increased in the same proportion so that the relation $1/\tau_A = \text{rate of formation of B}$ is maintained. But while the lifetime of A is decreased by about 20 times on going from a N₂-saturated to an O₂-saturated solution, the yield of formation of B is only slightly decreased (by 40% in the case of **1**). The same observations were made when NO was used as quencher.

The influence of oxygen on the yield of formation of B has been studied by measuring the value of the transient optical density at 500 or 520 nm a few microseconds after the excitation of solutions saturated with N₂, air, O₂, or a 1/1 mixture of O₂ and N₂. The ratio of the measured optical densities, OD/OD₀, gives the relative yield of formation of the polyene, ϕ/ϕ_0 , as a function of the oxygen concentration. Since oxygen quenches partially the sensitizer triplet state, the quantum yield of sensitization, $\phi^S = \phi_{ISC} k_{ET}[VB]/(k_1^S + k_Q^S[O_2] + k_{ET}[VB])$ has been calculated in

Scheme I



each case from the reciprocal lifetime of the xanthone triplet ($k_1^S = 1.3 \times 10^7 \text{ s}^{-1}$), its quenching rate constant by O₂ ($k_Q^S = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the rate constant for energy transfer, k_{ET} , and the VB concentration. The rate constants k_1^S , k_Q^S , and k_{ET} have been determined by measuring the lifetime of the xanthone triplet state as a function of O₂ and VB concentrations, and ϕ_{ISC} , the yield for intersystem crossing of xanthone, was assumed to be unity.

Addition of isopropyl iodide in the solution revealed an appreciable external heavy-atom effect on the lifetime of A with a bimolecular rate constant (determined by plotting $1/\tau$ as a function of the concentration of isopropyl iodide) approximately equal to $4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for **1**. However, the lifetime of A is not affected by the addition of compounds with a low triplet energy such as *trans*-stilbene and ferrocene ($E_T = 50$ and 39 kcal/mol , respectively) at concentrations up to $2 \times 10^{-2} \text{ M}$.

The results obtained with compounds **12** and **13** are entirely different:

The transient species B is not observed. This is in agreement with the fact that these two compounds do not undergo the reaction of photocyclization under triplet sensitization.

The compound **12** gives a transient species with an absorption spectrum similar with that of A but with a lifetime equal to 30 ns whereas the compound **13** gives a transient absorption between 355 and 400 nm, with a 60-ns lifetime, very similar to the triplet-triplet absorption of *trans*-stilbene.

Discussion

The triplet nature of A is supported by the rapid formation of this species under triplet sensitization (a few nanoseconds or less, so that a multiplicity change seems highly improbable) and by the decrease of its lifetime upon addition of O₂ or NO and by heavy-atom effect.

In a previous study,³ the transient A has been assigned to the triplet state of the vinylbiphenyl derivative (³VB) and it was postulated^{3,9} that the cyclization reaction occurs from the perpendicular conformation of this triplet species (³VB_p), leading to the two stereoisomers of the polyene (P₁ and P₂) according to the mechanism shown in Scheme I. In this scheme, as in the followings, the equilibrium between the planar and perpendicular triplets is assumed to be fast, i.e., the rate of interconversion being much larger than the rates of decay, as it appears to be for similar systems.¹⁰

With such a mechanism and with α being the fraction of ³VB in the perpendicular geometry, the lifetime of ³VB would be given by

$$1/\tau = (1 - \alpha)(k_1' + k_Q'[O_2]) + \alpha(k_1'' + k_Q''[O_2] + k_r) \quad (\text{I})$$

and the quantum yield of cyclization by

$$\phi = \phi^S \alpha k_r \tau \quad (\text{II})$$

From the experimental values in the absence of oxygen, $\tau_0 = 600 \text{ ns}$ and $\phi_0 \approx 0.6$ (for **1**) and with the usual values¹¹ for k_1' (10^5 s^{-1}) and k_1'' ($3 \times 10^7 \text{ s}^{-1}$), eq I and II give $k_r = 5 \times 10^7 \text{ s}^{-1}$ and $\alpha = 0.02$. Thus ³VB would be mainly planar (98%), and it should be quenched by ferrocene and stilbene since the energy of the

(10) Lazare, S.; Bonneau, R.; Lapouyade, R. *J. Phys. Chem.* **1984**, *88*, 18.

(11) From previous studies of the triplet state of many arylethylenic compounds (**10**, **22**) the following values of the reciprocal lifetime (k_1) and of the quenching rate constant by O₂ (k_Q) are considered as typical: $k_1' < 10^5 \text{ s}^{-1}$, $k_Q' = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the planar triplet and $k_1'' = 3 \times 10^7 \text{ s}^{-1}$, $k_Q'' = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the perpendicular triplet species.

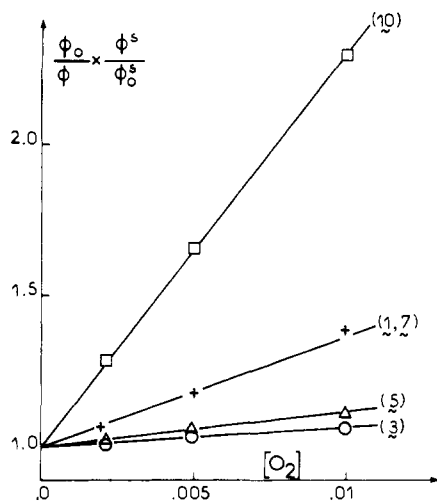


Figure 3. Stern-Volmer analysis of the influence of oxygen on the yield of cyclization. The concentration of oxygen in O_2 -saturated benzene is assumed to be 0.01 M under 1 atm of pressure.

Table I

	VB compound						
	1	2	3	5	7	10	12
τ of 3P (ns)	560	730	720	610	650	600	
$k_{ET}(10^9 \text{ M}^{-1} \text{ s}^{-1})$	6.8	7.2	8.5	7.6	7.5	8.0	
$k_Q\tau_0 (\pm 10\%)$	37	42	7.5	12	37	130	270 ^a
$k_Q (10^9 \text{ M}^{-1} \text{ s}^{-1})^b$	8	7	3	3	8	8.5	9

^a From estimated k_Q and measured τ_0 (30 ns). ^b Estimated values.

planar triplet of **1** is around 63 kcal/mol, from phosphorescence measurements.² Experimentally, the lifetime of **A** is not affected by stilbene and ferrocene: this is a first indication that **A** cannot be 3VB .

From eq II in the presence and in the absence of oxygen one gets $\phi/\phi_0 = (\phi^S/\phi_0^S)(\tau/\tau_0)$ and, with $k_Q = (1 - \alpha)k_Q' + \alpha k_Q''$, it comes from eq I

$$\tau_0/\tau = 1 + k_Q\tau_0[O_2] \quad (\text{III})$$

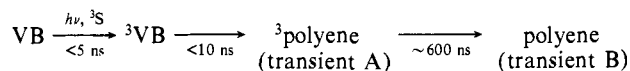
and then

$$(\phi_0/\phi)(\phi^S/\phi_0^S) = 1 + k_Q\tau_0[O_2] \quad (\text{IV})$$

A plot of eq IV is given in Figure 3 for several compounds and the $k_Q\tau_0$ values obtained from the slope of the straight lines of Figure 3 are listed in Table I. Since k_Q must be in the range $3\text{--}9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, depending on the relative fractions of planar and perpendicular triplet geometries,¹¹ the resulting lifetime of 3VB should be in the range 1–40 ns, i.e., much shorter than the 600-ns lifetime of **A**.

Therefore, the transient **A** is definitely not the triplet state of the VB compound. Besides, the fact that rigid compounds such as **3** or **5** give a very efficient sensitized cyclization proves that this reaction does not occur exclusively from the perpendicular geometry of 3VB , as postulated previously.⁹ Thus we need a new assignment for **A** and a new mechanism for the cyclization reaction.

It still remains that the transient species **A** has a triplet character and is a precursor of the polyene **P**. The only expected triplet intermediate between the 3VB produced by sensitization and the polyene is the polyene triplet state, in the following sequence of reactions:



This scheme of an adiabatic reaction in the triplet state allows us to account for all the experimental observations. We will demonstrate below that (a) the energy of 3P is lower than 23 kcal/mol, which explains the absence of quenching by stilbene and ferrocene; (b) the adiabatic reaction $^3VB \rightarrow ^3P$ is energetically

possible for most of the 2-vinylbiphenyl derivatives; (c) the lifetime of 3VB is, in most cases, shorter than 10 ns in agreement with the very fast build up of **A**; (d) the cyclization rate constant is around $3 \times 10^8 \text{ s}^{-1}$, indicative of a spin-allowed process; and (e) when the existence of a perpendicular 3VB is allowed by the molecular structure, the cyclization occurs from both the planar and perpendicular geometries of 3VB , which explains the lack of stereoselectivity of the reaction in these cases.

(a) Evaluation of the Triplet Energy of the Polyene. The orthoquinodimethane character of a part of the π -system of the polyene **P**, which can explain the large decrease of the $S_0 - S_1$ energy gap observed when going from the octahexaene ($\lambda_{\text{max}} \approx 360 \text{ nm}$) to the polyene **P** ($\lambda_{\text{max}} \approx 500\text{--}550 \text{ nm}$), should also lower the $S_0 - T_1$ energy gap. Thus the triplet energy of the polyene **P** should be much lower than 28 kcal/mol, the triplet energy expected for a linear hexaene.¹² It is even lower than 23 kcal/mol since the quenching of 3P by O_2 does not lead to a significant formation of singlet oxygen. This was shown by measuring the rate of disappearance of diphenylisobenzofuran (DPBF) upon continuous irradiation at 355 nm of aerated solutions of xanthone + naphthalene or **1** ($4 \times 10^{-2} \text{ M}$) + DPBF ($4 \times 10^{-5} \text{ M}$) in benzene. This rate is about ten times smaller with **1** than with naphthalene and is mainly (if not entirely) due to $^1O_2^*$ produced from the triplet states of **1** and xanthone.¹³

The triplet energy of the polyene **P** probably lies around that of π -conjugated systems with a $S_0 - S_1$ transition in the 500–550 nm range such as pentacene or spirilloxanthin, a linear polyene with 13 double bonds, i.e., between 22 and 18 kcal/mol.¹⁴ The polyene produced by photocyclization of *cis*-stilbene, the maximum absorption of which is around 450 nm, probably has a slightly higher triplet energy, in the range 21–25 kcal/mol.

(b) Energetics of the Reaction $^3VB \rightarrow ^3P$. The relative position of the energy levels of 3VB and 3P were estimated as follows. The relative position of the ground-state level of the initial aromatic and of the cyclized polyene was set from the enthalpies of formation of these two molecules, calculated as the sum of "group values" and "ring compound corrections" found in Benson's tables.¹⁵ Then the triplet energy is added to the ground-state level.

The triplet energy of the aromatics is 63 kcal/mol for **1** and 66.7 kcal/mol for **12**, from phosphorescence measurements.² In fact, the relevant triplet energy for **1** is probably a few kcal/mol higher than the value given by the phosphorescence because of the changes in the geometry of the biphenyl moiety between the triplet and ground states.¹⁶ For the 1-phenyl-1-(4-phenanthryl)ethylene, E_T must be around 60 kcal/mol, close to that of phenanthrene. The 1-phenyl-2-(2'-biphenyl)ethylene, **13**, must be considered as a substituted stilbene in the same way as the 1-phenyl-2-(β -naphthyl)ethylene. Since the triplet energy of the latter is 49 kcal/mol,¹⁷ close to that of stilbene, it must be around the same value for **13**.

(12) The triplet energy of linear polyenes was evaluated from the expression: $E_T (\text{kcal/mol}) = 9 + 120/N - 40/N^2$, N being the number of conjugated double bonds. This expression is taken from Said et al. (Said, M.; Maynau, D.; Malrieu, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 580) with the values of the coefficients adjusted in order to fit the known experimental values for $N = 2, 3, 8$, and 9, the two last ones being known to bracket the energy of singlet oxygen (see: Mathews-Roth, M.; Krinsky, N. I. *Photochem. Photobiol.* **1970**, *11*, 550 and references cited therein).

(13) A detailed analysis of these measurements for several VB compounds, in relation with the problem of rotamers, will be given elsewhere.

(14) (a) Birks, J. B. In "Photophysics of aromatic molecules"; Wiley-Interscience: New York, 1970, p 184; $E_T = 22 \text{ kcal/mol}$ for pentacene. (b) Bensasson, R.; Land, E. J.; Maudinas, B. *Photochem. Photobiol.* **1976**, *23*, 189; $E_T = 15 \text{ kcal/mol}$ for spirilloxanthin. (c) $E_T = 18 \text{ kcal/mol}$ for spirilloxanthin from the expression given in ref 12 with $N = 13$.

(15) Benson, S. W. In "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976; pp 272 and 273.

(16) Wagner (Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820) reports a 4 kcal/mol difference between the triplet energy determined by phosphorescence (E_{ph}) and the actual energy splitting (E_{00}) between the relaxed triplet and ground states of biphenyl. The steric effect of a large ortho substituent should increase both E_{ph} and E_{00} but whether it increases or decreases ($E_{00} - E_{ph}$) seems unpredictable. Thus, we consider this difference to be "a few kcal/mole" for the 2-vinylbiphenyls 1–8.

(17) Görner, H.; Eaker, D. E.; Saltiel, J. *J. Am. Chem. Soc.* **1981**, *103*, 7164.

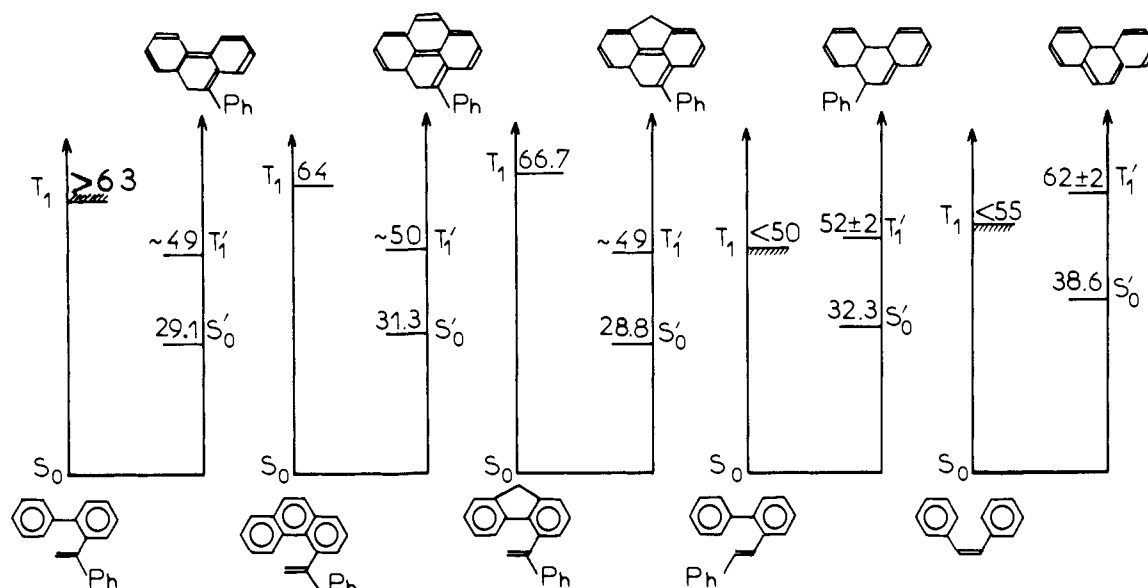
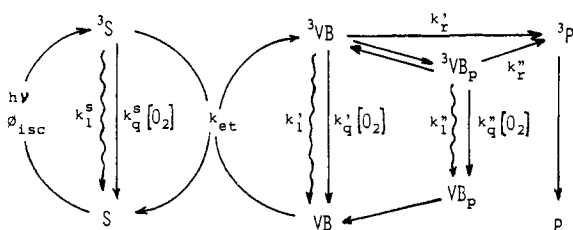


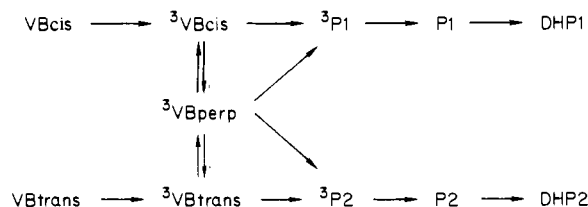
Figure 4. Diagram of the energy levels of the S_0 and T_0 states for some arylethylenic compounds and the related cyclic polyenes.

Scheme II



It then appears from the results presented in Figure 4 that an adiabatic cyclization reaction in the triplet state is energetically possible for the 1-phenyl-1-arylethylenes but impossible (or at least unfavorable) for the 1,2-diarylethylenes such as *cis*-stilbene and **13** which actually do not undergo the cyclization reaction under triplet-sensitized conditions.

(c) **Lifetime of 3VB and Cyclization Rate Constant of the Planar Triplet.** These two parameters can be obtained from the analysis of the effect of oxygen on the yield of photocyclization. But, first, we need a new reaction scheme, including 3P as an intermediate and accounting for the efficient cyclization from the planar 3VB . The framework of such a scheme should be



For most of the compounds investigated the species VB_{cis} and VB_{trans} are indistinguishable (and so are P_1 and P_2), and the reaction mechanism can be represented by Scheme II.

With α being the fraction of perpendicular triplet and with $k_x = (1 - \alpha)k_x' + \alpha k_x''$ (x being 1, r , or Q), the lifetime of 3VB is given by $1/\tau = k_1 + k_r + k_Q[O_2]$, and the quantum yield of formation of the polyene P is $\phi = \phi^S k_r \tau$.

From the measurement of ϕ in the presence and in the absence of oxygen one gets

$$(\phi_0/\phi)(\phi^S/\phi_0^S) = 1 + k_Q\tau_0[O_2]$$

with $1/\tau_0 = k_1 + k_r$. This expression is the same as eq IV and, therefore, the $k_Q\tau_0$ values given in Table I can be used directly.

For the rigid compounds **3** and **5**, in which the twisting of the double bond is very limited, the triplet state is essentially planar

and k_Q must be around $3 \times 10^9 M^{-1} s^{-1}$. Then, from $k_Q\tau_0 = 7.5$ and **12**, one gets $\tau_0 = 2.5$ and 4 ns for the compounds **3** and **5**, respectively. The cyclization rate constant, $k_r = 1/\tau_0 - K_1$, is around $4 \times 10^8 s^{-1}$ for **3** and $2.5 \times 10^8 s^{-1}$ for **5** since $k_1 \ll 10^6 s^{-1}$ for these planar triplets.

For the other compounds presented in Table I, the equilibrium between the planar and perpendicular triplets makes it impossible to accurately determine the lifetime of 3VB since K_Q will change from $3 \times 10^9 M^{-1} s^{-1}$ if the triplet is mainly planar to $9 \times 10^9 M^{-1} s^{-1}$ if the triplet is mainly perpendicular.¹¹ Using the value $k_Q = 5 \times 10^9 M^{-1} s^{-1}$ which certainly approximates the real k_Q value within a factor of two, one gets $\tau_0 = 8$ ns for **1** and **7**, in agreement with the rapid growth of **A**, and $\tau_0 = 26$ ns for **10**. In the latter case the growth of **A** should be measurable, but it is hidden by the absorption of a third transient species, **C**, which will be discussed later.

(d) **Geometry of the Reactive Triplet and Stereoselectivity.** In the case of compounds **5** and **6** the triplet-sensitized photocyclization gives only one stereoisomer of the product, the same as obtained by direct irradiation, i.e., the "trans" DHP. Since the "cis" DHP is known and is thermally stable,¹⁸ we conclude that the cyclization from the planar triplet is stereoselective. On the other hand, in the case of compounds in which a perpendicular triplet is possible and the DHP isomers can be distinguished, such as **4** and **7**, the sensitized reaction does give the two stereoisomers. In the case of **4**, a fast equilibrium between the two planar "cis" and "trans" and the perpendicular conformations of the triplet could explain the stereochemistry of the reaction even with the assumption of a nonreactive perpendicular triplet. But for **7**, in which a planar triplet state with a "trans"-cycloheptene ring seems quite impossible, the formation of 35% of "cis"-cyclized product¹⁸ can only be explained by a cyclization from the perpendicular triplet which, depending on the relative direction of the twisting motions of the biphenyl and of the double bond, can give the two DHP isomers as shown in Figure 5. Then one must consider that the perpendicular triplet of a compound such as **1** can give the cyclization reaction as well.

The rate constant for cyclization from the perpendicular triplet, k_r'' , can be evaluated as a function of α and k_r' from the expression

$$k_Q\tau_0 = \frac{\alpha k_Q'' + (1 - \alpha)k_Q'}{(\alpha(k_1'' + k_r'') + (1 - \alpha)(k_1' + k_r'))} \quad (V)$$

Assuming that the rate of cyclization from the planar triplet of

(18) Lapouyade, R.; Manigand, C.; Nourmamode, A. *Can. J. Chem.*, submitted.

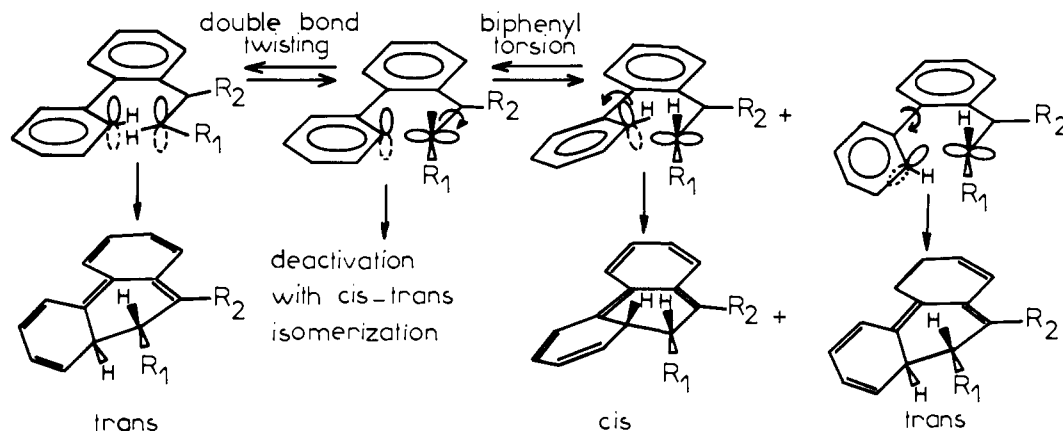
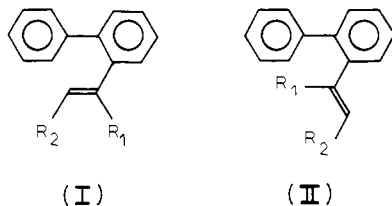


Figure 5. Postulated scheme for the cyclization of the perpendicular triplet. The two different stereoisomers are formed after the nonconcerted motions of twisting of the double bond by 90° and distortion of the biphenyl. The curved arrows indicate the direction of the twisting motions which lead from the initially planar molecule to the represented geometries.

1 and **7** is comparable to that determined above for **3** and **5**, i.e., $k_r' = 3 \pm 1 \times 10^8 \text{ s}^{-1}$ and that $0.7 \leq \alpha \leq 1.0$, and with the usual values of k_1' , k_Q' , k_1'' , and k_Q'' ,¹¹ and $k_{QT_0} = 37$ for **1** and **7**, eq V gives $k_r'' = 1.5 \pm 0.6 \times 10^8 \text{ s}^{-1}$: thus the perpendicular triplet of these VB derivatives would be nearly as reactive as their planar triplet.

This does not seem to be the case for the α -styrylfluorene **12**, the triplet state of which is essentially perpendicular¹⁰ and gives no detectable amount of cyclized product. The lack of reactivity of the triplet state of **12** may result from (i) an increased distance between the cyclizing vinyl and aromatic carbons, (ii) a change in the electronic charges on these carbons, and (iii) the nearly planar rigid geometry of the fluorene moiety which prevents the twisting motions involved in the cyclization of the biphenyl derivatives through the perpendicular triplet.

(e) **Rotamers, Transient C, and Quantum Yields.** In all the previous sections it was considered that the arylythylenic molecule has a conformation of type I in which the ethylenic double is suitably oriented to give the reaction. However, another stable conformation, type II, is also possible. The rotamers I and II



coexist probably in the ground state in proportions depending on the structure of the compound.^{19,20} For instance, the presence of the phenyl substituent should favor the structure I in **1–4** and **12**. Whether or not the rotamer distribution is changed during the energy-transfer step is not known, but once the molecule is in the triplet state, the exchange rate between the rotamers is probably much slower than that in the triplet decay.²¹ Therefore, in addition to the triplet state of rotamer I, the lifetime of which is short because it is limited by the rate of reaction, there should be the triplet state of rotamer II, unreactive because of unsuitable orientation of the double bond, the lifetime of which should vary from several μs , if this triplet is planar, to about 30 ns, if it is mainly perpendicular. We think that the third transient absorption (transient C) which is observed for compounds **5–8** in the region 360–400 nm and for **10** in the 400–500 nm range is

due to the triplet state of the rotamer II for the following reasons:

(i) This transient C is not observed for compounds **1–4** in which the percentage of rotamer II is expected to be low.

(ii) The transient C is formed quite rapidly ($< 10 \text{ ns}$), and its lifetime is around 2 μs for **5**, 60 ns for **6**, 40 ns for **7** and **8**, and 32 ns for **10**. These values correspond to a triplet state which would be planar for **5**, mainly perpendicular for **10** and to percentages of planar triplet around 50% for **6** and 20% for **7** and **8**. These fractions of planar/perpendicular geometries are those expected for the triplet state of these compounds on the ground of their structure.

(iii) The transient C is quenched by O_2 and, in the case of **5**, it is also quenched by *trans*-stilbene ($k_Q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

The existence of two rotamers affect the values of the quantum yields of the sensitized photocyclization reaction since both rotamers accept the energy of the sensitizer whereas only one can give the reaction. The quantum yield of cyclization of rotamer I calculated from the rate constants measured or evaluated above is very close to unity for the biphenyl derivatives considered in this study. The experimentally measured quantum yields ($\phi = 0.58$ for **1**, 0.89 for **2**, 0.46 for **5**, 0.37 for **6**, ...) could, possibly, give an evaluation of the percentage of rotamer I. Some other experiments, such as fluorescence measurements, are in progress to investigate this problem of rotamers.

Conclusion

The photocyclization of the triplet state of 2-vinylbiphenyls and related compounds is an adiabatic reaction energetically possible because of the high triplet energy of these molecules and the low triplet energy of the cyclic polyene given by the reaction. In contrast, *cis*-stilbene and 1-phenyl-2-(2'-biphenyl)ethylene do not undergo this reaction: most probably, the adiabatic cyclization is endoenergetic in these cases because of the low triplet energy of 1,2-diarylethylenes.

When the cyclization occurs from a planar triplet state, the stereochemistry of the product is well explained by a concerted stereospecific conrotatory reaction, as from the excited singlet. However, the reaction may appear as nonstereospecific when there is a fast equilibrium between the two planar "cis" and "trans" triplets. In the case of biphenyl derivatives, the cyclization occurring from the perpendicular triplet is an additional reason for the nonstereospecificity of the triplet-sensitized reaction.

The yield of cyclization from the planar triplet should be very close to unity and rather large from the perpendicular triplet of biphenyl derivatives. However, the experimental quantum yield of the reaction will also depend on the percentage of the geometrically favorable rotamer.

Experimental Section

The laser-flash-photolysis setup recently has been described.¹⁰ The xanthone sensitizer, in benzene solution, was excited by the third harmonic of the Nd-YAG laser. The concentration of xanthone was ad-

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justed to get an optical density around 1.5 at 355 nm and that of the olefinic acceptor was in the range 0.02-0.06 M in order to get a fast energy transfer.

The synthesis of several compounds has been described in previous papers: **1** and **12** in ref 2, **2** in ref 8, and **5-8** in ref 18. The others were prepared by reaction of 2-lithiobiphenyl (or 4-lithiofluorenyl) with the

appropriate ketones and dehydration of the resulting alcohols with P₂O₅.

Registry No. 1, 57704-78-6; 2, 83283-82-3; 3, 98509-50-3; 4, 75925-36-9; 5, 98509-51-4; 6, 10468-66-3; 7, 98509-52-5; 8, 98509-53-6; 9, 98509-54-7; 10, 98509-55-8; 11, 98509-56-9; 12, 57704-79-7; 13, 34662-94-7.

Application of the H.T.-n Mechanism of Photoisomerization to the Photocycles of Bacteriorhodopsin. A Model Study[†]

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Abstract: The H.T.-n process, recently introduced to account for the primary process of vision, has now been incorporated into a scheme for the two photocycles of bacteriorhodopsin. The current analysis is based on molecular model construction as well as photochemical and bioorganic reasoning. Specific molecular structures are proposed for BR¹, K¹, L¹, M-I, M-II, Photo-M, L', and M' in the trans-cycle. The pathways connecting these species are H.T.-14 for photochemical processes and conformational relaxation and B.P.-14,16 for thermal reactions. The latter also leads to relocation of the iminium hydrogen, hence initiating the proton pumping activity. The proposed structures are consistent with the known spectroscopic properties of these species. Two possible schemes are considered for the minor BR^c photocycle.

In an earlier report we introduced a new mechanism for geometric isomerization of polyenes which involves translocation of a single H atom from one side of the polyene chain to another with concerted rotation of the two adjacent C,C bonds. This motion was dubbed the H.T.-n process (Figure 1).¹ Application of the mechanism to the primary process of vision led to the proposal of the 10-*s-cis*,*all-trans* structure for bathorhodopsin. This structure satisfactorily accounts for all known spectroscopic and chemical properties of the primary photoproduct. The H.T.-n process is not believed to be competitively favored relative to the conventional one-bond rotation process of isomerization in unconstrained molecules, e.g., those in solution. However, for chromophores in which translational and rotational motions are restricted (e.g., by specific protein-substrate interactions at the two termini and by the limited space available due to the surrounding protein), the H.T.-n process could become the dominant isomerization pathway because the alternative one-bond-rotation process is more volume demanding. Bacteriorhodopsin (BR), like rhodopsin, contains a retinyl chromophore in a membrane protein binding site.² A close examination of the possible application of the H.T.-n mechanism to the known chemistry of the isomeric pigments and their intermediates is, therefore, of obvious interest.

The presence of two independent photocycles and the large number of intermediates suggest that BR is mechanistically more complex than rhodopsin. However, on the basis of the same approach of model construction and photochemical and mechanistic considerations that was successfully applied to rhodopsin, we can now formulate a complete and logical scheme for early stages of the BR photocycles. This scheme is the subject of this report.

Background on the Photocycles of the BR System

The photobleaching and dark regeneration processes of BR have been studied in great detail by fast kinetics and low-temperature spectroscopy by many research groups. The topic has been re-

viewed in several excellent articles.² The key intermediates for the photocycles are indicated in Figure 2, and a brief review of the experimental results is presented below.

The configurational integrity of the 13,14 bond of the retinyl chromophore is not maintained at room temperature, giving approximately equal amounts of *all-trans*- (BR¹) and 13-*cis*-BR (BR^c).^{2c} Light adaptation results in a slow 13-*cis* to *all-trans* conversion. At ≤0 °C where the dark adaptation process is suppressed, the light conversion to the BR¹ becomes complete. Light excitation generates a series of intermediates. From BR¹ the primary photoproduct is usually considered to be the red-shifted K¹ intermediate, although more recently a shorter-lived precursor (J) of K¹ has been detected in fast kinetic studies.⁴ Sequentially, K¹ is converted to the blue-shifted L¹ and the much more blue-shifted M-I. It is during the L¹ to M-I transition that the physiologically important proton-pumping activity is believed to originate, the product (M-I) being a deprotonated chromophore⁵ containing the 13-*cis* geometry.⁶ From kinetic arguments, M-I is believed to be in equilibrium with an isochromic M-II.⁷ A slower, probably catalytic process follows, resulting in the formation of the red-shifted O intermediate, containing the *all-trans* geometry.⁸ To complete the photocycle, O is converted to BR¹.

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[†] Photochemistry of Polyenes 23. For part 22 in the series, see ref 1, to which readers should consult for a more general discussion of the H.T.-n process. Abbreviations used in this paper: H.T.-n, hula-twist at center n (also known as C.T.-n: concerted twist at center n);¹ B.P.-14,16, bicycle-peddaling at bonds 14 and 16; BR, bacteriorhodopsin; BR¹, *all-trans*-bacteriorhodopsin; BR^c, 13-*cis*-bacteriorhodopsin.