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Diarylethene photoisometization and photocyclization mechanisms

M F Budyka

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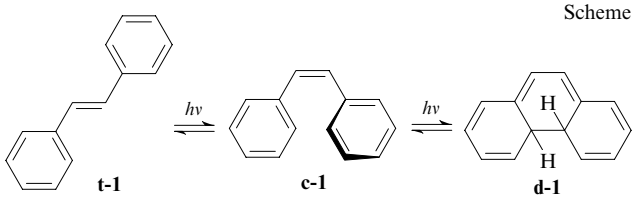
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Abstract. The mechanism of photoisomerization of diarylethenes is considered, including its multiplet, conformational and energetic aspects. The experimental data on the 'one bond flip' and 'hula-twist' photoisomerization mechanisms, the adiabatic and diabatic reaction channels and also on one-photon photocyclization of diarylethene *trans*-isomers are surveyed. The results of quantum chemical calculations of the potential energy surface along the reaction coordinates of diarylethene isomerization and cyclization are analyzed. The bibliography includes 179 references.

I. Introduction

Photoisomerization and photocyclization are the two major intramolecular reactions of diarylethenes. These reactions can be illustrated by the example of the simplest diarylethene, stilbene (**1**) (Scheme 1). Under the action of light, *trans*-isomer (**t-1**) transforms to *cis*-isomer (**c-1**) and the latter undergoes ring-closure to afford a dihydrocyclo product, in this particular case, dihydrophenanthrene (**d-1**). For stilbene, as for most diarylethenes, both reactions are reversible. In the presence of oxidizers, the dihydrocyclo product is oxidized; this is often used to prepare fused arenes.

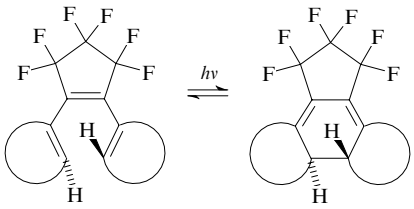
Scheme 1



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Studying the mechanism of photoisomerization and photocyclization is of interest from the viewpoint of acquiring fundamental knowledge of the mechanism of photochemical transformations[1–9] and also with the aim of optimizing various practical applications of diarylethenes as photochromes, luminophores, in memory storage devices, for the design of molecular photoswitches, *etc.*[10–33] In practice, only one of these reactions is used, while the other is undersirable side process that should be eliminated. Thus, in photochromes, which employ photocyclization, the photoisomerization is suppressed by securing the molecule in the *cis*-configurations by one of another method.[25–33] The most efficient way is to insert an ethylene group into an additional third ring, most often, the perfluorocyclopentene ring.



The notion 'photoisomerization mechanism' includes, at least, three different aspects conditionally referred to as multiplet, conformational and energetic aspects.

The multiplet aspect is associated with the type of'electronically excited state (singlet or triplet) in which the reaction proceeds (as a rule, these are the lower excited states S_1 or T_1). For direct excitation of stilbene and the majority of diarylethenes, the reactive state is S_1; hence, in the further text, if not specified otherwise, the reactions are considered for this state. For triplet sensitization of diarylethenes and also for excitation of diarylethenes having high rate constants for intersystem crossing, the isomerization occurs in the T_1 state. The identification of the singlet and triplet mechanisms requires special experiments on the effect of sensitizers and quenchers; from the standpoint of chemistry, these mechanisms are indistinguishable because produce one and the same set of isomers.

The conformational aspect of photoisomerization considers the particular way of restructuring of the diarylethene skeleton. The photoisomerization reaction can follow the 'one bond flip' and 'hula twist' mechanisms. These mechanisms are distinguished by the conformation of the product formed: the molecular conformation is retained when isomerization follows the former mechanism but changes in the case of the latter mechanism. Furthermore, the latter mechanism requires much smaller free volume for the reaction to proceed so that the photoisomerization can take place in viscous and even rigid matrices. Below, these mechanisms are briefly characterized.

The third, energetic aspect of photoisomerization is associated with the variation of the system energy when travelling along the reaction coordinate. The photoisomerization can proceed by diabatic or adiabatic channels. An adiabatic chemical reaction occurs without changes in the electronic state and in one and the same potential energy surface (PES).[34] As applied to photoisomerization of diarylethenes, this means that after the excitation of one isomer, the system travels along the PES of the excited state to reach the coordinate domain of the other isomer, which is followed by its deactivation and the transition to the ground state PES. Hence, for adiabatic photoisomerization, the reaction product is formed in the excited state, *i.e.*, virtually without any loss in energy. This is why under certain conditions the saved energy can be transferred to the substrate, which triggers the chain quantum reaction. In contrast, for the diabatic photoisomerization, the reaction products are formed in the ground state, *i.e.*, lose the excitation energy in the course of reaction. The diabatic and adiabatic mechanisms are usually distinguished based on the data of quantum chemical studies but sometimes they can be identified by the composition of the photostationary mixture and the observed quantum yield. This aspect of photoimerization is the focus of attention in the further text.

In addition to the aforesaid, mention should be made of yet another aspect of photoisomerization: the reaction can proceed in either radical or radical-ion state; the peculiarities of photoisomerization in these states were considered in a review.[7]

In contrast to photoisomerization, the photocyclization proceeds only in the singlet-excited state. As a rule, the photocyclization is considered separately from photoisomerization, because the study objects often represent compounds incapable of isomerization. The present review considers both intramolecular reactions of diarylethenes, because they proceed in one and the same excited-state PES. This is why the complete analysis of the routes of transformations of excited diarylethenes is impossible without the joint consideration of photoisomerization and photocyclization data. Thus, although photocyclization is the side and competitive reaction with respect to *cis*-isomer photoisomerization, in some experimental studies the kinetic data on *trans*-isomer photocyclization are used to elucidate the photoisomerization mechanism as either diabatic or adiabatic. However, as follows from quantum chemical calculations, the conclusions drawn in the latter studies appear to be controversial and admit another interpretation (see below).

Recently, considerable progress was achieved in understanding the detailed mechanism of reactions, first of all, owing to the development and application of time-resolved spectroscopy and, second, owing to the elaboration of new quantum chemical methods and appropriate software to be used in calculation of excited states and interpretation of experimental data. For example, the key role of conical intersections (regions of degenerate electronic states) in the molecular-level control over the selectivity and efficiency of photochemical reactions in fast internal-conversion processes was demonstrated.[35–37]

The majority of reviews published recently were devoted to applied aspects of diarylethene photochemistry, the possibility of using the photocyclization reaction switch not only the light absorption region (photochromism) but also fluorescence[13,19,29,30] and electrical,[11,13] magnetic[13] or chiral[31] properties. The peculiarities of photoswitching for diarylethenes adsorbed on the surface,[32] photochromism of diarylethenes in single crystals,[10,12] the problems of using diarylethenes in photochromic polymers,[28] as photochromic ligands in metal complexes[33] were considered. The general classification of organic photochromes was given in a review;[23] photochromic switches and the problems associated with the development of optoelectronic devices based on the diarylethene photocyclization reaction were surveyed.[25,27] Photonic molecular logical gates based on photoisomerization and photocyclization reactions were considered in a review.[18]

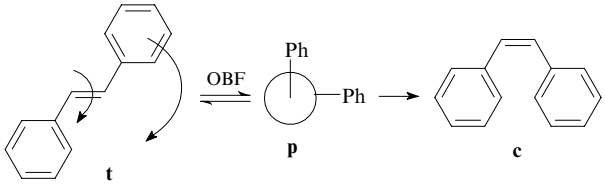
As to the theoretical studies of the mechanism of diarylethene photocyclization, there is a brief review of authors' studies on this problem.[14] Furthermore, the problems associated with the ratio of diabatic and adiabatic photoisomerization channels were surveyed, also based mainly on the own results of authors.[8,9]

Note that the terms *trans–cis*- and *cis–trans* photoisomerization often remain undistinguished, being equally used for designating the reaction reversibility. In the present review, these terms are considered as different in order to stress the particular direction of the process under consideration from *trans*- to *cis*-isomer and back.

II. Photoisomerization mechanisms

1. One bond flip and hula-twist mechanisms

First of all, let us consider the conformational aspect. The classical photoisomerization mechanism becomes clear if we consider the necessary geometrical changes that occur during the reaction. This mechanism is called one bond flip (OBF) or one bond twist (OBT).[1] According to this mechanism, in the excited state, the π-bond loosens and the aryl substituents twist with respect to one another to afford a conformer in which they take the orthogonal position (with the dihedral angle at the double bond of ~90°). This conformer is referred to as perpendicular (*perp*-conformer, **p**) and sometimes as the phantom state.



The perpendicular conformer corresponds to a minimum in the excited-state PES and a maximum in the ground-state (S_0) PES. Figure 1 shows a simplified scheme of potential energy curves for diarylethene isomerization,

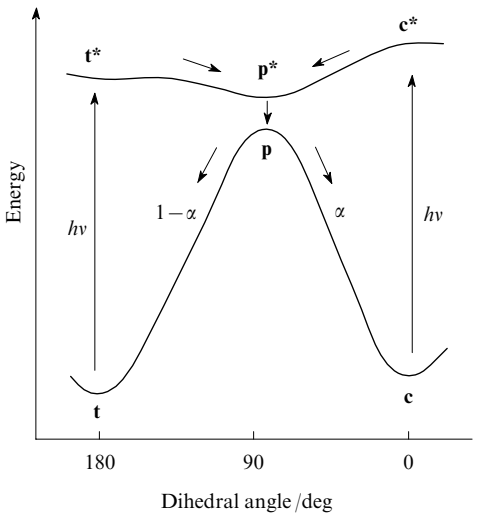
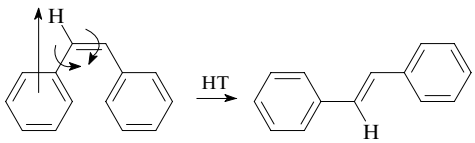


Figure 1. Simplified chart of potential energy curves for diarylethene isomerization.[3, 8]
Arrows point to the diabatic route of photoisomerization.

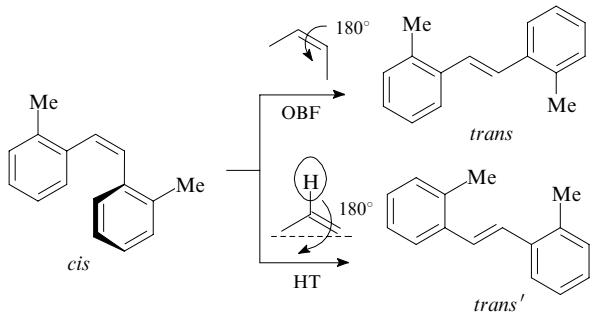
with the dihedral angle at the double bond taken as the reaction coordinate.

According to the OBF photoisomerization mechanism, as the substituents rotate around the double bond, they leave the molecular plane and circumscribe a cone. Such restructuring of the molecular geometry requires a wide free space, especially when a flatter *trans*-isomer isomerizes to a bulkier *cis*-isomer. This is why *trans*–*cis* photoisomerization is hindered in confined media, for instance, in solutions frozen to the glassy state.

Nonetheless, photoisomerization sometimes can proceed very fast and with a high quantum yield even under conditions of limited mobility. To explain this phenomenon, the mechanism that involves the rotation around two bonds was proposed and called the hula-twist (HT) mechanism,[38–42] because this molecular reorganization resembles movements of dancers in the well-known dance. According to the HT mechanism, in the excited state, the rotation proceeds around both the double bond and the adjacent single bond. As a result, formally speaking, only one CH group leaves the plane as if turning by 180° from one side of the molecule to the other, whereas the substituents are reoriented in the molecular plane.



Comparing the OBF and HT isomerization mechanisms shows that both produce one and the same geometrical isomer but different conformers (rotamers). The question of the conformational isomerism of diarylethenes is considered below; this problem has already been studied in detail (*e.g.*, see the review[43]). According to the OBF mechanism, only the molecular configuration changes while its original conformation remains unchanged. In the HT mechanism, both the molecular configuration and conformation change simultaneously. This effect is not manifested for all diarylethenes and is observable only for those compounds the conformers of which exhibit different spectra. For example, in 4,4′-dimethylstilbene, the conformers are undistinguishable, whereas for 2,2′-dimethylstilbene, the OBF and HT mechanisms produce two different conformers (*trans* and *trans′*).



The HT mechanism was proposed for explaining the *cis*–*trans*-photoisomerization of diarylethenes in frozen glasses at low temperatures, the reverse *trans*–*cis*-isomerization does not proceed under these conditions. Let us briefly consider the experimental procedure, insofar as there is disagreement on the interpretation of experimental data and also because, unlike the OBF mechanism, the HT mechanism is not yet generally accepted.

A solution of diarylethene cooled to the glassy state (~77 K) is illuminated with light up to cessation of spectral changes. Then, the reaction mixture is heated and recooled, while monitoring the spectral changes with respect to the spectrum taken immediately after illumination. This effect, *i.e.*, the spectroscopic changes upon refreezing was first observed by Alfimov *et al.*,[44] who assigned them to the formation of a non-equilibrium mixture of *s*-conformers upon photoisomerization. As the matrix is being heated to become softer, the equilibrium is resumed while the mixture composition and, correspondingly, its spectrum change, because different *s*-conformers exhibit slightly different absorption and luminescence spectra. Later, this effect was interpreted as evidence for the HT mechanism.

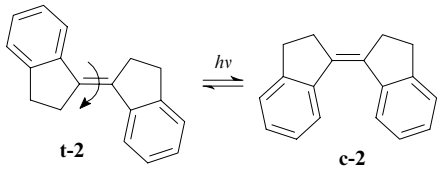
Thus, in the photoisomerization by the OBF mechanism, the subsequent spectral changes are associated with the redistribution of the contents of conformers to afford their equilibrium content,[45, 46] whereas for isomerization by the HT mechanism, the subsequent changes are associated with transformation of the less stable conformer to the more stable one. Both processes should induce changes in the observed spectra.

According to a recent study,[47] the *cis*–*trans* photoisomerization at low temperatures strongly depends on the matrix rigidity. In line with this, it was assumed[47] that the seeming disagreement on the photoisomerization mechanism in confined media can be explained by the fact that different authors used different matrices and some of them might fail to confine the conformer transformations.

It is obvious from the aforementioned that the HT mechanism was proposed and used mainly for interpreting the process of *cis*–*trans* photoisomerization in a rigid matrix. A possible example of the reverse *trans*–*cis* photoisomerization, particularly that proceeding in a liquid solution, is the photoisomerization of stilbene dendrimers.[48, 49] Dendrimers of the fourth generation were found to have almost the same properties, *i.e.*, similar quantum yields of

trans–*cis* photoisomerization (0.24–0.32) and fluorescence (0.43) and the same fluorescence lifetime (~10 ns). Presumably,[49] this points to the HT mechanism, because within the framework of the OBF mechanism it is hard to explain the absence of any dependence of photophysical and photochemical parameters on the size of substituents, which varies widely in the series of stilbenes under study.

Interesting results were obtained for photoisomerization of 1,1′-biindanylidene (**2**).



It was found that the excited *perp*-conformer of compound **2** has the lifetime several times longer as compared with stilbene.[50, 51] Insofar as for biindanylidene (**2**), OBF is the only possible mechanism of photoisomerization, whereas stilbene can also isomerize by the HT mechanism, it was concluded that the minimum energy path in the S_1-state PES corresponds precisely to isomerization by the HT mechanism.[51, 52] Based on this, it was assumed that the HT mechanism can occur not only in a rigid matrix but also for free molecules under 'ordinary' conditions without any limitations for mobility.[51, 52]

2. Adiabatic and diabatic mechanisms

Now we consider the energy aspect of photoisomerization. The reaction can proceed by either adiabatic or diabatic routes; the latter is also referred to as the non-adiabatic route where two negative prefixes are used simultaneously, the Latin 'non' and the Greek 'a'. The route of isomerization determines the energy of reaction products.

Upon photoexcitation, the majority of diarylethenes isomerize by the diabatic mechanism as shown in the simplified chart of potential curves (see Fig. 1). After excitation of a *trans*- or *cis*-isomer, the system drops to a potential energy minimum corresponding to *perp*-conformer (**p***). For stilbene, it was found that the excited *trans*-isomer (**t***) domain is separated from the **p***-minimum by a barrier with the height of 1200 cm^{-1} (3.43 kcal mol^{-1})[53] and the domain of excited *cis*-isomer (**c***) is separated by a barrier of no less than 40 cm^{-1} (0.11 kcal mol^{-1}).[54] In the vicinity of **p***-minimum, the molecule passes from the excited to the ground state. For the $S_1 \rightarrow S_0$ transition, this corresponds to the internal conversion, whereas for the $T_1 \rightarrow S_0$ transition, this corresponds to the intersystem crossing. According to quantum chemical calculations, the internal conversion proceeds through a conical intersection (see below).

Insofar as the minimum in the excited-state PES is located symmetrically above the maximum in the S_0-state PES, then upon the **p*** → **p** transition, the system can with equal probability find itself on either side of the barrier, which corresponds to the partitioning factor $\alpha \approx 0.5$ and is typical of two-way photoisomerization. The quantum yields of *trans*–*cis*- and *cis*–*trans* photoisomerization (φ_{tc} and φ_{ct}) are determined as $\varphi_{tc} = \varphi_{p^*}\alpha$ and $\varphi_{ct} = \varphi_{p^*}(1-\alpha)$, where φ_{p^*} is the quantum yield of the excited perpendicular state (**p***). Hence, it is clear that for $\alpha \approx 0.5$, the quantum yields of isomerization cannot exceed 0.5: $\varphi_{tc}, \varphi_{ct} \leqslant 0.5$.

Thus, for photoisomerization by the diabatic mechanism, rotation around the double bond starts in the lower excited state and ends in the ground S_0-state. The reaction is described by the following sequence of processes

$$\mathbf{t(c)} + h\nu \longrightarrow \mathbf{t^*(c^*)} \longrightarrow \mathbf{p^*} \longrightarrow \mathbf{p} \longrightarrow \alpha\,\mathbf{c} + (1-\alpha)\mathbf{t}$$

and, irrespective of the initial substrate (*trans*- or *cis*-isomer), affords a mixture of isomers. On illumination of the reaction mixture, a state is reached where the rates of *trans*–*cis*- and *cis*–*trans* photoisomerization reactions are equal. This state is called photostationary. The content of one or another isomer in the photostationary mixture depends on the ratio of quantum yields for the forward and reverse reactions and also on molar absorption factors of isomers at the exciting radiation wavelength and can be calculated by using the equation

$$[\varphi_{tc}\varepsilon_t(c_t)_{ps}]_\lambda = [\varphi_{ct}\varepsilon_c(c_c)_{ps}]_\lambda ,$$

where c_i is the isomer i concentration and ε_i is its molar absorption factor at the radiation wavelength λ. By varying the exciting light wavelength, it is possible to change the composition of the photostationary mixture.

The adiabatic reaction route is associated with the system travelling in the excited-state PES from one isomer configuration to the other, which is observed more often for the *cis*–*trans* photoisomerization

$$\mathbf{c} + h\nu \longrightarrow \mathbf{c^*} \longrightarrow \mathbf{t^*} \longrightarrow \mathbf{t}$$

This is explained by the fact that the **c*** → **t*** process is advantageous as regards energy, because on the energy scale, the *cis*-isomer lies higher than the *trans*-isomer and, on the whole, the PES descends from *cis*- to *trans*-isomer as shown in Fig. 2. At the same time, this arrangement of the terms for *trans*- and *cis*-isomers means that the reverse adiabatic *trans*–*cis* isomerization **t*** → **c*** is endothermic, which is unfavourable. Indeed, in contrast to *cis*–*trans* photoisomerization, the cases of adiabatic *trans*–*cis* photo-

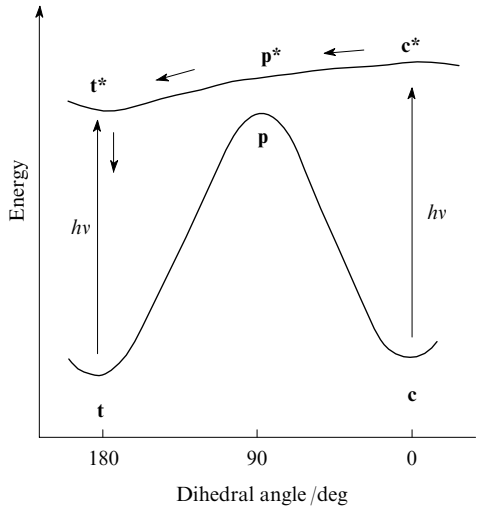


Figure 2. Simplified chart of potential energy curves for one-way adiabatic *cis*–*trans*-photoisomerization of diarylethenes.[3]

isomerization are not so numerous (and convincingly proved only for dihetarylethenes with the inverse stability of *trans*- and *cis*-isomers, see below).

Note the following basic differences between the two photoisomerization mechanisms. For the diabatic mechanism,

— photoisomerization always produces two isomers which form the photostationary mixture;

— both isomers are formed in the ground state;

— the theoretically maximum quantum yield does not exceed 0.5 (for $\alpha \approx 0.5$).

For the adiabatic mechanism

— photoisomeriation produces one isomer, and one isomer can be completely converted to the other;

— the isomerized product is formed in the excited state;

— the maximum theoretical quantum yield is 1, whereas the experimentally measured quantum yield may exceed 1 provided a chain quantum process arises as a result of the intermolecular energy transfer from the excited reaction product (*trans*-isomer) to the substrate (*cis*-isomer); this effect is observed for the one-way isomerization.

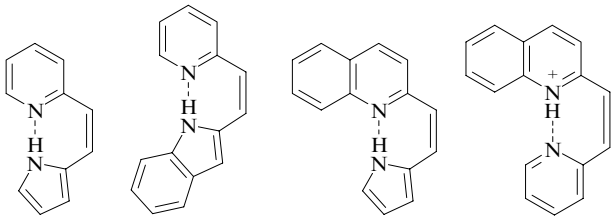
Thus, to prove that the reaction proceeds by the adiabatic route, it is necessary to detect the excited isomer (reaction product) after the excitation of the other isomer (reaction substrate). Insofar as the *trans*-isomer exhibits fluorescent properties, this was carried out for the reaction of *cis*–*trans*-photoisomerization. After excitation of the *cis*-isomer, the *trans*-isomer fluorescence was observed, which confirmed the adiabatic nature of photoisomerization.

This is a direct physical method of proof. Besides, there is an indirect chemical method that can be used to identify the adiabatic route of *trans*–*cis* photoisomerization, because the fluorescence quantum yield for the *cis*-isomer is much lower as compared with the *trans*-isomer, which complicates the use of the physical method. The chemical method employs 'one photon — two reactions' approach with photocyclization as the second reaction. As shown below, in this case, the interpretation of experimental data is not so obvious, because the observed effects can also be explained without invoking the adiabatic photoisomerization.

III. Experimental results and their interpretation

Based on the analysis of the excited-state potential energy curves, it is evident that the conditions favourable for adiabatic photoisomerization imply the absence of a high barrier between the two isomers, which might prevent the reaction, and also the absence of a deep minimum in the vicinity of *perp*-conformer, which might serve as a potential energy trap to direct the reaction along the diabatic route. Since owing to the steric repulsion between aryl substituents, the *cis*-isomer is usually unstable compared to the *trans*-isomer, the *cis*-isomer term lies in the energy scale higher than the *trans*-isomer term, which is favourable for the *cis*–*trans* photoisomerization by the adiabatic route but at the same time prevents the reverse *trans*–*cis* isomerization because exothermicity of one reaction means endothermicity of the other.

The endothermicity of *trans*–*cis* isomerization decreases as the terms of *cis*- and *trans*-isomers approach each other. Cases are known where the *cis*-isomer term drops in the energy scale even lower than the *trans*-isomer term; however, both terms are associated with specific interactions between two diarylethene fragments, which stabilize the *cis*-isomer. For example, the inversion of energies of *trans*- and *cis*-isomers was observed upon the intramolecular hydrogen bonding between the azole and azine nuclei in *cis*-1-(2-pyridyl)-2-(2-pyrrolyl)ethene (**3**),[55] *cis*-1-(2-indolyl)-2-(2-pyridyl)ethene (**4**)[56,57] and *cis*-1-(2-quinolyl)-2-(2-pyrrolyl)-ethene (**5**)[58] and also in analogous derivatives containing the 2-phenanthroline substituent[59] or between two azine nuclei in a salt of monoprotonated *cis*-1-(2-quinolyl)-2-(2-pyridyl)ethene (**6**).[60] As a result, the quantum yield of *trans*–*cis* photoisomerization increases[60] or the reaction even transforms into one-way *trans*–*cis* photoisomerization.[55,56]



3 **4** **5** **6**

Before considering particular cases of adiabatic photoisomerization, consider the rule of non-equilibration of excited rotamers (NEER).[43,61] According to the NEER rule, in the excited state, the distribution of rotamers (conformers) established in the ground state is conserved. During the excited-state lifetime, the system has no time to reach new equilibrium because double bonding of the quasi-single bonds is enhanced in the excited state of the ethylene group. This principle is not always strictly observed but in the photochemistry of 2-styrylnaphthalene and 2-styrylanthracene, it plays an important role allowing the reaction routes of different conformers to be distinguished (see below).

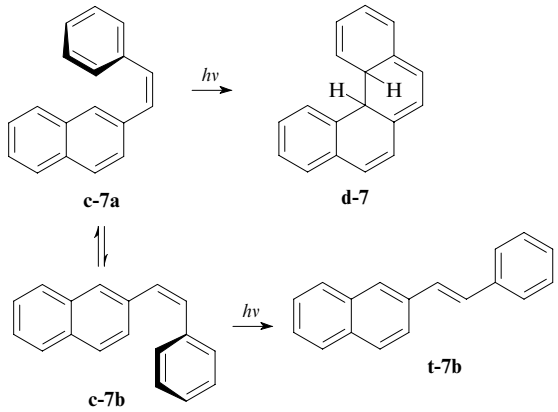
1. *cis*–*trans* Photoisomerization

Historically, adiabatic *cis*–*trans* photoisomerization was the first to be observed. This reaction was considered in a review[3] focused on the triplet state and also in recent reviews,[8,9] which also provide detailed descriptions of the analytical procedure for processing spectroscopic and kinetics data. First of all, we consider the examples of adiabatic *cis*–*trans* photoisomerization that have been convincingly proved, and then the cases of the reverse reaction of adiabatic *trans*–*cis* photoisomerization, which have been proved only indirectly.

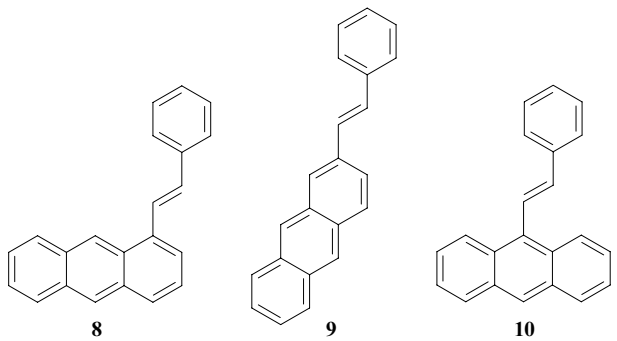
For stilbene, the adiabatic photoisomerization channel does not play any significant role but its very existence is of principal importance. The quantum yield of stilbene *cis*–*trans* photoisomerization is $\varphi_{ct} = 0.35$,[62] the contribution of the adiabatic reaction channel is $\varphi_{ct,ad} = 0.0016$ (in n-hexane).[63,64] This contribution was demonstrated by a sophisticated analysis of the fluorescence spectrum of *cis*-isomer (**c-1**) from which the spectrum of the *trans*-isomer (**t-1**) formed upon adiabatic photoisomerization was distinguished by using the principal component analysis with self-modelling (PCA-SM).

For 1-styrylnaphthalene, $\varphi_{ct} = 0.11$ (in methylcyclohexane–3-methylpentane mixture, MCH–3-MP), while nothing is known on the adiabatic *cis*–*trans*-photoisomerization.[65] For 2-styrylnaphthaline (**7**), $\varphi_{ct} = 0.30$ (MCH–

3-MP).[65] The adiabatic channel contribution is $\varphi_{ct,ad} = 0.02$ (MCH), which was also found by *trans*-isomer fluorescence upon *cis*-isomer excitation. It was shown that only *s-trans*-conformer **c-7b** is isomerized to produce *s-trans*-conformer **t-7b**, whereas excited *s-cis*-conformer **c-7a** undergoes ring closure to form dihydrobenzo[*c*]phenanthrene (**d-7**).[66,67] It was noted[66] that the properties of conformers can be distinguished as a result of 'striking application of the NEER principle'.



Styrylanthracene has three possible positional isomers: 1-styrylanthracene (**8**), 2-styrylanthracene (**9**) and 9-styrylanthracene (**10**). Styrylanthracenes **8** and **10** exhibit similar properties. For the latter, the conformational isomerism is absent (both solutions contain only one conformer); in nonpolar solutions, cyclization prevails over photoisomerization. The latter reaction proceeds mostly by the adiabatic singlet and triplet channels with the latter channel prevailing.[68–71] Thus, for styrylanthracene **8**, the quantum yield of one-way *cis–trans* photoisomerization is $\varphi_{ct} = 0.04$ (MCH–3-MP), the contributions of adiabatic singlet and triplet channels are 0.011 and 0.025, respectively, and photocyclization proceeds with the quantum yield of 0.44.[70] The adiabatic *cis–trans* photoisomerization was also observed for heteroanalogues of 9-styrylanthracene with a pyridine residue substituted for the phenyl group.[72]



Of all styrylanthracenes, compound **9** with the properties different from those of positional isomers **8**, **10** was studied most thoroughly.[73–76] As regards the structure, styrylanthracene **9** resembles styrylnaphthalene **7** and, like the latter, exists as a mixture of two *s*-conformers the photochemical behaviour of which obeys the NEER rule. Studies of the *cis*-isomer have shown that of two conformers only the *s-trans*-conformer enters into (one-way) *cis–trans* photoisomerization that proceeds completely *via* the adiabatic channel: $\varphi_{ct} = \varphi_{ct,ad} \approx 1$ (MCH–3-MP), whereas the *s-cis*-conformer undergoes photocyclization. Thus, for styrylanthracene **9**, the highly efficient conformer-specific adiabatic photoisomerization occurs.

The comparison of reaction quantum yields shows that in the stilbene–2-styrylnaphthalene–2-styrylanthracene series, the size effect is clearly observed, where the larger size of the aromatic substituent entails a larger contribution of the adiabatic photoisomerization channel to reach 100% for styrylanthracene; moreover, the reaction becomes one-way (one direction) and proceeds only in the **c*** → **t*** direction.

This effect can find explanation through the analysis of the relative position of potential energy curves for the lower excited states of different kinds. According to a proposed model,[77] the barrier between *trans*-isomer and *perp*-conformer in the excited state appears as a result of avoided crossing of terms of S_1 and S_2 states, which are inverted as regards energy when going from the *trans*-isomer to the *perp*-conformer. The particular type of these terms for *trans*-stilbene depends on the calculation method and the molecule geometry (see below). Within the framework, of a simplified model, in the vicinity of the vertical (Frank–Condon) transition of the *trans*-isomer, the lower excited diarylethene state can be characterized as 'aromatic' (S_{ar}), while in the vicinity of *perp*-conformer, it is described as the 'ethylene' state (S_{et}). When going along the reaction coordinate from the *trans*-isomer to the *perp*-conformer (**t*** → **p***), the system passes from the ascending PES branch of the S_{ar}-state to the descending PES branch of the S_{et}-state. As the aryl substituent size increases, the energy of its locally excited state decreases; hence, the term S_{ar} drops in energy below the term S_{et}, which hinders the **t*** → **p*** transition. (This results in localization of the excitation energy on the larger aromatic substituent, as manifested by the increase in the quantum yield of *trans*-isomer fluorescence.)

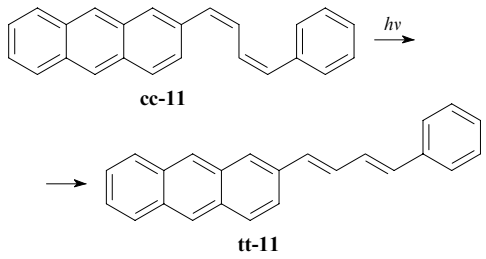
As a result, when travelling along the excited-state PES in the coordinate domain of the *cis*-isomer, the system slips past the 'perpendicular' minimum (which can disappear and even become a maximum if term **c*** also drops below term **p***) and finds itself in the *trans*-isomer coordinate domain, *i.e.*, the reaction proceeds by the adiabatic route **c*** → **t***. The position of the *trans*-isomer term below the *cis*-isomer term favours one-way adiabatic *cis–trans* photoisomerization.

The π-system of styrylphenanthrenes (22 electrons) is similar to the π-system of styrylanthracenes; however, there is no information on the adiabatic photoisomerization of these compounds.[65] Pyrene has a still larger π-system (24 electrons). Studying the photochemical properties of *cis*-isomers of diarylethenes with a pyrenyl substituent points to the adiabatic *cis–trans* photoisomerization in the singlet-excited state.[78,79]

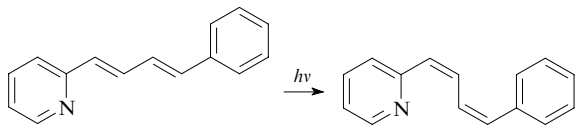
There are numerous examples of adiabatic *cis–trans* photoisomerization in the singlet-excited state for positional isomers of distyrylbenzene and its derivatives[80,81] and also for its heteroanalogues.[82–84]

The adiabatic routes of *cis–trans* photoisomerization of one of the double bonds in the butadiene moiety were observed for 1,4-diarylbutadienes and heteroanalogues.[85–89] For certain diarylbutadienes, absorption of a light quantum triggers the isomerization of simultaneously two double bonds in the butadiene moiety (one photon–

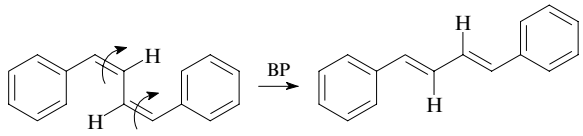
two bonds). For example, *cis*,*cis*-1-(2-anthryl)-4-phenylbuta-1,3-diene (**cc-11**) immediately transforms to *trans*,*trans*-isomer **tt-11**.[85]



An example of the reverse process is also known: illumination of *trans,trans*-1-(2-pyridyl)-4-phenylbuta-1,3-diene (**tt-12**) induces the one-photon reaction to afford *cis*,*cis*-isomer **cc-12**.[87]



Within the framework of the classical OBF mechanism, the 'one photon — two bonds' reaction is possible only if at least the first double bond isomerizes *via* the adiabatic channel. However, another explanation is possible for the 'one photon – two bonds' photoisomerization in butadienes, namely, in the excited state, the synchronous rotation of two neighbouring CH groups in the diene moiety resembling the rotation of bicycle pedals can occur; this is why the mechanism was named bicycle-pedal (BP).[46, 90 – 92]



Isomerization by the BP mechanism includes the direct transformation of the *cis*,*cis*-isomer to the *trans*,*trans*-isomer without transient involvement of the *cis*,*trans*(or *trans,cis*)-isomer. Insofar as the twist of aryl groups is ruled out, the free space requirements diminish, which makes easier the reaction in a rigid matrix.

2. *trans – cis* Photoisomerization

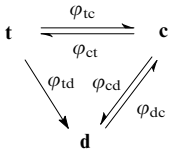
Note once again that the observation of an excited isomer as the reaction product is direct evidence for the adiabatic photoisomerization mechanism. The 'one photon – two bonds' method is indirect; its more general version, 'one photon – two reactions' is used in studying the photochemical properties of diarylethene *trans*-isomers. In the latter case, the second reaction is photocyclization. For *cis – trans* photoisomerization, the photocyclization is a competitive process; however, for the reverse *trans – cis* photoisomerization, the photocylization is used as the test for the photoisomerization mechanism. The method is based on the fact that diarylethene photocyclization proceeds in the singlet-excited *cis*-isomer.[93, 94] If the photocyclization product in the one-quantum process forms immediately upon *trans*-isomer excitation, the kinetics of photocyclization corresponds to the one-step reaction. This is believed to prove that the excited *cis*-isomer is transiently involved in the reaction, which is only possible if photoisomerization follows the adiabatic route.

Thus, upon the *trans*-isomer (**t**) excitation, the following sequence of processes is observed:

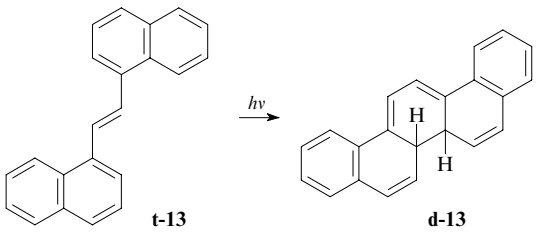
$$\mathbf{t} + h\nu \longrightarrow \mathbf{t}^* \longrightarrow \mathbf{c}^* \longrightarrow \mathbf{c} + \mathbf{d}$$

The parallel formation of the *cis*-isomer (**c**) and the dihydrocyclo product (**d**) requires that the experimental data be considered in terms of a more complicated reaction scheme. To the two consecutive reactions (photoisomerization and photocyclization) of classical Scheme 1, the third reaction, direct photocyclization $\mathbf{t} \rightarrow \mathbf{d}$ with the quantum yield φ_{td} should be added (Scheme 2). Probably, this reaction is also reversible, like two other reactions.[95]

Scheme 2



The method of determination of the photoisomerization mechanism by the kinetics of photocyclization was used for the first time in studying the photochemical properties of *trans*-di(1-naphthyl)ethene (**t-13**).[96] In this case, the photoisomerization product was 6a,6b-dihydropicene (**d-13**) with the absorption spectrum bathochromically shifted with respect to the spectra of *trans*- and *cis*-isomers, which allowed the kinetics of its formation to be selectively monitored by the increase in the optical density. Computer simulation of kinetic curves has shown that experimental data contradict the two-photon cyclization scheme of the *trans*-isomer with intermediate formation of the *cis*-isomer (see Scheme 1), but completely correspond to Scheme 2 with one-photon cyclization.

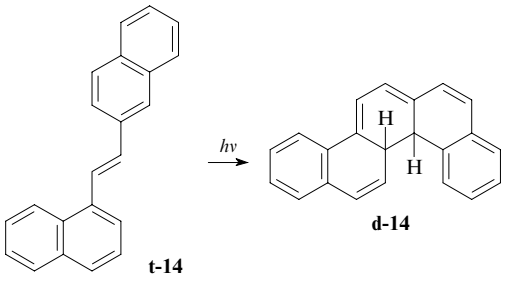


Based on the kinetic data for *trans*-isomer photocyclization supplemented by studies of photochemical properties of the *cis*-isomer, the whole set of quantum yields (in toluene) was obtained: $\varphi_{tc} = 0.09$ and $\varphi_{ct} < 0.015$ for photoisomerization; $\varphi_{cd} = 0.53$, $\varphi_{dc} = 0.70$ and $\varphi_{td} = 0.03$ for photocyclization. Hence, the adiabatic route contribution to the *trans – cis* photoisomerization was calculated as $\varphi_{tc,ad} = \varphi_{td}/\varphi_{cd}$ to be 0.057, which is comparable with the observed quantum yield φ_{tc}.

The one-photon character of *trans*-isomer photocyclization was confirmed by the linear dependence of the amount of formed dihydropicene **d-13** on the radiation intensity for the constant time of irradiation.[96]

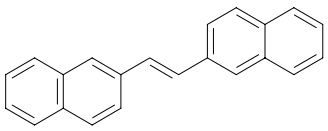
In ethanol and n-heptane, the photocyclization quantum yields of isomer **t-13** decreased to 0.02 and 0.006 – 0.009, respectively.[95] The cyclization of 1-(1-naphthyl)-2-(2-naphthyl)ethene (**14**) affords 12b,12c-dihydrobenzo[*c*]chrysene

(**d-14**). Studying the properties of dinaphthylethene **14** has shown that replacement of one 1-naphthyl group by a 2-naphthyl group induces a substantial decrease in the quantum yield of one-photon photocyclization for the *trans*-isomer (down to $\varphi_{td} = 0.001$ in n-heptane).[95]



t-14 **d-14**

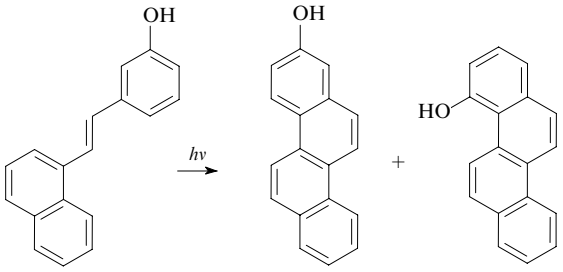
For di(2-naphthyl)ethene **15** with both 1-naphthyl moieties being replaced by 1-naphthyl moieties, no one-photon photocyclization was observed.[95,97]



15

Note that one of the mentioned publications,[95] besides the adiabatic photoisomerization, discussed also the relative contributions of the diabatic and adiabatic channels to the ring-opening reaction of dihydrophenanthrene derivatives.

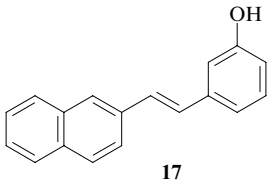
The one-photon photocyclization was observed for the *trans*-isomer of 1-(1-naphthyl)-2-(3-hydroxyphenyl)ethene (**16**).[98] This compound gives two isomeric photocyclization products, which are quickly oxidized in air to afford 4-hydroxychrysene (**d-16**) and 6-hydroxychrysene (**d-16′**); their mixture was isolated and characterized by spectroscopic methods.



16 **d-16** **d-16′**

For the reaction in cyclohexane, the following parameters were found: $\varphi_{tc} = 0.105$ and $\varphi_{ct} = 0.125$ for photoisomerization and $\varphi_{cd} = 0.45$ and $\varphi_{td} = 0.05$ for photocyclization; the adiabatic channel contribution $\varphi_{tc,ad} = 0.11$. In acetonitrile, the photoisomerization quantum yields changed insignificantly, whereas the cyclization yields decreased by one order of magnitude down to $\varphi_{cd} = 0.04$ and $\varphi_{td} = 0.005$.[98]

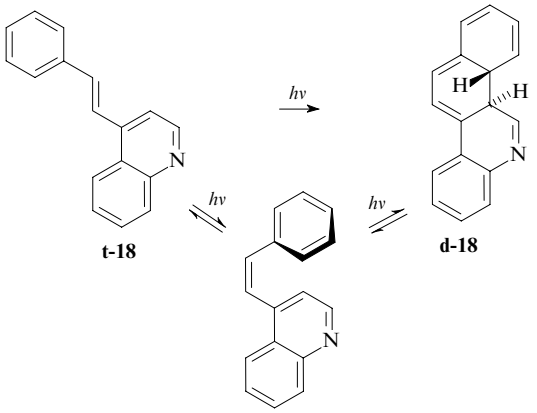
As seen from the comparison of molecular structures, each diarylethene considered above (**13**, **14** and **16**) had a 1-styrylnaphthalene structural moiety. An analogue of styrylnaphthene **16**, namely, a hydroxy derivative of 2-styrylnaphthalene **17**, did not enter into the reaction of one-photon photocyclization of the *trans*-isomer.[99]



17

The one-photon photocyclization of the *trans*-isomer was observed recently for 4- and 8-styrylquinolines, which are aza analogues of 1-styrylnaphthalene. For 2-styrylquinoline, the aza-analogue of 2-styrylnaphthalene, this reaction channel is absent.[100]

The primary photocyclization product of 4-styrylquinoline (**18**) is 4a,4b-dihydrobenzo[*i*]phenanthridine (**d-18**).[101,102] The initial segment of the kinetic curve of accumulation of compound **d-18** in hexane was linear without any induction period, which suggests that compound **d-18** forms immediately from *trans*-isomer **t-18** in the one-photon reaction. Based on this fact, the adiabatic mechanism of the *trans*–*cis* photoisomerization of 4-styrylquinoline was deduced. Treatment of the kinetic data produced the following quantum yields: $\varphi_{tc} = 0.39$, $\varphi_{ct} = 0.30$ and $\varphi_{td} = 0.013$.



t-18 **d-18**

c-18

The one-photon nature of photocyclization of *trans*-isomer **t-18** in hexane was confirmed by the linear dependence of the rate of dihydrophenanthridine **d-18** formation on the light intensity.[101]

When going from hexane to ethanol, the kinetic curve of accumulation of product **d-18** acquires the S-shape typical of a two-step (in our case, two-photon) reaction, which points to the diabatic mechanism of *cis*-isomer formation.[101] The effect of solvent polarity on the photoisomerization mechanism can be explained by taking into account the zwitter-ionic nature of the key intermediate, the excited perpendicular conformer **p***.[7] This is why, polar solvents are capable of stronger stabilization of conformer **p*** compared to excited *trans*-isomer **t***, thus deepening the potential energy minimum in the S_1-state PES (see Fig. 1) and directing photoisomerization along the diabatic route. Non-polar solvents destabilize state **p*** as compared with **t***, thus decreasing the potential energy minimum. As a result, the S_1 PES becomes more shallow in the vicinity of **p***-conformer, which favours the adiabatic route **t*** → **c***.

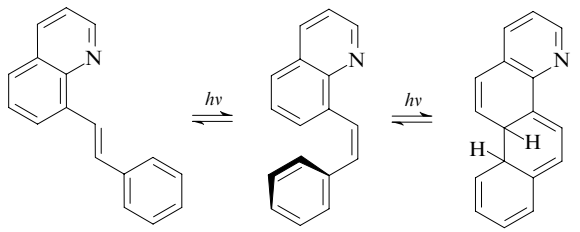
It was shown that halogen atoms present in the *para*-position of styryl fragment in 4-styrylquinoline have virtually no effect on the reaction kinetics, whereas the nitro group substantially accelerates the oxidation reaction;

among nitro derivatives, only the final nitrobenzophenanthridine with the quantum yield of 0.004 could be observed.[102]

There are controversial data on how the donor groups affect photocyclization. It was reported [103] that the photocyclization products of 4-styrylquinoline derivatives containing a methoxy or dimethylamino group in the *para*-position of the styryl moiety could be obtained in preparative yileds (~20%). However, these results could not be reproduced later;[104, 105] thus, it was concluded that electron-donating substituents inhibit the photocyclization.

It is interesting that protonation of 4-styrylquinoline was found to block photocyclization.[102] According to quantum chemical calculations, the possible reason for the absence of this reaction is considerable destabilization of the dihydrocyclo product as compared with the *cis*-isomer in the protonated form.[106, 107]

The photocyclization product of 8-styrylquinoline (**19**) is 10a,10b-dihydronaphtho[1,2-*h*]quinoline (**d-19**).[108]

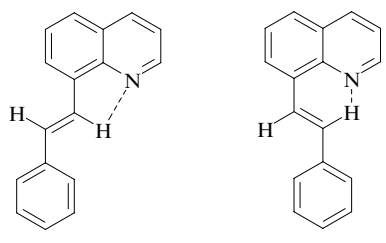


t-19 **c-19** **d-19**

Kinetic studies of photocyclization of *trans*-isomer **t-19** in hexane have shown that for this compound one can observe both the one-photon photocyclization with the quantum yield $\varphi_{td} = 0.009$ and the two-photon reaction with the quantum yields $\varphi_{tc} = 0.13$ in the first stage (*trans*-isomer photoisomerization) and $\varphi_{cd} = 0.23$ in the second stage (*cis*-isomer photocyclization); the quantum yield of *cis–trans* photoisomerization φ_{ct} was equal to 0.17.[108]

The presence of a two-photon channel of *trans*-isomer cyclization can point to the diabatic mechanism of *trans–cis* photoisomerization. However, taking into account the structural peculiarities of styrylquinoline **19**, another explanation of the two-stage reaction mechanism is possible. The *trans*-isomer of this compound is known to exist as two conformers (**t-19a** and **t-19b**) associated with the hindered rotation about the quasi-single bond between the ethylene group and the quinoline nucleus, where each conformer can be stabilized by an intramolecular hydrogen bond.[109]

Of two conformers of the *trans*-isomer, only **t-19a** can undergo ring closure to compound **d-19** immediately after photoisomerization to the *cis*-isomer, whereas the *cis*-isomer of conformer **t-19b** should first transform to *cis*-isomer of conformer **t-19a**. In the S_0 state, the conformers are in equilibrium. However, in the excited state, the equilibrium between conformers has no time to establish (the NEER principle). Hence, even if conformer **t-19b** isomerizes by the adiabatic mechanism, its ring-closure requires that *cis*-isomer of conformer **t-19b** be transformed to *cis*-isomer of conformer **t-19a**, which is possible only after the loss of excitation and the transition to the S_0 state. After this, the *cis*-isomer of conformer **t-19a** absorbs an additional light quantum and undergoes ring closure to afford compound **d-19**. Hence, only a part of *trans*-isomer **t-19** that is present in solution in the form of conformer **t-19a** can undergo one-photon photocyclization, whereas the photocyclization of conformer **t-19b** in either case (for diabatic or adiabatic photoisomerization) requires the absorption of two light quanta.



t-19a **t-19b**

For certain azadiarylethenes,[110–113] when going from the neutral to protonated form, the quantum yield of *trans–cis* photoisomerization was observed to increase to $\varphi_{tc} > 0.5$; for instance, for 2-styrylquinoline φ_{tc} increased from 0.2–0.27 to 0.62–0.83.[100, 112] These data may be considered as evidence for the adibatic reaction channel, as shown in Fig. 3 by dashed arrows, because for photoisomerization by the diabatic mechanism and the partitioning factor $\alpha = 0.5$, the quantum yields of isomerization cannot exceed 0.5 (see above). However, this effect can also be explained within the framework of the diabatic mechanism by assuming that the partitioning factor increases to $\alpha > 0.5$, which is possible if **p***-minimum shifts to the *cis*-isomer, as shown in Fig. 3 by solid arrows.

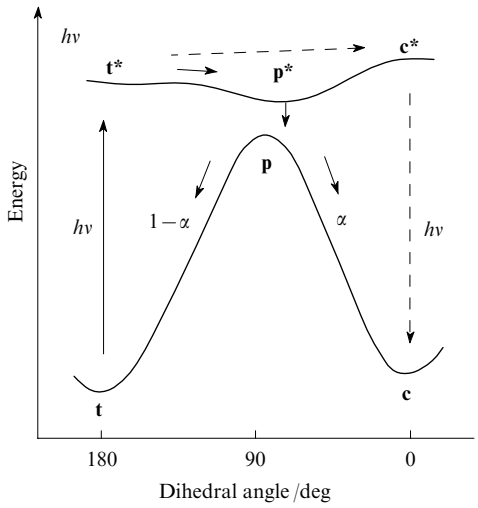


Figure 3. Chart of potential energy curves for photoisomerization of diarylethenes for $\varphi_{tc} > 0.5$: the shift of **p***-minimum to the *cis*-isomer in the diabatic route (solid arrows) or the adiabatic route (dashed arrows).[113]

To find the true reason for the increase in φ_{tc} for azadiarylethenes in the protonated form, further studies are necessary.

Summing up the consideration of experimental data on the diarylethene adiabatic photoisomerzation, it should be stated that the presence of the adiabatic reaction route was proved for *cis–trans* photoisomerization **c*** → **t*** by the direct observation of emission from the excited *trans*-isomer after irradiation of the *cis*-isomer. The contribution of this

reaction channel is negligibly small for stilbene but quickly increases with the increase in the diarylethene π-system to become major or even dominant for 22 or more π-electrons.

At the same time, in all known examples of adiabatic *trans*–*cis* photoisomerization, the conclusion on the presence of the adiabatic stage **t*** → **c*** was drawn based on one-photon photocyclization of the *trans*-isomer into the corresponding dihydrophenanthrene derivative, which is indirect evidence. Another interpretation of these experimental data is possible based on quantum chemical calculations (see the next section).

IV. Quantum chemical calculations of photoisomerization and photocyclization routes

A lot of publications were devoted to quantum chemical calculations of stilbene.[114–134] Different calculation techniques predict different geometry for the *trans*-isomer ground state S_0. The molecule may have a planar conformation with C_{2h} symmetry (see Refs 122, 134) or a non-planar structure with C_2 symmetry and with benzene rings rotated with respect to the ethylene fragment.[123, 125] Note that experimental studies may also produce one or another structure depending on experimental conditions, *i.e.*, the temperature and the stilbene phase composition (gas, solution or crystal) (*e.g.*, see Ref. 133). For the *cis*-isomer, all methods suggest a structure with C_2 symmetry or similar.[123, 125, 134]

For stilbene, the frontier molecular orbitals (MO), *i.e.*, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are localized on the central ethylene group, the former orbital being bonding and the latter being antibonding with respect to the central double bond. The neighbouring MO, *i.e.*, HOMO − 1 and LUMO + 1, are the linear combinations of orbitals localized on benzene rings.[120]

For the C_{2h} symmetry, *trans*-stilbene has three lower singlet-excited states: 1^1B_u, 2^1B_u and 2^1A_g, their relative positions depending on the calculation method. According to the results of the CASPT2 method,[120] the HOMO → LUMO transition in *trans*-stilbene corresponds to the 2^1B_u state, while the 1^1B_u state is described by a combination of HOMO → LUMO + 1 and HOMO − 1 → HBMO transitions. In contrast, the MS-CASPT2,[135, 136] TD-PBE0,[137] SF-BHHLYP [134] methods assign the HOMO → LUMO transition to the 1^1B_u state. According to the data of SF-BHHLYP [134] and TD-PBE0 methods,[137] in *cis*-stilbene, the HOMO → LUMO transition leads to the lower singlet-excited state S_1.

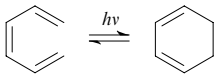
All quantum chemical methods predict the presence of a minimum in the excited state PES in the *trans*-isomer coordinate domain. The main changes in the *trans*-isomer structure in state S_1 are associated with less pronounced bond alternation in the ethylene group; moreover, the SA-2-CAS(2/2) [123] and SF-BHHLYP [134] methods predict the same alternations: the central double bond extends by 0.06 Å, and the adjacent quasi-single bonds shorten by 0.07 Å. This is explained by the electron transfer from the HOMO, which is bonding for the central bond, to the LUMO, which is bonding for side bonds in the ethylene group (and antibonding for the central bond).

For the excited *cis*-isomer in state S_1, the SA-2-CAS(2/2) method [123] predicts the similar structural changes, whereas on the SF-BHHLYP [134] and LR-TDDFT level,[137] the structure fails to be optimized and the system slides down the PES towards the cyclization product, dihydrophenanthrene (**d-1**). According to experimental data, the ratio of the excited *cis* -stilbene deactivation channels towards isomerization and towards cyclization is 7 : 3.[138, 139]

1. Photocyclization

Cyclization of diarylethenes is a 6π-electron electrocyclic reaction. According to the Woodword – Hoffmann principle of orbital symmetry conservation, cyclization is permitted in the excited state being a conrotatory process. Hence, after photocyclization, the substituents at the newly formed bond (in compound **d-1**, these are hydrogen atoms) are in the *trans*-configuration.

The simplest reaction substrate is hexa-1,3,5-triene (**20**). It undergoes ring closure to afford cyclohexa-1,3-diene (**21**). Due to formation of a new σ-bond, the hybridization of terminal carbon atoms in the hexatriene chain changes from sp^2 to sp^3.



20 **21**

The interconversion of compounds **20** and **21** represents the model reaction not only for photocyclization of diarylethenes but also for other photochromes. The reaction mechanism was elucidated by thorough experimental and theoretical investigations;[140–151] this is probably one of the best studied systems as regards the kinetics and the sequence of processes involving different states.[149] Figure 4 shows a simplified chart of potential energy curves for the model reaction, where the distance between terminal carbon atoms in hexatriene serves as the reaction coordinate.

In the half-chair conformation, the cyclohexadiene (**21**) molecule has C_2 symmetry and is in 1A state, which correlates with the doubly excited state 2A of hexatriene. Due to avoided crossing of terms 1A and 2A, in the ground state (S_0), a high barrier appears (characterizing the symmetry-forbidden thermal reaction), which, in the S_1 state

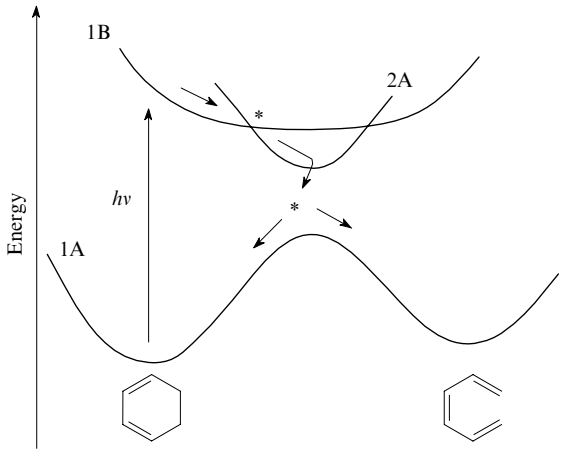


Figure 4. Qualitative chart of potential energy curves for ring opening in cyclohexa-1,3-diene.[149, 151]
Asterisks (*) mark the conical intersections that are beyond the figure plane. Arrows show the diabatic route of the photochemical reaction.

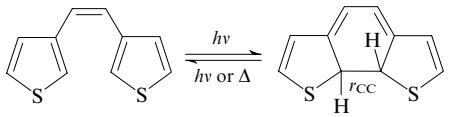
corresponds to a pericyclic (*peri**) minimum (for travelling along the reaction coordinate with retention of symmetry).

The lower excited state (S_1) of cyclohexadiene in the vicinity of the Franck–Condon transition is state 1B; it correlates with the symmetry-analogous state S_1 of hexatriene. After excitation to the 'spectroscopic' state 1B, the system passes first to the PES of state 2A and then to the PES of state 1A, both transitions being accomplished through the conical intersection (CI). Thus, the reaction begins in the excited state and ends in the ground state, *i.e.*, proceeds by the diabatic mechanism. This route is shown by arrows in Fig. 4. According to quantum chemical calculations by MS-CASPT2[145] and CASSCF[151] methods, to reach a conical intersection, bending vibrations that disrupt the system symmetry are required. This is consistent with experimental data on coherent oscillations of the wave packet: the presence of conical intersections provides the ultrafast transition between electronic states so that the reaction is completed in 200 fs.[149]

The main features of the model reaction are the same for diarylethene photocyclization, but the relative position of critical points depends strongly on the reactant structure. Thus in contrast to cyclohexadiene, the stilbene photocyclization product, dihydrophenanthrene, is thermally unstable. The thermal stability of the products of photocyclization of stilbene heterocyclic analogues, particularly, di(thienyl)ethenes, was once theoretically substantiated based on considering the correlational diagrams,[152] which gave impetus to the development in this research field, the synthesis of new compounds,[25,153] various practical applications of thermally stable photochromes (see Introduction).

The mechanism of diarylethene photocyclization (and the reverse ring-opening reaction) is studied by various quantum chemical methods[154–165] aimed at elucidation of how the structure affects the practically important parameters such as quantum yields of the forward and reverse reactions, the rate constant of thermal decomposition, the absorption spectra of open and closed forms. The mechanism of side reactions,[166] the mutual effect of two chromophore moieties in bichromophore derivatives are also investigated.[167–170]

Calculations of the simplest 1,2-di(3-thienyl)ethene (**22**) as the structural fragment in reactions of the majority of di(thienyl)ethenes have shown that the distances between the carbon atoms (r_{CC}) involved in reaction in state S_0 (1A) are ~3.4 and ~1.5 Å for *cis*-isomer **c-22** (open form) and dihydro product **d-22** (DHP, closed or ring form), respectively.[165]



c-22 **d-22**

In the S_0 state, these two forms are divided by a potential energy barrier, which determines the kinetics of the ring opening thermal reaction, *i.e.*, the thermal stability of the compound. The barrier height correlates with the energy difference between the DHP and the *cis*-isomer and substantially depends on the type of the aromatic nuclei.[14] The larger the energy difference, the lower the barrier (on the DHP side) and the lower the DHP stability. The thermal stability is higher for diarylethenes containing aromatic nuclei with a low aromatic stabilization energy.

Of two *cis*-isomer conformations, *i.e.*, those with parallel and antiparallel orientations of aromatic nuclei, only the latter (C_2 symmetry) is photocyclized. This is why the introduction of substituents that increase the population of the antiparallel conformation increases the reaction quantum yield, although other effects are possible.[156]

The analysis of the frountier MO in the S_0 state shows that for conrotatory rotation of aryl substituents in the *cis*-isomer, the structure of diarylethene LUMO provides the overlap of in-phase components of atomic orbitals localized on the hexatriene terminal atoms. Hence, LUMO is the bonding orbital for the newly formed bond and HOMO is antibonding, which favours the photochemical ring closure and prevents the thermal cyclization.[160,163,164] The analysis of MO provides qualitative prediction of the main features of the system behaviour in the thermal and photochemical reactions; however, complete picture can be obtained only based on the PES calculations.

According to TD-B3LYP calculations, there are two lower excited states in the vicinity of the Franck–Condon transition.[158] The one-electron HOMO → LUMO excitation corresponds to the permitted transition to state 1B of the ionic nature. State 2A has the covalent nature and is optically inert.

On excitation, the system passes first to state 1B and then, *via* the conical intersection, quickly drops to the PES of state 2A. The structure of the latter is determining for the ring closure and ring opening reactions in the excited state. CASSCF calculations revealed two minima on the 2A-PES.[157–159,165] The first minimum, in the coordinate domain of $r_{CC} \approx 1.5$ Å, corresponds to the excited DHP* (**d-22***). The second minimum is near the barrier in the S_0-PES, in the coordinate domain of $r_{CC} \approx 2.3$ Å; in the cited studies, it was assigned to excited *cis*-isomer **c-22***. However, by comparing with the data on hexatriene photocyclization (see Fig. 4), it can be concluded that the second minimum corresponds most probably to the pericyclic (*peri**) minimum that appears in the S_1-PES as a result of avoided crossing of terms 1A and 2A (in the coordinate domain of r_{CC}, where a barrier arises in the S_0-PES for the same reason, see Fig. 4). For certain di(thienyl)ethenes, a minimum appears in the coordinate domain of $r_{CC} > 4$ Å; it indeed pertains to the excited *cis*-isomer and is called 'non-reactive' minimum, in contrast to the reactive *peri* *-minimum in the vicinity of 2.3 Å.[156]

CASSCF calculations revealed several conical intersections between the S_1- and S_0-PES.[158,159] The conical S_1/S_0-intersection CI_{cycl} (designated in the cited studies as CI_3), which is crucial for photocyclization, lies in the vicinity of *peri**-minimum at $r_{CC} \approx 2$ Å. This conical intersection is achieved due to wide-amplitude torsion vibrations of one of thiophene rings, which distort the molecule and disrupt C_2 symmetry. This is why, to localize CI_{cycl}, one should take into account not only the distance r_{CC}, but also the second reaction coordinate, the dihedral angle between the thiophene ring and the ethylene group. In the S_0-PES, CI_{cycl} is the bifurcation point that leads to either *cis*-isomer or DHP. The ratio between contributions of deactivation routes is determined by the CI_{cycl} position with respect to the barrier in the S_0-PES; for model system **20**–**21,** the ratio is 1 : 1 (Ref. 147) (which can be compared with the partitioning factor α for diabatic photoisomerization, see Fig. 1).

The ring-closing reaction in the excited state proceeds *via* CI_{cycl} in virtually barrier-free fashion with a high quantum yield (up to $\sim$ 1.0). The same conical intersection represents a 'reaction funnel' for the excited DHP* too, being separated from the latter by an energy barrier in the S_1- PES. The presence of the barrier on the DHP* side is the key difference between photochemical ring closure and ring opening reactions. As a result of this difference, the quantum yield of the latter process is temperature dependent and as a rule low ($10^{-3}-10^{-4}$).[155, 165]

Substituents in aromatic nuclei that elongate the π-conjugated system lead to the bathochromic shift of the DHP long-wavelength absorption band and a decrease in the ring opening quantum yield. Both effects are associated with lowering down of the S_1-term of DHP*. This results in a decrease in vertical excitation energy and the simultaneous increase in the energy difference between DHP* and the *peri**-minimum that correlates with the quantum yield of ring opening.[157]

2. Photoisomerization

For diarylethene photoisomerization, the calculations of reaction routes by various quantum chemical methods qualitatively confirm the simplified chart of potential energy curves shown in Fig. 1. When going along the isomerization reaction coordinate from the *trans*-isomer to the *perp*-conformer, a low barrier appears due to the avoided crossing of two lower excited states.[120, 135] In the vicinity of *perp*-conformer, there is a minimum which corresponds, apart from the rotation of two aryl fragments by 90°, to pyramidalization of one of carbon atoms in the ethylene group.[123, 134]

According to high-level calculations, pyramidalization is associated with the second important coordinate that should be taken into account for adequate description of double-bond photoisomerization and localization of the conical intersection.[171–176] In the vicinity of perpendicular minimum, where only rotation by 90° around the central axis has taken place, the energy difference between states S_1 and S_0 is too large for fast internal conversion.[134, 174, 175] The rotation leads to unpairing of π-bond electrons to produce a biradical covalent state, whereas pyramidalization stabilizes the charge-separated state of the ethylene group. As a result, the energies of two states, the covalent and zwitter-ionic ones, approach each other, which creates conditions for the conical S_0/S_1-intersection. Here, it deserves mention that for the *n*-dimensional PES, the conical intersection represents not an individual point but a hypersurface in which the points with minimum energy (minimum energy CI, MECI) are localized.[171] The relative energies of the perpendicular minimum and MECI points in the photoisomerization reaction depend on the calculation method. The deactivation through MECI proceeds extremely quickly, which explains the short lifetime of the excited *perp*-conformer of stilbene.[54]

Recently, by using the SF-BHHLYP method,[134] the most comprehensive study of the stilbene S_1-PES was carried out along the coordinates of both intramolecular reactions, the main critical points were calculated and a chart was proposed the simplified version of which is shown in Fig. 5. It was found that even in the **p***-minimum, the pyramidalization of an ethylene carbon atom takes place to reach 70° in the point of conical intersection in the photoisomerization reaction route (CI_{iso}); as regards the energy,

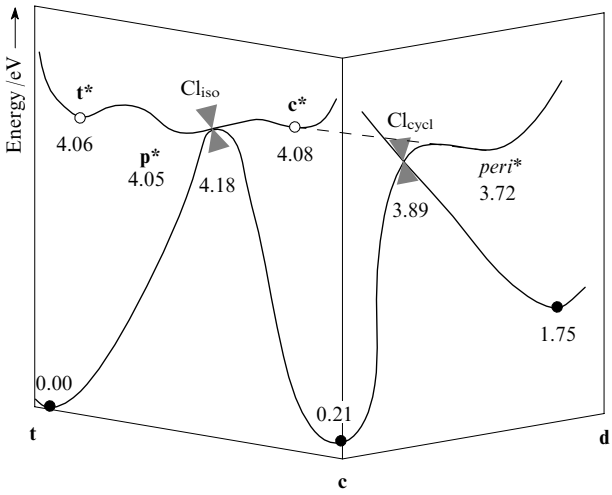


Figure 5. Chart of potential energy curves for S_0 and S_1 states of stilbene, according to the data of SF-BHHLYP calculations (energies are in eV).[134]

this point is 0.13 eV higher than **p***-minimum.[134] According to the SA-2-CAS(2/2) data, the energy difference between these points does not exceed 0.22 eV and, in ethylene, CI_{iso} coincides with the **p***-minimum.[171] At the same time, the MS-CASPT2 calculations predict[36] that CI_{iso} is also an absolute minimum in the stilbene S_1-PES (cyclization was not considered in that study).

Optimization of the excited *cis*-isomer carried out without geometry constraints by the SF-BHHLYP method[134] deduced a structure in which the distance between carbon atoms that form the bond in dihydrophenanthrene decreased from 3.22 Å (in the S_0-state) to 2.10 Å , and the neighbouring hydrogen atoms deviated from the molecular plane to different sides. For this reason, this state was assigned to the ring-closure product, dihydrophenanthrene, and designated as $(S_1)_{DHP}$; however, another interpretation is possible.

Taking into account the above data on the photocyclization mechanism, it appears more likely that point $(S_1)_{DHP}$ corresponds to the pericyclic minimum rather than to DHP with the already formed C–C bond; this is why it is designated as *peri** in Fig. 5. According to the SF-BHHLYP results,[134] this point is the global minimum in the stilbene S_1-PES and is lower in energy than **p***-minimum and the neighbouring conical intersection CI_{cycl} by 0.33 and 0.17 eV, respectively.

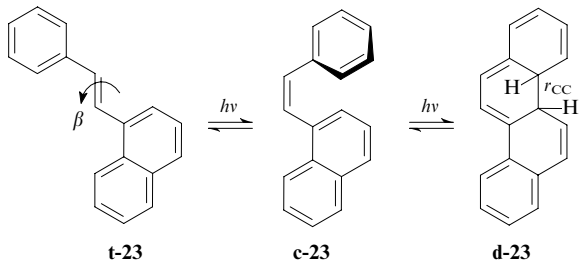
Based on the analysis of the excited-state PES, it was assumed[134] that in the vicinity of **p***-minimum, a part of molecules can avoid deactivation through CI_{iso} and continue their motion along the PES; moreover, this is easier on the side of the excited *cis*-isomer because the latter possesses the higher extra energy as compared with the excited *trans*-isomer. Thus the theoretical possibility of the adiabatic route of photoisomerization in both *cis–trans* and *trans–cis* directions is substantiated as well as the possibility of the direct one-photon formation of DHP from the *trans*-isomer.

As was shown in Section III, the one-photon photocyclization of the *trans*-isomer was experimentally observed for diarylethenes with the structure involving the 1-styrylnaphthalene moiety or for the aza analogue, styrylquinoline. To elucidate the routes of isomerization and

cyclization by using the semi-empirical PM3-CI method with configurational interaction, PES of the ground state and the lower singlet-excited state were calculated for 4-styrylquinoline (**18**)[177] and 1-styrylnaphthalene (**23**).[178] Model calculations of excited stilbene confirmed the applicability of this method to the posed problem.[177]

Scheme 3 shows the structural transformations of 1-styrylnaphthalene and depicts the reaction coordinates of isomerization (β) and cyclization (r_{CC}); in this particular case, the cyclization product (DHP) is 4a,4b-dihydrochrysene (**d-23**).

Scheme 3



First of all, the profiles (cross-sections) of S_0- and S_1-PES were calculated separately for variation of either the dihedral angle at the central double bond (angle β, isomerization reaction coordinate) or the distance r_{CC} between two carbon atoms that form the new ring (cyclization reaction coordinate). This afforded the 'classical' two-dimensional PES cross-sections qualitatively consistent with the well-known calculations of minimum energy paths (MEP) for isomerization and cyclization reactions.[178] A typical MEP (see Figs 1 and 4) represents a barrier in the ground state S_0 PES that corresponds to a minimum in the excited state S_1 PES. The latter minimum represents a perpendicular minimum for isomerization and a pericyclic minimum for cyclization.[178] For PM3-CI-level calculations, the minimum is absent in the coordinate domain of the *cis*-isomer in the S_1-PES; for optimization based on ground-state geometry, the system slides down to the pericyclic minimum. These results are comparable with high-level calculations for stilbene, with the only exception that the semi-empirical method fails to locate the conic intersection.

Further, the three-dimensional PES were calculated by scanning simultaneously the coordinates of two reactions: isomerization and cyclization. Figure 6 shows the PES of 1-styrylnaphthalene (**23**) (for the sake of simplicity, the PES domains outside the reaction zone are not shown).[178] The minima in S_1-PES correspond to saddle points of the first order in the lower S_0-PES. These points represent crossings between the energy valleys of *trans*- and *cis*-isomers and DHP; in two-dimensional cross-sections, they represent transition-state barriers for isomerization and cyclization. As for stilbene,[134] in the S_1-PES of styrylnaphthalene, the *peri**-minimum is the global minimum located 14 kcal mol^{-1} lower than the **p***-minimum.[178]

The calculations that simultaneously take into account the coordinates of two reactions identify new additional phototransformation routes of excited styrylnaphthalene. The three-dimensional S_1-PES shows the MEP from the *trans*-isomer to DHP that runs along the bottom of the valley and passes, first, through a perpendicular minimum and then through a pericyclic minimum (see Fig. 6). In this route, two low barriers are present with the heights of 3.23

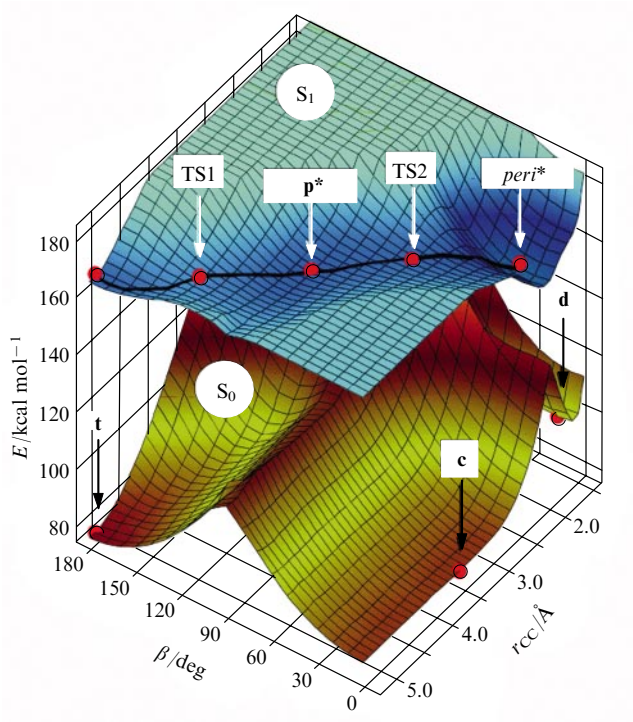


Figure 6. Potential energy surfaces of the S_0 and S_1 states of 1-styrylnaphthalene for scanning along the reaction coordinates of isomerization (angle β) and cyclization (distance r_{CC}), according to PM3-CI(2 × 2) data.[178]
Stationary points are designated by circles; the minimum energy path from the *trans*-isomer to the 'perpendicular' minimum and further to the pericyclic minimum is shown.

(TS1) and 0.95 kcal mol^{-1} (TS2).[178] Probably, this very route describes the experimentally observed one-quantum photocyclization of the *trans*-isomer. It is interesting that this route bypasses the coordinate domain of the *cis*-isomer, as can be clearly seen in Fig. 6.[178]

Analogous results were obtained for 4-styrylquinoline (**18**): in the S_1-PES, there is a minimum energy path from the *trans*-isomer to the dihydrocyclo product, which passes through the perpendicular and pericyclic minima but bypasses the coordinate domain of the *cis*-isomer.[177]

Thus, the quantum chemical calculations predict the absence of deep minima and high barriers in the PES of the S_1-state on route from the *trans*-isomer to DHP, which makes possible the direct one-photon cyclization of the *trans*-isomer in agreement with experimental data. At the same time, according to calculations, the reaction can proceed without participation of the excited *cis*-isomer, *i.e.*, the latter is not intermediate in the *trans*-isomer photocyclization, which leaves room for another interpretation of the above experimental data.

It is probable that from the perpendicular minimum, a part of excited molecules can pass to S_0-PES (diabatic photoisomerization), while the rest can reach the pericyclic minimum by a route shown in Fig. 6. In this case, two photochemical reactions of the *trans*-isomer, *i.e.*, photoisomerization and photocyclization, represent parallel rather than consecutive reactions with the bifurcation point in the S_1-PES in the vicinity of the perpendicular conformer. Hence, the experimentally observed direct one-

photon photocyclization of the *trans*-isomer to the corresponding ring product cannot serve as evidence for the adiabatic nature of *trans*–*cis*-photoisomerization.

As was noted above for stilbene, a minor but fundamentally important contribution of the adiabatic route to the *cis*–*trans* photoisomerization was revealed. Attempts were undertaken [95] to observe the reverse adiabatic *trans*–*cis* photoisomerization of stilbene and it was concluded that even if such channel exists, its quantum yield is not higher than 0.001.

At the same time, the recent calculations by the molecular dynamics SERID methods predict that the direct photocyclization of *trans*-stilbene to dihydrophenanthrene through the excited *cis*-stilbebe is possible for the *trans*-isomer excitation by a femtosecond pulse and should be observed experimentally.[179] Based on the results of SF-BHHLYP calculations of the stilbene S_1-PES, is was also assumed [134] that the adiabatic photoisomerization of stilbene is also possible in both *cis*–*trans*- and *trans*–*cis*-directions (although no minimum could be localized in the S_1-PES in the *cis*-isomer coordinate domain).

Summarizing the considered results of quantum chemical calculations, it is possible to correct the chart of potential energy curves for diarylethene photoisomerization and photocyclization, which was accomplished conveniently for the simplest diarylethene, stilbene. Figure 7 shows the simplified chart of potential energy surfaces for stilbene isomerization and cyclization in the S_0 and S_1 states. The chart takes into account that the internal conversion $S_1 \rightarrow S_0$ in the vicinity of perpendicular and pericyclic minima proceeds through a conical intersection. Dotted line shows the direct transition in the S_1-PES between the perpendicular and pericyclic minima, bypassing the coordinate domain of the *cis*-isomer.

According to Fig. 7, two routes are possible for one-quantum photocyclization (and photoisomerization) of the *trans*-isomer; the corresponding changes in the stilbene structure are shown in Scheme 4. Both routes begin in the ground state of the *trans*-isomer and end in the ground state of the *cis*-isomer and DHP but differ in intermediate stages in the excited state.

The classical route implies the consecutive formation of the *cis*-isomer and DHP, as shown by dashed arrows in Scheme 4. This route requires that the excited *cis*-isomer take part in the reaction as an intermediate; this is why the one-quantum photocyclization of the *trans*-isomer was so far considered as evidence for the adiabatic *trans*–*cis*-photoisomerization.

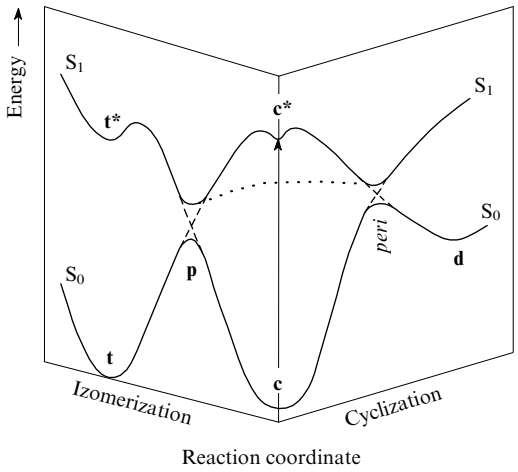
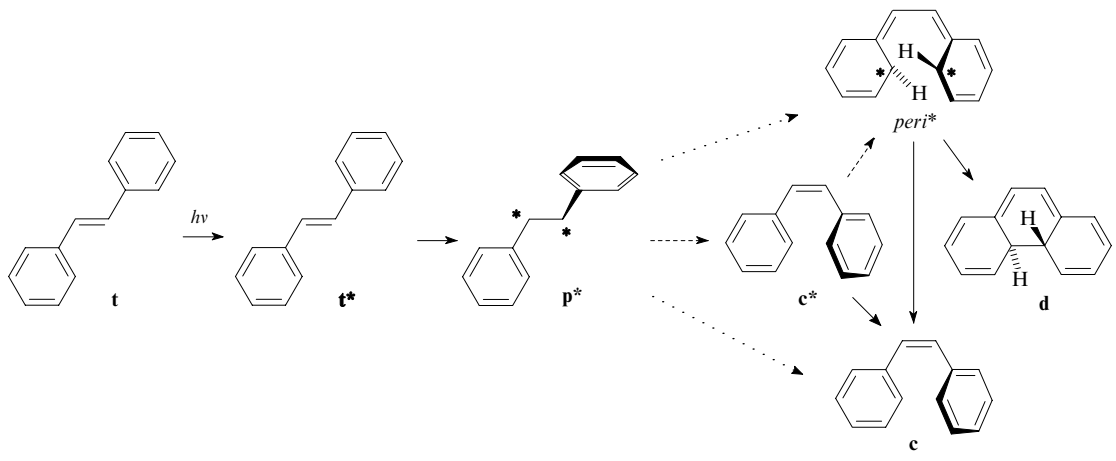


Figure 7. Chart of potential energy surfaces for isomerization and cyclization of stilbene in the S_0 and S_1 states.[178]
Dashed lines show the conical intersections in the vicinity of perpendicular and pericyclic minina; dotted line shows the minimum energy path between the perpendicular and pericyclic minima bypassing the coordinate domain of the *cis*-isomer.

Quantum chemical calculations have shown another possible route which involves the formation of the *cis*-isomer and DPH in two parallel reactions with a bifurcation point at the perpendicular conformer in the S_1 state, as shown by dotted arrows in Scheme 4.

The analysis of structural transformations on the reaction route (see Scheme 4) together with the results of SF-BHHLYP calculations for stilbene [134] also point to the direct transition from the perpendicular to pericyclic minimum (**p*** → *peri**). In the two-step route, first, two molecular groups rotate around the central bond to afford the *cis*-isomer geometry (**p*** → **c***), which is assumed [134] to be a slightly endothermic process (the reaction enthalpy is 0.03 eV). After this, the benzene rings approach each other and two hydrogen atoms bend to different sides of the molecular plane (**c*** → *peri**), which is an exothermic process (reaction enthalpy is −0.36 eV). The direct transition **p*** → *peri** involves the synchronous rotation around the central bond so that the benzene rings approach each other,

Scheme 4



while the hydrogen atoms deviate from the plane, which is a purely exothermic process (the reaction enthalpy −0.33 eV). To ultimately decide in favour of one or another route, one should localize the transition state and calculate the potential energy barrier in the **p*** → *peri** route.

Thus, the existing knowledge on the mechanism of *trans*–*cis* photoisomerization of diarylethenes should be revised, in particular, this concerns the conclusion that the reaction proceeds by the adiabatic route, which was drawn based on experimentally observed one-quantum photocyclization of the *trans*-isomer.

V. Conclusion

As follows from the above material, despite the numerous experimental and theoretical studies, several controversial issues are still to be clarified in the photochemistry of diarylethenes.

The dispute on the conformational aspect of photoisomerization mechanism goes on. It is still being discussed which of the two mechanisms, one bond flip or hula-twist operates. It is difficult to explain the experimental results on diarylethene photoisomerization under the conditions of confined molecular mobility (rigid matrix, bulky substituents) in terms of the OBF mechanism and they are usually interpreted in terms of the HT mechanism. The latter mechanism was also confirmed by comparing the photochemical properties of diarylethenes capable of isomerization only by the OBF mechanism with the properties of diarylaethenes capable of isomerization by both mechanisms.

Quantum chemical calculations demonstrate that during the diabatic photoisomerization of diarylethenes, similar to their diabatic photocyclization, the system deactivation ($S_1 \rightarrow S_0$ transition) due to internal conversion proceeds through the conical intersection. Comparing the results of calculations for two photoisomerization mechanisms (OBF and HT) shows that both mechanisms include the step of rotation around the double bond and their difference consists in the fact that, in terms of the OBF mechanism, the subsequent conical intersection S_1/S_0 is reached through the pyramidalization (rehybridization) of one of two carbon atoms, whereas for the HT mechanism, this proceeds through the rotation around the neighbouring single bond.

Questions also remain on the energy aspect of photoisomerization, namely, which route, diabatic or adiabatic, the reaction takes. The photophysical method that monitors the emission of the excited reaction product provides direct evidence for the adiabatic mechanism and is widely used when studying the *cis*–*trans* photoisomerization. The photochemical method is indirect being based on the principle 'one photon–two reactions', where the latter may be 'isomerization + isomerization' (one photon–two bonds) or 'isomerization + cyclization' under the assumption that at least the former reaction follows the adiabatic route. This method is used when studying *trans*–*cis* photoisomerization. The observed one-quantum photoisomerization of the *trans*-isomer is usually interpreted in terms of two consecutive reactions 'isomerization + cyclization', which is taken as evidence for the adiabatic photoisomerization mechanism.

However, the recent quantum-chemical calculations cast doubt on this interpretation of experimental data. It is probable that photoisomerization and photocyclization of the *trans*-isomer are the parallel rather than consecutive reactions, with bifurcation occurring in the excited state in a step where the system is in the coordinate domain of the perpendicular conformer.

To answer this question, it is necessary to carry out high-precision studies of the temperature effects and kinetics of formation of photoisomerization intermediates by using time-resolved spectroscopic methods and also to accomplish high-level quantum chemical calculations of the excited-state potential energy surface with simultaneous variation of the photoisomerization and photocyclization reaction coordinates.

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