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PHOTOCHEMISTRY

Adiabatic *trans-cis* Photoisomerization and Photocyclization of 8-Styrylquinoline

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Abstract—Kinetics of the photocyclization of *trans*-8-styrylquinoline into 10a,10b-dihydronaphtho[1,2-h]quinoline (4-azachrysene) was studied in hexane. It was found that in addition to the expected two-step (two-quantum) route with *trans-cis* photoisomerization occurring in the first step with a quantum yield of $\varphi_{tc} = 0.13$ with consequent photocyclization of the *cis*-isomer with a quantum yield of 0.23. The direct single-quantum photocyclization of the *trans*-isomer with a quantum yield of 0.009 is also observed. The latter observation indicates that the excited *trans*-isomer isomerizes without loss of excitation to the excited *cis*-isomer, which then undergoes cyclization, i.e., the *trans-cis* photoisomerization proceeds partially by adiabatic mechanism $t^* \rightarrow c^*$.

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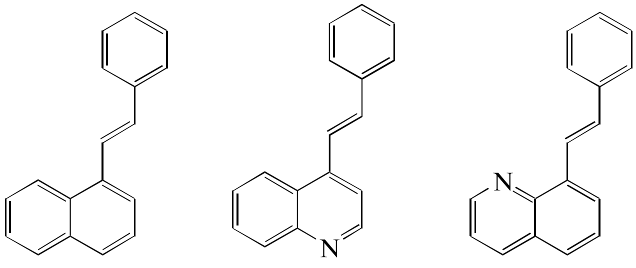
It was found that the *trans*-isomer of 4-styrylquinoline under irradiation isomerized into *cis*-isomer according to the adiabatic mechanism in hexane and according to the diabatic mechanism in alcohol [1]. It was pointed out that opposite to the adiabatic *cis-trans* photoisomerization, typical of diarylethylene subjected to one-way photoisomerization [2, 3], the adiabatic *trans-cis* photoisomerization was relatively rare event. This is rationalized in terms of the falling down the potential energy surface (PES) of the excited state along the reaction coordinate of the isomerization from the *cis*- to *trans*-isomer, therefore the adiabatic *trans-cis* isomerization is energetically unfavorable.

Several diarylethylenes capable of adiabatic *trans-cis* photoisomerization are known: 1,2-di(1-naphthyl)ethylene (**1N1N**) [4], 1-(1-naphthyl)-2-(2-naphthyl)ethylene (**1N2N**) [5] and the derivative of 1-styrylnaphthalene (**1SN**)—1-(1'-naphthyl)-2-(3'-hydroxyphenyl)ethylene (**1N3PhOH**) [6]. In all these compounds, at least one of the aryl substituents is the 1-naphthyl moiety. The analog of 1N3PhOH with the 2-naphthyl moiety does not posses this property [7].



ISN **4SQ** **8SQ**

Scheme 1.

4-Styrylquinoline (**4SQ**) is the aza-substituted analog of 1SN and involves azanaphthyl (4-quinolyl) fragment, in its structure. 8-Styrylquinoline (**8SQ**) is the other aza-analog of 1SN.

On the basis of the structural analogy, we propose that the adiabatic channel is also possible for the *trans-cis* photoisomerization of 8SQ as it is for 4SQ. It is documented that the photoisomerization of the *cis*-isomer 8SQ is complicated by the formation of dihydrocyclo product, which was identified by the absorption in the range of 400–450 nm [8]. It was pointed out that 8SQ was prone to photocyclization in a higher degree than 4SQ, but this reaction route was not studied in detail.

To reveal the mechanism of the 8SQ photoisomerization, we have used in this study the method based on the examination of the photocyclization kinetics, which can be applied for diarylethylenes entering in this reaction and forming thermally stable dihydrocyclo products. The photocyclization is the competitive reaction relative to the photoisomerization, but the mechanism of the photoisomerization, diabatic or adiabatic, can be revealed from the photocyclization kinetics [1]. This method was used for the first time for the confirmation of the adiabatic mechanism of the 1N1N photoisomerization [4].

The method is based on the fact that the photocyclization of diarylethylenes occurs in the excited singlet state of the *cis*-isomer [9, 10]. Therefore, the formation of dihydrocyclo product (**DHCP**) is a test on the presence of the excited *cis*-isomer in the reaction mixture. The formation of DHCP is readily observed by the absorbance changes in the visible range, because the absorption spectra of the photocyclization products are shifted bathochromically as compared to the spectra of the *trans*- and *cis*-isomers.

When the photoisomerization occurs by adiabatic mechanism

$$\mathrm{t} + h\nu \rightarrow \mathrm{t}^* \rightarrow \mathrm{c}^* \rightarrow \mathrm{c},$$

the excited *trans*-isomer (t*) isomerizes without energy loss to the excited *cis*-isomer (c*), which then can undergo cyclization to DHCP. If DHCP is formed in a single-quantum process directly upon excitation of the *trans*-isomer, the kinetics of DHCP formation corresponds to the one-step reaction. This indicates the intermediate participation of the excited *cis*-isomer in the reaction. This is possible only if the photoisomerization proceeds adiabatically.

When the photoisomerization occurs by diabatic mechanism via a perpendicular conformer (p)

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

the *cis*-isomer in the ground state is formed from the excited *trans*-isomer and is not able to undergo cyclization immediately (here α is the partitioning factor). In this case, the absorption of an extra light quantum is necessary for cyclization. When *trans*-isomer is a starting compound, the kinetics of the DHCP formation should correspond to the two-step reaction, and the induction period will be observed, which is necessary for the accumulation of some quantity of the *cis*-isomer in the reaction mixture.

The results obtained in this work confirmed the assumption made above about the presence of the adiabatic *trans-cis* isomerization for 8SQ. The study of the kinetics of the 8SQ photoisomerization shows that, when the *trans*-isomer is used as starting reagent, the photoisomerization occurs by both two-quantum and single-quantum routes. The latter means that the *trans-cis* photoisomerization of 8SQ occurs at least partially by the adiabatic mechanism (t*→c*), when the excited *cis*-isomer, which then undergoes cyclization, is formed from the excited *trans*-isomer.

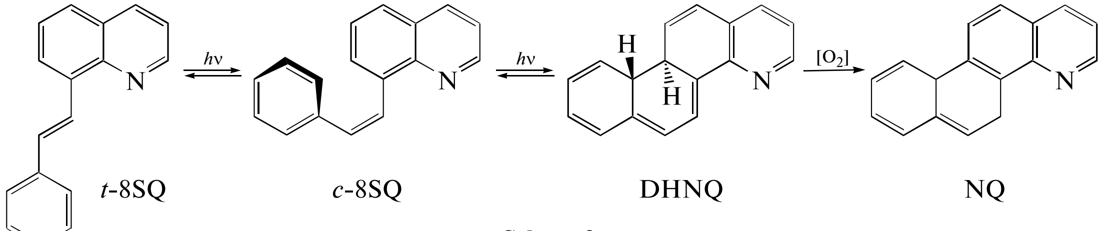
EXPERIMENTAL

8-Styrylquinoline (*trans*-isomer) was synthesized according to the known procedure [8]. Electronic absorption spectra of the *trans*-isomers were measured on a Specord M-40 spectrophotometer in hexane. A DRSh-500 mercury lamp was used as a source of the UV light. The spectral line 313 nm was isolated by a set of glass filters. Photochemical studies were carried out at room temperature in air-saturated solutions with $[8SQ] = (2–20) \times 10^{-5}$ mol/l in quartz cells with an optical path length of $l = 1$ cm, the light intensity measured by a PP-1 cavity detector or a ferrioxalate actinometer was $(3–10) \times 10^{-10}$ Einstein $\mathrm{cm^{-2}\ s^{-1}}$. The quantum yields were calculated by digital solution of a set of differential equations with a typical error of ±20%. The following values of the extinction coefficients were used: $\varepsilon_{313} = 13600$ and 5100 $\mathrm{M^{-1}\ cm^{-1}}$ for the *trans*- and *cis*-isomers, respectively, and $\varepsilon_{437} = 8000$ $\mathrm{M^{-1}\ cm^{-1}}$ for dihydronaphthoquinoline (the value measured for dihydrochrysene, the carbon analog, was used [11]).

Quantum chemical calculations of the 8SQ conformers in the ground state (S_0) were carried out by DFT B3LYP method with a 6-31G** basis of a GAUSSIAN program package [12]. The structures of the compounds were calculated with complete geometry optimization. The correspondence of the optimized structure to the minimum on PES was verified by the absence of the imaginary frequencies in the vibrational spectrum.

RESULTS AND DISCUSSION

The possible structural transformations of 8SQ under irradiation are shown in Scheme 2. The complete reaction scheme involves three steps: reversible *trans-cis* photoisomerization with consequent reversible photocyclization into primary DHCP, 10a,10b-dihydronaphtho[1,2-h]quinoline (**DHNQ**) in the case under study. The latter is oxidized irreversibly by the oxygen of the air into 4-azachrysene (naphtha[1,2-h]quinoline, **NQ**). This compound has a characteristic absorption spectrum with maximums 215 (28900), 235 (18070), 265 (67350), 296 (18460), 343 (2510), and 361 nm (2510 $\mathrm{M^{-1}\ cm^{-1}}$) [13].



Scheme 2.

The formation of NQ in insignificant amount with a preparative yield of 2–4% was observed earlier as a by-product in the photocyclization of 1-(1-naphthyl)-2-(3-pyridyl)ethylene, with 2-azachrysene (preparative yield of 50–60%) being the major product [13, 14]. In the photocyclization of 8SQ, 4-azachrysene (NQ) is the only reaction product.

The spectral changes occurring during irradiation of the solution of the 8SQ *trans*-isomer in hexane with the light with λ = 313 nm are shown in Fig. 1. In the initial stage of the photolysis (0–400 s, spectra *1*–*3*), a decrease in the absorption band of the *trans*-isomer in the range of 270–380 nm caused by the *trans*-*cis* photoisomerization and a simultaneous increase in a weak band in the long-wavelength range of 400–450 nm with a maximum at 437 nm are observed. By analogy with reactions of 4SQ [1], 1-styrylnaphthalene, and other diarylethylenes [15], we attributed the long-wavelength band to DHNQ, the primary photocyclization product (Scheme 2).

In the course of the following irradiation, a gradual increase in the short-wavelength band with a maximum at 267 nm is observed (spectra *4*–*8*) corresponding to NQ, the final oxidized photocyclization product. The increase in the NQ band at 267 nm continued also after scission of the irradiation, with an inversely proportional decrease in the DHNQ band at 437 nm being observed (Fig. 2). Both the decrease in the band at 437 nm and the increase in the band at 267 nm occurred according to the exponential law, with the

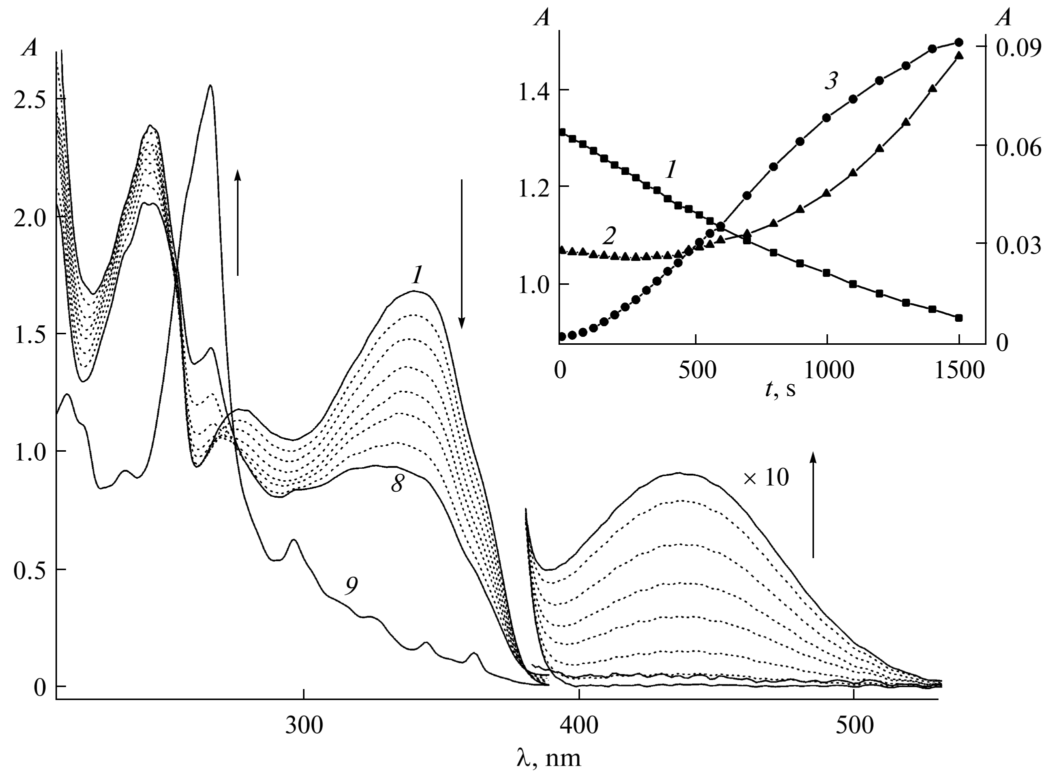
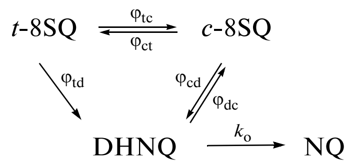


Fig. 1. Spectral changes of the air-saturated solution of *trans*-8-styrylquinoline (9.64×10^{-5} M) in hexane in the course of irradiation by the light with λ = 313 nm and intensity of 3.5×10^{-10} Einstein cm^{-2} c^{-1}, photolysis time, s: (*1*) 0, (*2*) 160, (*3*) 320, (*4*) 520, (*5*) 700, (*6*) 900, (*7*) 1200, (*8*) 1500, and (*9*) spectrum after irradiation of the reaction mixture for 30 min, storage in the dark and dilution. Inset: kinetics of the absorbance changes at the wavelength, nm: (*1*) 313 (*2*) 267 (left axis), and (*3*) 437 (right axis).

measured pseudo-first-order rate constant being equal to 2×10^{-4} s^{-1} and characterizing the oxidation of DHNQ into NQ.

The observed spectral changes agree well with a sequence of the structural transformations of 8SQ given in Scheme 2. The spectrum of the reaction mixture after long-term irradiation and storage in the dark for the completion of the thermal stage of the reaction (Fig. 1, spectrum *9*) is the additional evidence. The final product has absorption bands, which correspond by their position and intensity ratios to the absorption spectrum of NQ (see above).

As assumed above, the kinetic scheme of the DHNQ formation in addition to the two-step (two-quantum) route (φ_{tc}, φ_{cd}) shown in Scheme 2 may involve the reaction of the direct single-quantum cyclization of 8SQ into DHNQ with a quantum yield of φ_{td}, as shown in Scheme 3.



Scheme 3.

Taking into account all possible routes of the DHNQ formation and consequent reactions, the kinetics of the variations in the solution absorbance (*A*) upon irradiation of the reaction mixture is determined by a set of equations:

$$A = \varepsilon_t[t\text{-8SQ}]l + \varepsilon_c[c\text{-8SQ}]l + \varepsilon_{DHNQ}[\text{DHNQ}]l + \varepsilon_{NQ}[\text{NQ}]l, \quad (1)$$

$$d[t\text{-8SQ}]/dt = (-\varphi_{tc}A_t + \varphi_{ct}A_c)\, I_0(1-10^{-A})/(A\, l), \quad (2)$$

$$d[c\text{-8SQ}]/dt = (\varphi_t A_t - \varphi_{ct}A_c - \varphi_{cd}A_c + \varphi_{dc}A_d) \times I_0(1-10^{-A})/(A\, l), \quad (3)$$

$$d[\text{DHNQ}]/dt = (\varphi_{cd}A_c - \varphi_{dc}A_d + \varphi_{td}A_t) \times I_0(1-10^{-A})/(A\, l) - k_o[\text{DHNQ}], \quad (4)$$

$$d[\text{NQ}]/dt = k_o[\text{DHNQ}], \quad (5)$$

where A_i is the absorbance of the *i*th compound, ε_i is its extinction coefficient (M^{-1} cm^{-1}) at the irradiation wavelength, I_0 is the intensity of the light (milliEinstein cm^{-2} s^{-1}), l is the optical path length (cm) and k_o is the efficient rate constant of the DHNQ oxidation (s^{-1}).

This set of equations cannot be solved analytically or digitally, because involves both photochemical steps occurring only during irradiation and the thermal step occurring continuously. However, the set of Eqs. (1)–(5) may be reduced taking into account experimental results.

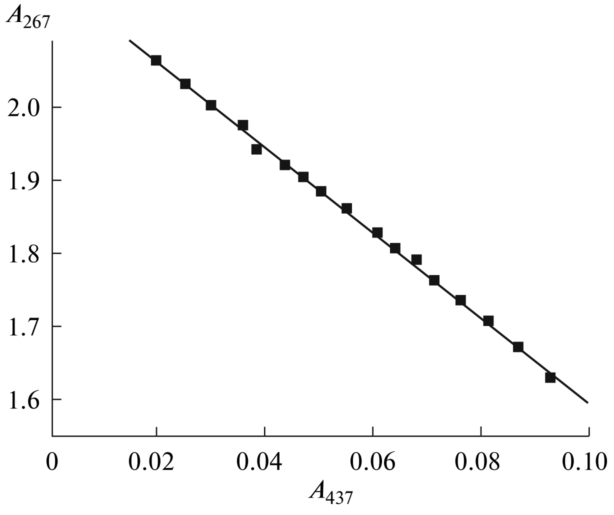


Fig. 2. Proportionality between the decrease in absorbance of DHNQ at λ = 437 nm and the increase in the absorbance of NQ at λ = 267 nm in the oxidation of DHNQ into NQ in the thermal study of the 8SQ photocyclization after scission of irradiation of the reaction mixture.

The measured rate constant of the thermal stage is 2×10^{-4} s^{-1} corresponding to transformation halflife of 58 min. Thus, the DHNQ oxidation is relatively slow reaction, which can be neglected in the initial stage of the photocyclization. This is also confirmed by the kinetic curve measured in the absorption maximum of NQ (267 nm, Fig. 1 inset, curve *2*), which shows the absence of NQ in the reaction mixture in the initial stage of the photolysis.

It should be pointed out that, in the UV spectral range, all components of the reactions mixture absorb, and the kinetic curves measured in this spectral range are the superposition of several curves. However, curve *1* (Fig. 1, inset) measured at the irradiation wavelength (313 nm) in the initial stage of the photolysis characterizes mainly the kinetics of photoisomerization. In the visible range (437 nm), only DHNQ absorbs, therefore curve *3* (Fig. 1, inset) reflects directly the changes in the DHNQ concentration.

Thus, in the initial stage of photocyclization, which is most interesting for the revealing the mechanism of photoisomerization, the reaction mixture contains three components, the *trans*- and *cis*-isomers and DHNQ, and the set of Eqs. (1)–(5) may be restricted by the reactions of photoisomerization and photocyclization. Moreover, to simplify the system in the initial stage of photoisomerization, the reverse photochemical reaction of the cycle opening can be neglected, because the DHNQ absorbance $A_d \ll A_t, A_c$.

The initial portion of the kinetic curve for the DHNQ formation measured at λ = 437 nm is shown in Fig. 3. To minimize the contribution of the thermal

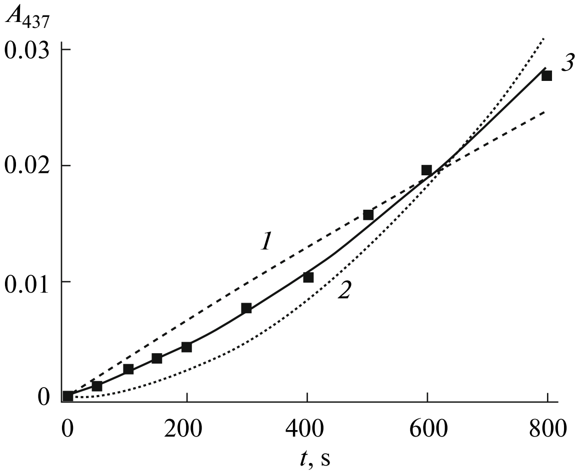


Fig. 3. Kinetics of the absorbance change at λ = 437 nm in the irradiation of the air-saturated solution of *trans*-8SQ in hexane by the light with λ = 313 nm. Points, experimental data; fitting curves, calculated with consideration of (*1*) a single-quantum route, (*2*) two-quantum route, and (*3*) the two routes of the DHNQ formation.

stage, each point was obtained in a separate experiment so that the overall time of the photolysis and registration of the spectrum takes less than 16 min for the last point. The experimental points and three variations of the approximating curves calculated on the assumption of only single-quantum route of the DHNQ formation (φ_{td}), only two-quantum route with the intermediate formation of the *cis*-isomer in the ground state (φ_{tc}, φ_{cd}), and considering both mechanisms (Scheme 3) are given in Fig. 3. In the fitting procedure, the least root-mean-square error for the determination of the absorbance $\Delta A = (\Sigma(A_{calc} - A_{exp})^2/m)^{1/2}$, where A_{calc} is the absorbance calculated by digital integration of the set of Eqs. (1)–(4), A_{exp} is the measured absorbance of the reaction mixture, and m is a number of experimental points in the kinetic curve, was minimized, with the values of the quantum yields being the fitting parameters [16]. One can see in Fig. 3, that the variation considering the both mechanisms of the DHNQ formation is optimal with the following values of the quantum yields of photoisomerization φ_{tc} =0.13 and $\varphi_{ct} = 0.17$ and of photocyclization $\varphi_{td} = 0.009$ and $\varphi_{cd} = 0.23$.

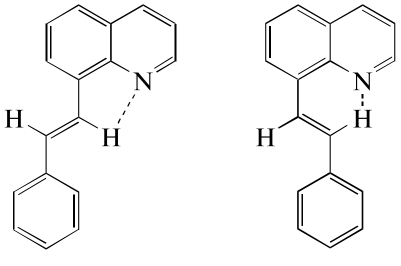
The value $\varphi_{tc} = 0.13$ (hexane) corresponds to the value $\varphi_{tc} = 0.12$ (cyclohexane) measured before [8]. The value $\varphi_{ct} = 0.20$ (ethanol [8]) is known for the back photoisomerization. This value is comparable with that obtained in this study. The values $\varphi_{tc} = 0.15$ and $\varphi_{cd} = 0.28$ [17] are known for 1SN, the carbon analog of 8SQ.

Thus, in comparison to 4SQ, for which $\varphi_{td} = 0.013$ [1], the reaction of the direct single-quantum photocyclization of the *trans*-isomer occurs with lower efficiency ($\varphi_{td} = 0.009$), and the two-quantum formation of DHNQ contributes mainly. The two-quantum photocyclization for 4SQ was observed in ethanol, and the change of the character of the photocyclization rate curves on passing from hexane to ethanol was accounted for by the change in the photoisomerization mechanism, from adiabatic in hexane to diabatic in ethanol [1].

As follows from the obtained data, the *trans-cis* photoisomerization for 8SQ also proceeds partially by adiabatic route, because the presence of the direct cyclization *t*-8SQ → DHNQ indicates the intermediate participation of the excited *cis*-isomer (c*), which is generated in the adiabatic reaction (t* → c*) from the excited *trans*-isomer.

The two-quantum route of the DHNQ formation upon excitation of the *trans*-isomer of 8SQ indicates the intermediate participation of the *cis*-isomer in the ground state, and the absorption of the second light quantum is necessary for its cyclization. Similarly to the case of 4SQ, this may be accounted for by the fact that a portion of the excited *trans*-isomer isomerizes by the diabatic route ($t^* \rightarrow p^* \rightarrow p \rightarrow \alpha c + (1 - \alpha)t$).

However, taking into account the specific structure of 8SQ, another explanation is possible for the two-step mechanism of photoisomerization of this compound. It is known that the *trans*-isomer of 8-SQ exists in the form of two conformers (rotamers), A and B, due to hindered rotation around quasi-single bond between the ethylene group and quinoline moiety [18].



A B

In the case of 1SN and 4SN, only one conformer A exists in the solution, because conformer B is sterically hindered and unstable due to repulsion of the hydrogen atoms in the *peri*-position of the naphthalene (quinoline) moiety and at the β-carbon atom of the ethylene group. The steric hindrance disappears in 8SQ, because the nitrogen atom is in the *peri*-position. Therefore, it was assumed that conformers A and B should be almost isoenergetic [18]. To estimate the relative stability of the two conformers, we carried out the quantum-chemical calculations by the B3LYP/6-31G** method.

The calculation shows that conformer A is more stable than conformer B by 1.01 kcal mol^{-1}, and, if this relationship is the same in solution, the content of the conformers in the equilibrium mixture is 85 and 15%, respectively. The calculation also shows that both conformers have planar structure and are stabilized with the intramolecular hydrogen bond. The distance between the atoms of nitrogen and hydrogen at the α-carbon atom of the ethylene group in the five-membered pseudo-cycle is 2.33 Å in conformer A, and the distance between the atoms of nitrogen and hydrogen at the β-carbon atom of the ethylene group in the six-membered pseudo-cycle is slightly smaller and equal to 2.25 Å in conformer B. These two values are lower than the sum of the van der Waals radii, which is equal to 2.65 Å for the nitrogen and hydrogen atoms [19].

Only conformer A from the two conformers of the *trans*-isomer can undergo cyclization into DHNQ after photoisomerization into the *cis*-isomer, whereas the *cis*-isomer of conformer B should first converts to conformer A. The conformers in the ground state (S_0) are in the equilibrium. However, the equilibrium between the conformers (rotamers) in the excited states has no time to be established (the principle of nonequilibration of excited rotamers (NEER)), due to the enhancement of the double bond character of the single bonds in the ethylene group in the excited state [20]. Therefore, even if the isomerization of the *trans*-isomer of conformer B occurs by the adiabatic mechanism, the conversion of the *cis*-isomer of conformer B into conformer A is necessary for the cyclization, which is possible only after the loss of the excitation and the transition into the S_0 state. Then the *cis*-isomer of conformer A absorbs an addition light quantum and undergoes cyclization to DHNQ. Hence, only a fraction of the 8SQ *trans*-isomer, which is in the form of conformer A in the solution, is able to undergo the cyclization into DHNQ after absorption of a single light quantum. For the cyclization of conformer B, the absorption of two light quanta is necessary in any case, in diabatic and adiabatic photoisomerization.

Thus, the study confirmed the assumption about possibility of the adiabatic *trans-cis* photoisomerization of 8SQ made in the Introduction Section. When *trans*-isomer is used as a starting reagent, the photocyclization occurs by both two-quantum and single-quantum route. The latter indicates that the *trans-cis* photoisomerization of 8SQ at least partially occurs by the adiabatic mechanism, when the excited *trans*-isomer affords the *cis*-isomer also in the excited state.

As was mentioned in the Introduction Section, the back adiabatic *trans-cis* isomerization is a relatively rare event in comparison with the adiabatic *cis-trans* isomerization, and all known diarylethylenes entering this reaction have 1-naphthyl moiety or its aza-analog, quinolinyl moiety, in their structure.

The results obtained in this study confirm this empiric regularity. It is clear that, for the occurrence of the adiabatic *trans-cis* photoisomerization, it is necessary that the potential energy surface of the excited state was flattened with the absence of high barriers and deep minimums at the t* → c* path, and the introduction of the naphthyl (quinolinyl) substituent into the diarylethylene molecule assist this. To reveal the peculiarities of the PES structure in the S_1 states of these compounds, the quantum-chemical calculations of the photoisomerization paths are necessary.

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