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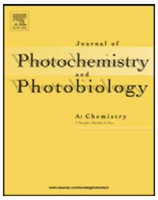

Solvent-driven adiabatic *trans*-to-*cis* photoisomerization of 4-styrylquinoline

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Direct one-stage photocyclization of *trans*-4-styrylquinoline to dihydrobenzo[i]phenanthridine (DHBP) in *n*-hexane with a quantum yield of 0.013 was observed. The kinetics of the photochemical transformations and an effect of the excitation intensity on the yield of DHBP were studied. In ethanol photocyclization proceeded in two stages with intermediate formation of the *cis*-isomer in the ground state. These facts imply a diabatic reaction pathway for *trans*-to-*cis* photoisomerization of 4-styrylquinoline in ethanol and an adiabatic pathway in hexane.

1. Introduction

Photoisomerization of diarylethylenes is known to occur by one-bond-flip mechanism in fluid solutions and by hula-twist mechanism in confined media [1–3]. One-bond-flip photoisomerization in turn can follow diabatic or adiabatic pathway [4,5]. The first one means that an excited perpendicular conformer (p^*), corresponding to the minimum at 90° on the lowest excited singlet or triplet potential energy surface (PES) along the double bond torsional coordinate, is a reaction intermediate (Fig. 1a). The radiationless deactivation to the ground state PES with a maximum (p) at 90° is followed by relaxation to either *cis*- or *trans*-isomer:

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

$$c + h\nu \rightarrow c^* \rightarrow p^* \rightarrow p \rightarrow \beta c + (1-\beta)t$$

where α and β are partitioning factors, and structures of the p^* conformers can differ on going from c^* or t^* side.

Adiabatic photoisomerization takes place fully on the excited state PES with the formation of one excited isomer from another. A bright example of adiabatic reaction is "one-way" *cis*-to-*trans* photoisomerization (Fig. 1b). Many styrylanthracenes and other diarylethylenes bearing large aromatic groups with low-energy local (aromatic) excited states undergo one-way photoisomerization [6]:

$$c + h\nu \rightarrow c^* \rightarrow t^* \rightarrow t$$

The less common case is an adiabatic process in the reverse direction,

$$t + h\nu \rightarrow t^* \rightarrow c^* \rightarrow c$$

because PES is generally descending from the excited *cis*-isomer to the *trans*-one.

To the best of our knowledge there are only three examples of the singlet state $t^* \rightarrow c^*$ isomerization of stilbenic compounds: adiabatic photoisomerization of *trans*-di(1-naphthyl)ethylene (1N1N) [7], *trans*-1-(1-naphthyl)-2-(2-naphthyl)ethylene (1N2N) [8] and *trans*-1-(1′-naphthyl)-2-(3′-hydroxyphenyl)ethene (1N3PhOH) [9]. A special case is adiabatic one-way $t^* \rightarrow c^*$ isomerization of some aza-diarylethenes where intramolecular hydrogen bonds may stabilize *cis*-isomer, inducing energy inversion of the t^* and c^* species, for example, in l-(2′-pyridyl),2-(2″-indolyl)ethene [10,11].

The direct experimental evidence for the adiabatic photoisomerization is the observation of an excited isomer during excitation of another geometric isomer [4,12]. Formation of a photocyclization product – dihydrophenanthrene analogue – upon excitation of the *trans*-isomer is also an evidence for the adiabatic $t^* \rightarrow c^*$ isomerization, since cyclization can proceed only via the excited *cis*-isomer.

Thus, despite being a competitive side reaction with respect to photoisomerization, photocyclization however can be used to examine the reaction mechanism – diabatic or adiabatic – of the photoisomerization reaction. Namely the fact of the photocyclization product – 4a,4b-dihydrobenzo[i]phenanthridine (DHBP) – formation upon excitation of the *trans*-isomer of 4-styrylquinoline we used in the present report to conclude about adiabatic mechanism of the styrylquinoline *trans*-to-*cis* photoisomerization.

In the literature there are somewhat controversial data about photochemical properties of 4-styrylquinoline (4SQ) and

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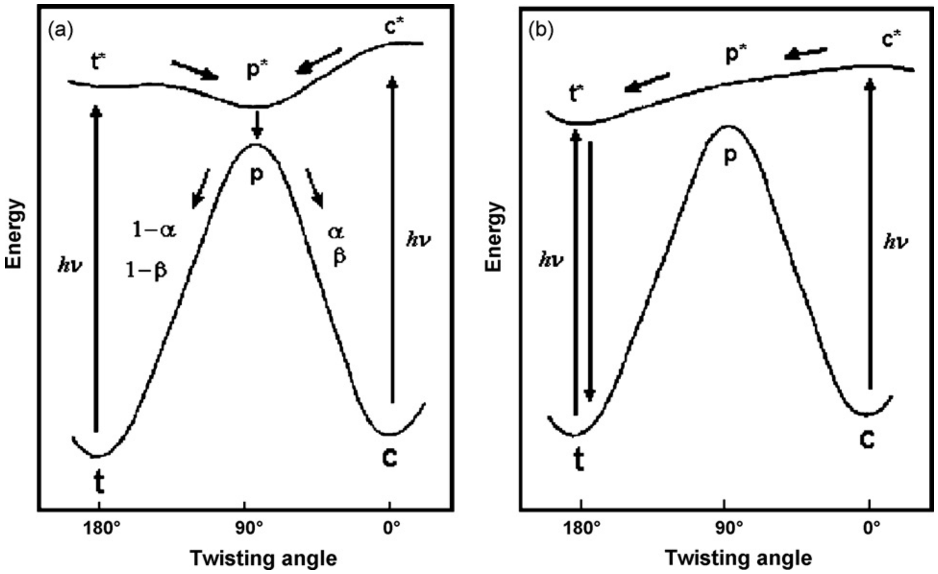


Fig. 1. Schematic potential energy curves of the ground and excited states of diarylethylenes for twisting around the double bond: (a) classical diabatic photoisomerization and (b) "one-way" adiabatic *cis*-to-*trans* photoisomerization.

derivatives. Galiazzo et al. [13] have marked at a qualitative level that the *cis*-isomer of 4SQ displays low tendency to photocyclization in apolar solvents and does not cyclize at all in polar solvents. Bartocci et al. [14] have discussed in detail fluorescence and photoisomerization reaction, but said nothing about photocyclization. Wang and Ho have described spectral and fluorescent properties of 4-(4′-dimethylaminostyryl)quinoline saying nothing about its photochemistry [15]. Earlier we have investigated the effect of substituents in the styryl fragment of 4SQ and found that nitro derivative both isomerizes and cyclizes whereas amino group prevents photocyclization [16].

In the present paper we investigated the effect of solvent polarity on photochemistry of 4SQ. This compound was found to cyclize in both apolar and polar solvents, and upon direct excitation of the *trans*-isomer the photocyclization proceeds as one-step reaction in apolar solvent and as two-step reaction (via *cis*-isomer) in polar solvent, implying adiabatic reaction pathway for *trans*-to-*cis* photoisomerization in the first case and diabatic pathway in the second case.

2. Experimental

4-Styrylquinoline was synthesized by known procedure [13]. The absorption spectra were recorded with a Specord M-40 spectrophotometer, using a 1-cm quartz cuvette.

A DRSh-500 mercury lamp was used as a source of UV light; the spectral lines at 313 and 365 nm were isolated by a set of glass filters; light intensity was $(1–20) \times 10^{-10}$ Einstein cm^{-2} s^{-1} (measured with a PP-1 cavity detector or a ferrioxalate actinometer). Photochemical studies were performed at room temperature with air-saturated solutions (solute concentration $(2–20) \times 10^{-5}$ mol l^{-1}). Quantum yields were calculated by numerical solution of a set of differential equations, error is typically ±20%; the following values of molar extinction coefficient were used: $\varepsilon_{313} = 20{,}400$ and 7000 M^{-1} cm^{-1} for *trans*- and *cis*-isomer, respectively, and $\varepsilon_{422} = 8000$ M^{-1} cm^{-1} for dihydrobenzophenanthridine (assumed to be the same as that of the hydrocarbon analogue dihydrochrysene [17]).

3. Results and discussion

Trans-4SQ possesses broad vibrationless absorption band at 320 nm (in *n*-hexane, Fig. 2, spectrum 1), which disappeared during irradiation with UV light (313 or 365 nm) with simultaneous appearance of sharp band with maxima at 259 and 266 nm and much less intense band with maximum at 422 nm (Fig. 2, spectra 2–10).

The long-wavelength band obviously belongs to the product of the photocyclization reaction – DHBP [18,19], and intense short-wavelength band – to its oxidation product, benzo[i]phenanthridine (BP, Scheme 1). The latter is an aza-derivative of chrysene, photocyclization product of 1-styrylnaphthalene [18]. The observed transformations correspond to the following scheme of the chemical reactions, which takes into account that both photoisomerization and photocyclization are reversible reactions whereas oxidation occurs irreversibly (Scheme 1).

This assignment is supported by the spectral variations which have been observed after finishing irradiation and keeping the solution in the dark. The DHBP absorption band at 422 nm disappeared simultaneously with the increase of the BP absorbance in the 250–260 nm region, and linear correlation was observed between

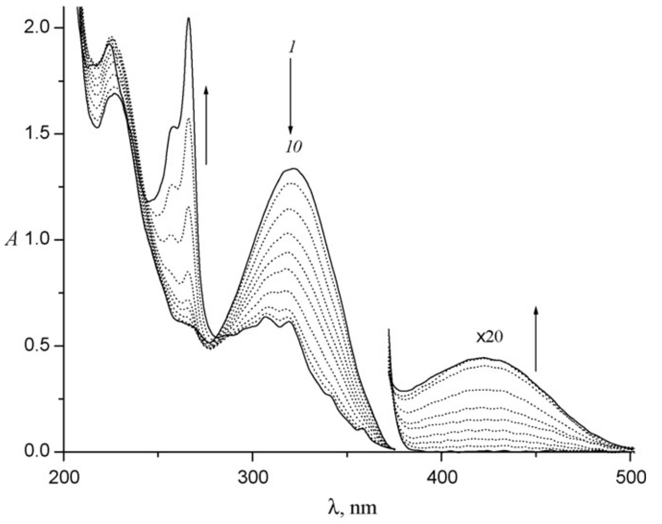
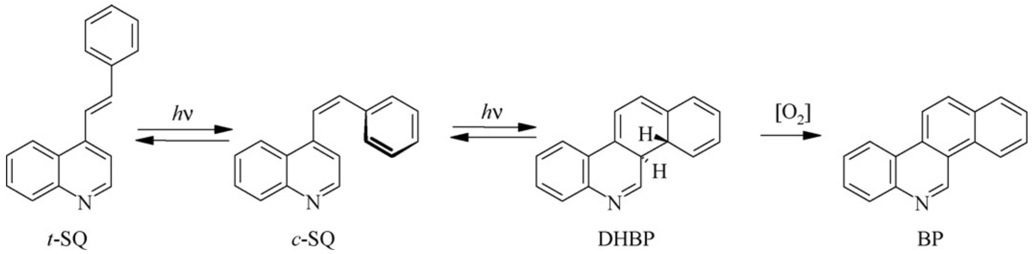


Fig. 2. Spectral variations during irradiation of air-saturated solution of *trans*-4-styrylquinoline (6.25×10^{-5} M) in *n*-hexane with light of 313 nm, intensity 2.43×10^{-10} Einstein cm^{-2} s^{-1}, irradiation time, s: 0 (1), 40 (2), 120 (3), 210 (4), 300 (5), 400 (6), 600 (7), 1000 (8), 1500 (9) and 2100 (10).



Scheme 1.

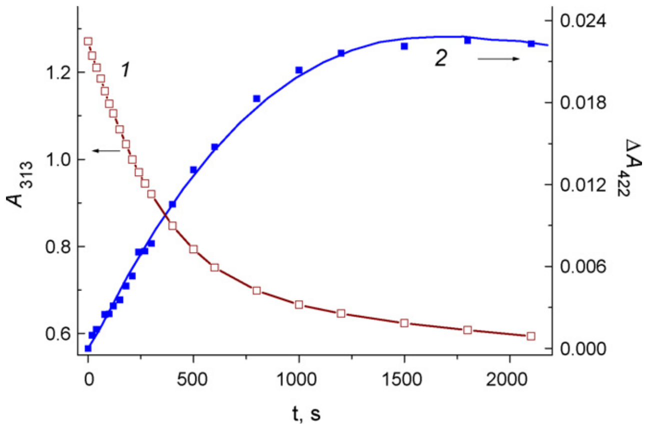


Fig. 3. Kinetics of absorbance change at (1) 313 nm (left axis) and (2) 422 nm (right axis) during irradiation of air-saturated solution of *trans*-4-styrylquinoline in *n*-hexane with light at 313 nm.

DHBP absorbance decrease and BP absorbance increase. Obviously, this transformation characterizes the (thermal) oxidation of DHBP to BP by atmospheric oxygen. The decay of DHBP absorption and increase of BP absorption followed a first order kinetics with the same rate constant $k = 7.1 \times 10^{-4}\,s^{-1}$ at 25 °C.

During irradiation of the *trans*-SQ in air-saturated ethanol we observed similar spectral variations as in *n*-hexane, absorption band of the *trans*-isomer being shifted to 331 nm and that of DHBP to 443 nm. Kinetics of the absorbance change at irradiation wavelength (313 nm) and at long-wavelength band in the range 400–450 nm is shown in Fig. 3 (*n*-hexane) and Fig. 4 (ethanol). Inasmuch as all components of the reaction mixture absorb at 313 nm, the kinetic curve at 313 nm is complex superposition of different curves, however, at the early stage of irradiation it characterizes mainly the *trans*-isomer decay. As compared with short-wavelength region, the only absorbing compound in the long-wavelength range is DHBP, so absorbance increase (decrease) in this range can be related directly to the rate of DHBP formation (decay).

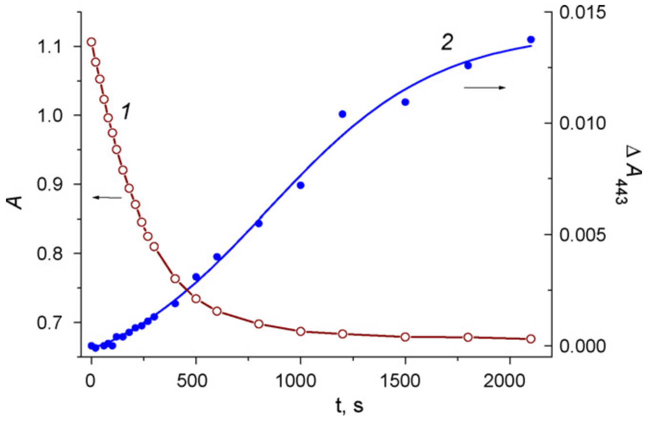


Fig. 4. Kinetics of absorbance change at (1) 313 (left axis) and (2) 443 nm (right axis) during irradiation of air-saturated solution of *trans*-4-styrylquinoline in ethanol with light at 313 nm.

As can be seen from comparison of Figs. 3 and 4, in spite of the comparable kinetics of the *trans*-isomer decay in *n*-hexane and ethanol (curve 1), kinetics of DHBP formation differs fundamentally in two solvents. In *n*-hexane, formation of DHBP begins from the initial stage of irradiation (Fig. 3, curve 2), but in ethanol DHBP is formed with induction period (Fig. 4, curve 2). Kinetic curve 2 in Fig. 3 unequivocally proves the DHBP formation directly upon excitation of *trans*-4SQ.

Two-stage formation of the cyclization product from *trans*-isomer (Scheme 1) demands the sequential absorption of two photons, one photon per each photochemical stage. So, starting from irradiation of the *trans*-isomer, one should expect for the S-shaped kinetic curve of the DHBP formation with some induction period, as it is observed in ethanol.

However, single-stage formation of DHBP from *trans*-4SQ without induction period in *n*-hexane demands the direct reaction of the *trans*-4SQ to DHBP photocyclization to be added to Scheme 1, as it is shown in Scheme 2.

According to Scheme 2, we can write the following set of differential equations for the system under consideration:

$$\frac{d[t\text{-4SQ}]}{dt} = -k_{tc}[t\text{-4SQ}] + k_{ct}[c\text{-4SQ}] - k_{td}[t\text{-4SQ}] \qquad (1)$$

$$\frac{d[c\text{-4SQ}]}{dt} = k_{tc}[t\text{-4SQ}] - k_{ct}[c\text{-4SQ}] - k_{cd}[c\text{-4SQ}] + k_{dc}[\text{DHBP}] \qquad (2)$$

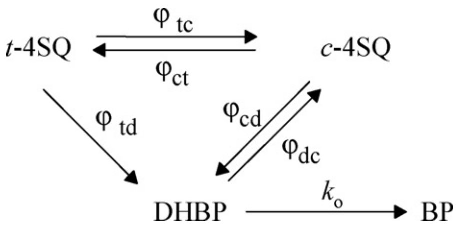
$$\frac{d[\text{DHBP}]}{dt} = k_{cd}[c\text{-4SQ}] - k_{dc}[\text{DHBP}] + k_{td}[t\text{-4SQ}] - k_{o}[\text{DHBP}] \qquad (3)$$

$$\frac{d[\text{BP}]}{dt} = k_{o}[\text{DHBP}] \qquad (4)$$

with rate constants:

$$k_{ij} = \varepsilon_i \varphi_{ij} I_o \frac{(1 - 10^{-A})}{A} \qquad (5)$$

where ε_i is the compound i extinction coefficient ($M^{-1}\,cm^{-1}$) at the irradiation wavelength, φ_{ij} is the quantum yield for the $i \to j$ transformation, I_o is the light intensity (milliEinstein $cm^{-2}\,s^{-1}$), and A is total absorbance of reaction mixture at the irradiation wavelength. Thermal ("dark") oxidation of dihydrophenanthrene is known to take place through several stages [20,21]. In our case oxidation of



Scheme 2.

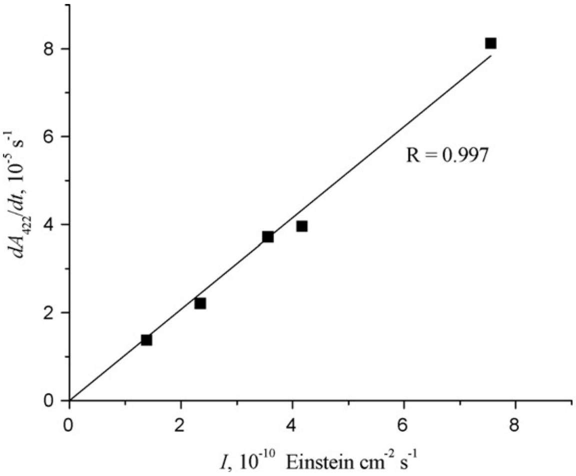


Fig. 5. The rate of DHBP formation in n-hexane as a function of the irradiation light intensity.

DHBP is characterized by a pseudomonomolecular rate constant k_o, Eq. (4).

When k_o is small, the primary cyclization product (dihydrocycloproduct) is stable to oxidation, as in the case of 1N1N [7] and 1N2N [8]. When k_o is large, dihydrocycloproduct is not observed and cyclization kinetics can be obtained directly by monitoring oxidation product formation, as in the case of 1N3PhOH [9].

As compared to previously investigated cases, full treatment of the kinetic scheme for 4SQ is complicated due to simultaneous reactions of DHPB formation (photochemical) and oxidation (thermal). However, the oxidation reaction can be neglected at the early stages of irradiation. Additionally, calculations show that up to 10% conversion of t-4SQ in n-hexane the main components of reaction mixture (>99.5%) are only *trans*- and *cis*-isomers. Computer-assisted processing of experimental data according to Eqs. (1)–(3) within this time period gave $\varphi_{tc} = 0.39$ and $\varphi_{ct} = 0.30$. The quantum yield of t-4SQ direct photocyclization to DHBP (φ_{td}) was calculated from the initial slope of the kinetic curve 2 in Fig. 3, $\varphi_{td} = 0.013$.

Additional evidence for the direct t-4SQ to DHBP cyclization in n-hexane was obtained from the effect of excitation light intensity. At the early stages of irradiation, when $[t\text{-4SQ}] \gg [c\text{-4SQ}], \gg[\text{DHBP}]$, and $\gg[\text{BP}]$, $A \sim \varepsilon_t[t\text{-4SQ}]l$, so the rate of DHBP formation, measured as absorbance increase at 422 nm, can be found from Eq. (3):

$$\frac{dA_{422}}{dt} \sim aI_o \quad (6)$$

where $a = \varepsilon_{d,422}\varphi_{td}(1 - 10^{-A})$. The rate of DHBP formation should increase linearly with excitation intensity, with a slope of a. Such linear dependence was corroborated experimentally, Fig. 5. From Fig. 5, the slope was found to be 1.07×10^5 s cm^2 Einstein^{-1}, to give $\varphi_{td} = 0.013$, in full agreement with the value from the kinetic data.

Thus, during irradiation of the *trans*-isomer of 4SQ in n-hexane, photocyclization to DHBP proceeds without induction period, as it follows from reaction kinetics, and the reaction rate is linearly dependent on the light intensity. Therefore, the ring closing process occurs under direct excitation of the *trans*-isomer in single stage, i.e. in monophotonic process.

Photocyclization of stilbene-like molecules is known to occur via *cis*-isomers in the lowest singlet excited state [22,23]. Formation of DHBP from the *trans*-isomer by a monophotonic process in hexane can only be explained by participation of the excited *cis*-isomer which is formed in adiabatic isomerization $t^* \rightarrow c^*$. On the other hand, absence of DHBP on the early stages of the *trans*-isomer irradiation in ethanol signifies absence of the excited *cis*-isomer in this case, that implies diabatic isomerization $t^* \rightarrow p^* \rightarrow p \rightarrow c$.

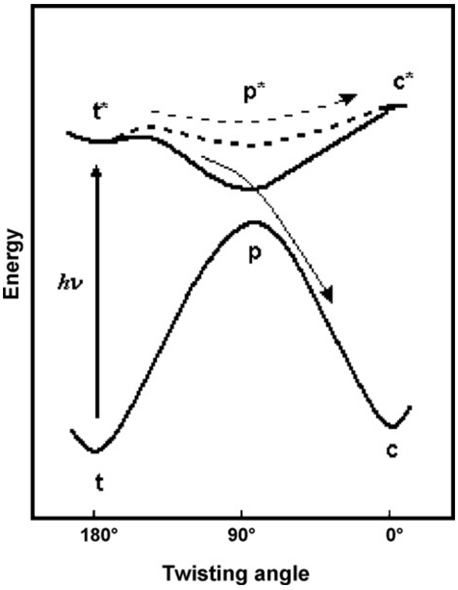


Fig. 6. Solvent polarity effect on the shape of the excited state potential energy surface: solid line—polar solvent, diabatic photoisomerization; dashed line—apolar solvent, adiabatic photoisomerization.

The effect of solvent polarity on photoisomerization is explained taking into account zwitterionic character of the intermediate perpendicular conformer p^* [5,14]. Polar solvents stabilize the p^* configuration more than the excited t^* isomer, deepening the potential minimum on the S_1 PES and directing photoisomerization along diabatic pathway, solid arrow in Fig. 6. Apolar solvents destabilize the p^* configuration relative to the t^* form, decreasing the p^*-minimum. The S_1 PES becomes more flat in the region of the p^* configuration that favors the $t^* \rightarrow c^*$ adiabatic pathway (dashed arrow in Fig. 6).

It is worth noting that high-level quantum chemical calculations show that the absolute minimum on the excited state PES is not a true minimum, but rather a conical intersection (CI), and that at least two molecular coordinates – twisting and pyramidalization – are required for description of photoisomerization [24]. The former coordinate electronically decouples the two groups (connected by double bond), whereas the latter stabilizes a charge-transfer electronic state. The resulting intersection arises from the interaction of covalent and charge-transfer states. Depopulation of the excited state occurs through the CI.

One can see that, in fact, calculations clarify the nature of "potential trap" on the pathway of the system movement from t^* to c^* side on the excited-state PES. Polar solvents stabilize the excited charge-transfer state and make the corresponding CI more easily accessible, whereas apolar solvents destabilize this state and allow the system to avoid potential trap. Thus, more detail model results in the same conclusion as predicted by simplified model depictured in Fig. 6: solvent polarity should affect the photoisomerization mechanism.

4. Conclusion

Thus, clear evidence is obtained for adiabatic *trans*-to-*cis* photoisomerization of 4-styrylquinoline in n-hexane. As already has been mentioned in introduction, there are numerous examples of adiabatic $c^* \rightarrow t^*$ photoisomerization, since *trans*-isomer is lower in energy than *cis*-one and the excited-state potential energy surface is generally descending from the latter to the former. However, only few examples of the back adiabatic $t^* \rightarrow c^*$ photoisomerization are found. Experimental results presented here, in combination with earlier works, allow us to determine a structural factor that favors adiabatic $t^* \rightarrow c^*$ photoisomerization. All known compounds undergoing this reaction include in their structure the fragment of 1-naphthyl group or its aza-analogue—4-quinolyl group. Obviously, naphthyl (quinolyl) substituent near the double bond of diarylethylene modifies the shape of potential energy surface (relative energies of the t^*, p^* and c^* configurations) in such a manner that promotes the adiabatic $t^* \rightarrow c^*$ transformation. High-level quantum chemical calculations can disclose the peculiarities of the excited-state potential energy surfaces and clarify the role of naphthyl (quinolyl) group.

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References

[1] J. Saltiel, J.L. Charlton, in: P. de Mayo (Ed.), Rearrangement in Ground and Excited States, vol. 3, Academic Press, New York, 1980, p. 25.
[2] J. Saltiel, Y.-P. Sun, in: H. Durr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990, p. 64.
[3] R.S.H. Liu, G.S. Hammond, Proc. Natl. Acad. Sci. U.S.A. 97 (2000) 11153.
[4] G. Bartocci, G. Galiazzo, E. Marri, U. Mazzucato, A. Spalletti, Inorg. Chim. Acta 360 (2007) 961.
[5] G. Bartocci, U. Mazzucato, A. Spalletti, Trends Phys. Chem. 12 (2007) 1.
[6] T. Arai, K. Tokumaru, Chem. Rev. 93 (1993) 23.
[7] M.F. Budyka, V.F. Razumov, O.D. Laukhina, Chem. Phys. Lett. 279 (1997) 327.
[8] S.P. Kazakov, V.F. Razumov, M.V. Alfimov, High Energy Chem. 38 (2004) 249.
[9] P. Bortolus, G. Galiazzo, G. Gennari, I. Manet, G. Marconi, S. Monti, Photochem. Photobiol. Sci. 3 (2004) 689.
[10] F.D. Lewis, B.A. Yoon, T. Arai, T. Iwasaki, K. Tokumaru, J. Am. Chem. Soc. 117 (1995) 3029.
[11] T. Arai, M. Obi, T. Iwasaki, K. Tokumaru, F.D. Lewis, J. Photochem. Photobiol. A: Chem. 96 (1996) 65.
[12] J. Saltiel, A.S. Waller, Y.P. Sun, D.F. Sears Jr., J. Am. Chem. Soc. 112 (1990) 4580.
[13] G. Galiazzo, P. Bortolus, G. Gennari, Gazz. Chim. Ital. 120 (1990) 581.
[14] G. Bartocci, U. Mazzucato, A. Spalletti, Recl. Trav. Chim. Pays-Bas 114 (1995) 459.
[15] S.L. Wang, T.I. Ho, J. Photochem. Photobiol. A: Chem. 135 (2000) 119.
[16] M.F. Budyka, N.I. Potashova, N.V. Biktimirova, T.N. Gavrishova, High Energy Chem. 42 (2008) 220.
[17] T. Wismontski-Knittel, G. Fischer, E. Fischer, J. Chem. Soc., Perkin Trans. II (1974) 1930.
[18] E.V. Blackburn, C.E. Loader, C.J. Timmons, J. Chem. Soc. (C) (1970) 163.
[19] K.A. Muszkat, Top. Curr. Chem. 88 (1980) 89.
[20] A. Bromberg, K.A. Muszkat, J. Am. Chem. Soc. 91 (1969) 2860.
[21] A. Bromberg, K.A. Muszkat, A. Warshel, J. Chem. Phys. 52 (1970) 5952.
[22] F.B. Mallory, C.W. Mallory, Org. React. 30 (1984) 1.
[23] W.H. Laarhoven, Recl. Trav. Chim. Pays-Bas 102 (1983) 185.
[24] B.G. Levine, T.J. Martinez, Ann. Rev. Phys. Chem. 58 (2007) 613.