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# Femto/Picosecond Transient Absorption Study of Perimidinespirocyclohexadienone Derivatives Ring-Opening Dynamics

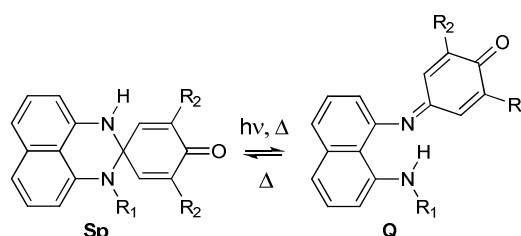
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**Abstract:** The ring-opening dynamics of perimidinespirocyclohexadienone derivatives has been studied by means of time-resolved spectroscopy in cyclohexane and acetonitrile solutions. It has been established that molecular isomerisation leading to the open isomer occurs against the background of the  $S_1$ - $S_0$  internal conversion of the cyclic form. In addition, the features of the observed spectral changes in the cyclohexane made it possible to distinguish formation of the photoproduct in the  $T_1$  state and its relaxation via intersystem crossing to the singlet ground state. The corresponding assignments for transient absorption bands were performed on the basis of TD-DFT calculation.



Scheme 1.

## Introduction

One of the main tasks in the development of new photochromic compounds is the establishment of mechanisms of photoinitiated processes leading to a change in their spectral properties. Obviously, the information obtained will determine the effective scope of application of a specific type of photochromic molecules, for instance, as structural elements of biological functions control, photo-driven molecular switches, media for optical data recording and storage.<sup>[1-3]</sup>

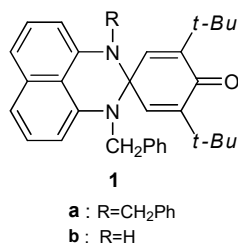
The present paper discusses the mechanisms that govern the photoinduced processes in perimidinespirocyclohexadienone (spiropyrimidine) derivatives, one of the classes of spiroheterocyclic compounds revealing photo- and thermochromic properties.<sup>[4,5]</sup> Irradiation of the solution of perimidinespirocyclohexadienones **Sp** ( $R_1=H$ , Alk;  $R_2=t-Bu$ ) by actinic light results in their reversible coloration due to the appearance of a longwave absorption band assigned to the ring-opened isomers **Q** with quinoneimine structure that was confirmed by X-ray diffraction analysis<sup>[6,7]</sup> (Scheme 1). The proposed mechanism of the photochromic reaction involved two stages: cleavage of a C-N bond in the first singlet excited state leading to a zwitterionic (biradical) intermediate formation and intramolecular proton transfer as a final step.<sup>[6]</sup> It is important to note that photochromic transformations were observed only in cases where at least one of the substituents at the nitrogen of the perimidine ring was a hydrogen atom.

The hypothesis of the existence of an intermediate on the reaction path of the interconversion of closed and open isomers of two related spiroperimidine compounds, 2,3-dihydro-2-spiro-7-(8'-imino-7,8-dihydronaphthalen-1'-amine)perimidine and 2,3-dihydro-2-spiro-4-[8-aminonaphthalen-1(4H)-one]perimidine, was proposed by Norikane et al.<sup>[8]</sup> This presumption was based upon the character of changes of the transient absorption intensities related to the initial isomer and photoproduct. At the same time no specific transient absorption that could be attributed to such an intermediate was observed in the range of wavelengths from 350 to 750 nm. Thus, the nature of the supposed intermediate species remained unclear.

Mechanism of the thermal cleavage of spiro-bond and formation of the colored isomer of spiropyrimidine **Sp** ( $R_1=H$ ,  $R_2=H$ ) was studied by means of quantum-chemical methods.<sup>[9]</sup> The calculation results showed that  $C_{\text{spiro}}-N$  bond cleavage and proton transfer occur concertedly at the ground state potential energy surface (PES). The ring-opening reaction on the  $T_1$  PES, in contrast, turned out to be a multi-step process. Moreover, it was established that the studied thermal rearrangement involves singlet-triplet states PES crossing. Thus, there is every reason to suggest that the intermediate species formed during the corresponding photoreaction may belong to the triplet state. The aim of the present paper is to shed light on the photoinitiated processes accompanying the formation of the open isomers of perimidinespirocyclohexadienones applying time-resolved spectrometry with conjunction of quantum-chemical calculations in order to clarify the interpretation of the experimental results.

## Results and Discussion

The experimental strategy for studying photoinduced processes in perimidinespirocyclohexadienons involved measurements of the transient spectra of non-photochromic compound **1a** and photochromic one **1b** (Scheme 2).



Scheme 2.

Obviously, the replacement of the hydrogen at the nitrogen atom by a benzyl group would significantly increase the energy barrier of rearrangement leading to the formation of the colored form thereby depriving compound **1a** of photochromic properties.

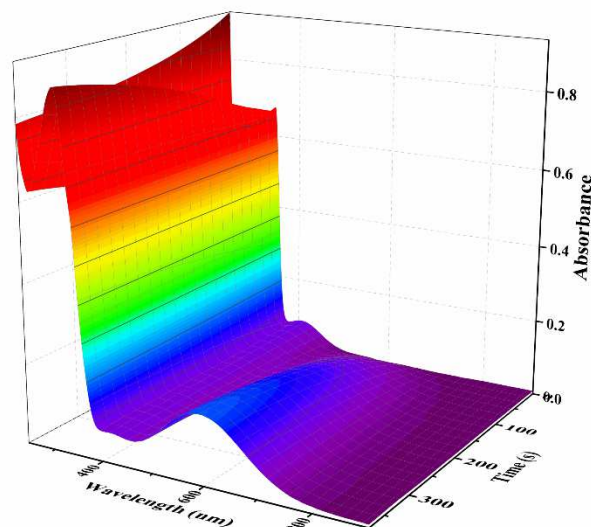
Thus, the transient spectra of **1a** will reflect photoinduced processes at the stage of bond cleavage and should indicate the presence of an intermediate with a broken C-N bond if one exists. The second experiment with a photochromic compound **1b** were to complement the first and have to demonstrate the full spectral dynamics including at the step of formation of the colored products. The measurements were carried out in solvents of different polarity to establish environmental effects on the observed processes.

Ground state electronic absorption spectra of **1a,b** exhibit a long-wavelength absorption with maxima at 344-348 nm and molar absorptivities  $\epsilon = (13.54-15.3) \cdot 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$ , as well as an order of magnitude less intense bands with maxima located at 408-424 nm ( $\epsilon = (1.28-1.53) \cdot 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) (Table 1, Figure S1). Irradiation of **1b** in its long-wavelength absorption region results in the appearance of broad band with maxima at 595 and 616 nm attributed to the open isomer of **1b** in cyclohexane and acetonitrile solution, respectively (Figure 1). In contrast, continuous irradiation of **1a** under the same conditions, as expected, did not lead to any spectral change.

**Table 1.** Spectral characteristics of the cyclic (**Sp**) and open (**Q**) isomers of perimidinespirocyclohexadienones **1a,b** in cyclohexane and acetonitrile solution.

Solvent	$\lambda_{max}, \text{nm} (\epsilon, 10^3, \text{M}^{-1}\text{cm}^{-1})$			
	1a-Sp	1a-Q	1b-Sp	1b-Q
Cyclohexane	344 (13.76) 424 (1.28)	-	345 (13.54) 418 (1.42)	616 (4.27)
Acetonitrile	347 (15.79) 420 (1.31)	-	348 (15.30) 408 (1.53)	595 (3.92)

After cessation of irradiation, thermal discoloration of the spiroperimidine **1b** solutions occurs due to thermal recyclization reaction. The lifetimes of the colored forms depend on the solvent and decrease with increasing of its polarity ( $1.22 \cdot 10^5 \text{ s}$  in cyclohexane vs.  $1.02 \cdot 10^5 \text{ s}$  in acetonitrile)



**Figure 1.** Photoinduced spectral changes of **1b** in acetonitrile solution after 436 nm irradiation ( $[C]=5.9 \cdot 10^{-5} \text{ M}$ ,  $T=293 \text{ K}$ ).

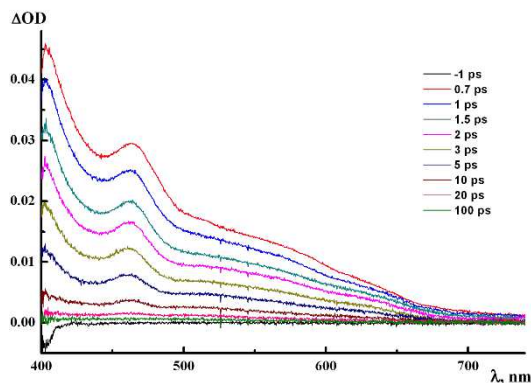
At the same time, irradiation of the colored solutions with 546 or 574 nm mercury lamp did not accelerate the bleaching, that may be regarded as evidence of the absence of the reverse photoreaction **1b-Q**  $\rightarrow$  **1b-Sp**. Furthermore, in the temperature range from 77 to 293 K, neither fluorescence nor phosphorescence was detected. Transient absorption spectra of the compound **1a** in cyclohexane solution, recorded 0.7 ps after excitation, consist of peaks at 403 and 463 nm, shoulders at 582 and 612 nm and structureless absorption of low intensity in the range 650-750 nm (Table 2, Figure 2). Subsequent spectral changes up to 100 ps are associated with a decrease of absorption intensity in the entire spectral region of observation while maintaining the shape of the initial spectrum. Neither spectral shift nor spectral narrowing is observed in this time window. The kinetics of spectral changes in the entire range has predominantly monoexponential character with a time constant of 2.6 ps (Figure S2). Similar spectral pattern has been detected in acetonitrile solution, however, the lifetime of the excited state in this case is longer and amounts to 4.4 ps (Table 2, Figures S3, S4).

**Table 2.** Spectral and kinetic characteristics of primary photoinduced processes in perimidinespirocyclohexadienone **1a**.

Solvent	$\lambda_{max}, \text{nm}$	$\tau_1, 10^{-12} \text{ s}$
Cyclohexane	403, 463, 582sh, 624sh, 650-750	2.6
Acetonitrile	405, 443sh, 544sh, 612sh, 650-750	4.4

Features of the above spectral changes can be explained by the internal conversion of the relaxed  $S_1$  excited state of the cyclic form **1a-Sp**. On the other hand, one cannot totally reject, upon excitation, the possibility of the formation of an intermediate with a broken C-N bond that would be instantaneously quenched by the Internal conversion process or a species with a much-weakened C-N bond strength not going as far as breaking the bond. Absorption of such a species can be significantly less intense (due to low concentration, for instance) or very close to the  $S_1$  state absorption and then completely hidden by the more

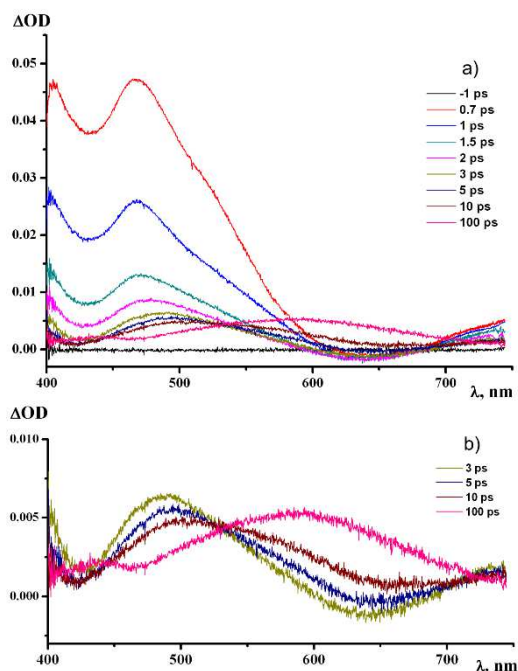
intense absorption bands related to the internal conversion process ( $S_0 \leftarrow S_1$ ). Nevertheless, the observed spectral dynamics (Figure 2) may be considered as predominantly decay of the  $S_1$ - $S_n$  absorption of **1a-Sp**.



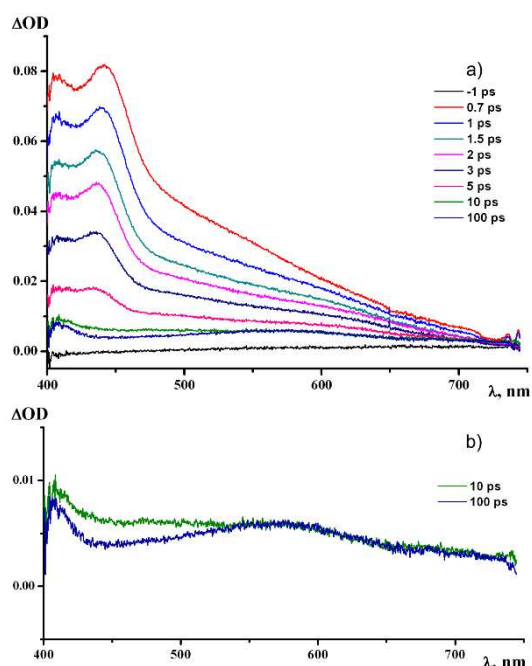
**Figure 2.** Transient absorption spectra of **1a** ( $10^{-3}$  M, 293 K) in cyclohexane at different pump-probe time delays in the 0-100 ps range after excitation at 375 nm ( $12 \mu\text{J}$  per pulse). The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation (negative peak at 400 nm for the -1 ps spectrum is an artefact).

The following experiments with photochromic compound **1b** were to demonstrate the further development of the photoreaction. Pump-probe experiment of photochromic spiroperimidine **1b** in cyclohexane solution 0.7 ps after the excitation pulse afforded transient absorption spectrum with maxima at 405 and 467 nm. Subsequent spectral evolution over a period of 0.7 – 3 ps was manifested in more than 7-fold decay of absorption at the band maxima and appearance of the absorption in the region of 487 nm and above 750 nm (Figure 3a). This process can be characterized by a time constant of 0.4 ps (Figure S5). As the main feature of the spectral changes in the time interval of 3 - 100 ps, one can distinguish three isosbestic points arising as a result of decay of the bands at 487 nm and 750 nm and appearance of the new ones at 439 nm and 597 nm (Figure 3b). These two bands are located in the spectral range of the open form isomer of **1b** absorption spectrum. The time constant of this process is considerably larger than that of previous one and equal to 12.4 ps (Figure S6). Please note the presence of a negative signal around 630 nm at the early stage of the spectral evolution. This signal cannot be assigned to a bleaching signal since the ground state of **1b** has no absorption in this spectral range. The only explanation is that this negative signal comes from the stimulated emission from the  $S_1$  state of the **1b** species. The kinetics of this process is mixed with the appearance of the band at 597 nm. This point confirms the very short-lived character of the  $S_1$  state of cyclic **1b** isomer which is consistent with the absence of detected fluorescence emission.

In acetonitrile, noticeable changes of the initial form of the spectrum **1b** were detected only 10 ps after excitation and manifested in the appearance of a long-wavelength maximum at 576 nm (Figure 4b). In the period of 0.7 – 10 ps, the character of the spectral dynamics is qualitatively similar to that observed for the non-photochromic compound **1a** (Figure 4a).



**Figure 3.** Transient absorption spectra of **1b** ( $10^{-3}$  M, 293 K) in cyclohexane at different pump-probe time delays in the 0-100 ps range (a) and 3-100 ps range (b) after excitation at 375 nm ( $12 \mu\text{J}$  per pulse). The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

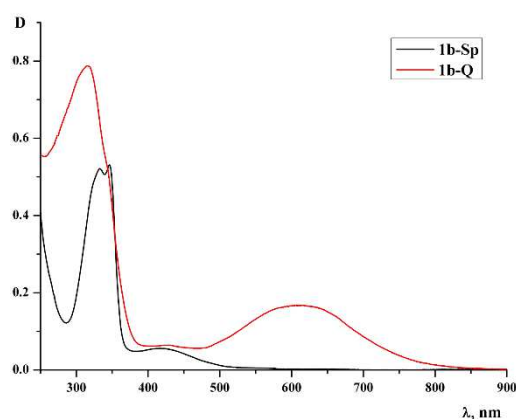


**Figure 4.** Transient absorption spectra of **1b** ( $10^{-3}$  M, 293 K) in acetonitrile at different pump-probe time delays in the 0 – 100 ps range (a) and 10 – 100 ps range (b) after excitation at 375 nm ( $12 \mu\text{J}$  per pulse). The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

The described spectral changes can be characterized by a single time constant of 2.4 ps (Figure S7).

The noticeable qualitative similarity of the observed spectral pattern for **1a** and **1b** at the initial stages of the photoreaction

suggests that in both cases it reflects the internal conversion of  $S_1$  excited state of the cyclic isomer. On the other hand, the transient absorption with maxima at 439 and 597 nm in cyclohexane and at 576 nm in acetonitrile should be attributed to the reaction product - open isomer **1b-Q** in the singlet ground state. This is clearly seen in the comparison of the transient absorption spectrum of **1b** in cyclohexane at the 100 ps pump-probe time delay after impulse excitation (Figure 3b) and the absorption spectrum of photoproduct **1b-Q** obtained after continuous irradiation (Figure 5). In the region of 400 - 750 nm, the absorption spectrum of photoproduct **1b-Q** includes a broad long-wavelength absorption band in the region of 500 - 750 nm and a short-wavelength low-intensity absorption band in the region of 400 - 500 nm (Figure 5). At the same time, the  $\Delta OD(\lambda)$  spectrum with a delay of 100 ps (Figure 3b) demonstrates a fairly good coincidence of both the long-wavelength and short-wavelength bands, indicating the formation of the ring opening product **Q** in the ground state 100 ps after the excitation pulse.



**Figure 5.** Absorption spectra of cyclic (**1b-Sp**) (black curve) and photoinduced opened (**1b-Q**) (red curve) after 365 nm CW irradiation ( $t_{ir}=1300$  s) forms of perimidinespirocyclohexadienone **1b** ( $3.9 \cdot 10^{-5}$  M, 293 K) in cyclohexane.

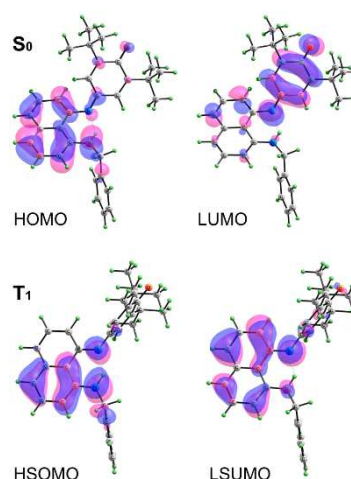
Arising of the above bands immediately after decay of the initial transient absorption indicates that, against the background of the process of internal conversion, molecular isomerization should take place including C-N bond cleavage and intramolecular proton transfer.

Transient absorption spectra shown at Figures 3 and 4 points that the major part of the spectral changes associated with this process turns out to be hidden behind the more intense absorption of  $S_1$ - $S_n$ . However, decay of this band in cyclohexane occurs noticeably faster than in more polar acetonitrile unveiling the final stage of the photoreaction (Figure 3b). As can be seen from the data obtained (Figure 3b), the appearance of the final reaction product is preceded by the formation of a certain intermediate species with transient absorption at 487 nm and above 750 nm. Obviously it cannot be a structure on the  $S_0$  PES, since, as already shown,<sup>[6]</sup> the structure with a broken C-N bond corresponds to the transition state on this surface. On the other hand, if the transition structure belonged to the  $S_1$  PES, then the time constant associated with its transition to the ground state would be comparable with that of internal conversion of the cyclic form **1a-Sp** (Table 1). However, the experiment revealed a significantly slower process with the time constant of 12.4 ps.

Therefore, it is most likely that the unknown intermediate is a reaction product minimum on the  $T_1$  PES. Thus, changes of the transient absorption of **1b** in cyclohexane solution in the time interval of 3 - 100 ps can be attributed to the  $T_1$ - $S_0$  intersystem crossing. Assuming that the transition absorption maxima are fairly close to the position of the corresponding maxima of the stationary spectra, for qualitative assignment of the observed absorption bands, the singlet and triplet stationary spectra of the open isomer **1b-Q** were calculated in the framework of time-dependent density functional theory (TD-DFT) (Tables 3, 4, Figure 6).

**Table 3.** Excitation energies  $E_{ex}$  (eV) (absorption maxima (nm) are given in parentheses) and oscillator strengths  $f$  of the first three singlet transitions of **1b-Q** isomer according to the TD-DFT calculation in cyclohexane solution.

Method of calculation	Transition	$E_{ex}$	$f$
TD-PBE0/6-311+G(d,p)	$S_0 \rightarrow S_1$	1.6790 (738)	0.2044
	$S_0 \rightarrow S_2$	2.5835 (480)	0.0179
	$S_0 \rightarrow S_3$	2.7723 (447)	0.1156
TD-PBE0-1/3/6-311+G(d,p)	$S_0 \rightarrow S_1$	1.9049 (651)	0.2206
	$S_0 \rightarrow S_2$	2.8157 (440)	0.0138
	$S_0 \rightarrow S_3$	3.0114 (412)	0.0990
TD-CAM-B3LYP/6-311+G(d,p)	$S_0 \rightarrow S_1$	2.3662 (524)	0.2331
	$S_0 \rightarrow S_2$	3.0534 (406)	0.0008
	$S_0 \rightarrow S_3$	3.3595 (369)	0.0434
TD-wB97XD/6-311+G(d,p)	$S_0 \rightarrow S_1$	2.4891 (498)	0.2077
	$S_0 \rightarrow S_2$	3.0451 (407)	0.0052
	$S_0 \rightarrow S_3$	3.4988 (354)	0.0243



**Figure 6.** The frontier molecular orbitals involving in the  $S_0 \rightarrow S_1$  (HOMO-LUMO) and  $T_1 \rightarrow T_2$  (HSOMO-LSUMO) transitions of **1b-Q** isomer calculated using PBE0-1/3/6-311+G(d,p) and UPBE0-1/3/6-311+G(d,p) methods in cyclohexane solution. (shown at 0.03 a.u contour threshold)

**Table 4.** Excitation energies  $E_{ex}$  (eV) (absorption maxima (nm) are given in parentheses) and oscillator strengths  $f$  of the first five triplet transitions of **1b-Q** isomer according to the TD-DFT calculation in cyclohexane solution.

Method of calculation	Transition	$E_{ex}$	$f$
TD-UPBE0/6-311+G(d,p)	$T_1 \rightarrow T_2$	1.391 (891)	0.0955
	$T_1 \rightarrow T_3$	1.490 (832)	0.0000
	$T_1 \rightarrow T_4$	2.053 (604)	0.0008
	$T_1 \rightarrow T_5$	2.468 (502)	0.0095
	$T_1 \rightarrow T_6$	2.569 (483)	0.0125
TD-UPBE0-1/3/6-311+G(d,p)	$T_1 \rightarrow T_2$	1.533 (809)	0.1032
	$T_1 \rightarrow T_3$	1.616 (767)	0.0000
	$T_1 \rightarrow T_4$	2.364 (525)	0.0006
	$T_1 \rightarrow T_5$	2.614 (474)	0.0100
	$T_1 \rightarrow T_6$	2.728 (454)	0.0133
TD-UCAM-B3LYP/6-311+G(d,p)	$T_1 \rightarrow T_2$	1.658 (748)	0.1066
	$T_1 \rightarrow T_3$	1.736 (714)	0.0000
	$T_1 \rightarrow T_4$	2.668 (467)	0.0102
	$T_1 \rightarrow T_5$	2.765 (448)	0.0144
	$T_1 \rightarrow T_6$	2.877 (431)	0.0001
TD-UwB97XD/6-311+G(d,p)	$T_1 \rightarrow T_2$	1.637 (757)	0.1049
	$T_1 \rightarrow T_3$	1.690 (734)	0.0000
	$T_1 \rightarrow T_4$	2.611 (475)	0.0103
	$T_1 \rightarrow T_5$	2.740 (452)	0.0178
	$T_1 \rightarrow T_6$	2.889 (429)	0.0008

The best agreement with the experiment for the lowest singlet transition (Table 3) was obtained using PBE0-1/3 functional while CAM-B3LYP and wb97XD overestimated and PBE0 underestimated the excitation energy. Thus, transient absorption maxima at 597 and 439 nm can be attributed to the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transitions, respectively. On the other hand, the lowest triplet excitation (Table 4) is reproduced better in the calculations employing wb97XD and CAM-B3LYP functionals. From this point of view transient absorption maxima at 750 and 487 nm can be assigned to the  $T_1 \rightarrow T_2$  and  $T_1 \rightarrow T_4$  transitions, respectively. The lowest energy singlet transition of **1b-Q** is accompanied by a pronounced charge transfer from pyrimidine to the cyclohexadienone moiety of the molecule, while lowest energy triplet excitation is associated with redistribution of electron density within pyrimidine fragment (Figure 6). Thus, the spectral changes observed in the 3 – 100 ps time interval in cyclohexane can be considered as a decay of the two triplet absorption bands (487 and 750 nm) and the appearance of the new ones related to the ground state (439 and 597 nm).

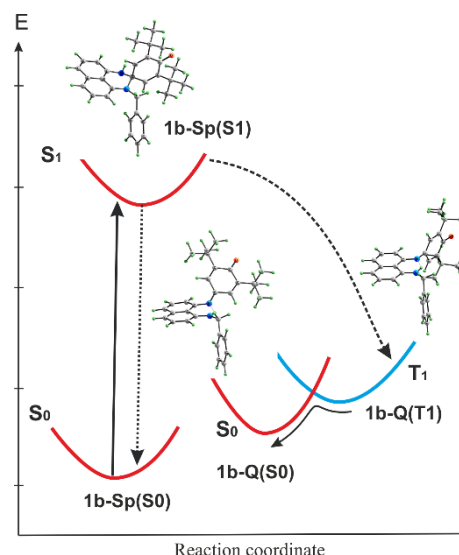
An additional argument in favor of the correctness of the above assignments can be calculated spectral characteristics of the

cyclic isomers of **1a** and **1b** in the ground state, which are in good agreement with experiment. (Tables S1-S4)

**Table 5.** Spectral characteristics of primary photoinitiated processes in perimidinespirocyclohexadienone **1b**.

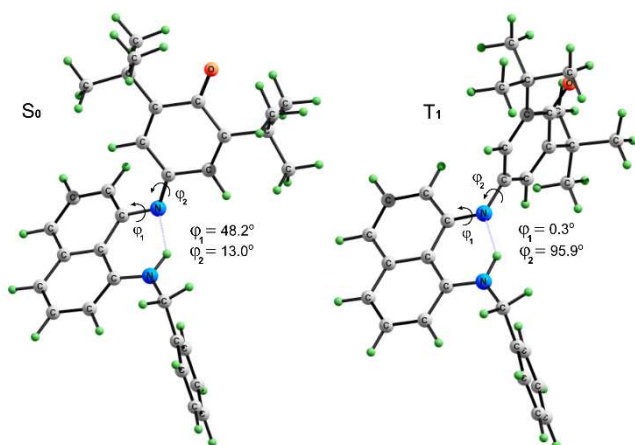
	<b>1b-Sp</b> ( $S_1$ )	<b>1b-Q</b> ( $T_1$ )	<b>1b-Q</b> ( $S_0$ )
Cyclohexane	405, 467, 522sh, 650-750	487, 750	439, 597
Acetonitrile	406, 442, 522sh, 600-730	-	576

Based on theoretical estimates and experimental data (Tables 2 - 5, Figures 2 - 4), the spectral dynamic of **1b** can be considered as follows. Excitation of the cyclic form of spiroperimidines **1b** into the long-wavelength absorption band leads to the population of  $S_1$  excited state of the cyclic isomer **1b-Sp** ( $S_1$ ). Note that no relaxation process from the Franck-Condon region is observed in our case since the bands assigned to the first excited singlet state  $S_1$  do not move over time nor do they exhibit band structuring and narrowing phenomena. This can be explained by the weak excess energy deposited in the  $S_1$  state by the 375 nm laser excitation, weak relaxation phenomena are expected to be observed in this case. The relaxed  $S_1$  state of the cyclic isomer serves as a starting point for two parallel processes: internal conversion of the cyclic isomer to the ground state and the photochemical isomerization including at the final step the formation of the open isomer **1b-Q** ( $T_1$ ) on the  $T_1$  PES, which then converts to the ground state photoproduct **1b-Q** ( $S_0$ ) via  $T_1/S_0$  intersystem crossing (Figure 7).



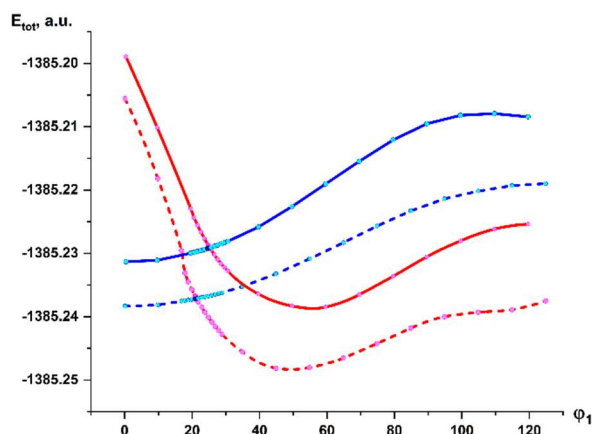
**Figure 7.** Schematic energy profile of ring-opening photoreaction of perimidinespirocyclohexadienone **1b-Sp**

It is logical to assume that the mechanism of the latter includes a certain structural isomerization. As can be seen from the comparison of the structures of the photoproduct in the  $T_1$  and  $S_0$  states (Figure 8), the most probable reaction path leading to  $T_1/S_0$  intersystem crossing will include rotation of the iminocyclohexadienone fragment around the C-N bond associated with a change in the angle  $\phi_1$ .



**Figure 8.** Optimized structures of **1b-Q** isomer on the  $S_0$  and  $T_1$  PES calculated using PBE0-1/3/6-311+G(d,p) and UPBE0-1/3/6-311+G(d,p) methods in cyclohexane solution.

Scanning the  $T_1$  PES along the rotation angle  $\phi_1$  from the minimum point of the open form **1b-Q** ( $T_1$ ) ( $\phi_1 = 0$ ) (Figure 9) revealed the existence of  $T_1/S_0$  intersection point at a rotation angle  $25.3^\circ$  in cyclohexane and  $21.3^\circ$  in acetonitrile.



**Figure 9.** Total energy profiles of **1b-Q** isomer on the  $T_1$  PES along the rotation coordinate  $\phi_1$  (blue) and their projections on the  $S_0$  PES (red) calculated using UPBE0-1/3/6-311+G(d,p) methods in cyclohexane (solid lines) and acetonitrile (dashed lines) solutions.

Thus, in acetonitrile, to reach the  $T_1/S_0$  intersection point, a smaller structural change in **1b-Q**( $T_1$ ) and, accordingly, the associated change in energy are required, which should ultimately lead to an increase in the rate of the transition to the ground state in a more polar medium. On the other hand, decay of the  $S_1 \rightarrow S_n$  absorption band in acetonitrile occurs noticeably slower than in less polar cyclohexane. As a result, this intense absorption totally obscures all the spectral changes accompanying the formation of the photoproduct in the acetonitrile. The opposite situation is observed in cyclohexane, that made it possible to observe spectral changes at the final stage of the reaction. The details of the **1b-Sp**( $S_1$ ) $\rightarrow$ **1b-Q**( $T_1$ ) process associated with the C-N bond cleavage and proton

transfer, in particular, the transition point to the triplet surface, remain unclear and require additional theoretical studies.

As already noted, the observed spectral dynamics of **1b** at the initial stages of the development of photoreaction reflects the occurrence of two parallel processes: internal conversion and photoinduced isomerization. Thus the experimentally obtained time-constant of the transient absorption spectra decay recorded 0.7 ps after excitation may be considered as a gross constants characterizing these processes. In the framework of one experiment, it is impossible to separate the corresponding rate constants. However, an assessment can be made (Table 6), if we assume that the internal conversion of **1b-Sp** ( $S_1$ ) is carried out with an efficiency close to that of the deactivation of the  $S_1$  state of **1a-Sp**.

The data presented in the Table 6 indicate that during the formation of the photoproduct **1b-Q** the fastest process is associated with isomerization of the cyclic isomer from the first singlet excited state into the open form on the  $T_1$  PES, and the slowest is its transformation into the singlet ground state.

**Table 6.** The rate constants of photoinduced transformations in **1b** in cyclohexane solution.

$S_1(S_1) \rightarrow S_1(S_0)$ $\downarrow$ $Q(T_1)$	$S_1(S_1) \rightarrow S_1(S_0)$	$S_1(S_1) \rightarrow Q(T_1)$	$Q(T_1) \rightarrow Q(S_0)$
$k_1 + k_2, 10^{12} \text{ s}^{-1}$ $(1/(k_1+k_2), 10^{-12} \text{ s})$	$k_1, 10^{12} \text{ s}^{-1}$ $(\tau_1, 10^{-12} \text{ s})$	$k_2, 10^{12} \text{ s}^{-1}$ $(\tau_2, 10^{-12} \text{ s})$	$k_3, 10^{12} \text{ s}^{-1}$ $(\tau_3, 10^{-12} \text{ s})$
2.5 (0.4)	0.39 (2.6 <sup>a</sup> )	2.11 (0.47)	0.08 (12.4)

<sup>a</sup> taken from the Table 2

## Conclusion

The spectral pattern of photoinitiated ring-opening dynamics of perimidinespirocyclohexadienone derivatives studied using time-resolved spectroscopy in cyclohexane solution indicated that the formation of the reaction product occurs against the background of the internal conversion of  $S_1$  excited state of the cyclic isomer. No spectral changes indicating the presence of an intermediate after cleavage of the C-N spiro bond and preceding intramolecular proton transfer were detected. The final stage of ring-opening process includes the formation of the open isomer on the triplet surface with a subsequent transition to the ground state via  $T_1-S_0$  intersystem crossing as a result of rotation of the iminocyclohexadienone fragment. According to the theoretical estimates in a more polar medium the rate of this transition will increase. An approximate evaluation of the rate constants of the observed processes revealed the significant differences between them. The formation of the reaction product in the triplet state is the fastest process, and its transition to the singlet state is the slowest.

TD-DFT calculations of the spectral properties of the open isomer in the singlet and triplet states verified the assignment of the recorded spectra.

The mechanism of formation of the photoproduct in the  $T_1$  state after excitation remains unclear and requires additional research.

## Experimental Section

Perimidinespirocyclohexadienones 1a,b were synthesized, purified by alumina column chromatography with hexane/toluene (2.5:1), recrystallized from 1-propanol (1a) and octane (1b), and provided to us by Dr. V. Komissarov [10,11]. Compounds purity is better than 95%.

1',3'-Dibenzyl-3,5-di-tert-butyl-1'H,3'H-spiro[cyclohexane-1,2'-perimidine]-2,5-dien-4-one (1a). Yellow crystals from 1-propanol. M.p. 192-194 °C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ, ppm): 1.02 (s, 18 H, tert-C<sub>4</sub>H<sub>9</sub>), 4.47 (s, 4 H, CH<sub>2</sub>), 6.56 (s, 2 H, H-2, H-6), 6.48-7.40 m (16 H, ArH). Elemental analysis calcd for C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O, %: C 84.41; H 7.46; N 5.18, found, %: C 84.47; H 7.40; N 5.02.

1'-Benzyl-3,5-di-tert-butyl-1'H,3'H-spiro[cyclohexane-1,2'-perimidine]-2,5-dien-4-one (1b). Dark yellow crystals from octane. M.p. 161-163 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>NO<sub>2</sub>, δ, ppm): 1.20-1.40 (m, 18 H, tert-C<sub>4</sub>H<sub>9</sub>), 4.27 (s, 2 H, CH<sub>2</sub>), 5.75 (s, 1 H, NH), 6.69 (m, 1 H, ArH), 6.94 (s, 2 H, H-2, H-6), 7.03 (m, 1 H, ArH), 6.70-7.62 (m, 9 H, ArH). Elemental analysis calcd for C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>O, %: C 82.76; H 7.61; N 6.22, found, %: C 82.97; H 7.55; N 6.29.

Spectrophotometric grade acetonitrile and cyclohexane solvents were obtained from Aldrich. The <sup>1</sup>H NMR spectra were obtained on "Varian Unity-300" (300 MHz) spectrometer at 20 °C, the signals were referred with respect to the signal of residual protons of deuterio-solvent CDCl<sub>3</sub>. The electronic absorption spectra and kinetic curves of thermal recyclization reactions of the studied compounds have been recorded on an "Agilent 8453" spectrophotometer equipped with a temperature-controlled cell. Irradiation light was brought into the thermostated cell compartment at 90° from a 200 W high-pressure mercury lamp "Newport" equipped with glass filters for allocation of mercury lines. The irradiation intensity has been calculated using light power measurement data with a "Newport 2935" optical power meter. The irradiation intensity at 365 and 546 nm has been found to be (0.8–1.2)·10<sup>-5</sup> and (0.6–1.1) 10<sup>-4</sup> Einstein L<sup>-1</sup> s<sup>-1</sup> correspondingly. Fluorescence emission was tested using an Eclipse Varian spectrofluorimeter. All measurements were performed on 10<sup>-3</sup>M solutions circulating in a 2 mm thick flow cell (equipped with 200 μm thick CaF<sub>2</sub> windows). The apparatus used for obtaining the femtosecond transient absorption measurements has been described previously.[12] In the present investigation, 377 nm pump pulses (100 fs, 1 kHz) were obtained by frequency doubling the output of the amplified Ti-Sapphire laser tuned at 756 nm in a 300 lm thick BBO Crystal. The pump energy at the sample was ~10 μJ (~1 mJ/cm<sup>2</sup>). The broadband white light continuum probe pulses were generated by focusing 756 nm, 1 μJ pulses in a CaF<sub>2</sub> plate. In order to avoid rotational diffusion effects on the absorption spectra, the pump polarization was set at the magic angle (54.7°) relative to the probe. Spectra were recorded over the 400–740 nm spectral ranges and were corrected from GVD effects. The time resolution measured within the 2 mm thick flow cell was better than 300 fs.

## Computational Section

All computations were carried out with Gaussian 09<sup>[13]</sup> program package by means of DFT and TD-DFT methods. Since the accuracy of such calculations varies greatly, depending on the type of functional choice and the nature of a particular electronic transition,<sup>[14]</sup> along with conventional parameter-free hybrid density functional PBE0<sup>[15]</sup>, long-range corrected functionals ωB97XD<sup>[16,17]</sup> and CAM-B3LYP<sup>[18]</sup> were used as well as modified version of PBE0 - functional PBE0-1/3<sup>[19]</sup> comprising the PBE generalized-gradient functional with a predefined amount of exact exchange of 1/3. 6-311+G(d,p) and 6-31G(d,p) sets were applied to the calculations of **1b** and **1a** derivatives, respectively. Frequency calculations at the optimized geometries were performed to confirm that the structures were at local minima. The singlet and triplet transition energies of species interested were obtained with TD-DFT methodology at the same level of approximation. The polarizable continuum model (PCM)<sup>[20-22]</sup> is used for evaluating the (bulk) solvent effects. Unrestricted calculations were employed for the open shell systems.

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