

Effect of steric *para*-tert-butyl substitutes on primary photoprocesses in stilbene

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Introduction of steric *para*-tert-butyl substitutes was shown to stabilize the structure of molecules in the near-planar *trans*-form. The symmetrical introduction of two tert-butyl substitutes led to changes of fluorescent and lasing properties of molecules. In that case, the probability of *trans* → *cis*-isomerization in **III** molecule decreased, but *cis* → *trans*-isomerization probability in **IV** increased conversely, and the molecule fluoresced. The emitting property of stilbene was improved several times at such substitutes.

Introduction

Thanks to nonrigid structure of the stilbene molecule (Ph–CH=CH–Ph) at radiative excitation, phenyl rings may rotate around the double bond, which leads to the competition between radiative and nonradiative processes. One of the primary ultraspeed photoprocesses in stilbene is *photoisomerization* that proceeds for a femtosecond interval and leads to weak fluorescence and lasing of the compound (the quantum yield of fluorescence is ~ 0.03–0.08 depending on the properties of a medium^{1–3}).

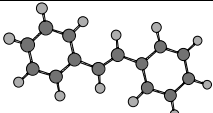
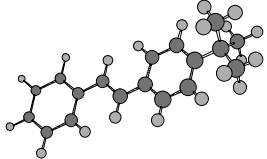
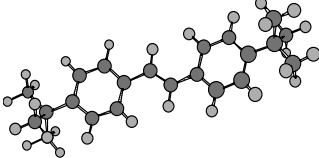
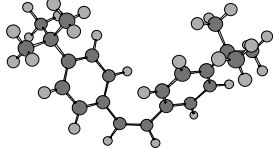
Earlier we have reviewed various mechanisms of this reaction for stilbene, in particular, we described the singlet and triplet mechanisms.⁴ One of the commonly recognized ways of *trans*-stilbene isomerization is rotation of phenyl rings around the ethylene bond in S_1^* state of $\pi\pi^*$ -type. The potential barrier for the rotational motion in the first excited state for *trans*-

stilbene is so low (~ 14 kJ/mol for the *trans*-species and ~ 5 kJ/mol for the *cis*-species³), that the possibility to obtain fluorescence and lasing of the compound and its substituted species is determined only by the external experimental conditions. Earlier^{5,6} we have described in detail the experiment on obtaining *trans*-stilbene lasing and the corresponding experimental conditions.

Introduction of substitutes of various nature and geometry significantly affect the primary photoprocesses in stilbene and its spectral-luminescent properties. The effect of the position of the steric substitute and its nature on the properties of a molecule was demonstrated in Refs. 5 and 7, which treated the methyl-substituted structures in different positions.

This paper is devoted to the effect of steric tert-butyl substitutes on the reaction of photoisomerization and changes in the spectral-luminescent properties of the stilbene molecule. The structure of the objects under study is summarized in Table 1.

Table 1. Structure of the molecules under study

Compound	Title	Structure	Substitutes
I	<i>Trans</i> -stilbene		—
II	4- <i>Trans</i> -tert-butyl-stilbene		<i>para</i> -C(CH ₃) ₃
III	4,4'- <i>Trans</i> -ditertbutyl-stilbene		<i>para</i> -C(CH ₃) ₃
IV	4,4'- <i>Cis</i> -ditertbutyl-stilbene		<i>para</i> -C(CH ₃) ₃

The experimental technique of studying the spectral-luminescent properties and the layout of the experimental setup were described in detail in Ref. 5. To understand the observed properties of the compounds, we have analyzed the photoprocesses in the stilbene molecule (**I**) and its tert-butyl substituted species (**II–IV**), using theoretical methods of quantum chemistry, as well as considered the effect of nonradiative processes on quenching the luminescence.

To optimize the geometry of the chosen objects, we used ChemOffice 6.0 software (including Chem3D Pro 5.0 and ChemDraw Pro 5.0), which allows the simulation and analysis of chemical structures and has a convenient graphical interface. Chem3D Pro 5.0 employs the methods based on the molecular mechanics and used for quantum-chemical calculations, as well as semiempirical methods (AM1, PM3, MINDO/3, MNDO, MNDO-d) for optimization of the model, conformational search, molecular dynamics, etc.⁸ The spectral-luminescent properties were calculated using our original software based on the quantum-chemical method of partial neglect of differential overlap with spectroscopic parameterization (PNDO/S).^{9–11} Such complex approach permitted us to conduct the conformational analysis of the chosen objects, construct the energy level structures for them, and estimate the rate constants of different photoprocesses in molecules after radiational excitation.

Results and discussion

Introduction of substitutes of the methyl and butyl types usually has no effect on the nature of absorption bands, leading to their broadening and blurring of the vibrational structure, as well as bathochromic shift.¹² The main role of these substitutes

is to change the geometry of the molecule, which results in variation of photophysical and spectral-luminescent properties of the initial compound.

Table 2 summarizes the experimental spectral-luminescent characteristics of the studied compounds in ethanol and hexane solutions. As can be seen, the peak of the longwave band in the absorption spectra of dissolved stilbene and its substituted species falls within the interval of 300–320 nm with a partly resolved vibrational structure. All the compounds under study demonstrate breakdown of the mirror symmetry in the absorption and fluorescence spectra and the large Stokes shift $\Delta\nu \sim 4000 \text{ cm}^{-1}$, indicating a change of the molecular geometry in the excited state.¹³

Trans-stilbene (**I**) is a weakly fluorescing compound with the quantum yield of 0.05 in ethanol and 0.11 in hexane (Table 2). Introduction of two steric tert-butyl substitutes in the *para*-form practically does not change the form of the spectra with respect to *trans*-stilbene itself, but almost threefold increases the quantum yield of fluorescence (for molecule **III** it is 0.18 in ethanol and 0.31 in hexane).

The *cis*-form of stilbene does not fluoresce because of practically barrierless photoisomerization. Appearance of fluorescence in *cis*-form **IV** (with the quantum yield of 0.16 in ethanol and 0.2 in hexane) is indicative of the important role of steric substitutes in the reaction of isomerization. Besides, molecule **IV** generated laser radiation (1–2 pulses were observed).

The calculated spectral characteristics for *trans*-stilbene are given in Tables 3 and 4, and the scheme of excited electronic states is depicted in Fig. 1, where arrows show different photoprocesses in the molecule and their constants (full data on calculation of plane *trans*-stilbene are presented in Ref. 4).

Table 2. Spectral-luminescent properties of *trans*-stilbene and its substituted species as obtained experimentally in ethanol and hexane

Compound	λ_{abs} , nm		$\varepsilon \cdot 10^{-3}$, liter/(mol · cm)		λ_{fl} , nm		Φ_{fl}		$\Delta\nu$, cm^{-1}	
	ethanol	hexane	ethanol	hexane	ethanol	hexane	ethanol	hexane	ethanol	hexane
I	308	308	25.8	30.8	348	346	0.05	0.11	3200	3600
II	313	312	31.4	40.0	354	355	0.06	0.07	3660	3930
III	316	315	35.0	29.3	358	358	0.18	0.31	3760	3770
IV	304	304	11.0	27.5	359	357	0.16	0.2	5030	4840

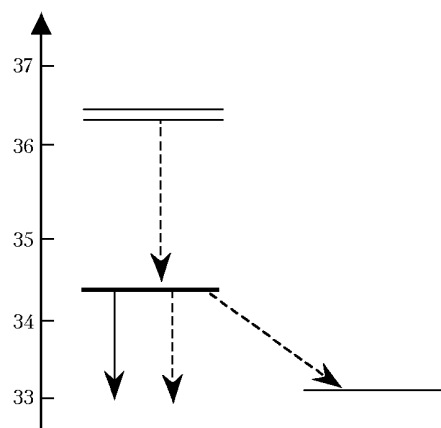
Table 3. Energies (ε_j) and types of molecular orbitals (MO), energies (E_i) and types of electronic $S_0 \rightarrow S_i$ transitions, configurational (RV) structure of the plane molecule **I***

MO number	ε_j , eV	Transition	E_i , cm^{-1}	RV structure
32	−9.30	1 $\pi\pi^*$	34294	0.968 34 \rightarrow 35) + 0.150 34 \rightarrow 36) + 0.164 31 \rightarrow 38)
33	−9.30	2 $\pi\pi^*$	36202	0.665 34 \rightarrow 37) + 0.477 32 \rightarrow 35) + 0.397 31 \rightarrow 36)
34(LUMO)**	−7.68	3 $\pi\pi^*$	36206	0.647 34 \rightarrow 36) − 0.490 33 \rightarrow 35) + 0.386 31 \rightarrow 37)
35(HOMO)***	0.41	4 $\pi\sigma^*$	38845	0.955 34 \rightarrow 39) + 0.241 31 \rightarrow 40) − 0.146 29 \rightarrow 39)
36	1.58	5 $\pi\sigma^*$	41203	0.929 34 \rightarrow 40) + 0.283 31 \rightarrow 39) − 0.138 31 \rightarrow 44)

* Theoretical values as calculated by the PNDO/S method. ** The lowest unoccupied molecular orbital. *** The highest occupied molecular orbital.

Table 4. Spectral characteristics and rate constants of photoprocesses in plane *trans*-stilbene molecule as calculated by the PNDO/S method (FC state)

State (S_i)	λ_{abs} , nm	Type	Oscillator strength	Constants, s^{-1}
S_1	292	$\pi\pi^*$	1.210	$k_r(S_1 \rightarrow S_0) = 10^9$ $k_{ic}(S_1 \rightarrow S_0) = 10^4$ $k_{isc}(S_1 \rightarrow T_7) = 7 \cdot 10^8$
S_2	276	$\pi\pi^*$	0.029	
S_3	276	$\pi\pi^*$	0.041	
S_4	257	$\pi\sigma^*$	0.000	
S_5	243	$\pi\sigma^*$	0.002	

**Fig. 1.** Scheme of energy levels for plane *trans*-stilbene (I in Table 1) as calculated by the PNDO/S method: radiative (—) and nonradiative (---) photoprocesses.

The longwave absorption band is formed by the intense $\pi\pi^*$ -transition $S_0 \rightarrow S_1^*$ with the wavelength of 292 nm and the oscillator strength ~ 1.21 . According to the calculation, the radiative constant from state S_1^* was $\sim 10^9 s^{-1}$, and the constant of nonradiative internal conversion into state S_0 was $\sim 10^4 s^{-1}$. Along with nonradiative deactivation of the singlet state energy, efficient intercombination conversion into T_7^* -state due to the nonradiative channel: $S_1\pi\pi^* \rightarrow T_7\pi\pi^*$ [$k_{isc} = 7 \cdot 10^8 s^{-1}$] with the following degradation by

the system of triplet states down to T_1 is possible. As can be seen, two photoprocesses in the Frank–Condon (FC) excited state, namely, the radiative process and the intercombination conversion compete with each other.

According to the quantum-chemical calculations for the plane *trans*-stilbene molecule in state S_1 , the significant part of the charge from the phenyl rings flows to the atoms of the double bond. The considerable increase in population of the atoms of $-C=C-$ bond, being in sp^2 -hybridization, can lead to transition into sp^3 -hybridization, which is accompanied by elongation of this bond and possible rotation of phenyl fragments in the molecule.¹⁴ Table 5 summarizes the populations P_{AB} of the bonds for plane *trans*-stilbene in the ground and excited fluorescence states as calculated by the PNDO/S method, as well as the bond lengths in these states estimated according to the population values. As can be seen, the geometry of the molecules in the steady fluorescent (SF) state differs from that in the Frank–Condon (FC) state. The bond between the 7th and 8th carbon atoms of the double bond elongates ($l(\text{SF}) = 1.34 \text{ \AA}$; $l(\text{FC}) = 1.42 \text{ \AA}$), while those between the 4th, 7th, and 8th, 9th atoms shorten by 0.04 \AA .

These data were used to model the structure of *trans*-stilbene in SF state S_1^* according to the data from Table 5 and to calculate its spectral-luminescent characteristics. The change of the molecular geometry leads to significant bathochromic shift of the first $\pi\pi^*$ -transition ($\Delta\nu \sim 4000 \text{ cm}^{-1}$). The triplet level T_7^* is close to the state S_1^* and has a strong spin-orbital interaction with it, which leads to the increase of the constant of intercombination conversion up to $10^{10} s^{-1}$. Therefore, the theoretical quantum yield of fluorescence of *trans*-stilbene is 0.05, which coincides with the experimentally observed one.

Optimization of the geometry of the tert-butyl substituted structures by the AM1 and PM3 methods has shown that molecule **II** can exist in the plane conformation, as the *trans*-form of molecule **III**.

Table 5. Calculated populations (P_{AB}) and bond lengths (l , \AA) for *trans*-stilbene

Bond	$P_{AB}(S_0)$	$P_{AB}(S_1)$	$l(\text{FC})$, \AA	$l(\text{SF})$, \AA
1–2 (12–13)	0.921	0.883	1.3954	1.4106
1–6 (11–12)	0.924	0.886	1.3939	1.4091
2–3 (13–14)	0.926	0.951	1.3917	1.3817
5–6 (10–11)	0.926	0.952	1.3937	1.3833
3–4 (9–14)	0.980	0.906	1.4067	1.4363
4–5 (9–10)	0.986	0.911	1.4025	1.4325
4–7 (8–9)	0.834	0.934	1.4526	1.4126
7–8	1.068	0.877	1.3438	1.4202

Introduction of steric tert-butyl substitutes leads to stabilization of the molecules in the ground-state plane conformations, which best describe the experimental absorption spectra. The structure of molecule **IV** in the *cis*-form has the twist and torsion angles (rotations of the phenyl rings around the double and single bonds) $\theta = 45^\circ$ and $\varphi = 30^\circ$ (for the structures see Table 1).

Table 6. Calculated spectral characteristics and rate constants of different photoprocesses in molecule **II in FC state**

State (S_i)	λ_{abs} , nm	Type	Oscillator strength	Constants, s^{-1}
S_1	295	$\pi\pi^*$	1.337	
S_2	283	$\pi\pi^*$	0.056	$k_r(S_1 \rightarrow S_0) = 10^9$
S_3	277	$\pi\pi^*$	0.037	$k_{ic}(S_1 \rightarrow S_0) = 10^5$
S_4	259	$\pi\sigma^*$	0.000	$k_{isc}(S_1 \rightarrow T_7) = 10^7$
S_5	243	$\pi\sigma^*$	0.042	

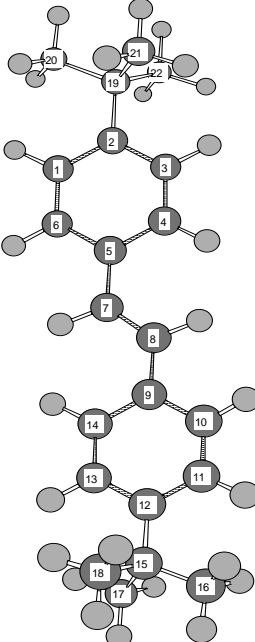
Analysis of the calculated spectral-luminescent characteristics of molecule **II** shows that introduction of only one substitute in the *para*-form produces no significant changes in the scheme of energy levels of the molecule (Table 6). Spectrally, a small longwave shift is observed, along with the increase of the oscillator strength ~ 1.34 of the first intense $\pi\pi^*$ -transition forming the band peak. Weak fluorescence of molecule **II** (with the quantum yield of 0.06 in ethanol and 0.07 in hexane) indicates that this substitution is a weak obstacle for photoisomerization at radiative excitation.

Symmetric introduction of two steric tert-butyl substitutes into *trans*-stilbene leads to prevalence of radiative decay after excitation with the geometry unchanged (FC state). As compared to it, the rate of nonradiative and intercombination conversion for molecule **III** decreases four orders of magnitude ($k_r = 10^9 s^{-1}$, $k_{ic} = 10^5 s^{-1}$, $k_{isc} = 10^5 s^{-1}$ in Table 7).

Table 7. Calculated spectral characteristics and rate constants of photoprocesses in *cis*- and *trans*-forms of molecules **III and **IV** in the FC state**

Structure	State (S_i)	λ_{abs} , nm	Type	Oscillator strength	Constants, s^{-1}
III	S_1	300	$\pi\pi^*$	1.412	
	S_2	284	$\pi\pi^*$	0.001	$k_r(S_1 \rightarrow S_0) = 10^9$
	S_3	283	$\pi\pi^*$	0.112	$k_{ic}(S_1 \rightarrow S_0) = 10^5$
	S_4	263	$\pi\sigma^*$	0.000	$k_{isc}(S_1 \rightarrow T_7) = 10^5$
	S_5	246	$\pi\sigma^*$	0.000	
IV	S_1	290	$\pi\pi^*$	0.489	
	S_2	285	$\pi\pi^*$	0.171	$k_r(S_1 \rightarrow S_0) = 10^8$
	S_3	279	$\pi\pi^*$	0.015	$k_{ic}(S_1 \rightarrow S_0) = 10^5$
	S_4	257	$\pi\sigma^*$	0.001	$k_{isc}(S_1 \rightarrow T_7) = 10^{10}$
	S_5	250	$\pi\sigma^*$	0.010	

Table 8. Populations (P_{AB}) and bond lengths (l , Å) for molecule **III as calculated by the PNDO/S method**

	Bond	$P_{AB}(S_0)$	$P_{AB}(S_1)$	$l(\text{FC})$, Å	$l(\text{SF})$, Å
	1–2 (11–12)	0.985	0.944	1.3996	1.4160
1–6 (10–11)	0.913	0.939	1.3919	1.3815	
2–3 (12–13)	0.978	0.934	1.4027	1.4203	
5–6 (9–10)	0.982	0.910	1.395	1.4238	
3–4 (13–14)	0.928	0.953	1.391	1.3810	
4–5 (9–14)	0.981	0.914	1.4025	1.4293	
5–7 (8–9)	0.837	0.933	1.4518	1.4134	
8–7	1.069	0.895	1.3441	1.4137	
12–15 (2–19)	0.804	0.808	1.5053	1.5037	

However, due to the decrease in the population of the double bond in state S_1^* of molecule **III** (Table 8) at excitation, after the vertical FC transition the bond lengths in the molecule redistribute, and the molecule relaxes into the SF state. At such a change in the geometry, the radiative constant decreases as compared to the intercombination constant ($k_r = 8 \cdot 10^8 \text{ s}^{-1}$, $k_{ic} = 10^6 \text{ s}^{-1}$, $k_{isc} = 2 \cdot 10^9 \text{ s}^{-1}$). In this case, the theoretical quantum yield of fluorescence of molecule **III** is 0.28. Ultraspeed *trans* \rightarrow *cis*-isomerization in the excited state is still efficient, but symmetric introduction of tert-butyl substitutes reduces its probability, hampering rotation of the phenyl rings and, correspondingly, the reaction itself.

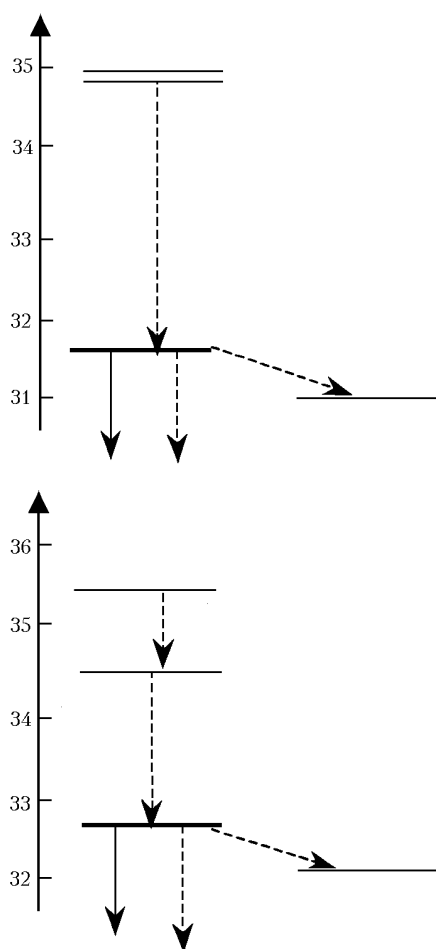


Fig. 2. Schemes of energy levels of *cis*- and *trans*-molecules **III** and **IV** as calculated by the PNDO/S method: radiative (—) and nonradiative (----) photoprocesses.

According to the calculations, for the *cis*-form of molecule **IV** in the FC state, the main channel for degradation of the excitation energy is intercombination conversion with the constant $k_{isc} = 10^{10} \text{ s}^{-1}$ (see Table 7 and Fig. 2) because the triplet level T_7^* is close to the level S_1^* . The prevalence of nonradiative photoprocesses and the low intensity of transition $S_0 \rightarrow S_1^*$ (with the oscillator strength ~ 0.49) must lead to the absence of fluorescence, characteristic of all the *cis*-forms of

stilbene, in molecule **IV**. However, this molecule still has the quantum yield of 0.16 in ethanol and 0.2 in hexane, which is quite comparable with that of the *trans*-form of molecule **III**. *Cis*-isomers **IV** absorb in the shorter-wave region as compared to *trans*-forms **III**, but the peaks in the fluorescence spectra of the both compounds fall at the same wavelengths (see Table 7), and the quantum yields of fluorescence of the both compounds are also close.

The calculations of the bond populations showed that the transition into S_1^* (FC) excited state is accompanied by loosening of the $-\text{C}=\text{C}-$ bond. Symmetric introduction of two steric tert-butyl substitutes into *cis*-stilbene facilitates *cis* \rightarrow *trans*-isomerization. As a consequence, molecule **IV** relaxes into the SF state with the flat *trans*-conformation. This is indicated by the dependence of the total molecular energy on the conformation of molecules **III** and **IV** in the excited FC and SF states (Table 9). It can be seen from Table 9 that after efficient *cis* \rightarrow *trans*-isomerization the *cis*-form of molecule **IV** relaxes to the flat *trans*-conformation with the total energy of -655.1 and -654.5 eV, while the total energy of the *trans*-form of molecule **III** in the SF state is -655.5 eV. Thus, it can be concluded that molecules **III** and **IV** on the potential surface of excited S_1^* state after the Frank–Condon transition fall in the same potential minimum, from which they then transit radiatively into the ground state.

Table 9. Dependence of the total molecular energy on conformation for molecules **III** and **IV** in S_1^* state

Conformation	Excited state	Energy, eV
<i>Trans</i> -form III	FC	-666.3
<i>Trans</i> -form III	SF	-655.5
<i>Cis</i> -form IV	FC	-523.5
<i>Cis</i> -form IV	SF	-627.8
<i>Trans</i> -form IV (torsion angle of 20°)	SF	-655.1
<i>Trans</i> -form IV plane	SF	-654.5

Conclusions

Thus, we have shown that

– the main competitive photoprocesses for the nonrigid structure of stilbene are the radiative process and nonradiative intercombination conversion;

– the molecular geometry and bond lengths change at excitation of the molecule. In particular, elongation of the double bond leads to the possibility of rotation of the phenyl rings around it and isomerization in excited S_1^* state, and the ring rotations result in the significant bathochromic shift of the first $\pi\pi^*$ -transition ($\Delta\nu \sim 4000 \text{ cm}^{-1}$). The constant of intercombination conversion increases up to 10^{10} s^{-1} , which leads to a low quantum yield of fluorescence of the molecules;

– introduction of steric tert-butyl substitutes stabilizes the molecular geometry in the plane *trans*-form, while symmetric introduction of two substitutes

in the *para*-form changes the fluorescent and lasing properties. The probability of *trans* → *cis*-isomerization in molecule **III** decreases, while the probability of *cis* → *trans*-isomerization in molecule **IV** increases, and the molecule transits into the luminescent form. As a consequence, the emitting properties of the substituted molecules improve several times;

– the strongest factor affecting photoisomerization and phototransformations of the molecules is creation of the corresponding external conditions, under which the nonradiative processes begin to compete with the radiative ones.

Acknowledgments

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