

# Investigation of spatial structure, spectral and photophysical properties of stilbene-substituted (1.4-bis(styryl)benzene, 4-phenylstilbene)

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The geometry of stilbene-substituted (4-phenylstilbene (II), 1.4-bis(styryl)benzene (III)) was investigated by methods of quantum chemistry. The spectral-luminescent characteristics and rate constants of various molecular photoprocesses are calculated. From calculations, high oscillatory force of the first  $\pi\pi^*$ -transition and the predominance of radiation constant over the rest photoprocesses cause the high luminescent properties of the compounds. The substitution leads to increase of the quantum yield of molecular luminescence by several times (for II – 0.95 in heptane; for III – 0.7 in toluene).

Molecules with «nonrigid» structure,<sup>1,2</sup> such as stilbene and its substituents<sup>3–5</sup> are of a special interest nowadays. It is explained by wide prospects in practical use of their optical properties. Specifically, a series of stilbene-substituted with good luminescent properties and photostability can be applied as active mediums for lasers in dyes of the blue–green range.<sup>6</sup> And, on the contrary, using the definite types of substituents, one can obtain the compounds with good nonlinear optical properties, which can be applicable for limiting the high-power optical radiation (optical radiation limiters).

Besides, the stilbene-substituted are efficiently used at present for obtaining films with photosensitive properties, and when producing systems for information recording and reproduction. Therefore, studying of spectral molecular properties, photophysical processes, and the influence of substituents on primary photoprocesses in stilbene, is of great importance.

However, some problems concerning the primary stilbene photoisomerization have not been studied yet. The lifetime of the electronically excited stilbene molecule in the  $S_1^*$ -state makes about 320 fs at  $\lambda = 312$  nm.<sup>7</sup> Excitation leads to the vibration-hot intermediate products, which are formed for several hundreds of femtoseconds.<sup>8</sup>

There is a great deal of opinions about isomerization mechanism. Some works<sup>9,10</sup> present the review of suggested singlet and triplet photoisomerization mechanisms, but somewhat consensus is absent up to now. The Nobel winner Ahmed Zewail<sup>7,11</sup> had conducted investigations with the use of femtosecond technology and femtochemistry, which, possibly, will solve the problem.

The results of theoretical quantum-chemical investigation of a series of *cis*- and *trans*-stilbene conformers allow describing the photoisomerization mechanism. As follows from calculations of

populations and bond lengths in the ground and excited stilbene states, and on the basis of Ref. 12, the stilbene excitation leads to the increase in population of the  $\pi$ -atomic orbitals of  $-C=C$ -bond, being in  $sp^2$ -hybridization. It can lead to the transition into  $sp^3$ -hybridization of these atoms and the double link elongation that admits rotation of phenyl rings around it (isomerization). Thus, the molecular geometry is subjected to changes at excitation with predominance of nonradiative photoprocesses.<sup>13</sup>

As it was shown earlier, the nature and the geometry of the substituent, as well as its position at substitution appreciably affect the stable isomers, their spectral-luminescent properties and primary photoprocesses. Specifically, the introduction of space groups (for instance, such as  $-CH_3$ ) in *ortho*- and  $\alpha$ -position (introduction of substituent into the ethylene unit of  $-C=C-$  stilbene) leads to the steric *cis*-forms and nonradiative properties. Introduction of basic centers (for instance, nitrogen atom into one of phenyl rings), which affect the charge density distribution in the molecule, three-fold increases the fluorescence quantum yield in comparison with *trans*-stilbene.<sup>14</sup>

The introduction of two volume tertbutyl-substituents into the *para*-position also causes a significant increase of the quantum yield.<sup>13</sup> In this case, the emergence of *cis*-form of the tertbutyl-substituted molecule specifies a great value of volume substituents in the isomerization reaction. Besides, the *cis*-forms of stilbene-tertbutylsubstituted, and the products of stilbene ring formation (phenanthrene and its substituents) show bright nonlinear optical properties,<sup>15</sup> that makes them prospective for using as optical radiation limiters.

This work is dedicated to theoretical investigations of the stilbene-substituted spectral-luminescent and photophysical properties by quantum chemistry methods: 4-phenylstilbene (II) and 1.4-bis(styryl)benzene (III) (Table 1), as well as to the

effect of substitution on spectral properties and photoisomerization. These compounds are known as good luminophores; however, the reasons of these radiative properties and the photoprocesses in these compounds are of a special interest.

**Table 1. Structure of the investigated molecules**

№	Name	Structure
I	<i>trans</i> -Stilbene	<i>trans</i> -Ph-HC=CH-Ph
II	4-phenylstilbene	Ph-HC=CH-Ph-Ph
III	1,4-bis(styryl)benzene	Ph-HC=CH-Ph-HC=CH-Ph

The scientific group of the Institute of Single Crystals in Khar'kov<sup>16</sup> has synthesized these structures and the experts of the Siberian Physicotechnical Institute<sup>17</sup> have analyzed their spectral-luminescent properties presented in Table 2.

**Table 2. Experimental spectral-luminescent properties of the compounds<sup>17,18</sup>**

№	$\lambda_{\text{abs}}$ , nm	$\varepsilon \cdot 10^{-3}$ , l/(mole · cm)	$\lambda_{\text{fl}}$ , nm	$\varphi_{\text{fl}}$	$\Delta\nu$ , cm <sup>-1</sup>
I	308	25.8	348	0.05	3200
II	327	38.5	376	0.90	3900
III	357	59.0	413	0.78	4000

Note.  $\lambda$  is the wavelength;  $\varphi_{\text{fl}}$  is the fluorescence quantum yield;  $\Delta\nu$  is the Stokes shift

Table 2 shows that luminescent characteristics of the molecules II and III are appreciably improved as compared to the *trans*-stilbene themselves; the substitution has led to a considerable increase in the fluorescence quantum yield of the compounds: 0.9 in toluene for II; 0.78 in heptane for III. The role of photoisomerization is reduced in this case, and the probability of radiation process from the excited state is increased.

Optimization of molecular geometry of II and III by the semiempirical methods AM1 and PM3 points that molecules in the ground state exist predominantly in the plane *trans*-form. Addition of a phenyl ring for the molecule II or the phenyl ring with one more ethylene link (-CH=CH-Ph, molecule III) in *pair*-position of the *trans*-stilbene leads to the molecular geometry stabilization in plane conformations described by the experimental absorption spectra of the compounds.<sup>18</sup>

For studying the photophysical and spectral properties of molecules II and III, the quantum-chemical calculations were conducted by the INDO/S method, which allows obtaining the broad spectral information: energies of the excited states, moments and forces of oscillators for transitions, nature of absorption bands, rate constants of different processes occurring in the molecule after excitation by light.<sup>19,20</sup> Table 3 presents the calculated data for the investigated molecules.

Complementary addition of a phenyl ring to the *pair*-position of the *trans*-stilbene leads to the increase of the conjugated  $\pi$ -system of the molecule and to the objective long-wave shift in the absorption spectrum. However, transition and form of the spectrum do not change appreciably in this case. The force of the oscillator and intensity of the first  $\pi\pi^*$ -transition were increased. Calculation of population and bond lengths for the molecule II in the ground and excited  $S_1^*$ -states shows only insignificant change in geometry at excitation of the molecule II. Thus, the rate of radiation photoprocess is much higher, than nonradiative internal and intersystem conversions. High theoretical value of the fluorescence quantum yield of the compound II ( $\varphi_{\text{fl}} \sim 0.95$ ) agrees with experimental value.

As well as in *trans*-stilbene, the intensive maximum in absorption and fluorescence spectrum forms the  $\pi\pi^*$ -transition  $S_0 \rightarrow S_1^*$  in the molecule III, polarized along the long molecular axis. Addition of one more ethylene link with a phenyl ring (-CH=CH-Ph) in *pair*-position of the *trans*-stilbene leads to the double increase in oscillator force of the first intensive transition. A significant bathochromic shift is observed in the absorption spectrum for III as compared to the stilbene. Calculation of population and bond lengths for III in the ground and excited  $S_1^*$ -state specifies a weak change in ethylene link lengths at excitation in several parts per hundreds of angstrom. Thus, unlike the *trans*-stilbene, for which excitation causes the double link loosening and rotation of phenyl rings, this process does not occur in the molecule III; the probability of photoisomerization is small; the molecules remain predominantly in *trans*-conformations.

**Table 3. Spectral characteristics, constants of photoprocesses, bond populations of the molecular *trans*-forms, calculated by the INDO/S method, and bond lengths**

№	Frank-Condon state				Fluorescent $S_1^*$ -state				
	$S_i$	$\lambda_{\text{abs}}$ , nm	$f$	$k$ , c <sup>-1</sup>	$P_{AB}$ and $l$ , Å	$\lambda_{\text{fl}}$ , nm	$f$	$k$ , c <sup>-1</sup>	$P_{AB}$ and $l$ , Å
I	1 $\pi\pi^*$	292	1.21	$k_r \sim 10^9$ $k_{ic} \sim 10^4$ $k_{isc} \sim 7 \cdot 10^8$	$P_{AB}(-C=C-) = 1.068$ $P_{AB}(-C-C=C) = 0.834$ $l(-C=C-) = 1.344$ $l(-C-C=C) = 1.453$	334	1.37	$k_r \sim 8 \cdot 10^8$ $k_{ic} \sim 3 \cdot 10^5$ $k_{isc} \sim 10^{10}$ $\varphi_{\text{fl}} \sim 0.07$	$P_{AB}(-C=C-) = 0.877$ $P_{AB}(-C-C=C) = 0.934$ $l(-C=C-) = 1.421$ $l(-C-C=C) = 1.412$
	2 $\pi\pi^*$	276	0.03			288	0.02		
	3 $\pi\pi^*$	277	0.04			287	0.01		
II	1 $\pi\pi^*$	320	1.76	$k_r \sim 10^9$ $k_{ic} \sim 10^7$ $k_{isc} \sim 10^8$	$P_{AB}(-C=C-) = 1.051$ $P_{AB}(-Ph-Ph) = 0.867$ $l(-C=C-) = 1.361$ $l(-Ph-Ph) = 1.465$	360	1.93	$k_r \sim 10^9$ $k_{ic} \sim 10^6$ $k_{isc} \sim 10^7$ $\varphi_{\text{fl}} \sim 0.95$	$P_{AB}(-C=C-) = 0.912$ $P_{AB}(-Ph-Ph) = 0.922$ $l(-C=C-) = 1.416$ $l(-Ph-Ph) = 1.443$
	2 $\pi\pi^*$	288	0.02			297	0.02		
	3 $\pi\pi^*$	278	0.01			286	0.01		
III	1 $\pi\pi^*$	332	2.20	$k_r \sim 10^9$ $k_{ic} \sim 10^5$ $k_{isc} \sim 10^9$	$P_{AB}(-C=C-) = 1.067$ $P_{AB}(-C-C=C) = 0.835$ $l(-C=C-) = 1.344$ $l(-C-C=C) = 1.451$	373	2.29	$k_r \sim 2 \cdot 10^9$ $k_{ic} \sim 10^5$ $k_{isc} \sim 6 \cdot 10^8$ $\varphi_{\text{fl}} \sim 0.76$	$P_{AB}(-C=C-) = 0.966$ $P_{AB}(-C-C=C) = 0.890$ $l(-C=C-) = 1.385$ $l(-C-C=C) = 1.432$
	2 $\pi\pi^*$	292	0.02			302	0.02		
	3 $\pi\pi^*$	277	0.01			283	0.01		

Note.  $f$  is the oscillator force;  $k$  are the photoprocess constants;  $P_{AB}$  are the bond populations;  $l$  are the bond lengths.

In the excited state of the *trans*-stilbene, close arrangement to the  $S_1$ -state of the triplet level  $T_5$ , with a high spin-orbit interaction, leads to a high value of the singlet-triplet conversion up to  $10^{10} \text{ s}^{-1}$ , which predominates over other photoprocesses. It causes low radiation properties of *trans*-stilbene; the theoretical value of the luminescence quantum yield makes 0.07.

For molecules II and III, the introduction of substituents affected on the energy scheme of electronic-excited states and photophysical processes. A long-wave shift is observed in the excited state for the very triplet level with singlet-triplet conversion in the *trans*-stilbene, it leads to the constant drop of this photoprocesses by 2 or 3 orders. The radiation process in this case plays the prevailing role; therefore, the compounds under investigation have good luminescent properties.

The calculations of spectral-luminescent properties have shown that radiation characteristics of the substituted molecules II and III are noticeably improved as compared to the *trans*-stilbene (fluorescence quantum yield for II is 0.9; for III is 0.78), that agrees with the experimental data.

Calculation of bond populations specifies that photoisomerization process in *trans*-forms of II and III is unlikely as compared to the similar process in stilbene.

The Substitution leads to the isomerization inhibition at excitation. High force of the oscillator of the first  $\pi\pi^*$ -transition and predominance of the radiation constant over other photoprocesses lead to the high luminescent properties of the compounds.

Thus, the investigated stilbene-substituted (*4*-phenylstilbene and *1.4*-bis(styryl)benzene) are good luminophores and can be recommended for the use as laser-active media and in organic electronics.

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