

Quantum-chemical study of nitrogen atom effect on spectral-luminescent characteristics of *trans*-stilbene molecule

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Absorption spectra of *trans*-stilbene and its substituted form: *4-methyl-3'-azastilbene* are calculated using the Intermediate Neglect of Differential Overlap/Spectroscopic (INDO/S) quantum-chemical method. Energy level diagrams are drawn and analyzed and the rate constants of different photophysical processes in the both molecules are obtained. The effect of the nitrogen atom on spectral properties of the *trans*-stilbene molecule is studied.

Introduction

It is well-known that *trans*-diarylethylenes, including stilbene, fluoresce, but do not phosphoresce.¹ The quantum yield of *trans*-stilbene fluorescence at the room temperature is 0.03–0.08, and the fluorescence lifetime is about 100 ps (Ref. 2). This low quantum yield is mostly caused by the reaction of photoisomerization, which proceeds with high probability in the excited state. The main channels of degradation of the *trans*-stilbene excited state are radiationless deactivation into the ground state and photoisomerization giving the *cis*-form in the ground state; radiative deactivation of the *trans*-stilbene excited state is improbable.

Experimental data evidence that the absorption spectrum of stilbene solutions (in alcohol, methylcyclohexane, hexane, petroleum-ether, methyl and ethyl alcohols, isooctane, methylpentane) includes an intense longwave band in the region of 320–270 nm with partly resolved vibrational structure already at the room temperature.¹ For the *trans*-isomer in ethanol $\lambda_{\text{abs}} = 308 \text{ nm}$, $\epsilon_{\text{max}} = 28500 \text{ l}/(\text{mol} \cdot \text{cm})$ (Ref. 3). Since the quantum yield of *trans*-stilbene fluorescence in solutions at the room temperature is 0.03–0.08 and the fluorescence lifetime is $\sim 100 \text{ ps}$, it can hardly be expected that *trans*-stilbene is capable of lasing. However, lasing of this compound when pumped by an excimer XeCl* laser with the wavelength of 308 nm was recently discovered.⁴ Under the experimental conditions, the lowest vibrational states of the S_1^* state were populated. The high intensity and the steep leading edge of the pump pulse, as well as the high concentration of *trans*-stilbene ($\sim 5 \cdot 10^{-3} \text{ mol/l}$) led to stimulated emission before the molecule had time to overcome the potential barrier at the expense of the energy of thermal motion of neighboring molecules and went into the *cis*-form.

The *4-methyl-3'-azastilbene* molecule (Fig. 1), which is hereinafter called *azastilbene*, is the stilbene molecule having the heterocyclic nitrogen atom and a

methyl group in its structure. An unshared electron pair is located on the *n*-orbital of the nitrogen atom and not connected with π -electrons of the phenyl ring. Transitions of the $n\pi^*$ -type arise in the system of electronic excited states. The *azastilbene* molecule under study falls in the IV type of molecules according to the Nurmukhametov–Shigorin–Plotnikov classification. In molecules of this type, the states S_1^* and T_1 are $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$, respectively. The longwave absorption band is due to the $\pi\pi^*$ -transition. The probability of intercombination conversion is high in molecules of this type $S_{\pi\pi^*} \rightarrow T_{n\pi^*}$ and the phosphorescent $T_{\pi\pi^*}$ state is efficiently populated. A feature of such molecules is that the $n\pi^*$ absorption band is hidden by more intense $\pi\pi^*$ bands.¹

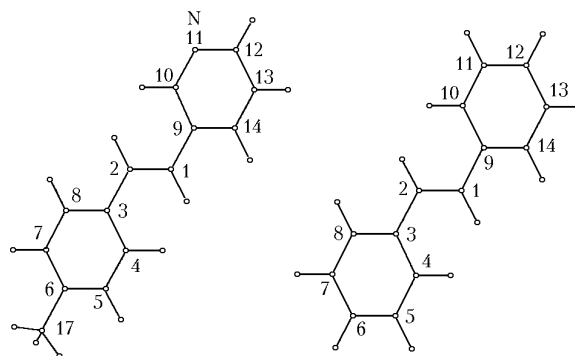


Fig. 1. Structure of *trans*-stilbene and *azastilbene* molecules.

Substituents usually change the structure and intensity of spectral bands of the initial compound, but keep their number, and cause the bathochromic shift and the increase in the intensity of the bands. Substituents of $-\text{CH}_3$ type almost always lead to smearing of the spectral structure of electronic bands.¹ The results of studying the spectral-luminescent properties of methyl-substituted stilbene are given in Ref. 4. It is shown that methyl substitution in different

positions of *trans*-stilbene phenyl rings only slightly affects the position of the fluorescence and absorption spectra. In Ref. 4, spectral characteristics of various aza-substituted stilbenes were studied experimentally as well. It was shown that introduction of heterocyclic nitrogen into one of phenyl rings leads to the threefold increase of the quantum yield of fluorescence in both ethanol and hexane. However, the lasing efficiency in this case remains the same as for *trans*-stilbene. The spectral-luminescent and lasing properties of *azastilbene* are presented in Table 1.

Table 1. Spectral-luminescent characteristics of *azastilbene*⁴

λ_{abs} , nm		λ_{fl} , nm		Quantum yield of fluorescence		λ_{las} , nm		Efficiency, %	
Ethanol	Hexane	Ethanol	Hexane	Ethanol	Hexane	Ethanol	Hexane	Ethanol	Hexane
313	312.5	374	362	0.18	0.32	374.8	361.8	2.1	6.0

Calculation technique

In calculations, we used the semi-empiric Intermediate Neglect of Differential Overlap (INDO) method with spectroscopic parameterization (INDO/S).⁵⁻⁷ Artyukhov with co-authors has developed a suit of computer programs for calculation of spectral properties for a wide range of molecules. The method was parameterized in such a way as to reconstruct the energy of excited states using limited allowance for the configuration interaction, including single-excited configurations.

An important advantage of the INDO/S method is a correct description of singlet and triplet terms, as well as correct consideration of the basic types of interaction. The INDO/S method rather accurately calculates the transition moments and oscillator strengths for transitions between excited states, as well as the energies of the excited states. Besides, it well determines the nature of absorption bands and the type of transitions. The rates of internal conversion were estimated by the equations described in Ref. 7. The efficiency of the processes of intercombination conversion was determined based on matrix elements of the operator of spin-orbit interaction in the single-center approximation.⁷

The advantage of the INDO/S method used in this work is that we can predict the emission properties of the considered molecule. Having drawn the energy level diagram of electronic excited states and knowing the oscillator strengths, dipole transition moments, and rate constants of photophysical processes, we can interpret and simulate some or other processes proceeding in the molecule after the quantum absorption event.

Results and discussion

As a result of our calculations, we obtained the spectral data for plane *trans*-stilbene and *azastilbene*. Introduction of the nitrogen atom does not disrupt the

aromaticity of the heterocyclic ring, the nitrogen unshared pair does not take part in the aromatic system, and the aromatic sextet is almost unchanged. Based on the calculated results, we drew the energy diagrams of the occupied and vacant molecular orbitals (MO) of the *trans*-stilbene molecule and determined their nature (Fig. 2). It can be seen from the diagram that the topmost occupied molecular orbitals with the energy from -7.65 to -11.12 eV are of π -type. At excitation of the molecule electronic transitions from these occupied orbitals to the lowest vacant orbitals of the π^* - and σ^* -

types are observed. The longwave band is formed by the transition of the $\pi\pi^*$ -type with the wavelength of 287 nm (transition from the 34th occupied MO to the 35th vacant MO, Fig. 3) and the oscillator strength ~ 1.15 ; the dipole moment of the *trans*-stilbene molecule is zero in the ground and excited states because of high symmetry of the molecule (Table 2).

Table 2. Spectral characteristics of plane *trans*-stilbene

State	Type	Wavelength, nm	Oscillator strength
S_1	$\pi\pi^*$	287	1.149
S_2	$\pi\pi^*$	276	0.000
S_3	$\pi\pi^*$	276	0.041
S_4	$\pi\sigma^*$	250	0.000
S_5	$\pi\sigma^*$	239	0.003
S_6	$\pi\pi^*$	223	0.000
S_7	$\pi\pi^*$	210	0.000
S_8	$\pi\pi^*$	209	0.654
S_9	$\pi\sigma^*$	208	0.000
S_{10}	$\pi\pi^*$	202	0.726

For the plane *trans*-stilbene molecule, the wave function of the first excited singlet state is formed by the following transitions from the occupied MO to the vacant one:

$$\psi(S_1) = 0.968 | 34 \rightarrow 35 \rangle + 0.150 | 34 \rightarrow 36 \rangle + 0.164 | 31 \rightarrow 38 \rangle.$$

Based on the calculated results, the rate constants of various photoprocesses in the *trans*-stilbene molecule were estimated. Since the radiation constant (10^8 s⁻¹) is several orders of magnitude larger than the constant of radiationless conversion to the state S_0 (10^4 s⁻¹), we can say that the radiative channel of degradation of the excited state of plane *trans*-stilbene dominates over the radiationless one. Nevertheless, due to the high probability of isomerization, in a solvent the quantum yield of fluorescence of this molecule is low (0.03–0.08) (Ref. 2).

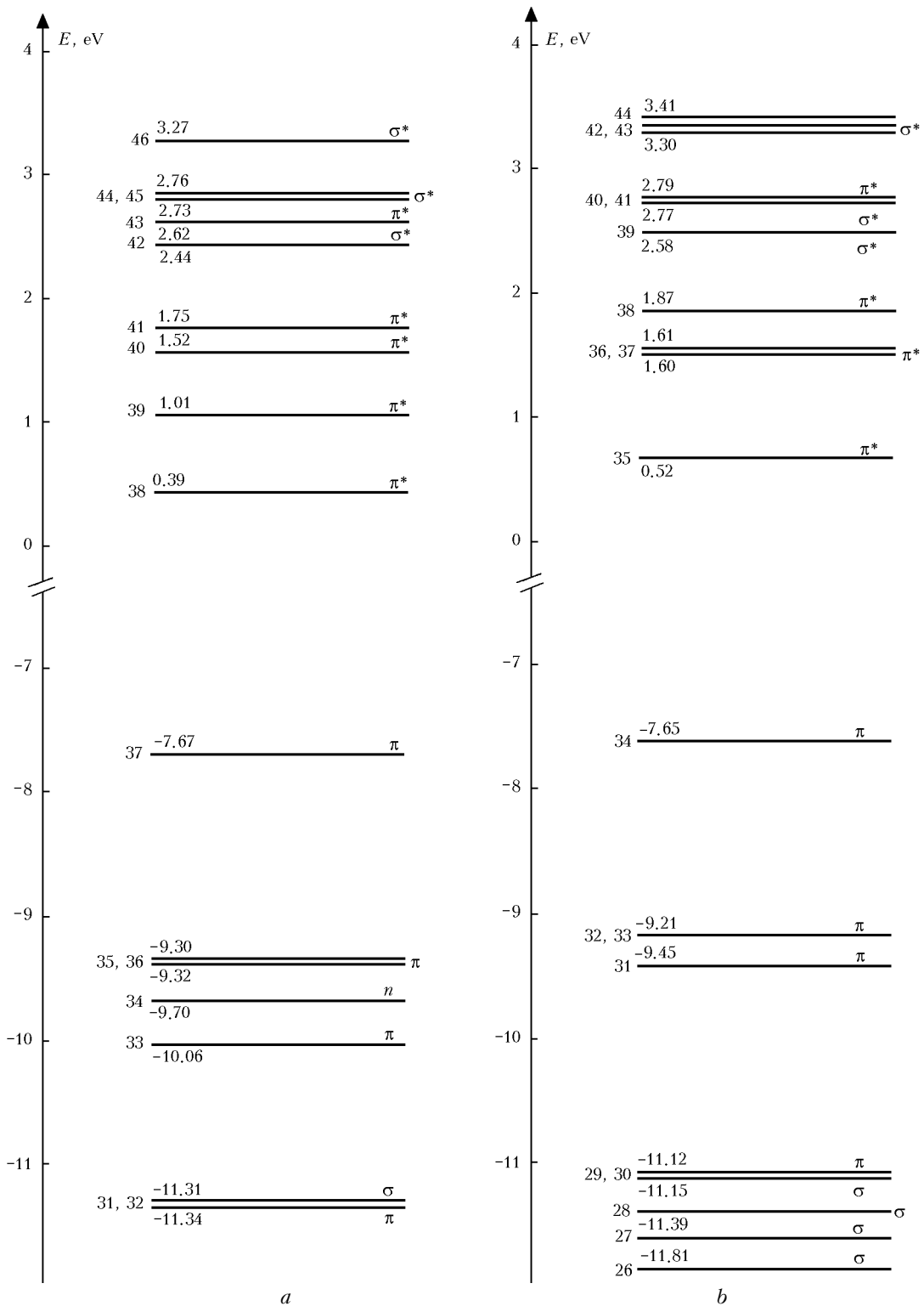
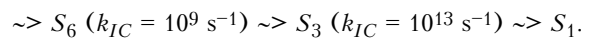
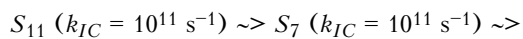


Fig. 2. Energy of occupied and vacant molecular orbitals: plane *azastilbene* (a) and plane *trans-stilbene* (b).

Two channels are possible for energy degradation from higher singlet states. The first channel is the degradation through singlet states of the $\pi\pi^*$ nature (Fig. 3):



At population of singlet excited states of the $\pi\sigma^*$ -type through effective singlet-triplet conversion between the states S_4 , $\pi\sigma^*$ and T_8 , $\pi\pi^*$, the triplet degradation of the excited state is possible:

$$S_9 (k_{IC} = 10^{10} \text{ s}^{-1}) \rightsquigarrow S_5 (k_{IC} = 10^{12} \text{ s}^{-1}) \rightsquigarrow \\ \rightsquigarrow S_4 (k_{ST} = 10^{10} \text{ s}^{-1}) \rightsquigarrow T_8.$$

In the *azastilbene* molecule, molecular orbitals of the n -type arise (the 34th occupied MO with the energy of -9.7 eV, see Fig. 2) and the electronic transitions of the $n\pi^*$ -type appear. The topmost occupied MO of the π -type has the energy of -7.67 eV, and the longwave absorption band is formed by the transition of the $\pi \rightarrow \pi^*$ -type with the wavelength of 287 nm (transition from the 37th occupied MO to the 38th lowest vacant MO). The upper occupied molecular orbitals of the *azastilbene* and *trans-stilbene* molecules have almost the same energy, and the lowest vacant MO for *azastilbene* is 0.13 eV lower (see Fig. 2). The observed bathochromic shift of the longwave absorption band of

azastilbene is caused by lowering of the lower vacant molecular orbital.

For the *azastilbene* molecule the wave functions of the first two excited singlet states form the following transitions from the occupied MO to the vacant one:

$$\begin{aligned} \psi(S_1, \pi\pi^*) &= 0.952 |37 \rightarrow 38\rangle + \\ &+ 0.145 |37 \rightarrow 40\rangle - 0.167 |35 \rightarrow 41\rangle, \\ \psi(S_2, n\pi^*) &= -0.851 |34 \rightarrow 39\rangle - \\ &- 0.475 |34 \rightarrow 38\rangle + 0.150 |34 \rightarrow 41\rangle. \end{aligned}$$

Introduction of heterocycle and methyl group breaks the stilbene symmetry about the ethyl bond, and the *azastilbene* molecule acquires a dipole moment (Table 3). The appearance of the dipole moment can be explained considering the results presented in Tables 4

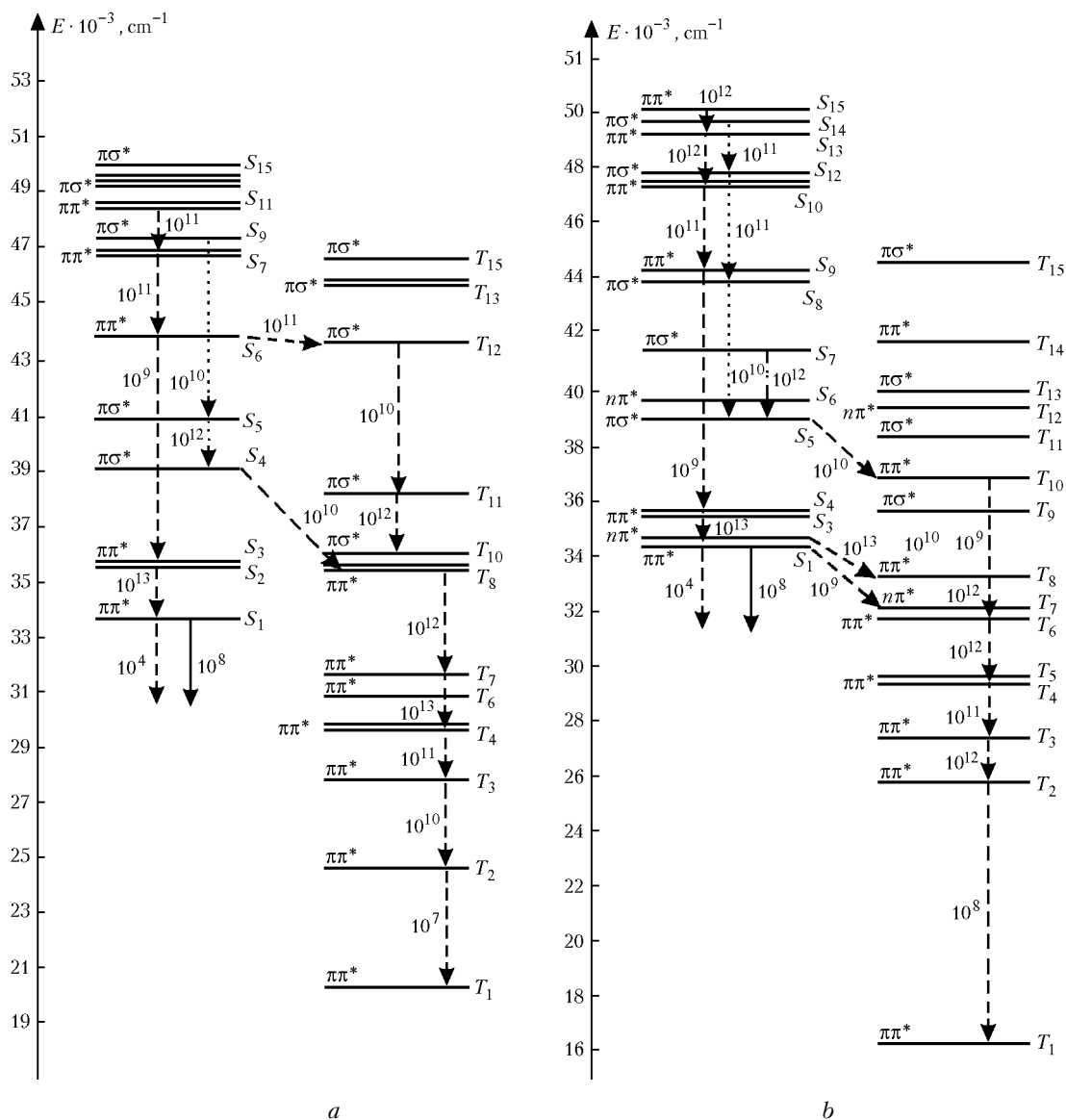


Fig. 3. Energy diagram of electronic excited states as calculated by the INDO/S method: plane *trans-stilbene* (a) and plane *azastilbene* (b).

to 6 on the change of electron density at the carbon atoms and nitrogen atom for the molecules of *trans*-stilbene and *azastilbene*. It can be seen that the nitrogen atom in the *azastilbene* molecule (the 11th atom, Table 4) in the ground state S_0 has a very high negative charge as compared with other atoms (because the nitrogen atom has an unshared electron pair) and the electron density of carbon atoms of phenyl rings shifts toward the nitrogen atom. If we divide the *azastilbene* molecule into fragments (phenyl rings with substituents and double ethylene bond), we can see that the highest electron density in the ground state is concentrated at the phenyl ring with the nitrogen atom.

Table 3. Spectral characteristics of *azastilbene*

State	Type	Wavelength, nm	Oscillator strength	Dipole moment, D
S_1	$\pi\pi^*$	292	1.201	4.60
S_2	$n\pi^*$	289	0.006	1.75
S_3	$\pi\pi^*$	281	0.063	3.56
S_4	$\pi\pi^*$	280	0.031	7.23
S_5	$\pi\pi^*$	256	0.000	3.99
S_6	$n\pi^*$	251	0.000	2.11
S_7	$\pi\sigma^*$	242	0.005	3.56
S_8	$\pi\pi^*$	229	0.001	4.93
S_9	$\pi\pi^*$	226	0.001	4.86
S_{10}	$\pi\pi^*$	211	0.164	7.52

Quite similar situation is in the excited singlet state S_1 . The electron density from the 3rd, 6th, 10th, and 12th carbon atoms shifts toward the nitrogen atom. This

explains the increasing intensity of the first absorption band. The electron density of the phenyl ring with the methyl group shifts toward the phenyl ring with the nitrogen atom, and the resulting charge of the former is negative, while the resulting charge of the latter is positive (Table 5). The qualitatively different situation is observed in the excited singlet state S_2 of the $n\pi^*$ -type. The electron charge at excitation is transferred from the nitrogen atom to other atoms; the 9th, 10th, and 12th carbon atoms are also donors of electron density and have the positive charge (see Table 4).

The dipole moment of the *trans*-stilbene molecule is zero, because it is symmetric about the double ethylene bond $C=C$. The distribution of electron density among atoms in the ground and excited states of the *trans*-stilbene molecule obeys some symmetry, and the charges at the corresponding symmetric atoms are the same (see Table 4). If we consider a change of the electron density at fragments of the *trans*-stilbene molecule (phenyl rings and double ethylene bond), then in the symmetric molecule the whole electron density is mostly concentrated at phenyl rings, whose electron charge is negative. In the first excited singlet state the electron charge is transferred from the phenyl rings to the ethylene bond $C=C$ (see Table 5).

The calculation shows that the bands of the $n\pi^*$ -type are not observed in the experimental absorption spectrum of *azastilbene*. In particular, the $S_0 \rightarrow S_2$ absorption band is not observed, because the band of $n\pi^*$ -type is overlapped by the more intense band of the $\pi\pi^*$ -type.

Table 4. Effective atomic charges at excitation of *trans*-stilbene and *azastilbene* molecules

Atom number	<i>Azastilbene</i>						<i>Trans</i> -stilbene					
	S_0	S_1	S_2	S_3	S_4	S_5	S_0	S_1	S_2	S_3	S_4	S_5
1	-0.056	-0.045	-0.100	0.002	0.020	-0.032	-0.041	-0.056	-0.009	-0.017	-0.014	0.035
2	-0.038	-0.082	-0.89	0.005	0.034	-0.015	-0.041	-0.056	-0.009	-0.017	-0.014	0.035
3	-0.007	0.046	-0.030	0.039	0.059	-0.051	0.005	0.010	0.024	0.019	-0.103	-0.071
4	-0.020	-0.016	-0.035	-0.073	0.002	0.003	-0.023	-0.019	-0.034	-0.030	-0.003	-0.075
5	-0.034	-0.019	-0.037	-0.095	-0.011	-0.016	-0.024	-0.027	-0.051	-0.047	-0.013	-0.040
6	0.005	0.047	-0.027	0.052	0.076	0.100	-0.027	-0.018	-0.002	-0.007	0.073	0.073
7	-0.032	-0.019	-0.036	-0.088	-0.014	-0.015	-0.023	-0.026	-0.050	-0.045	-0.023	-0.015
8	-0.017	-0.012	-0.033	-0.072	0.008	-0.014	-0.021	-0.017	-0.031	-0.028	-0.039	-0.007
9	0.002	-0.020	0.051	0.019	0.045	-0.152	0.005	0.01	0.024	0.019	-0.103	-0.071
10	0.167	0.215	0.012	0.189	0.016	0.193	-0.023	-0.019	-0.034	-0.030	-0.003	-0.075
11	-0.442	-0.469	0.015	-0.460	-0.580	-0.434	-0.024	-0.027	-0.051	-0.047	-0.013	-0.040
12	0.159	0.100	0.174	0.165	0.180	0.228	-0.027	-0.018	-0.002	-0.007	0.073	0.073
13	-0.027	-0.019	-0.073	-0.026	-0.072	-0.028	-0.023	-0.026	-0.050	-0.045	-0.023	-0.015
14	0.026	-0.040	-0.163	0.015	-0.100	-0.036	-0.021	-0.017	-0.031	-0.028	-0.039	-0.007
17	-0.013	-0.006	-0.012	-0.007	-0.005	-0.014	-	-	-	-	-	-

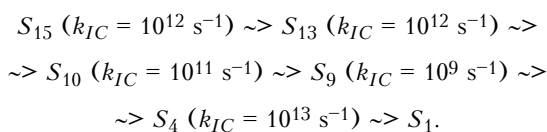
Table 5. Effective charges at fragments of atoms in the ground and excited states of the *trans*-stilbene molecule

Fragment number	Atom number	Charge change					
		S_0	S_1	S_2	S_3	S_4	S_5
1	9 – 14, 20 – 24	-0.001	0.014	-0.033	-0.026	-0.013	-0.058
2	3 – 8, 15 – 19	-0.001	0.014	-0.033	-0.026	-0.013	-0.058
3	1, 2, 25, 26	0.002	-0.027	0.066	0.051	0.025	0.115

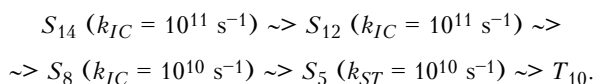
Table 6. Effective charges at fragments of atoms in the ground and excited states of the azastilbene molecule

Fragment number	Atom number	Charge change					
		S_0	S_1	S_2	S_3	S_4	S_5
1	11	-0.442	-0.469	0.015	0.460	0.580	0.434
2	9 - 14, 20 - 23	-0.009	-0.096	0.129	0.091	-0.475	-0.141
3	1, 2, 24, 25	-0.005	-0.041	-0.049	0.087	0.322	-0.001
4	3 - 8, 15 - 19, 26 - 28	0.014	0.137	-0.080	-0.178	0.153	0.142

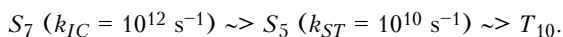
If the molecule finds itself at higher singlet excited states, energy degradation through singlet states of the $\pi\pi^*$ -type to the state S_1 is possible (see Fig. 3):



At population of high singlet excited states of the $\pi\sigma^*$ -type, triplet degradation through the singlet-triplet conversion between the states S_5 , $\pi\sigma^*$ and T_{10} , $\pi\pi^*$ is possible (see Fig. 3):



The triplet mechanism of degradation of the excited state also takes place, if the molecule is in the S_7 , $\pi\sigma^*$ -state:



Comparing the radiation constant (10^8 s^{-1}), the constant of radiationless conversion into the state S_0 (10^4 s^{-1}), and the constants of singlet-triplet conversion from the state S_1 to T_7 ($k_{ST} = 10^9 \text{ s}^{-1}$) and from S_2 to T_8 ($k_{ST} = 10^{13} \text{ s}^{-1}$), we can conclude that the transition to the triplet state is most probable among all processes in the azastilbene molecule.

The experimental data⁴ show that introduction of heterocyclic nitrogen into one of phenyl rings leads to the about threefold increase of the quantum yield of fluorescence as compared with *trans*-stilbene depending

on the solvent ($\phi_{trans} = 0.03-0.08$; $\phi_{aza} = 0.18-0.32$). The increase in the oscillator strength and intensity of the first transition is connected with the transfer of the electron density to the nitrogen heteroatom. However, the quantum yield for the azastilbene molecule remains small as compared with unity, and the lasing efficiency remains low (2.1–6.0%, Ref. 4). Such a low lasing efficiency is likely caused by the efficient singlet-triplet conversion, as well as the reaction of isomerization, characteristic of stilbene and its derivatives, which can follow the triplet mechanism.⁸

References

1. R.N. Nurmukhametov, *Absorption and Luminescence of Complex Organic Compounds* (Khimiya, Moscow, 1971), 216 pp.
2. J.S. Roseanne, S.T. Repines, A.Z. Szarka, and R.M. Hochstrasser, *J. Chem. Phys.* **98**(8), 6291–6315 (1993).
3. O.G. Bekker, *Introduction to Photochemistry of Organic Compounds* (Khimiya, Leningrad, 1976), 378 pp.
4. L.G. Samsonova, T.N. Kopylova, N.N. Svetlichnaya, and O.S. Andrienko, *Atmos. Oceanic Opt.* **13**, No. 3, 262–264 (2000).
5. G.V. Maier, V.Ya. Artyukhov, O.K. Bazyl', T.N. Kopylova, N.R. Rib, and I.V. Sokolova, *Electronic Excited States and Photochemistry of Organic Compounds* (Nauka, Novosibirsk, 1997), 231 pp.
6. V.Ya. Artyukhov and A.I. Galeeva, *Izv. Vyssh. Uchebn. Zaved., Ser. Fiz.*, No. 11, 96–100 (1986).
7. G.V. Maier, *Photophysical Processes and Lasing Capability of Aromatic Molecules* (Tomsk State University Publishing House, Tomsk, 1992), 265 pp.
8. A.N. Terenin, *Photonics of Dye Molecules and Relative Organic Compounds* (Nauka, Leningrad, 1967), 616 pp.