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Experimental study and calculations of spectral-luminescence properties of cyanine dye

Spectral-luminescence properties of monomers and dimers of cyanine dye were studied. Concentration dependence of absorption and fluorescence spectra was measured for dye solutions. Obtained data reveals formation of cyanine dimers at high concentrations. The most optimal configuration and optical properties of molecular aggregates of studied dye were predicted by using of complex analysis of spectral data and quantum-chemical calculations. Obtained results could be used for developing of systems with predicted properties.

Key words: cyanine, dimers, spectral-luminescence properties, aggregation, quantum-chemical calculations.

Dyes as sensitizers are the most important component for the dye-sensitized solar cell because they are used for light absorption and electron injection into the semiconductor [1]. Cyanine dyes are stand out from all the classes of organic dyes due to high absorptance of light [2]. The main advantages of these dyes are extremely high extinction coefficients, and tunable absorption spectra across the visible and near infrared region of spectrum.

In this study polymethine dye, the structural formula of which is shown in Figure 1, was selected.

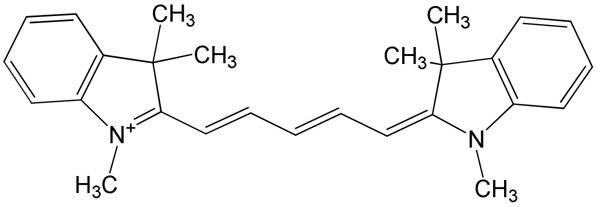
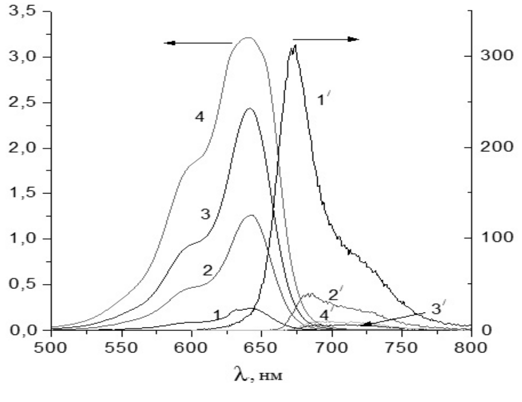


Figure 1. Structure of cyanine dye

Concentration dependence of absorption and fluorescence spectra of cyanine dye K in ethanol solutions was studied. Dye concentration in used samples was equal to 10^{-6}, 10^{-5}, $5\cdot10^{-5}$, 10^{-4}, $2\cdot10^{-4}$, $5\cdot10^{-4}$ mol/l. Absorption spectra were measured with a Cary-300 spectrophotometer (Agilent, USA) and fluorescence spectra were measured with a spectrofluorimeter Cary Eclipse (Agilent, USA). The absorption and fluorescence spectra of dye, depending on the dye concentration are shown in Figure 2.



1, 1′ — 10^{-5}; *2, 2′* — $5\cdot10^{-5}$; *3, 3′* — 10^{-4}; *4, 4′* — $2\cdot10^{-4}$ (in mol/l)

Figure 2. The concentration dependence of the absorption (1–4) and fluorescence (1'–4') (λex=590 nm) spectra of dye at various concentrations

As could bee seen from the figure, considerable broadening of the spectrum is occurs with increasing of dye concentration in solution. The maxima of absorption spectra in short-wavelength region and change of the ratio of optical density of main peak (at 642 nm) and shoulder (at 600 nm) were registered also. When the dye concentration is equal to $2\cdot10^{-4}$ mol/l, the deformation of the absorption spectrum is observed. The maximum of fluorescence spectra with increasing dye concentration was shifted to longer wavelengths by about 30 nm at growth of dye content. The maximum intensity of the fluorescence was observed for a solution with dye concentration equal to 10^{-5} mol/l. Further increase in the content of the dye lead to the decreasing of fluorescence intensity. For a solution with a dye concentration of $5\cdot10^{-4}$ mol/l, the emission of dye is almost quenched. However, an increase of the Stokes shift of the dye spectra (Table 1) was registered. The change in the wavelength of excitation of fluorescence spectrum does not change the position of the emission bands.

Table 1

Spectral parameters of dye at different concentrations in the solutions

Concentration, mol/l	10^{-6}	10^{-5}	$5\cdot10^{-5}$	10^{-4}	$2\cdot10^{-4}$	$5\cdot10^{-4}$
$^{a}\lambda_{1\ max}$, nm	642	642	644	642	640	625
$^{a}\lambda_{2\ max}$, nm	600	600	600	600	–	–
$\Delta\lambda^{a}_{1/2}$, nm	40	39	41	42	68	84
D	0,03	0,2	1,3	2,4	3,0	3,4
$^{f}\lambda_{max}$, nm	662	674	685	688	697	–
$^{f}\lambda_{max}$, nm	720	720	723	720	–	–
$\Delta\lambda^{f}_{1/2}$, nm	36	31	49	50	52	–
I, o, e,	137	313	40	7	11	–
$\Delta\lambda_{st}$, nm	20	32	41	46	57	–

To explain the obtained results excitation spectra of dye were measured (Fig. 3).

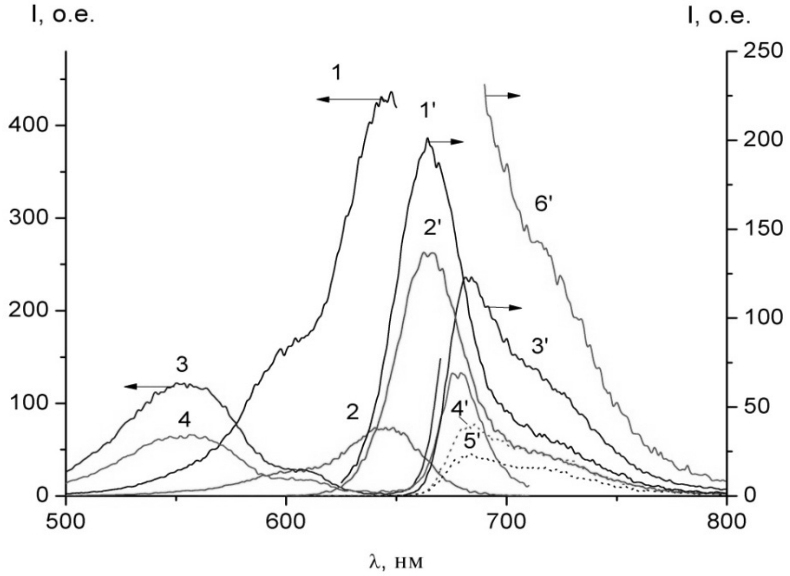


Figure 3. Fluorescence excitation spectra (1–4) and fluorescence (1'–6') K1 dye in solution at various concentrations of 10^{-6} mol/l: *1* — λ_{ex}= 660 nm; *2* — λ_{ex} = 720 nm; *1'* — λ_{ex} = 615 nm; 2' — λ_{ex} = 590 nm; to a concentration of $5\cdot10^{-5}$ mol/l: *3* — λ_{ex}= 680 nm; *3* — λ_{ex}= 720 nm; *3'* — λ_{ex}= 550 nm; *4'* — λ_{ex}= 590 nm; *5'* — λ_{ex}= 615 nm; *6'* — λ_{ex}= 680 nm

For a solution with dye concentration equal to 10^{-6} mol/l, the band with a maximum at 645 nm and a shoulder around 600 nm exhibits in the spectrum of the fluorescence excitation. A more intense band was recorded under the registration at λ = 662 nm (curve 1). Accordingly, the greater the intensity has a band that was excited with λ_{ex} = 615 nm (curve 1').

When the concentration was grown in the fluorescence excitation spectra, along with the band around 600 nm, there are two bands with maxima at 550 and 675 nm (curves 3 and 4) exhibits. Upon irradiation of solution with light at $\lambda_{ex} = 590$ nm and $\lambda_{ex} = 615$ nm the bands with maxima at 688 and 720 nm appears in luminescence spectra. The maximum at the 688 nm is bathochromically shifted by 26 nm relative to the same parameter for a solution with a concentration equal to $C = 10^{-6}$ mol/l. In this case the fluorescence intensity which is excited in a shoulder absorption spectrum K1 is higher than the fluorescence excited at 615 nm (curve 4'). More intense luminescence band were recorded at excitation of the dye emission at 550 nm (curve 3') and at 680 nm (curve 6'). Thus, the data suggest the process of molecular aggregation in solution with a high concentration of the dye molecules. Since new bands have not been registered in the absorption and fluorescence spectra, that is most typical for the case of formation of molecular aggregates, including a large number of molecules, it can be assumed that dye forms dimers.

In the second part of our study we calculate the conformation and spectral-luminescence properties of cyanine molecular aggregates. The calculations were performed by the density functional theory (DFT) using the software package Gaussian 09. Optimization of geometry was carried out using the three-parameter hybrid method Beke with the correction gradient-correlation functional Lee, Yang and Pará (B3LYp) and standard basis set 6–311 + + G (d, p).

The optimized geometry of the dye molecule is shown in Figure 4.

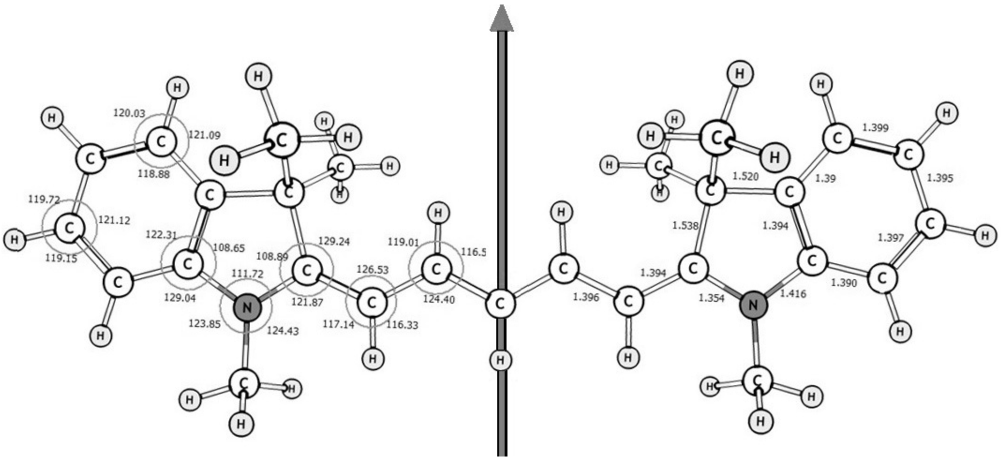


Figure 4. Calculated structure of dye. At the right — values of bond lengths (Å), at the left — values of valence angles (deg); an arrows indicate the orientation of dipole moments (m¼ 2.14 D)

The dipole moment of the molecule in the ground state K1 is equal to 2.138 D. The maximum projection of the dipole moment for the dye molecule oriented in the plane of the molecule and is directed along the short axis. For this dye charges on the atoms are distributed symmetrically.

Figure 5 shows an electronic absorption spectrum of dye obtained from the calculation. As can be seen from the figure, the spectral maximum is located at the wavelength of λ = 553,73 nm and corresponds to the transition from the ground to the first excited singlet state. The oscillator strength is equal to 1.0. The oscillator strength is spectroscopic dimensionless quantity, through which the probability of quantum transitions in the emission process, photoabsorption and the Coulomb excitation of atomic, molecular or nuclear systems is expressed [3].

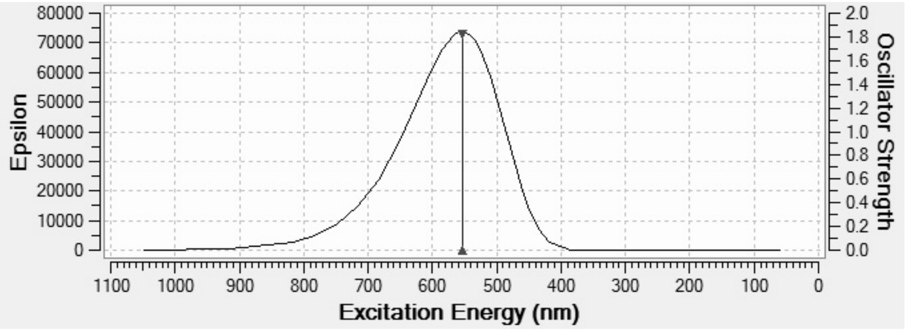


Figure 5. The calculated electronic spectrum of dye molecule

Table 2 shows the results of calculation of energy (*E*), the oscillator strength (*f*), polarization of transition (P_i) and the nature of the S_0-S_i transitions in the dye molecule.

Table 2

Results of the calculation of the spectral characteristics of dye

Condition	E, cm^{-1}	λ, nm	f	k_r, s^{-1}	P$_i$	D	E_{exp}, cm^{-1}	λ_{exp}, nm
S_1 ($\pi\pi^*$)	18051	554	1	$2.8\cdot10^8$	Y	2.138	15625	640
S_2 ($\pi\pi^*$)	28818	347	0.019	$7.72\cdot10^7$	X	0	–	–
S_3 ($\pi\pi^*$)	32895	304	0.023	$1.45\cdot10^8$	Z	0	–	–

Fugure 6 shows the distribution of electron density of molecular orbital (MO) of dye.

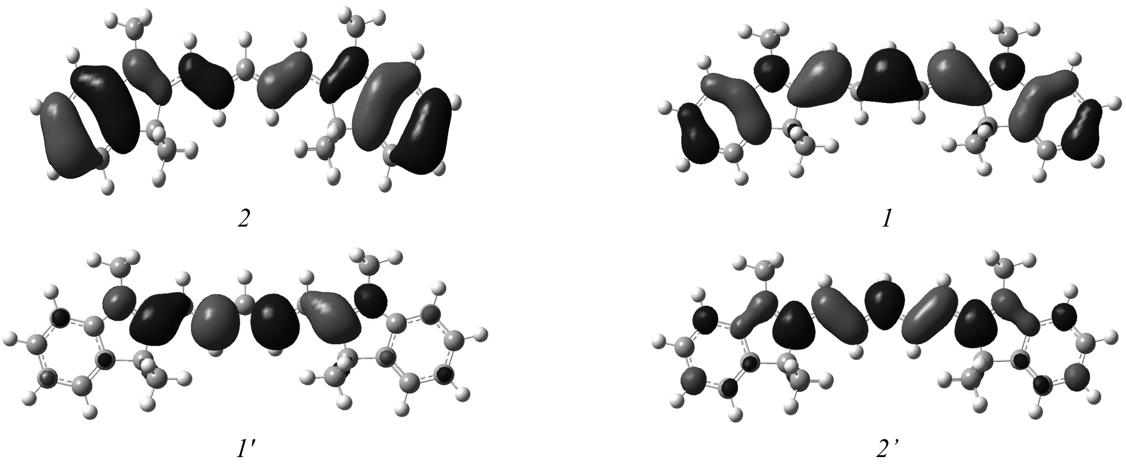


Figure 6. MO involved in the formation of the excited electronic states of dye

Configuration decomposition (CD) of MOs is shown below, where the 1, 2, 3, etc. — numbering of occupied MO from the top, and the numbering of free MOs starts from the lowest unoccupied orbital and designated as 1', 2', 3', etc.

$\Psi(S_1) = -0{,}143|2\rightarrow2'\rangle + 0{,}674|1\rightarrow1'\rangle$
$\Psi(S_2) = -0{,}103|3\rightarrow2'\rangle + 0{,}613|2\rightarrow1'\rangle - 0{,}275|1\rightarrow2'\rangle$
$\Psi(S_3) = 0{,}299|5\rightarrow1'\rangle + 0{,}550|3\rightarrow1'\rangle - 0{,}193|2'\rightarrow2'\rangle$

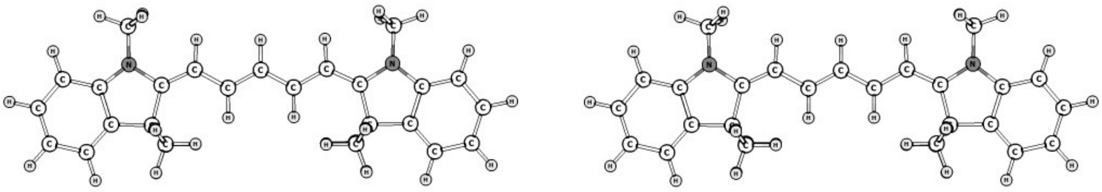
Is evidence that the transition S_0–S_1 is formed almost one configuration of MO |1 → 1'> with some admixture of configuration |2 → 2'>. This transition is formed at the promotion of an electron between the MOs that have the same distribution of MO and involved atomic orbitals (AO), i.e. by orbitals that have a maximum overlapping area.

Whereas opposite case is observed in the case of formation of the S_2-state. The calculation showed that despite of transition moments of configurations |2 → 1'> and |1 → 2'> is big, but are located on different fragments of the molecule, which leads almost to zero in the oscillator strength of strasition from ground to second-excited state.

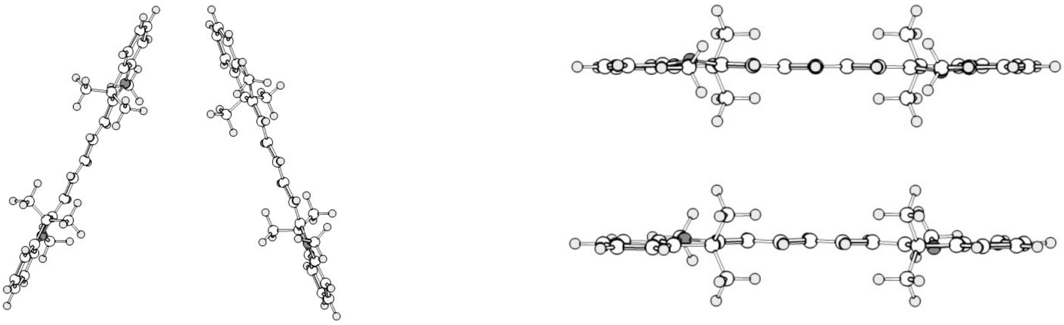
In experiment it was shown that absorption and fluorescence spectra could be attributed as to monomers as to dimers. At the next stage the configuration of dimers was calculated by the method of molecular mechanics. It will allow to predict the most probable type of dimers of dye.

The 3 configurations of dye dimers were selected for calculations and they are presented in Figure 7. The choice of the distance between the studied molecules was selected in such a way that there is no overlap of the van der Waals radii of molecules (the optimal distance between the molecules is equal to 3.6 Å).

The results of the calculation were shown that for the conformation, where the dye molecules are located in the same plane, has energy of 58.04 kcal/mol. The value of energy for the conformation 2 (a dimer of the «Christmas tree» or «house of cards») is equal to 65.43 kcal/mol. The conformation 3 is energetically less favorable for dye (*E* = 70.02 kcal/mol). So, the dye molecules in solution at high concentration of dye most probably form dimers of the first conformation (the «plane» dimers).



1 — «plane» dimer

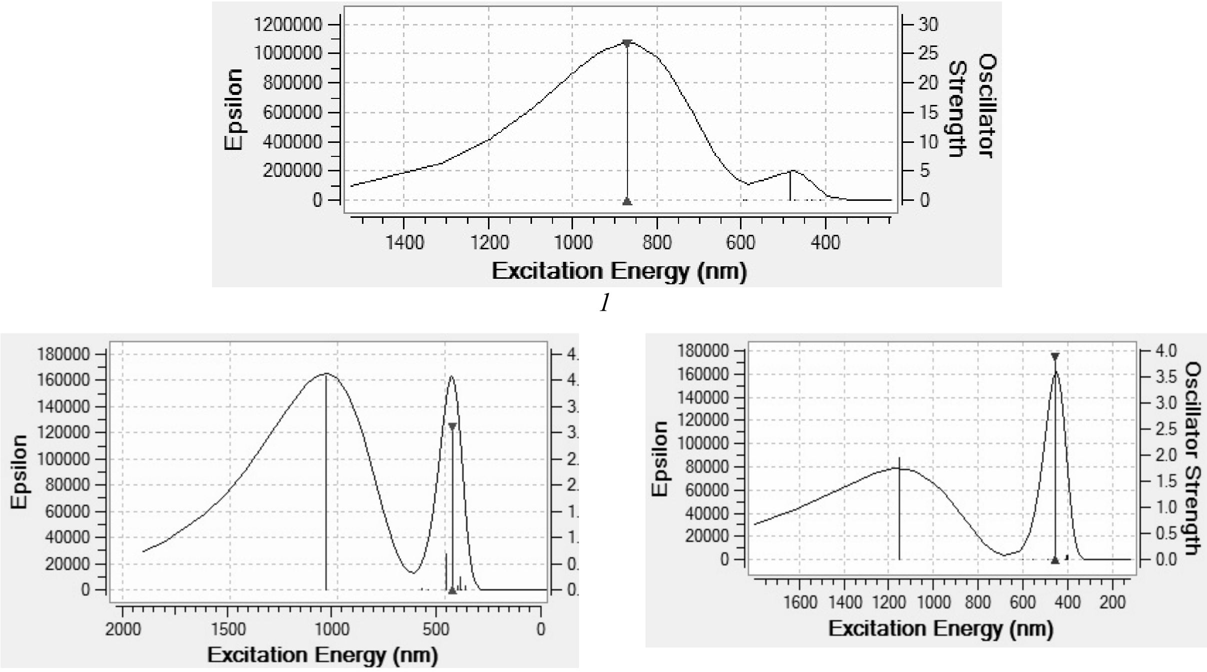


2 — dimer of «christmas tree» type

3 — «sandwich» dimer

Figure 7. The calculated conformation of dye dimers

Further electronic spectra were calculated for these conformations of dye dimers (Fig. 8, Table 3).



1

2

3

Figure 8. The calculated spectra of electronic absorption spectra of dye dimers for various conformations

Table 3

Calculated spectral parameters of the dye dimers

Condition	Dimer conformation					
	1		2		3	
	E, nm	*f*	*E*, nm	*f*	*E*, nm	*f*
$S_1^{'}$	870.30	26.5083	1053.55	4.0828	1119.91	2.3483
S_1	595.58	0.0002	602.20	0.0162	601.61	0.0118
$S_1^{''}$	483.55	4.8091	464.90	3.1156	457.15	3.8749
S_2	474.38	0.0445	437.79	0.0872	410.44	0.0053

As can be seen from the figures, the obtained spectra coincide with Davydov’s exciton model of molecular aggregates [4]. In this model the interaction of monomer molecules in the dimer leads to the splitting of the excited electronic level S_1 into two sublevels S1’ and S1». To clear up the origin of short-wavelength maximum in the experimental spectra of dye absorption consider the CD and localization of MOs for dimer (Fig. 9).

As could bee seen the state S_1 is formed by the same MO as in the monomer molecule. The positive coefficients determine the maximum oscillator strength for the transition of S_0-S_1’. In the formation of states S_1’ and take part MOs that are localized in both molecules included in the molecular dimer. For other dimers excited states are formed by the same MOs.

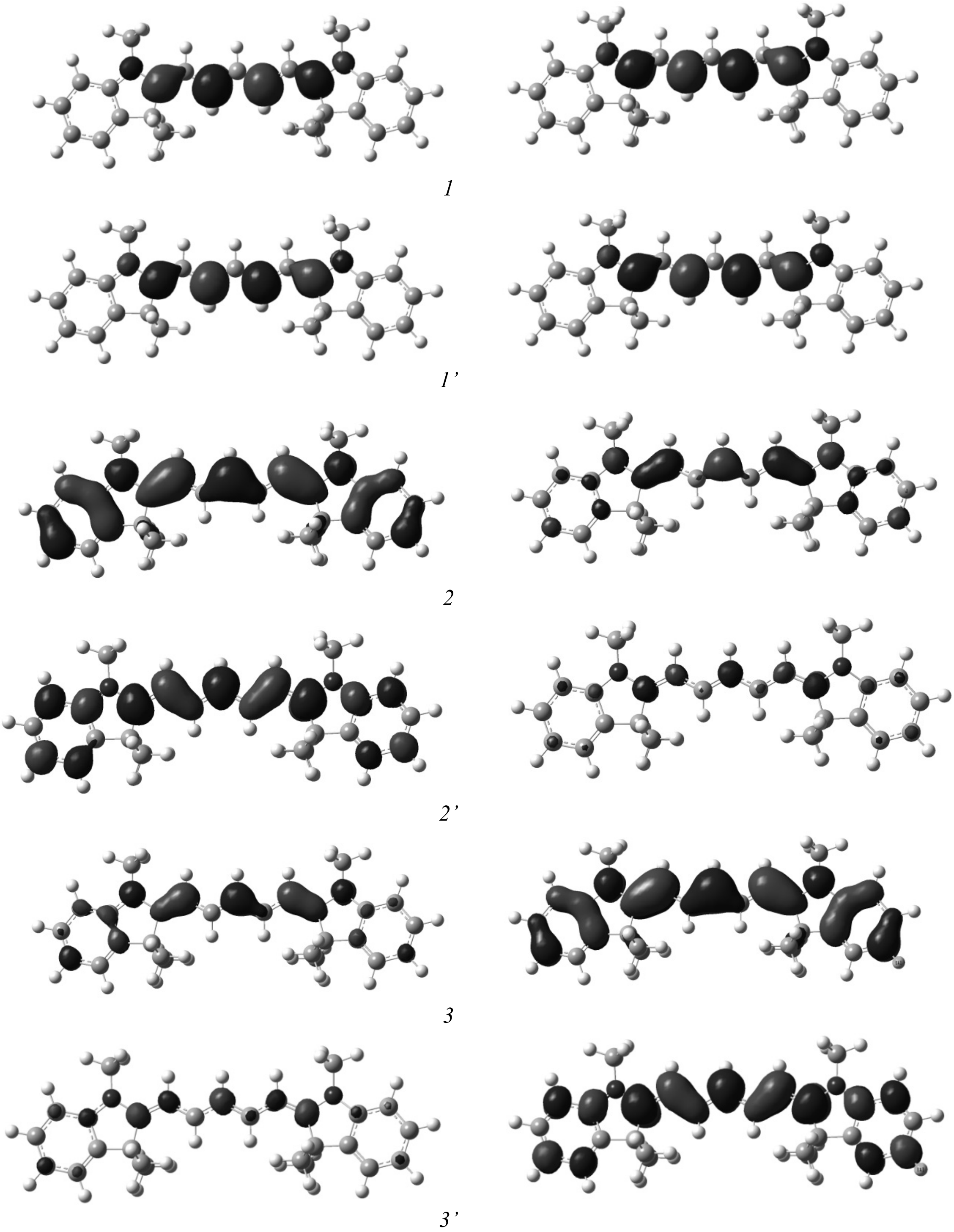


Figure 9. MO involved in the formation of the excited electronic states of «plane» dimer

$\Psi (S_1') = -0,11|3\rightarrow3'> + 0,1096|2\rightarrow2'> + 0,662|1\rightarrow1'>$
$\Psi (S_1) = -0,100|3\rightarrow1'> + 0,502|2\rightarrow1'> - 0,412|1\rightarrow2'> - 0,148|1\rightarrow3'> - 0,115|1\rightarrow9'> - 0,100|1\rightarrow10'>$
$\Psi (S_1\text{»}) = -0,404|3\rightarrow1'> - 0,157|2\rightarrow1'> - 0,254|1\rightarrow2'> + 0,452|1\rightarrow3'>$
$\Psi (S_2) = -0,158|3\rightarrow1'> + 0,403|2\rightarrow1'> + 0,448|1\rightarrow2'> + 0,252|1\rightarrow3'>$

The observed results are consistent with the conclusions of the work [5] where it was shown that at the absence of intermolecular interaction all electronic states of dimers will be doubly degenerate. Thus the «monomeric» state S_1 is split and shifted in energy into two sublevels S1' and S1» [5]. As can be seen from the calculation results, the oscillator strength of the transition in the split state is less than for the «monomeric» state.

Thus, studies have shown that for studied dye the largest luminescence was registered for solution with concentration of 10^{-5} mol/l. With a further increase in dye concentration there is a noticeable decrease fluorescence intensity was registered. The deformation of absorption spectra bands was observed at a dye concentration of $2\cdot10^{-4}$ mol/l or higher. To explain experimental results the quantum-chemical calculations of the dye monomer and the dimers were carried out. Conformational search of dye dimers showed that the most optimum is a configuration in which the molecules are arranged in one plane. It was shown that allowed the electron-excited state of dye is split in dimers. The transition that formed by the redistribution of the electron density between the same molecular fragments as monomeric molecule is most allowed. In the formation of electronically excited states of the dimer participate the MOs that localized in both molecules included in the molecular dimer.

The findings and further studies of polymethine dyes may be used at using of these dyes in the basic science and technological applications such as organic solar cells and organic LED, photosensors, optical drives, chemical indicators, etc.

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Д. Темирбаева, Е. Селиверстова, Н.Х. Ибраев, А. Ищенко

Цианинді бояғыштың спектрлі-люминесценттік қасиеттерін тәжірибелік тұрғыдан зерттеу және есептеу

Мақалада цианинді бояғыштың мономер мен димерлерінің спектрлі-люминесценттік қасиеттері зерттелген. Бояғыш ерітінділерінің жұтылу және флуоресценция спектрлерінің концентрациялық тәуелділігі тәжірибе жүзінде талданған. Алынған мәліметтер цианиннің димерлері ерітінділердің жоғары концентрациясында қалыптасатынын көрсеткен. Зерттелетін бояғыштың молекулалық агрегаттардың неғұрлым оңтайлы конфигурациясы мен оптикалық қасиеттері спектрлік нәтижелер және кванттық-химиялық есептеулердің кешенді талдауы арқылы анықталған. Ол нәтижелер болжамды қасиеттері бар жүйелер жасау үшін қолданылуы мүмкін.

Д. Темирбаева, Е. Селиверстова, Н.Х. Ибраев, А. Ищенко

Экспериментальное исследование и расчет спектрально-люминесцентных свойств цианинового красителя

Исследованы спектрально-люминесцентные свойства мономеров и димеров цианинового красителя. Экспериментально изучена концентрационная зависимость спектров поглощения и флуоресценции растворов красителя. Полученные данные свидетельствуют о формировании димеров цианина при высоких концентрациях. Посредством комплексного анализа спектральных данных и квантово-химических расчетов спрогнозированы наиболее оптимальная конфигурация и оптические свойства молекулярных агрегатов исследуемого красителя. Полученные результаты могут быть использованы для создания систем с прогнозируемыми свойствами.

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