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ARTICLE in DYES AND PIGMENTS · DECEMBER 2015

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Nature of the lowest electronic transitions of thia- and quinocyanines with fluorinated polymethine chain



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ARTICLE INFO

Article history:

Received 24 February 2015

Received in revised form

24 July 2015

Accepted 27 July 2015

Available online 5 August 2015

Keywords:

Polymethine dyes

Fluorinated polymethine dyes

Thia- and quinocyanines with fluorinated

polymethine chain

Electron transitions

Absorption spectra, fluorescence anisotropy

Quantum-chemical calculations

ABSTRACT

Quantum-chemical and spectroscopic study of fluorine atoms as substituents in the trimethine and pentamethine chain influence on the electronic structure in polymethine dyes has been performed. According to the calculation data that were experimentally confirmed by RCA and ¹³C NMR spectroscopy fluorination of polymethine chain leads to the small C–C bond lengths changes in chromophore and appreciably changes of the atomic charges. It was established that the introduction of fluorine atoms in the chromophore is accompanied by the significant shifting of the frontier and nearest levels and hence by changing the electronic transitions energies. The simultaneous analysis of the absorption and fluorescence excitation anisotropy spectra as well as results of the calculations of electronic transitions has shown that the S₀ → S₁ transition is more sensitive to the fluorine substituents than the S₀ → S₂ transition.

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1. Introduction

The well-known polymethine dyes have been studied for more than a century, but intensive investigations continue due to the permanent extension of their applications, that first of all based on their non-linear properties (see, for example, the reviews [1–3] and references cited therein). Owing to their strong and selective absorptions across broad spectral regions, this class of linear conjugated molecules has proved to be attractive for applications as fluorescent probes in chemistry and biology, as active and passive laser media, as photosensitizers, for optical data storage and as electroluminescence materials [1–5]. The expansion of the polymethine dyes utilization logically stimulates their investigation by both spectral and quantum-chemical methods to help molecular design of new perspective dye molecules. The typical polymethines, especially, cyanines with nitrogen containing terminal groups demonstrate the high intensive (extinction up to 250–300,000 M^{−1}cm^{−1}) and narrow (30–50 nm) spectral band connected with S₀ → S₁ electronic transition. By variation of the

chemical structure, for e.g., the length of the conjugated chain and/or topology of the terminal residues, the longwavelength absorption band maximum could be shifted from UV to near IR region. To effective influence to the higher electronic transition of the dyes using as non-linear optical materials [3,5], it is necessary to modify the both chain and terminal groups by specific ways. In a case when polymethine dyes use as non-linear optical materials [3,5], it is often necessary to modify additionally both the chain and terminal groups to effective influence just on higher electronic transitions nature. One of the most effective chemical design pathways is an introduction of the heteroatoms. The previous study has shown that the replacement of the hydrogen in the polymethine chain of the cyanine dyes by fluorine atom with its high electronegativity could considerably affects not only on the positions of the first absorption band [6–9], but also on the energy of the second electronic transition [10]. As a further development of this conception, the investigation of new cyanine dyes with the fluorines in the open polymethine chain and with terminal groups of variable basicity were performed. The detailed analysis of the influence of the replacing of one or several hydrogen atoms in the polymethine chain by corresponding number of fluorine atoms on equilibrium molecular geometry, charge distribution and electronic transitions in both first and next higher excited states was performed.

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2. Materials and methods

The general structures of the investigated dyes are presented in Fig. 1. Methods of the synthesis of corresponding thiacyanines **1–3** and **7–9**, quinocyanines **4–6** and **10–12** were described earlier [6–11].

NMR (nuclear magnetic resonance) spectra. All NMR measurements were carried out on Varian GEMINI 2000 spectrometer with ^1H and ^{13}C frequencies of 400.07 and 100.61 MHz, respectively at 293 K. Tetramethylsilane was used as a standard for δ (NMR chemical shifts) scale calibrating. ^1H NMR spectra were recorded with spectral width 8000 Hz and numbers of points 32,000; ^{13}C NMR spectra were recorded with spectral width 30,000 Hz and numbers of points 128,000. 1H–1H COSY [12] spectra were acquired into 2048 (F2) and 512 (F1) time-domain data matrix and 2048 (F2) \times 2048 (F1) frequency-domain matrix after zero-filling.

NOESY [13] spectra were acquired, if necessary, with parameters similar to COSY spectra. Mixing times were determined preliminary from T1-measurement experiment for each sample by a conventional inversion-recovery method. Heteronuclear chemical shift correlation (HETCOR) [14] was used to determine ^1H – ^{13}C attachment with 2048 (F2) \times 256 (F1) time-domain matrix and 2048 (F2) \times 1024 (F1) frequency-domain matrix after zero-filling. The average value of one bond constant JCH was set to 140 Hz. HETCOR for determination long range correlation had very similar parameters and average value of multibond C–H coupling constant was set to 8 Hz.

UV–Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in acetonitrile and ethylene glycol (spectral grade).

The fluorescence excitation spectra and anisotropy of fluorescence excitation spectra are performed using a CM 2203 spectrofluorimeter (Solar, Belarus). The fluorescence excitation anisotropy spectra were measured in viscous solutions to reduce rotational reorientation and at low concentrations ($C \approx 10^{-6}$ M) to avoid reabsorption of the fluorescence. The anisotropy, calculated by $r(\lambda) = \frac{I_{\parallel}(\lambda) - G \times I_{\perp}(\lambda)}{I_{\parallel}(\lambda) + G \times 2 \times I_{\perp}(\lambda)}$, is measured by setting the emission wavelength, typically near the fluorescence maximum, with a fixed polarization. Then, the fluorescence intensity is recorded as a function of excitation wavelength λ at polarizations parallel ($I_{\parallel}(\lambda)$) and perpendicular ($I_{\perp}(\lambda)$) to the emission polarization. A G-factor expresses sensitivity ratio of detection system for perpendicular and parallel polarized light [15].

The quantum-chemical calculations were performed to study the dependence of the electron structure and electronic transitions on molecular constitution. The equilibrium geometry of dye molecules in the ground state was optimized by the non-empirical DFT/6-31G(d,p)/B3LYP methods (package Gaussian 03 [14]); the Mulliken charges were used. The electronic transition characteristics were

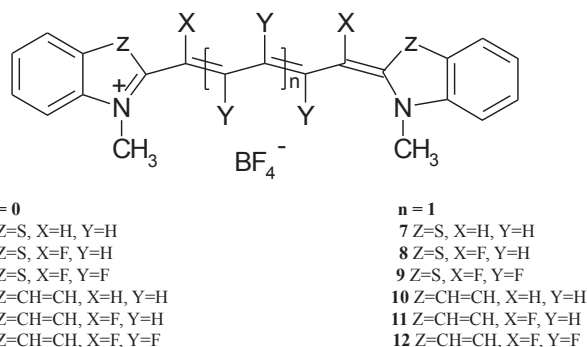


Fig. 1. Formulae of dyes investigated.

calculated by the non-empirical (TD/DFT/6-31G(d,p)/B3LYP) method and semi-empirical ZINDO method. Of course, there are not the perfect coinciding of the calculated and experimental data (what is typical for this approach [16,17]); however it's enough to analyze correctly the nature of the electronic transitions.

3. Results and discussion

3.1. Equilibrium molecular geometry

The calculations of the equilibrium molecular geometry showed that conjugated part of all molecules is planar that is typical for π -electron systems [18]. Only there exist certain spatial hindrances between the terminal groups and polymethine chain in the quinocyanines. One can see from Fig. 2a that the torsion angle between quinolinium residue and chain is equal $\varphi_1 \approx 12^\circ$ in the unsubstituted dye **4**, while the disturbance of the molecular planarity somewhat increases upon replacing of the hydrogen atom in the α -position of the chain by the more bulky fluorine atom in the dye **4** and **6** with the fluorinated chain, so that the angle between the planes of the chain and terminal group reaches $\varphi_1 \approx 24^\circ$, as it is shown in Fig. 2b. Besides, the calculations show that the nearest part of the chain is also out of plane and the next torsion angle is equal to $\varphi_2 \approx 14^\circ$. Because of the such spatial hindrances, the other conformers of the dye **6** obtained by the rotation of the terminal group can exist with the different torsion angles as presented in Fig. 2c.

The existence of cyanine dyes conformational structures was previously demonstrated in Refs. [19,20]. Their origins can be connected with steric hindrance, caused by quinoline nucleus. The optimized molecular geometry of dye **6** and its unsubstituted analogue **4** are shown in Fig. 2. As seen from Fig. 2 even in the unsubstituted dye's chain exist steric hindrance that is caused by

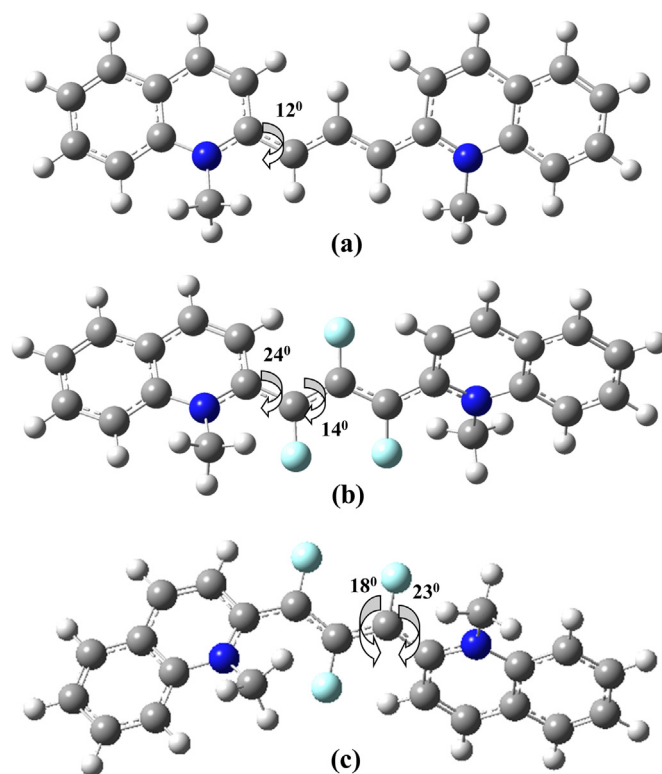


Fig. 2. Optimized molecular geometry of unsubstituted quinocarbocyanine **4** (a) and two conformers of fluorinated analogue **6** (b, c).

repulsion of bulky methyl groups on the nitrogen atom and the hydrogen atom in the α -position. Due to this steric hindrance a quinoline nucleus is rotated by 12° towards to the polymethine chain. Calculations predict a much greater steric hindrance in dye 6 with fluorine atoms (Fig. 2b): rotation on the first bond in the polymethine chain reaches 24° , in addition, there is also a rotation by 14° on the second bond. Consequently, it's make possible the existence of other conformers with transition into *cis*-conformation of one or even both terminal heterocycles.

One of main distinguishing characteristic of the polymethines is known to be equalizing of the carbon–carbon (C–C) bonds within the polymethine chain, in contrast to the polyenes [19,20]. In fact, Fig. 3 demonstrates that the calculated CC-bonds within the open chain of the unsubstituted dyes 1, 4, 7 and 10 are practically equalized and equal to $\approx 1.4 \pm 0.015$ Å, only the utmost bonds (connecting the chain with the residues) in the dyes polymethine chain with the quinolinium residues are slightly increased (up to 1.422 Å). In the same time, the elongation of the polymethine chain ($n = 1 \rightarrow n = 2$) causes an appearance of the certain lengths alternation of the neighbouring bonds from both chain ends to the chain center, particularly, in the substituted dicarbocyanines.

As regards to the sensitivity of the effects on the terminal groups, the performed calculations show that increasing of donor strength of the terminal residues upon going from the thiacyanines to the quinocyanines is accompanied by lengthening of the utmost bonds, and hence to increasing of the bond lengths alternation along the chain from its ends to its center, in exact accordance with the theoretical postulation about dependence of the amplitude of the bond lengths alternation on the donor properties of the terminal groups [21]. This tendency is hold true for both carbocyanine and dicarbocyanine.

The replacing of the hydrogen atoms in the chain by the fluorines is seen from Fig. 3 to affect only slightly towards the bond lengths, so that the equalizing of the neighbouring bonds lengths remains. Nevertheless, the lengths of the utmost left and right bonds somewhat increase, while lengths of the other bonds, on the contrary, decrease (at approximately 0.01 Å), in comparison with the corresponding unsubstituted thia- and quinocyanine. This fact could be connected with the relative increasing of the terminal groups basicity (discussed above): it was established that terminal

residues with the higher basicity introduction causes increasing of the bond orders (and hence length) alternation from the center of the polymethine chain to its ends [21]. The calculations were performed both for *cis*-isomer and all *trans*-isomers. Analysis of obtained bond lengths showed that they are practically the same.

The negligible influence on the lengths of the bonds involved the carbon atoms connected with the fluorine atoms is confirmed experimentally by RCA spectroscopy [8]: it was established that bond lengths in the chain of the thiacyanocyanine with the totally fluorinated chain 3 are equal: 1.399; 1.384; 1.378 and 1.411 Å and are approximate to the bond lengths in the unsubstituted dye 1: 1.391; 1.383; 1.384 and 1.393 Å (molecules in the crystal are unsymmetrical because of the unsymmetrical disposition of the counter ions in the unit cell).

3.2. Charge distribution in polymethine chain

As opposite to the bond lengths, the calculations reveal that the atomic charges in the chromophore are appreciably sensitive to the fluorine atoms introduction. Fig. 4 demonstrates the significant alternation of the electron densities along the chromophore extended between nitrogen atoms (so-called Kuhn's chain [22]); it is a characteristic property of the polymethine dyes, in contrast to the polyenes with their equalizing of the electron densities at the carbon atoms [19–21]. Comparison the charge distributions in the chain of the unsubstituted and fluorinated cyanines shows that the chemical modification of the dyes by replacing of the hydrogen atoms by the fluorine atoms (Fig. 4) causes the drastic change of the charge distribution at that carbon atoms which are bounded with the fluorines: in the α, α' -positions in the disubstituted dyes 2, 5, 8 and 11; and in totally fluorinated polymethine chain 3, 6, 9 and 12. Because of the substantial polarization of the C–F bond, the sizeable positive charge is located at the carbon atoms in the substituted positions, while the calculations give the negative charges for the all carbons in the dyes 1, 4, 7 and 10. As regards to the order (or phase) of the alternation (of the excess or deficit of electronic densities) in the chain of the α, α' -disubstituted dyes in comparison with the unsubstituted cyanines, the amplitude of the alternation of electronic densities (or charges) increasing appreciable. In contrast to the dyes with only two fluorine substituents in

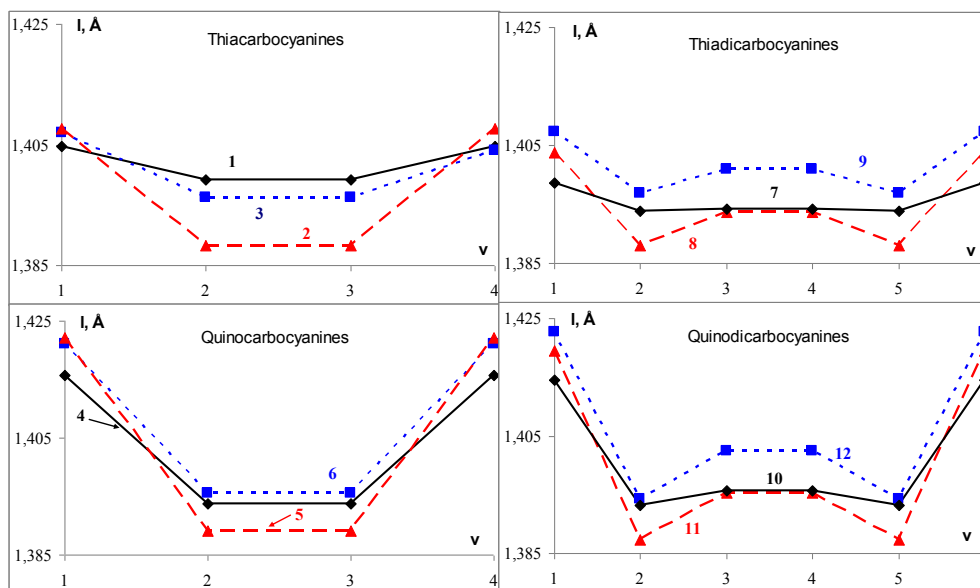


Fig. 3. Bond lengths in the chain of the dyes 1–12 (unsubstituted —; disubstituted — —; total substituted ······).

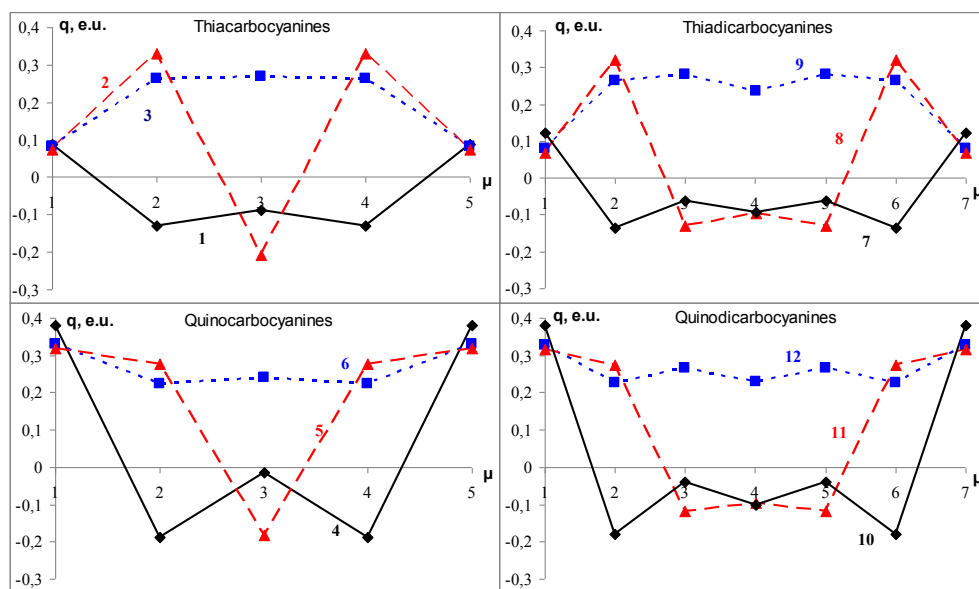


Fig. 4. Charges at the carbon atoms in the chain of the dyes 1–12 (unsubstituted —; disubstituted ----; total substituted).

the polymethine chain, the calculations give the evident equaling of the atomic charges in the chain of the totally substituted dyes **3**, **6**, **9** and **12**. In the same time, it is to be specially mentioned that the charge at the carbon atom of the each terminal group connected with chain do not practically change. Also, Fig. 4 shows that the charge distribution in the polymethine chain is weakly sensitive to the number of the vinylenes groups, i.e. it is similar in both carbo- and dicarbocyanines. In contrast, the basicity of the terminal residues (going from thiocyanines to the quinocyanines) causes the appreciable change of the atomic charges in the polymethine chain.

Such appreciable changes of the electron densities at the carbon atoms in the open polymethine chain of the fluorinated dyes causes redistribution of the total positive charge between the molecular fragments - the chain and both terminal groups. It is to be taken in consideration that the fragmentary charges in the conjugated system of the cyanine dyes depend directly on the donor strength of the terminal groups. Brooker [23] proposed to testify donor strength of the terminal groups as their ability to transfer the electron density from terminal residues to the polymethine chain; He have named this property *basicity*. The calculated summary charges located in the different fragments of the dyes total chromophore investigated are presented in Table 1.

Table 1
Charge distribution between chain and terminal groups in dyes 1–12.

Dye	n	Chain	$\sum q_{\mu}(TG_1)$	$\sum q_{\mu}(\text{Chain})$	$\sum q_{\mu}(TG_2)$	$\Delta q_{\mu}(C)$
1	0	CHCHCH	+0.489	+0.022	+0.489	
2		CFCHCF	+0.522	-0.044	+0.522	+0.066
3		CFCFCF	+0.5105	-0.021	+0.5105	+0.043
4	0	CHCHCH	+0.547	-0.094	+0.547	
5		CFCHCF	+0.5345	-0.069	+0.5345	-0.025
6		CFCFCF	+0.575	-0.150	+0.575	+0.056
7	1	CHCHCHCHCH	+0.475	+0.050	+0.475	
8		CFCHCHCHCF	+0.4565	+0.087	+0.4565	-0.037
9		CFCFCFCFCF	+0.5035	-0.007	+0.5035	+0.057
10	1	CHCHCHCHCH	+0.532	-0.064	+0.532	
11		CFCHCHCHCF	+0.5125	-0.025	+0.5125	-0.039
12		CFCFCFCFCF	+0.5605	-0.121	+0.5605	+0.057

Remark: $\sum q_{\mu}$ is a total sum of the atomic charges within the molecular fragment, where the summation runs over atoms including hydrogens, carbons and heteroatoms; $\Delta q_{\mu}(C) = \sum q_{\mu}(\text{substituted chain}) - \sum q_{\mu}(\text{unsubstituted chain})$.

In exact accordance with Brooker's statement about the basicity as a characteristic of the donor strengths of the terminal groups, translating from the thiocyanines with any lengths of both unsubstituted and substituted polymethine chain to the corresponding quinocyanine is regularly accompanied every time by transferring of the electron density from both terminal groups to the open chain, that directly point out the higher donor ability of the quinoline residue in comparison with the thiazole residue. In all quinocyanines, the total charge located in the chain is negative, its quantity being the maximum in the dyes **6** and **12** with totally fluorinated chain and minimum in the disubstituted dyes **5** and **11**.

In respect of the fluorine substituents influence, Table 1 shows that the total electron densities in the chain estimated quantitatively by the value $\Delta q_{\mu}(C) = \sum q_{\mu}(\text{substituted chain}) - \sum q_{\mu}(\text{unsubstituted chain})$ decreases in the carbocyanines (excepting the α, α' -disubstituted thiocarbocyanine **2**) and increases in all dicarbocyanines.

3.3. ^{13}C chemical shifts

It is well-known that the considerable cyanine-like alternation of the charges at neighboring carbon atoms is confirmed experimentally by NMR spectroscopy: the ^{13}C chemical shifts (δ_{μ}) for the neighboring carbon atoms are shifted in the opposite field, that agrees with the calculated electron density values at the atoms [24,25]. It is logically that the measured NMR spectra of the dyes studied are sensitive to the introduction of the fluorine atoms in the chromophore. The observed ^{13}C chemical shifts for the carbon atoms in the polymethine chain as well as the carbon atoms of the terminal groups connected with the chain of thia- and quinocarbocyanines are presented in Fig. 5.

In the first place, all signals along the chain alternate regularly in the neighboring positions, in the good accordance of the calculated atomic charges, especially, in the unsubstituted dyes **1** and **4**. Going over from thiocarbocyanine **1** to the dye **4** with the more basic terminal quinolinium residues is accompanied by decreasing of the chemical shifts values for the atoms in the positions with the positive charges, that is connected with the higher transformation of the electron density from terminal groups to the polymethine chain in the more basic quinocyanine dyes (see Table 1). Also, Fig. 5

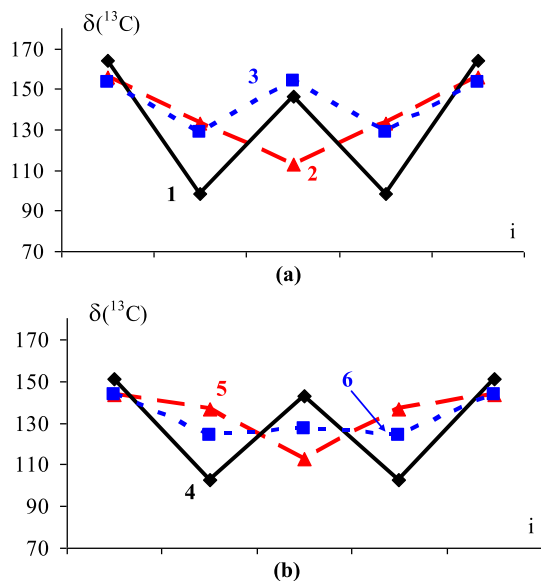


Fig. 5. Chemical shifts of carbon atoms in the chain of the dyes 1–3 (a) and 4–6 (b).

shows the high sensitivity of the chemical shifts to the change of the chemical constitution of the dyes by replacing of the hydrogen atoms to fluorine atoms in the chain. Therefore, two fluorine atoms in the α,α' -positions of both thiacyanine **2** and quinocyanine **5** cause the significant downfield movement of the chemical shifts for the corresponding carbon atoms, while signals for the atoms in central position move upfield, in comparison with unsubstituted dyes in full coincidence with the changes of the calculated charges at these atoms.

Unlike, replacing of all hydrogens in the chain by fluorine atoms (Fig. 5) remains in the same order of the alternation of chemical shifts, but their alternation amplitudes are appreciable lower. It should be noted that the signals for the carbon atom of both terminal heterocycles connected with the chain in both totally substituted dyes, **3** and **6**, as well as for the atom in the *meso*-position of the dye **3** are close to the signals in the corresponding unsubstituted dyes. In the same time, the signals of two carbon atoms in α,α' -positions of the chain are moved downfield, whereas chemical shift for the atom in the *meso*-position of the quinocarbocyanine **6** is observed in the more downfield, in the concordance with the distribution of the calculated charges at the corresponding carbon atoms. As a general conclusion, the changes of the chemical shifts in the ^{13}C spectra confirm the changes of the charge distribution upon introduction of the fluorine atoms in the polymethine chain of the both cyanine dyes series.

3.4. Energy levels of essential MOs

The modification of the constitution of the polymethine chain by replacing of the hydrogen atoms by fluorines should be naturally accompanied by the appreciable changes in electron structure, including the distribution of the charges at the atoms, bond lengths, positions of the electron levels and electronic transitions. Though, at the beginning, let's consider the discrepancy in the positions of the frontier and nearest levels involving in the lowest electronic transitions in the thia- and quinocarbocyanines, **1** and **4**, correspondingly. The performed calculation gives that the going from dye **1** to its quinoanalogue **4** (Fig. 6) is accompanied with the appreciable shifting up of the lowest vacant levels and slight shifting down of the highest occupied levels. Also, one can see that

HOMO-1 is the totally delocalized orbital similarly to the HOMO and LUMO while HOMO-2 and HOMO-3 are degenerated local orbitals (without the participation of the chain carbon atoms) in the thiacyanocyanine **1**, in contrast to the quinocarbocyanine **4** with its degenerated local orbitals HOMO-1 and HOMO-2. It is worth to note that both mentioned dyes differs essentially by the distances between the lowest and next vacant levels as well as between the highest and the next deep occupied levels, that leads to the change of nature of the second electronic transition.

Any modification of the cyanine dyes chemical constitution by change of the terminal groups constitution, the polymethine chain lengths and introduction of fluorine atoms is naturally accompanied with the corresponding change of the molecular levels positions, that is clearly seen from Fig. 7 where the energies of the two lowest vacant and two highest occupied MOs are presented. So, providing the same polymethine chain (the same length and the same substituents), as a rule, the frontier levels are positioned higher in the quinocyanines (excepting only the unsubstituted carbocyanines), that agree with the higher basicity of the quinolinium terminal residues. In the same time, the calculations do not give the similar dependence of the energies of the nearest to frontier orbitals, LUMO+1 and HOMO-1. Also, there are no strict regularity in the change of the positions of levels upon lengthening of the polymethine chain.

Further, Fig. 7 shows some tendency in influence on energy levels positions by hydrogens replacement to fluorine atoms. One can see that going over from the unsubstituted dyes to the corresponding disubstituted dyes and then to the totally fluorinated cyanines causes the shift of levels down, with the exception of both lowest vacant levels of the thiacyanocyanines **1**, **2**, **3**, where these levels shift up; as well as, the effect of two fluorines introduction on the HOMO is seen from Fig. 7 to be negligible.

The change in the positions of the frontier electron levels results, firstly, in the change of the lowest electronic transitions energies.

3.5. Electronic transitions and spectral characteristics

Besides the RCA and NMR ^{13}C spectra, the influence of the modification of the polymethine chromophore by the fluorine atoms can be determined experimentally by a measurement of the electronic transitions energies via absorption/fluorescence and fluorescence excitation anisotropy spectra. The typical spectra of the dyes **8**, **9**, **10** and their derivatives are shown in Fig. 8, while the measured spectral characteristics are collected in Table 2.

It could be expected that the two lowest electronic transitions should be most suitable for such investigation. So, spectral effect of the change of energy of the first electronic transition can be detected by the shift of the longwavelength band in the absorption spectrum, while the change of energy of the second transition can be detected by the shift of the minimum in the anisotropy spectrum. One can see from Fig. 8 that the second transition does not exhibit itself in the absorption spectra because of its negligible oscillator strengths. According to previously obtained results dyes with fluorinated polymethine chain characterized by conservation of the symmetry of the absorption and fluorescence spectra, that points on the stability of the excited fluorescence state [10]. However, the measurements give the substantial decreasing of the quantum yield upon going from unsubstituted cyanines to their fluorinated analogues.

For the sake of an illustration, the scheme of the lowest electronic transitions in the unsubstituted thia- and quinocarbocyanine (**1** and **4**) is presented in Fig. 6, while the calculated characteristics of the lowest transitions of the all dyes are collected in Table 3. Analysis of the calculated data has shown that the first electronic

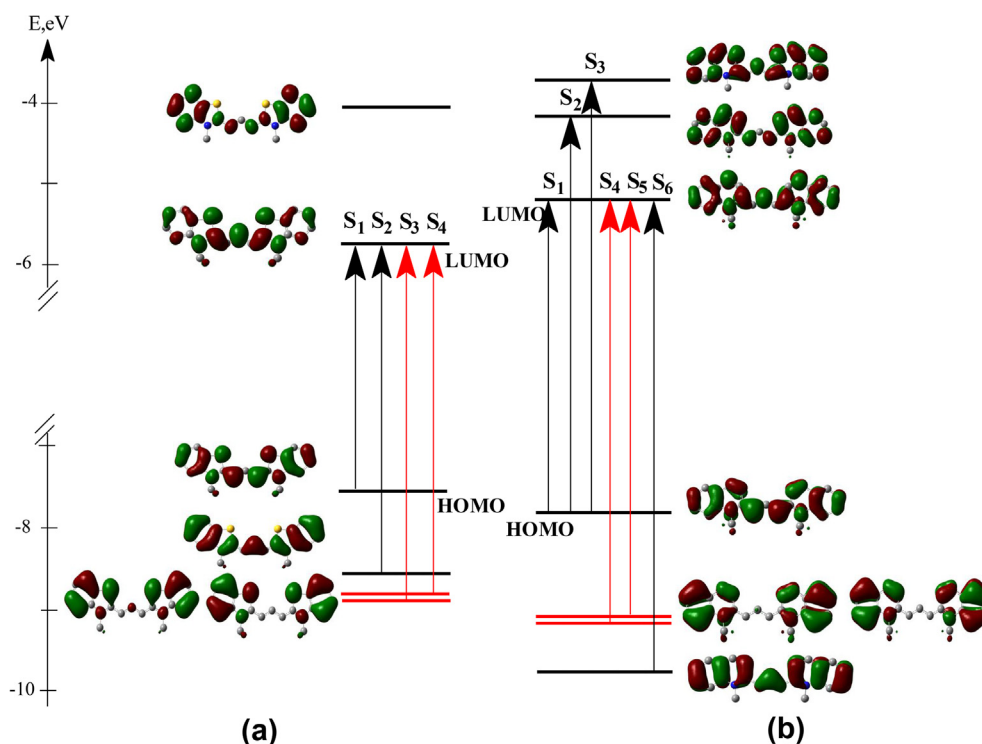


Fig. 6. Scheme of electron levels and shapes of MOs: a) dye 1; b) dye 4.

transition in all dyes studied is practically described by only electron configuration involving the frontier levels: $|S_0 \rightarrow S_1\rangle \approx |HOMO \rightarrow LUMO\rangle$. In contrast, the nature of the second transition in the thiacyanines **1–3**, **7–9** and in the quinocyanines **4–6**, **10–12** differs principally. One can see from both Table 3 and Fig. 6 that this transition involves the different MOs:

$|S_0 \rightarrow S_2\rangle \approx |HOMO-1 \rightarrow LUMO\rangle$ in thiacyanines **1–3**, **7–9**;
 $|S_0 \rightarrow S_2\rangle \approx |HOMO \rightarrow LUMO+1\rangle$ in quinocyanines **4–6**, **10–12**;

It is to be emphasized, that the second transition is described by only electron configuration in both dye series. Thus, the $|S_0 \rightarrow S_2\rangle$ transition involves the two orbitals of the same symmetry; hence it is polarized perpendicularly to the polymethine chain, according to its symmetry $A_1 \rightarrow A_1$, in contrast to the symmetrical first electronic transition ($A_1 \rightarrow B_1$) polarized along polymethine chain. The performed calculations are seen from Table 3 to give the negligible oscillator strength for the second transitions, $f_2 < 0.02$, in contrast to the substantial values for the first transition: $f_1 \approx 1–2$, that is

why the second transition does not manifest itself in the absorption spectra. Experimentally, it can be detected by fluorescence excitation anisotropy spectra which is measured by polarized light and hence points distinctly the positions of the electronic transitions with different polarization (in respect to their first transition [15]); it is obtained as the first minimum in the corresponding spectra (Fig. 8).

As a preliminary, it is to be noted that the change of the transition energy $\Delta E_{i \rightarrow j}$ is defined not only by the changes of the positions of the involved levels, ε_i and ε_j , but also by the change of the integrals of the Coulomb (J_{ij}) and resonance (K_{ij}) interaction between i -th and j -th MOs, according to the following equation [18]:

$$\Delta E_{i \rightarrow j} = \varepsilon_j - \varepsilon_i + 2K_{ij} - J_{ij} \quad (1)$$

Both integrals depend directly on the shape (coefficients) of the involved MOs, but there is not an exact correlation between the changes of the transition energies and changes of the energies of the levels involved.

Comparison of the calculated characteristics (Table 3) and corresponding spectral data collected in Table 2 shows the meaningful disagreement between the calculated wavelength of the first electronic transition and obtained position of the longwavelength of the band maximum. It is typical disadvantage of the TD DFT method upon calculation of the electronic transitions of the polymethine dyes, especially, with the higher vinyls [16]. The semi-empirical method ZINDO as seen from Table 3 to give more realistic wavelengths, i.e. there is rather better agreement with the experimental data for the both transitions.

Nevertheless, taking into consideration the considerable values of the first and second transitions splitting (that agrees experimentally with the spectral data), we can assume that the calculations give correctly the order sequence of some lowest electronic transitions, i.e. the calculated characteristics could be used for the

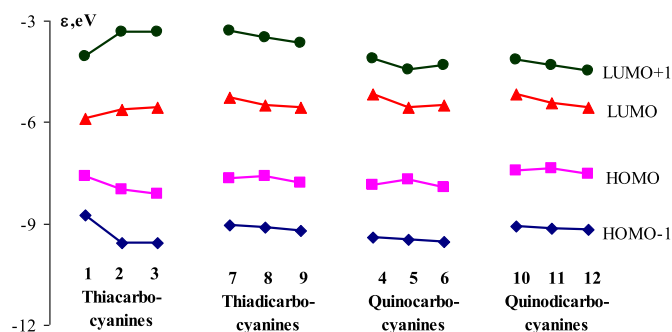


Fig. 7. MO energies in unsubstituted (**1**, **4**, **7**, **10**), disubstituted (**2**, **5**, **8**, **11**), totally substituted (**3**, **6**, **9**, **12**) dyes.

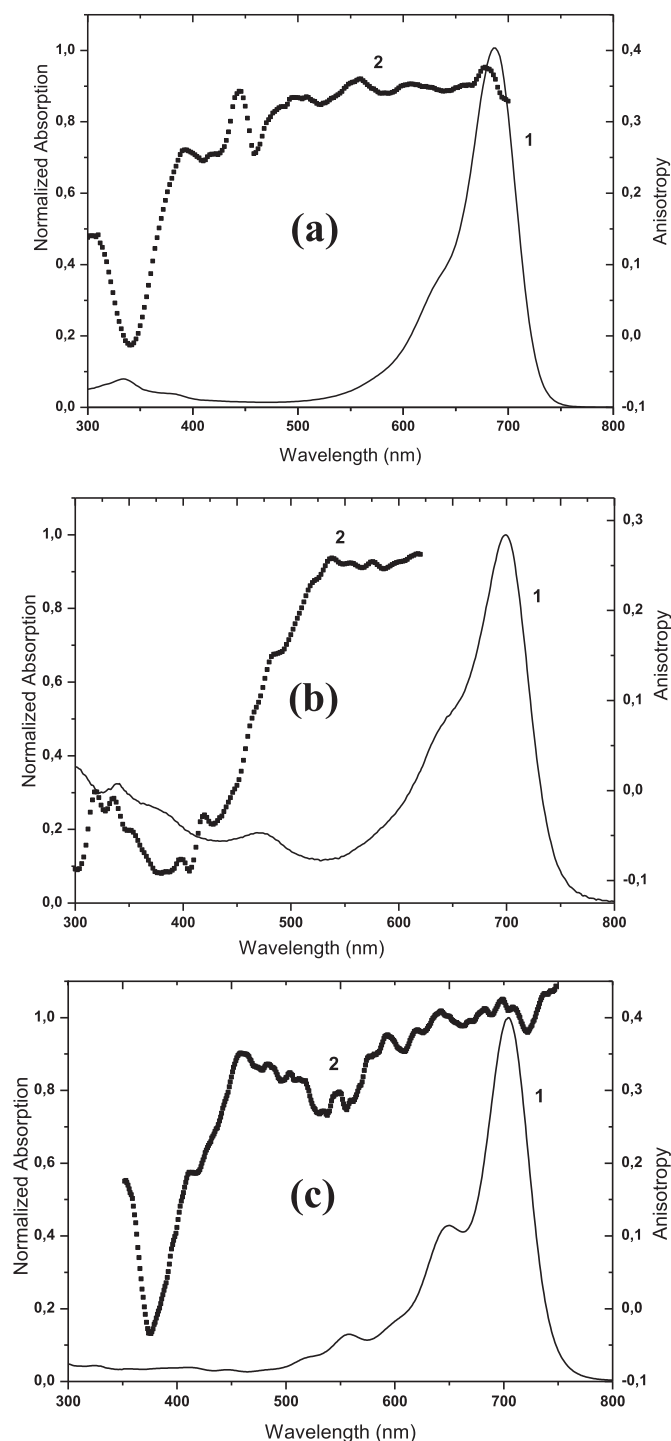


Fig. 8. Absorption (1) and excitation anisotropy spectra (2) measured in fluorescence peaks for dyes **8** (a), **9** (b), **10** (c), correspondingly.

analysis of the nature, at least, of the first and second transitions, as well as for the qualitative estimation of the effects of the chemical constitution modification of the cyanine dyes investigated.

Here, we are restricted only by the transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ detected experimentally.

It's well-known that the first electronic transition in the cyanine dyes [1–3,15,16,21,23] is polarized parallel to polymethine chromophore and manifested itself by high intensive and narrow longwavelength band in the absorption spectra. This band is regularly shifted bathochromically upon introduction of new

vinylene group upon ≈ 100 nm. This effect is illustrated in Table 2 for the unsubstituted quinocyanines **4**, **10** and fluorinated thiacyanines **3**, **9**.

As regards to second transition, the combined spectral and quantum-chemical investigations show that it is polarized perpendicularly to the first transition and hence it manifested as the first minimum in the excitation anisotropy spectra [3]. The excitation anisotropy spectra with the typical minimum at 300–400 nm for the two thiadicarbocyanines: difluorinated dyes **8** and **9** with totally fluorinated polymethine chain are given in Fig. 8. Similarly to the position of the longwavelength band maximum in the absorption spectrum, the minimum in the excitation anisotropy spectrum is sensitive to the modification of the investigated dyes chemical constitution. The shapes of the spectral curves of the other thiacyanines are similar; the positions of their maxima and minima are given in Table 2. It is worth to note that the experimental distance between the longwavelength band maximum and minimum in the excitation anisotropy spectra is comparatively large, that are in good agreement with the calculated difference of the wavelengths of the first and second electronic transitions: $\Delta\lambda(S_1-S_2) = \lambda(S_0 \rightarrow S_1) - \lambda(S_0 \rightarrow S_2)$. Thus, we can state that the observed comparatively deep minimum in the excitation anisotropy spectrum of the thiacyanines is undoubtedly connected with the second transitions involving the HOMO-1 and LUMO. Also Table 3 allows to consider HOMO and HOMO-1 as two splitting MOs generating from the initial donor orbitals of both terminal groups, similarly to other symmetrical and symmetrical cationic polymethine dyes [25].

In contrast to the thiacyanines, the second (as well as third) electronic transition in the quinocyanines is not connected with the next occupied levels, but with HOMO and LUMO, that is demonstrated in Fig. 6b and in Table 3. Thus, it could be expected the principal change in the fluorescence excitation anisotropy spectra. Indeed, comparison of the really measured anisotropy spectrum of the quinocarbocyanine **4** with spectrum of any thiacyanine confirms this assumption. Besides the sharp deep minimum at the same spectral region 330 nm, as for the thiacyanine [10], the wide minimum appears at the shortwavelength spectral region at the approximately 425–475 nm in the anisotropy spectrum of quinocarbocyanine **4** (see Table 2). Our measurements have shown the similar depression (wide minimum) at 450–550 nm in the spectrum of vinylog **10** (see Fig. 8c).

It follows from Fig. 6b that calculations of the quinocarbocyanine **4** predict the existence of an electronic transition starting from another splitting donor orbital, |HOMO-3 \rightarrow LUMO>, which is similar to the second transition in the corresponding thia analogue **1**, starting from the second splitting occupied donor orbital: |HOMO-1 \rightarrow LUMO>. Taking into consideration the same nature of the electronic transitions (|HOMO-3 \rightarrow LUMO> in the dye **4** and |HOMO-1 \rightarrow LUMO> in the dye **1**), we could assume that the deep minimum at ≈ 330 nm in the anisotropy spectrum of the quinocyanine (see Table 2) is connected with the higher $\pi \rightarrow \pi^*$ transition | $S_0 \rightarrow S_6$ >, as it is shown in Fig. 6b.

Therefore, the observed wide minimum in the anisotropy spectra of quinocyanines should be connected with two higher transitions involving the same HOMO and two vacant orbitals: LUMO + 1 and LUMO + 2.

Besides, analysis shows that there exist also electronic transitions starting from the local MOs, as one can see from Fig. 6. The performed calculations gives that the energies of such transitions in the thiacyanines **1–3**, **7–9** are higher than the energies of the first two transitions involving splitting donor MOs: |HOMO \rightarrow LUMO> and |HOMO-1 \rightarrow LUMO>; due to their low oscillator strength the local transitions practically are not manifested themselves in the absorption spectra.

Table 2
Spectral characteristics of dyes **1–11**.

Dye	n	Chain	Absorption (CH ₃ CN)			Anisotropy		
			λ_{\max} , nm	$\Delta\lambda_{\max}$, nm	V, nm	λ_{\min} , nm	$\Delta\lambda_{\max}$, nm	V, nm
1	0	CHCHCH	555			340		
2	0	CFCHCF	586	31		—	—	
3	0	CFCFCF	578	23		350	10	
7	1	CHCHCHCHCH	658		103	380		40
8	1	CFCHCHCHCF	686	28	100			
9	1	CFCFCFCFCF	692	34	114	395	15	45
4	0	CHCHCH	605			≈ 330 425–475		
5	0	CFCHCF	670	65		—		
6	0	CFCFCF	632, 667	27, 62		—		
10	1	CHCHCHCHCH	705		100	340 450–550		
11	1	CFCHCHCHCF	764	59	96	—		

Comments. $\Delta\lambda = \lambda(\text{substituted}) - \lambda(\text{unsubstituted})$; $V = \lambda(n = 2) - \lambda(n = 1)$.

Table 3
Characteristics of lowest electron transitions of dyes **1–12** were calculated by TD-DFT and ZINDO (in bracket).

Dye	n	Chain	Transition	λ , nm	f	Symmetry	$\Delta\lambda$, nm	V, nm	Main configuration
1	0	CHCHCH	$S_0 \rightarrow S_1$	472 (507)	1.394	B ₁			$ S_0 \rightarrow S_1 > \approx$ $ HOMO \rightarrow LUMO>$
			$S_0 \rightarrow S_2$	397 (343)	0.014	A ₁			$ S_0 \rightarrow S_2 > \approx$ $ HOMO-1 \rightarrow LUMO>$
2	0	CFCHCF	$S_0 \rightarrow S_1$	494 (547)	1.376	B ₁	22 (40)		
			$S_0 \rightarrow S_2$	351 (351)	0.022	A ₁	−46 (8)		
3	0	CFCFCF	$S_0 \rightarrow S_1$	472 (549)	1.502	B ₁	0 (44)		
			$S_0 \rightarrow S_2$	347 (359)	0.022	A ₁	−50 (16)		
7	1	CHCHCHCHCH	$S_0 \rightarrow S_1$	500 (565)	2.044	B ₁		28 (58)	
			$S_0 \rightarrow S_2$	358 (353)	0.014	A ₁		−39 (10)	
8	1	CFCHCHCHCF	$S_0 \rightarrow S_1$	538 (610)	1.996	B ₁	38 (55)	44 (63)	
			$S_0 \rightarrow S_2$	373 (368)	0.007	A ₁	15 (15)	22 (17)	
9	1	CFCFCFCFCF	$S_0 \rightarrow S_1$	531 (631)	2.049	B ₁	31 (66)	59 (82)	
			$S_0 \rightarrow S_2$	371 (383)	0.004	A ₁	13 (30)	24 (24)	
4	0	CHCHCH	$S_0 \rightarrow S_1$	479 (578)	1.630	B ₁			$ S_0 \rightarrow S_1 > \approx$ $ HOMO \rightarrow LUMO>$
			$S_0 \rightarrow S_2$	390 (365)	0.001	A ₁			$ S_0 \rightarrow S_2 > \approx$ $ HOMO \rightarrow LUMO + 1>$
			$S_0 \rightarrow S_3$	349 (329)	0.191	B ₁			$ S_0 \rightarrow S_3 > \approx$ $ HOMO \rightarrow LUMO+2>$
			$S_0 \rightarrow S_4$	340 (322)	0.030	A ₁			$ S_0 \rightarrow S_4 > \approx$ $ HOMO-1 \rightarrow LUMO>$
			$S_0 \rightarrow S_5$	338 (318)	0.085	B ₁			$ S_0 \rightarrow S_5 > \approx$ $ HOMO-2 \rightarrow LUMO>$
			$S_0 \rightarrow S_6$	312 (311)	0.005	A ₁			$ S_0 \rightarrow S_6 > \approx$ $ HOMO-3 \rightarrow LUMO>$
5	0	CFCHCF	$S_0 \rightarrow S_1$	535 (632)	1.449	B ₁	56 (54)		
			$S_0 \rightarrow S_2$	421 (384)	0.001	A ₁	31 (19)		
6	0	CFCFCF	$S_0 \rightarrow S_1$	528 (634)	1.544	B ₁	49 (56)		
			$S_0 \rightarrow S_2$	406 (380)	0.001	A ₁	16 (15)		
10	1	CHCHCHCHCH	$S_0 \rightarrow S_1$	531 (653)	2.219	B ₁		52 (75)	
			$S_0 \rightarrow S_2$	423 (388)	0.001	A ₁		33 (23)	
			$S_0 \rightarrow S_3$	377 (342)	0.245	B ₁		28 (13)	
			$S_0 \rightarrow S_4$	347 (333)	0.021	A ₁		7 (11)	
			$S_0 \rightarrow S_5$	346 (321)	0.008	B ₁		8 (3)	
			$S_0 \rightarrow S_6$	339 (319)	0.007	A ₁		27 (8)	
11	1	CFCHCHCHCF	$S_0 \rightarrow S_1$	578 (705)	2.126	B ₁	47 (52)	43 (73)	
			$S_0 \rightarrow S_2$	449 (408)	0.002	A ₁	26 (20)	28 (24)	
12	1	CFCFCFCFCF	$S_0 \rightarrow S_1$	588 (718)	2.049	B ₁	57 (65)	60 (84)	
			$S_0 \rightarrow S_2$	445 (414)	0.004	A ₁	22 (26)	39 (34)	

* $\Delta\lambda = \lambda(\text{substituted}) - \lambda(\text{unsubstituted})$; $V = \lambda(n = 2) - \lambda(n = 1)$.

Unlike, the second and third higher transitions involving the degenerated local orbitals (HOMO-1 and HOMO-2) in the quino-cyanines (Fig. 6b) are intermediate between the three transitions starting from the same HOMO (S_1 , S_2 , S_3) and the transition involving the delocalized HOMO-3 (S_6 , second splitting donor MO) and LUMO. Table 3 shows that the calculated oscillator strengths of both local transitions, f_4 and f_5 , are too low to be detected in the absorption spectra. It can be supposed that they could be mixed somewhat with other higher configurations ($|HOMO \rightarrow LUMO + 1, 2 >$) of the same symmetry. In contrast, the next higher transition, $S_0 \rightarrow S_6$, involving the second splitting donor orbital HOMO-3 (and hence should be considered as the coupled transition with first transition) is seen

from Table 3 to be sharply observed in the anisotropy spectrum as the deep minimum at ≈ 330 nm.

Now, let us consider the spectral effects of the fluorine atoms introduction in the cyanine dyes chromophore in detail.

The effect of two fluorine atoms. It is to be preliminarily noted that the non-empirical TD DFT method predicts the nonrealistic negative effect for the second transition (hypsochromic shift of the minimum in the anisotropy spectrum) in the thiocarbocyanines **1–3**, **7–9**, that contradicts the ZINDO calculation and experimental data. In the other cases, the calculated effects by both methods agree qualitatively with the obtained spectral results. Besides, there is a better agreement between the calculated and experimental

effects than between the wavelengths values obtained from the spectra and quantum-chemical calculations.

According to the well-known Forster-Dewar-Knott's rule (FDK's rule) [26–28], introduction of the donor substituents in the odd positions of the polymethine chain should cause the bathochromic shift, in contrast to the even positions where such modification of the chemical constitution should causes the opposite spectral effects. However, analysis above enables to consider the fluorine atom as a combine π -donor and σ -acceptor substituent, that could complicate usage of the conclusions basing on the perturbation theory.

The calculations performed in Table 3 give that replacing of two hydrogen atoms by fluorine atoms leads to decreasing energies of both $|S_0 \rightarrow S_1\rangle$ and $|S_0 \rightarrow S_2\rangle$ electronic transitions, that is in a good agreement with the bathochromic shifts of both maximum of the longwavelength band in the absorption/fluorescence spectra and of the minimum in the anisotropy spectrum upon going from unsubstituted dyes to the corresponding dyes with two fluorines in the α, α' -positions in polymethine chain. In the thiacyanine series, this effect somewhat increases upon chromophore lengthening, while the influence of two fluorine atoms in the quinocyanines is not practically sensitive to the length of the chain. Also, excepting thiacyanines 1–2, calculation shows weak sensitivity of the effect to the basicity of the terminal groups.

The spectral effects measured experimentally agree with the predicted data. Table 2 shows that only bathochromical shifts are observed upon symmetrical introducing of two fluorine atoms in α, α' -positions of the polymethine dyes 2, 5 and 8, 11 in a good agreement with FDK's rule. Unlikely to the weak sensitivity of the calculated effects on the basicity of the terminal groups, the experimental shift, $\Delta\lambda_{\max}$, is seen from Table 2 to increase twice upon going from the thiacyanines (dye pair 1 \rightarrow 2) to the corresponding dyes with the quinolinium residues (dye pair 4 \rightarrow 5). While the lengthening of the polymethine chain does not affect appreciably on the measured value $\Delta\lambda_{\max}$: 31 nm for the dye pair 1 \rightarrow 2 and 28 nm for the dye pair 7 \rightarrow 8.

One can see from Table 3 that spectral effect on the second transition should be appreciably lower, in comparison with the first electronic transition, that is confirmed by comparing calculated and experimental data (Table 2).

It is evident that the certain difference in the values of the effects in the carbo- and dicarbocyanines can result in the vinylenic shifts, i.e. spectral effects on the positions of the spectral band upon introduction of new vinylenic group in the polymethine chain: $V = \lambda(n = 2) - \lambda(n = 1)$. One can clearly see that the calculated parameter V increases regularly upon fluorine atoms introduction in the polymethine chain. The obtained spectra confirm these predictions, although the observed effects of the lengthening chain as seen from Table 2 to exceed nearly twice the calculated vinylenic shifts. In respect of the higher transitions, the calculations predict the essential lower vinylenic shifts, however comparison with experimental effects is difficult because of the deficiency of the measured values for the comparing dye pairs.

The effect of total fluorination of the polymethine chain. As a preliminary, we must to take into consideration that the totally substituted carbo- and dicarbocyanine contains the different number of the fluorine atoms in the open polymethine chain. Also, it is worth to mention that the introduction of the fluorine atom in the even position should cause the opposite effects, in comparison with the odd position, in accordance with FDK's rule. Thus, we could observed the cumulative effects in the dyes with the totally fluorinated chain.

As regards to the methods of the calculations, the semi-empirical ZINDO approximation gives more realistic effects that the non-empirical TD DFT method, especially, for the thiacyanines 1–3.

The main general conclusion is following: total replacement of the all hydrogen atoms in the polymethine chain by the fluorine atoms should be usually accompanied by the further decreasing of the electronic transitions energies: particularly $S_0 \rightarrow S_1$; and somewhat lower $S_0 \rightarrow S_2$, in comparison with only two fluorine substituents in the chromophore. In the carbocyanines with three substituents, the total effect increases upon increasing of the basicity of the terminal groups: from 44 nm (dye 3, ZINDO) to 56 nm (dye 6). In contrast, the calculation shows that influence of the five fluorines in the dicarbocyanines should be practically non-sensitive to nature of the terminal residues: 66 nm for the thiadicarbocyanine 9, and 65 nm for the quinodicarbocyanine 12.

In the same time, Table 2 points that the observed effects $\Delta\lambda_{\max} = 23$ nm upon going from the unsubstituted thiacyanines 1 to the dye 3 with three fluorine atoms in the chain is accompanied by decreasing spectral effects, in compare with dye pair 1 \rightarrow 2 with $\Delta\lambda_{\max} = 31$ nm; this means that the introduction of the π -donor fluorine atom in the even position leads to the hypsochromic shift of the longwavelength band in the absorption spectra. In the dicarbocyanine 9, the observed spectral effect should consist from two opposite components: bathochromic shift caused by three fluorine atoms in the three even positions (α, α', γ) of the chain, and hypsochromic shift caused by two fluorines in the odd (β, β') positions. As a result, the calculated spectral effect of the totally fluorinated polymethine chain regularly increases upon going from the thiacyanines to their higher vinylogs. In the pair quinocarbocyanines 4 \rightarrow 6, determination of the spectral effect becomes complicated because possible existence of two stereo isomers with the different band maxima (Fig. 9); the performed calculation results in increasing of the transition energy upon isomerisation of the dye 6. As seen from Fig. 9, two peaks are observed in the absorption spectra in weakly polar methylene chloride: 634 nm and 667 nm. The distance between them is 780 cm^{-1} that is much less than vibrational transition frequency ($\approx 1200\text{--}1300\text{ cm}^{-1}$). The ratios of bands intensity are changed in more polar solvents (DMF, CH_3CN) (Fig. 9). Probably the appearance of these peaks is connected with the presence of two conformers in solution at different wavelengths of the first electronic transition and with different sensitivity to the solvent polarity. As seen from Fig. 2b, steric hindrances are practically the same as in the molecule 6. Therefore *cis*-conformer of dye 6 also has nonplanar structure of chromophore. Important to note that in the asymmetric mono-*cis*-isomer the symmetrical distributions of charge are broken and as a

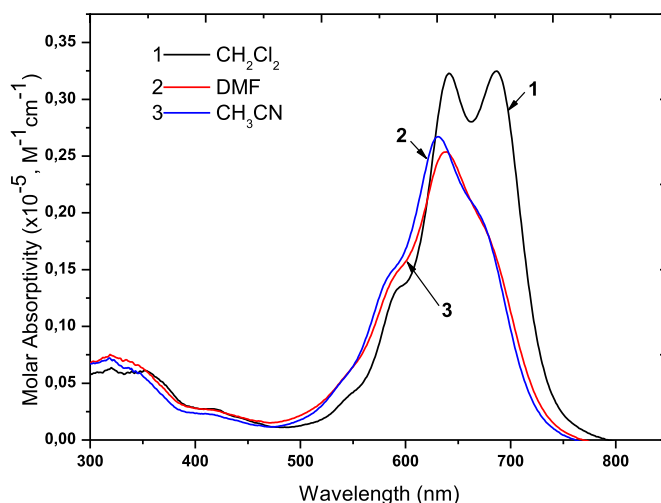


Fig. 9. Absorption spectra of the dye 6 in CH_2Cl_2 (1), DMF (2), CH_3CN (3).

result a dipole moment appeared. This fact can explain the difference in sensitivity of different conformers to the solvent polarity.

For the all-trans configuration (with more longwavelength band maximum), the spectral effect is seen from Table 2 to be close to the effect in the pair of the dyes **4** and **5** with two fluorine atoms in the chain.

It is logical that increasing of the effects upon lengthening of the chain should caused the increasing of the vinylene shift for totally fluorinated dyes; one can see from Table 3 that the parameter V reaches 82 nm for the pair of the dyes **3** → **9** and 84 nm for the pair of the dyes **6** → **12**, i.e. it does not dependent practically on the basicity of the terminal groups. The conclusions based on the calculated data are in the good agreement with the measured spectral results. However, the experimental vinylene shift is obtained only for the thiacyanine series: it increases somewhat ($V = 114$ nm), in comparison with this parameter for unsubstituted dyes **1** → **7** (103 nm) or disubstituted cyanines **2** → **8** (100 nm). Unfortunately, the similar experimental estimation of the vinylene shift for the quinocyanine series could not be obtained, as far as the synthesis of dicarbocyanine **12** with the total replaced chain proves unsuccessful.

4. Conclusions

Thus, the replacement of the hydrogen atoms in the polymethine chain of thia- and quinocyanines by the fluorine atoms affects only slightly on the bond lengths, so equalizing of the lengths of the neighboring bonds remains which agrees with RCA data published in Ref. [8].

In contrast, the atomic charges in the chromophore are appreciably sensitive to the introduction of the fluorine atoms, because of the substantial polarization of the C–F bond; that is in a good agreement with changes of ^{13}C chemical shifts. Also, there is a redistribution of the total positive charge between the molecular fragments: the chain and both terminal groups.

Going from dyes with unsubstituted chain to their fluorinated analogues is accompanied by the significant shift of the frontier and nearest levels and hence by the energies of the electron transitions change. Obtained effects in the absorption spectra are exceed the shifts in the fluorescence excitation anisotropy spectra that

correlate with the calculated changes of the wavelengths of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions.

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