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

CrossMark

Oksana I. Chernega [a], Svitlana M. Levchenko [b,*], Aleksey B. Ryabitskii [a], Andrii O. Gerasov [a], Oleksiy D. Kachkovskii [a], Yurii L. Yagupolskii [a]

[a] Institute of Organic Chemistry, National Academy of Sciences, Murmanskaya Str. 5, Kyiv 02094, Ukraine
[b] Institute of Molecular Biology and Genetics, National Academy of Sciences, Zabolotnogo Str. 150, Kyiv 03680, Ukraine

ARTICLE INFO

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 ^{13}C 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 $S_0 \rightarrow S_1$ transition is more sensitive to the fluorine substituents than the $S_0 \rightarrow S_2$ transition.

© 2015 Elsevier Ltd. All rights reserved.

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 $S_0 \rightarrow S_1$ 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.

---

* Corresponding author. Tel.: +380 99 220 97 04.
E-mail address: sveta.levchenko@gmail.com (S.M. Levchenko).

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].
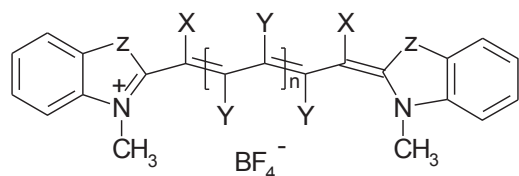
NMR (nuclear magnetic resonance) spectra. All NMR measurements were carried out on Varian GEMINI 2000 spectrometer with ^{1}H and ^{13}C frequencies of 400.07 and 100.61 MHz, respectively at 293 K. Tetramethylsilane was used as a standard for d (NMR chemical shifts) scale calibrating. ^{1}H NMR spectra 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) × 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 [1]H–[13]C attachment with 2048 (F2) × 256 (F1) time-domain matrix and 2048 (F2) × 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 $r(\lambda) = \frac{I_{II}(\lambda) - G \times I_{\perp}(\lambda)}{I_{II}(\lambda) + G \times 2 \times I_{\perp}(\lambda)}$, 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 ($I_{II}(\lambda)$) 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 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 $\varphi_1 \approx 12°$ 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 $\varphi_1 \approx 24°$, 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 $\varphi_2 \approx 14°$. 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
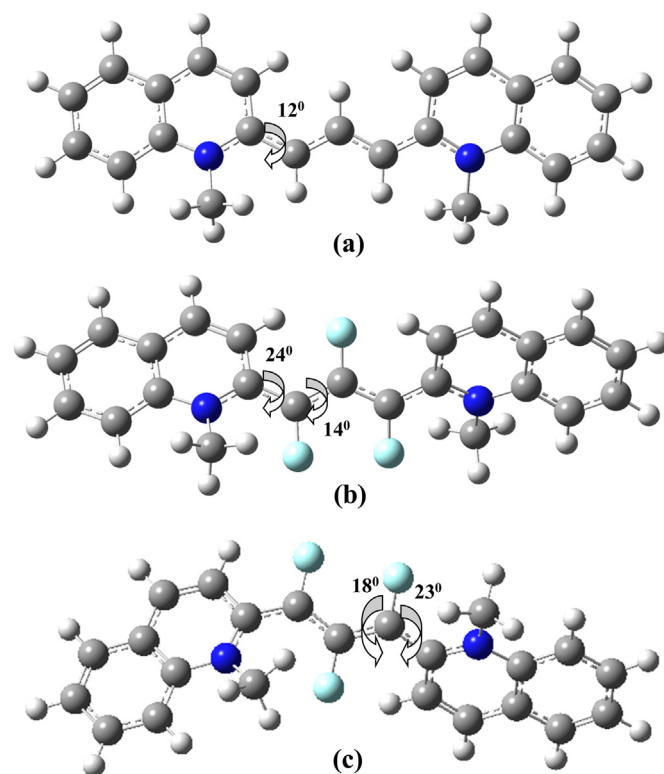

(a)

(b)

(c)

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

Fig. 1. Formulae of dyes investigated.

n = 0
1 Z=S, X=H, Y=H
2 Z=S, X=F, Y=H
3 Z=S, X=F, Y=F
4 Z=CH=CH, X=H, Y=H
5 Z=CH=CH, X=F, Y=H
6 Z=CH=CH, X=F, Y=F

n = 1
7 Z=S, X=H, Y=H
8 Z=S, X=F, Y=H
9 Z=S, X=F, Y=F
10 Z=CH=CH, X=H, Y=H
11 Z=CH=CH, X=F, Y=H
12 Z=CH=CH, X=F, Y=F