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Electronic properties of polymethine systems. 10. Electron structure and absorption spectra of cyanine bases

A.D. Kachkovsky*, N.V. Pilipchuk, V.V. Kurdyukov, A.I. Tolmachev

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmans'ka str. 5, Kyiv 94, 02660 Ukraine

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Abstract

Complex quantum-chemical and spectral studies of the features of the electron structure and absorption spectra of the bases' derivatives of the symmetrical cyanine dyes are performed. It is found that moving from cationic cyanines to their neutral bases is accompanied by a drastic increase in the bond length alternation, equalizing the electron densities at atoms in the chromophore and by sharp shifting up of the molecular levels. Spectral bands in the absorption spectra of the bases are essentially wider and lower intensive and hypsochromically shifted, what is suggested to be connected with different nature of the first electron transition in the cyanine dyes and their bases.

Keywords: Cyanine dyes; Bases; Electron structure; Absorption spectra; Quantum-chemical calculation

1. Introduction

Neutral bases of cyanine dyes are compounds closely related to the original ionic polymethines and can be considered just as their de-alkylated derivatives. Also, they are the most easily interpretable donor–acceptor conjugated systems. In the case of the simplest streptocyanines **1**, their bases can be presented by formulas **2**:

$$(H_3C)_2N^+ = CH - (CH = CH)_n - N(CH_3)_2 \Rightarrow H_3CN = CH - (CH = CH)_n - N(CH_3)_2$$

1 Cyanine dyes (**Str**) **2** Cyanine bases (**Str-B**)

Similar to other related classes of linear π-electron compounds (for example, polymethine dyes, α,ω-disubstituted polyenes, merocyanines), cyanine bases are used in various applications: spectral sensation [1,2], fluorescent labels [3,4] and probes [5–8], materials for non-linear optics [9], etc. Unlike the original cyanine dye with their narrow and high-intensive bands in the absorption and fluorescence spectra [10], bases exhibit, especially, in polar solvents, wide and structureless spectral bands which show a considerable Stokes' shift. This is connected with a specific intramolecular charge transfer (ICT) process upon excitation, in contrast to transferring of an electron density only on the adjacent atoms in the related ionic polymethine dyes (see, for example, [11] and references therein). Due to the features in their spectral properties, the cyanine bases are the finest fluorescent sensors: in combination with a crown fragment as the complexing moiety, cyanine bases are themselves fluorescent quenchers, but complexation with metal cations is accompanied by a drastic increase in quantum yields, by a factor of 100–1000 [7,8,11].

Although bases differ chemically from the corresponding cyanines, structurally both related classes of the organic dyes contain the same π-electron shell (the same number of π-electrons). The only, but principal, distinction between cyanines and their bases lies in the fact that the two-coordinated nitrogen atoms (for example, in formulas **2**) have the electron configuration

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* Corresponding author. Fax: +38 044 573 26 43.
E-mail address: iochkiev@ukrpack.net (A.D. Kachkovsky).

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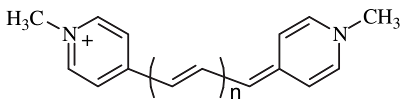
N($tr^2trtr\pi$) while the electron configuration of the three-coordinated nitrogen is N($trtrtr\pi^2$). In the topological (Huckel) approximation, this difference is practically negligible (only the Coulomb integral is varied), and hence cannot explain the substantial changes in the spectral properties. Taking into consideration only the electron–electron interaction, one can describe the features of the electron structure of the neutral bases, and correctly interpret their spectral data connected with specific nature of the electron transitions, in comparison with the cationic cyanine dyes.

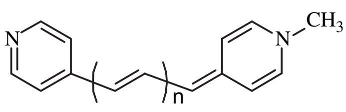
Earlier, we have considered in detail the molecular geometry and electron distribution at atoms in the ground and excited states in the symmetrical polymethine dyes, in particularly, in the symmetrical cyanines [12–14]. This article presents the results of the systematic both quantum-chemical and spectral studies of the features of the electron structure and electron transitions as well as of the absorption spectra of the bases of cyanine dyes.

2. Objects and methodology

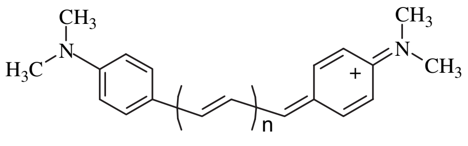
Since by definition, the bases are derivatives only of dyes containing nitrogen atom which can change its valency, here we will restrict our consideration to a specific



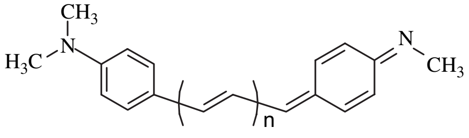
3 (Py)



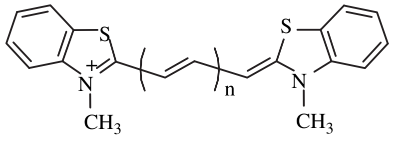
4 (Py-B)



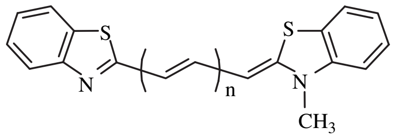
5 (PhN)



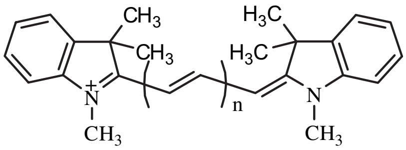
6 (PhN-B)



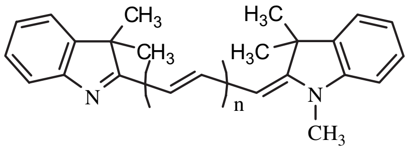
7 (BT)



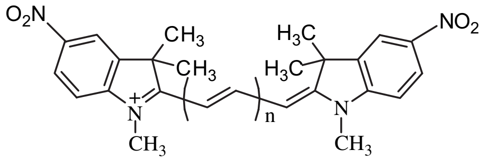
8 (BT-B)



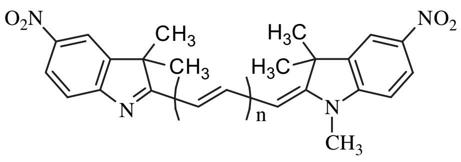
9 (In)



10 (In-B)



11 (NO2-In)



12 (NO2-In-B)

type of dyes, symmetrical cyanines **1**, **3**, **5**, **7**, **9**, **11** and their de-alkylated derivatives, cyanine bases **2**, **4**, **6**, **8**, **10**, **12**.

Some of these compounds were synthesized to investigate experimentally their absorption spectra. Synthesis of the corresponding cyanine dyes and their bases are given in Ref. [15]. Absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100.

The equilibrium geometry of dye molecules in the ground state was optimized by the ab initio and AM1 methods (with the gradient of 0.01 kcal/mol). The electron transition characteristics were calculated in AM1 approximation using 30 the lowest singly excited configurations.

3. Results and discussion

3.1. Molecular geometry of the polymethine chain

We will begin with a consideration of the difference between cyanine dyes and related bases from their equilibrium molecular geometry. It was postulated by Daehne et al. in the framework of his triad theory [16] that polymethine dyes are characterized by an equal lengths of the carbon–carbon bond in the conjugated chain, in contrast to the another type of the linear π-electron molecules, polyenes, in which the bond lengths exhibit the considerable alternation, so that the difference in the lengths of two adjacent bonds reaches a limit of 0.08 Å [17].

To compare the molecular geometry of three different types of linear π-electron systems, polymethines, polyenes and donor–acceptor compounds, we have calculated the optimized geometry for the model molecules with the simplest end groups and with the same chain length ($n = 5$): streptocyanine **1**, its base **2** and corresponding polyenes **13**:

$$(H_3C)_2N{-}(CH{=}CH)_5{-}N(CH_3)_2 \qquad \mathbf{13}\,(\mathrm{Pe})$$

The calculations were performed in framework of the well known and much used ab initio approximation (STO 6-31G** basis set); the obtained lengths of the CC-bonds are presented in Fig. 1.

One can see that in fact, the calculations give the CC-bond lengths are equal for the streptocyanine **1** and are considerably alternated for the polyene **13**. The molecular geometry of the base **2** is following from Fig. 1 to resemble more closely to that of the polyene **13**: in the middle of the chain, the bond lengths practically coincide.

It is a common practice to characterize a bond length alternation (BLA) by its amplitude: $\Delta l_\mu = |l_\mu - l_{\mu+1}|$, where μ are the number of bonds [18]. As an example, the calculated values Δl_μ for the vinylogous series of cyanine dyes **5** (PhN) and their bases **6** are presented in Fig. 2. There are two principal distinctions between cyanine and bases in their BLA parameter. Firstly, the magnitudes of the values Δl_μ in the middle of the chain of the both types of the conjugated systems differ significantly from each other. Secondly, in the bases, BLA is only weakly sensitive to the chain length, while the lengthening of the chain in the corresponding cyanine dyes leads the parameter Δl_μ for the pair of the bonds at the chain ends regularly increases, so that the difference in the bond length alternation at the chain ends in the cyanines and bases gradually decreases.

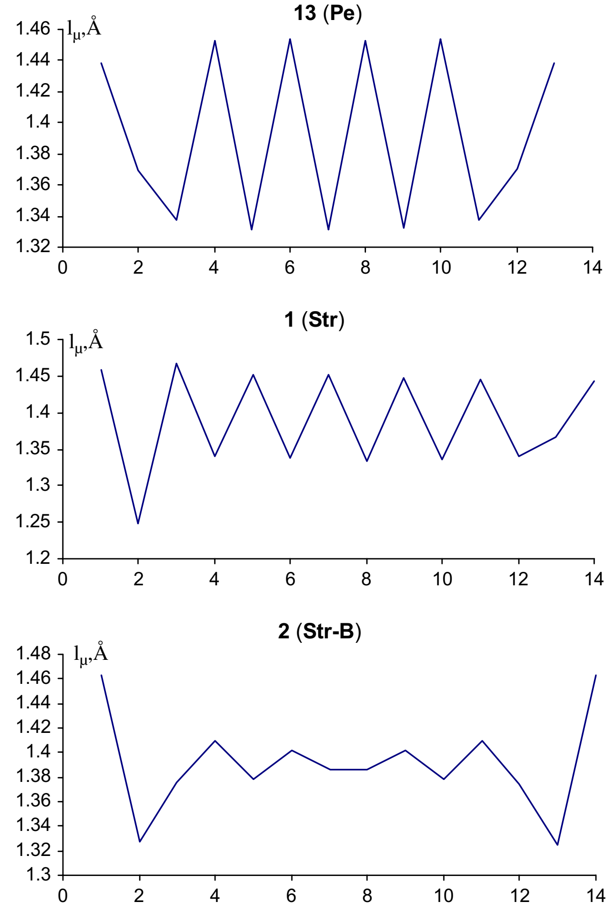


Fig. 1. Calculated (ab initio) lengths of the carbon–carbon bonds in the conjugated molecules ($n = 5$).

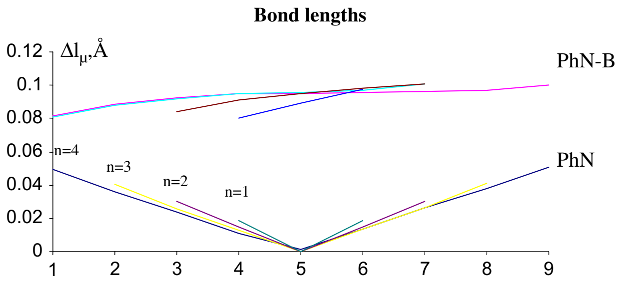


Fig. 2. Bond lengths alternation, Δl_μ, in the chain of the dyes **5** and bases **6** (AM1).

Similar trends are obtained for other cyanine dyes and their bases, except for the dyes with the relative long polymethine chain ($n = 4$–6) where the symmetry breaking could occur [13,19].

Also, the bond orders and hence bond lengths in the chain have been found to depend on nature of the terminal residues. For the quantitative estimation of the influence of terminal residues, the convenient theoretical model of linear conjugated systems with the quasi-long polymethine chain has been elaborated [20,21]. In this model, the donor influence of end group on the electronic properties of conjugated chain can be estimated quantitatively by means of its topological index Φ_o, which was called as an electron donor ability. It characterizes the ability of terminal residues to donate the π-electron density to the carbon atoms of the polymethine chain or, more correctly, to shift the modes of the frontier MOs from their positions in non-substituted polymethines. For the molecules with stable closed electron shell, the parameter Φ_o magnitude is usually positive and falls within interval: $0^\circ \le \Phi_o \le 90^\circ$.

Calculated indices for the heterocycles used as end groups in the studied dyes are follows:

Φ_o: Py − 76°; BT − 50°; In − 40°; PhN − 14°

Similarly to the donor strength of the end groups, we can introduce, in the same approximation, a special parameter, an electron acceptor ability, Ω_o. While the index Φ_o is connected with a position of the modes of the highest occupied MO (HOMO), the acceptor properties should correspond to a position of the lowest unoccupied orbital (LUMO). In the approximation of linear conjugated systems with the quasi-long polymethine chain, it leads to change of the topological index by following way: $\Phi'_o = 90^\circ - \Phi_o$. Roughly, neglecting the difference in Coulomb integrals for the two- and three-coordinated nitrogen atoms, we can put:

$$\Omega_o \equiv \Phi'_o = 90^\circ - \Phi_o$$

Then, for the bases derived from the symmetrical cyanines, indices Ω_o and Φ_o should change oppositely and we will use mainly only the parameter Φ_o:

Ω_o: Py − 14°; BT − 40°; In − 50°; PhN − 76°

In Fig. 3, the values Δl_μ calculated for the both cyanine and bases upon the same chain length ($n = 3$) are presented. One can see that the bond lengths are practically equal in the chain of the cyanine dyes containing the end groups with the middle and high index Φ_o (In and Py), while the dye with the low basic residues (PhN) gives the regular increase in the BLA amplitude from the middle of the chain to its ends (Fig. 3a). More significantly, influence of the end group topology is reflected in the bases (Fig. 3b); the degree of the BLA in indocyanine base with middle indices ($\Phi_o = 40^\circ$, $\Omega_o = 50^\circ$) is close to that in the dyes, especially, in the middle of the chain. At the same time, a deviation of the index Φ_o (and simultaneously an opposite deviation of the index Ω_o) from the centre magnitude, 45°, causes the sharp increase in the BLA amplitude, the slope of the function $\Delta l_\mu = f(n)$ from the acceptor residue to donor that for the base **4** (Py-B) and **6** (PhN-B) being opposite (Fig. 3b).

3.2. Electron density distribution

According to Daehne theory [16], polymethine dyes and polyenes differ from each other by distribution of charges or electron densities in the conjugated chain. So, in contrast to the neutral symmetrical polyenes with totally equalized π-electron densities at the carbon atoms, the charges at carbons along the chain in cationic polymethine dyes are highly alternated. The degree of this alternation can be estimated also by its amplitude: $\Delta q_\mu = |q_\mu - q_{\mu+1}|$, where q_μ is an electron

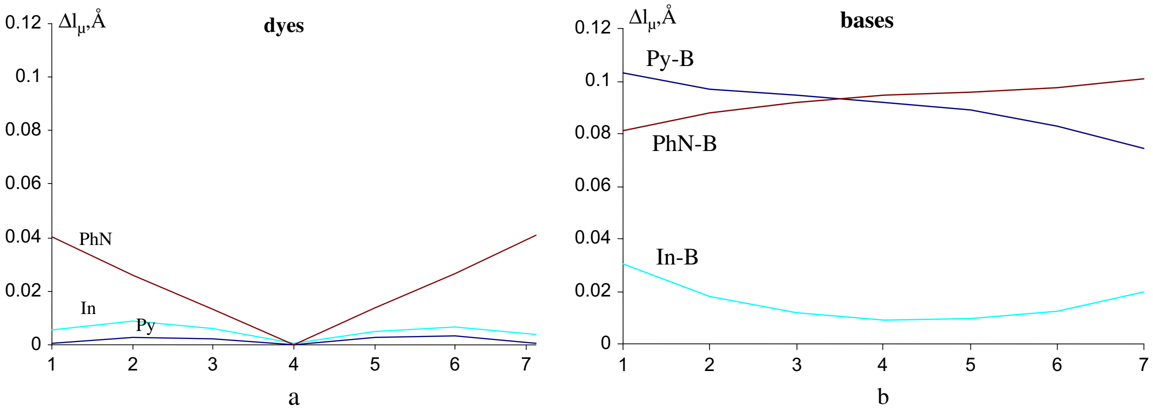


Fig. 3. Bond lengths alternation, Δl_μ, of the dyes (a) and corresponding bases (b) with the same chain ($n = 3$).

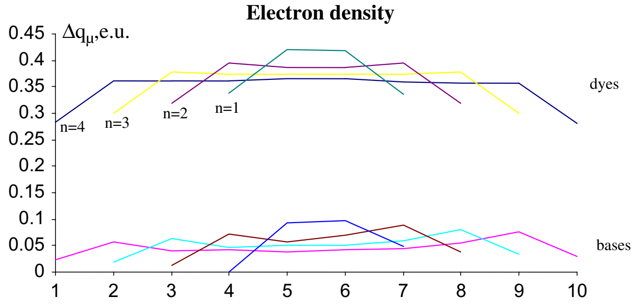


Fig. 4. Electron density alternation (at carbon atoms), Δq_μ, in the chain of the dyes **5** and bases **6** (AM1).

density at the μ-th atom. Fig. 4 presents the dependence of the calculated values Δq_μ on a number of vinylene groups in the polymethine chain of the dye series **5** (PhN) and corresponding bases **6** (PhN-B). One can see that there is also a degree of the alternation of the charges for the bases. However, comparison shows that the amplitude Δq_μ in the chain middle of the bases **6** is lesser, practically by a factor of 5–7, than in the related charged cyanines **5**. Unlike the symmetrical distribution of the electron densities in the cyanine dyes, the values Δq_μ in the chain of the bases change slightly along the chain from one end group to another.

Also, the amplitudes of the charge alternation in the cyanine and their bases exhibit different sensitivity to nature of the terminal groups. One can see from Fig. 5 that the charge distribution in the chain of the bases is more responsive to the donor strength of the corresponding residue, especially, close to door end group.

3.3. Positions of electron levels and molecular stability

Now, let us consider the dispositions of the lowest vacant level and the highest occupied level that influence directly on the stability of the molecules. It is well known [22] that whereas the solutions of the cyanine dyes are relatively stable, the base solutions demonstrate high unstability, especially upon going to molecules with more longer polymethine chain.

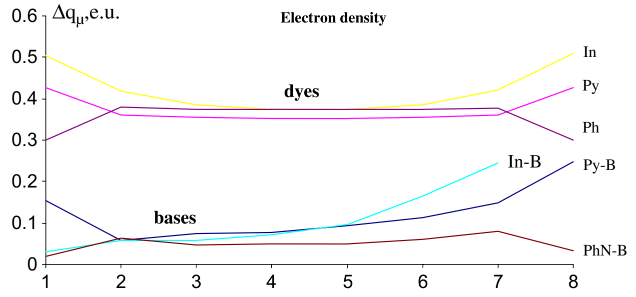


Fig. 5. Electron density alternation, Δq_μ, in the dyes and bases with the same chain ($n = 3$).

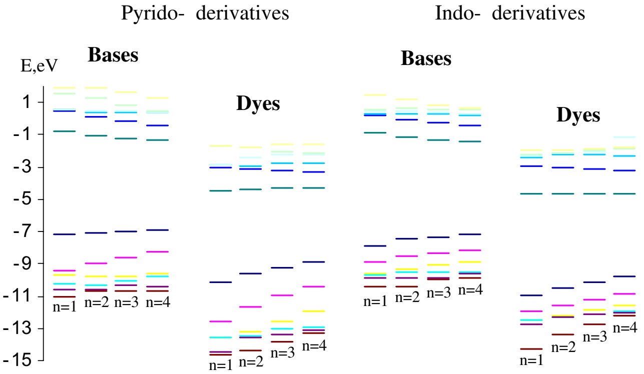


Fig. 6. Positions of the electron levels in dyes **3** (Py), **9** (In) and bases **4** (Py-B), **10** (In-B).

We have found that solutions of cyanine bases are not stable, in contrast to relative stable dye solutions. Because of stability, the only freshly prepared solutions of the cyanine bases have been used for spectral measurements.

The difference in the electron occupancies at carbon atoms (atomic charges) or at bonds (bond orders which correlate with bond lengths) seems likely not to explain adequately such difference in stability of two related types of conjugated compounds. An additional information can be obtained upon comparing of the positions of the electron levels and hence basicity. Fig. 6 shows the positions of the frontier and nearest to the levels for the vinylogous series of the thiacyanines N, indocyanines N and corresponding bases. One can see that going from the charged cyanine dye to the neutral base is accompanied by the sharp shifting up of the electron levels and simultaneously by increase in the energy gap. Another principal difference between two types of the π-systems studied is connected with their sensitivity to the chain length. Introducing of vinylene groups causes the regular decrease in the energy of the LUMO and increase in the energy of the HOMO in the bases what is typical property of the neutral conjugated systems [14]. While cationic cyanine dyes have a solitonic level (LUMO) which is practically insensitive to the length of the chain.

Thus, we assume that the considerable destabilisation of HOMO in the bases comparing with the related cyanine dyes could be treated as an increase in the electron donor properties and hence reactivity.

3.4. Absorption spectra and nature of electron transitions

Experimentally, the difference between cyanine dyes and their bases manifests itself most pronounced in absorption spectra. As examples, the long wavelength bands of the vinylogous series of thiacyanine **7** (BT) and

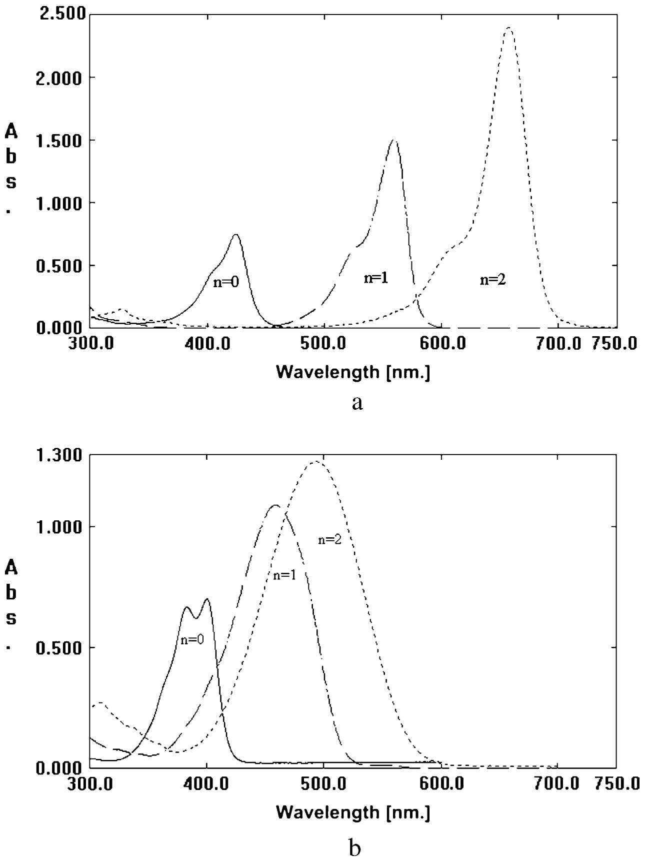


Fig. 7. Absorbtion spectra of the ethanol solutions of the thiacyanines **7** (a) $c = 1 \times 10^{-5}$ m/l and their bases **8** (b) $c = 2 \times 10^{-5}$ m/l.

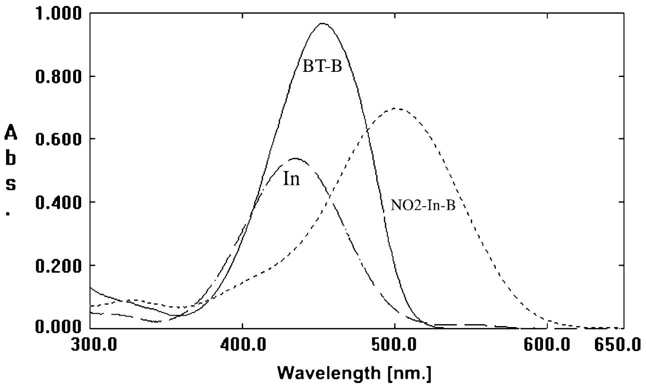


Fig. 8. Absorbtion spectra of the ethanol solutions of the bases **8**, **10**, **12**, with the same chain ($n = 1$); qualitative spectra.

corresponding bases **8** (BT-B) are presented in Fig. 7. There are considerable changes in absorption spectra upon going from one compound type to another. The cyanine dyes **7** ($n = 0$, 1, 2) exhibit high intensive and narrow spectral bands with the shoulder at the short wavelength side which correspond to the higher vibronical transitions, $0 \rightarrow 1'$ (Fig. 7a). The lengthening of the polymethine chromophore by introducing vinylene groups causes the bathochromic shift of the band maximum on 135 nm ($n = 0$ and $n = 1$) and on 98 nm ($n = 1$, 2). Small increase in the first vinylene shift (135 nm) compared with the usual value of 100 nm is explained by a interaction between two sulfur atoms in the monomethinecyanine **7** ($n = 0$) which leads to the hypsochromic shift of the band maximum [23,24].

In contrast, the spectral bands of the bases are followed from Fig. 7b to be substantially wider and to be markedly shifted in the short wavelength region, in comparison with the corresponding cyanine dyes. The vinylene shifts are essentially lesser, 59 nm ($n = 0$, 1) and 34 nm ($n = 1$, 2); and decreases upon going to the higher vinylogs.

We have also measured absorption spectra of the carbocyanine bases ($n = 1$) containing the indolenine (**10**, In-B) and 5-nitro-indolenine residues (**12**, NO2-In-B) as end groups with lower basicity; their bands are presented in Fig. 8. All spectra are similar, differing only by their band maxima, especially in polar solvents (see also Table 1). Although, it is to be noted that the absorption spectra of the studied bases are only weakly sensitive to solvent polarity (compare the data obtained in ethanol, acetonytryl and toluene). Also, Fig. 7 shows that the chain lengthening leads the intensity of the spectral bands to increase regularly in both cyanine dyes and bases.

On the contrary, the influence of the chain length on the bandwidth in two compared series is opposite. In Tables 1 and 2, the obtained bandwidths at the half-intensity, $\Delta\nu_{1/2}$, are presented. Comparing the corresponding data, one will readily see that the $\Delta\nu_{1/2}$ values for the thiacyanine dyes **7** decrease considerably for the each next member of the series, while introducing of the vinylene groups in the chain of the bases **8** is accompanied by increase in the bandwidth. At the same time, providing the same length of the chain, the widths of the absorption bands for the indo- and 5-nitro-indocarbocyanine bases (**10** and **12**) are close, independent of solvent polarity (Table 1).

Thus, the absorption spectra of the cyanine dyes and related bases, follow from Figs. 7 and 8 as well as from Tables 1 and 2, differ principally between each other in their intensity, selectivity and sensitivity to the chromophore length. We suggest that such spectral distinctions are connected with different nature of the electron transitions in the cationic cyanine dyes and neutral bases. It was earlier proposed to use the diagrams of the

Table 1
Band maxima, λ_{max}, and bandwidths, $\Delta\nu_{1/2}$, of the bases **8**,**10**,**12**

Bases	Acetonitrile		Toluene		Ethanol	
	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})
8 (BT)	452	3721	449	3670	459	3607
10 (In)	435	4130	435	4092	447	4036
12 (NO2-In-B)	500	4057	488	3827	505	4073

Table 2
Bandwidths, $\Delta\nu_{1/2}$ (cm^{-1}) of the cyanines **7** and their bases **8**

7 (BT) − **8** (BT-B)	Base	Dye
$n = 0$	3142	2074
$n = 1$	3721	1105
$n = 2$	3970	908

electron density redistribution upon excitation to characterize the location (and hence nature) of the electron transitions [25]. Quantitatively, the redistribution is calculated as follows: $\Delta q_\mu = q_\mu^* - q_\mu^{\text{o}}$ where q_μ^* and q_μ^{o} are the electron densities at the μ-th atom in the excited and ground states. As examples, the diagrams of the changes of the electron densities upon the $S_0 \rightarrow S_1$ transition for the thiadicarbocyanine **7** ($n = 2$) and corresponding bases **8** ($n = 2$) are depicted in Fig. 9. One can see that the first electron transition in the cyanine is accompanied by the considerable transferring of the electron density from the atoms in odd positions of the polymethine chain what is typical picture for the ionic polymethine dyes with their specific narrow and highly intensive absorption long wavelength bands [21,25]. Unlike the cyanine dye, the redistribution of the electron density in the base is seen from **9** to resemble more closely with the innermolecular charge transferring (ICT) from the donor part of the molecule to its acceptor part, except the carbon atom of the donor residue which is connected with the chain where the considerable deficit of the electron density is in the ground state. Additionally, some atoms of the donor heterocycle are involved in the first transitions.

Also, our calculation has shown that there is a considerable difference in the change of the bond orders upon excitation in the cyanine dyes and bases. It should be directly connected with difference in the widths of the spectral bands, so as $\Delta\nu_{1/2}$ values were shown to correlate with the so-called root-mean square change of the bond order upon excitation, δ, which is calculated by following formula [26]:

$$\delta = \sqrt{\sum p_\mu^* - p_\mu^0} \tag{1}$$

where p_μ^* and p_μ^0 are the orders of the μ-th bond in the excited and ground states; summing runs over all bonds. The calculated magnitudes δ for the vinylogous series of thia- and indocyanines (**7**, **9**) altogether with the corresponding bases (**8**, **10**) are given in Table 3. Comparison of data shows that values δ for the bases are essentially larger than for the cyanine dyes. Also, the dependence of the δ value on the number of the vinylene groups in the chain is opposite for both types of the investigated compounds, which is in a good agreement with the regularities in width of the spectral bands and hence can explain the considerable increase in the absorption bandwidths in the bases (compare with Tables 2 and 3).

Summarizing, we can conclude that cationic cyanine dyes and their bases differ from each other not only by their equilibrium geometry, electron density distribution and positions of the molecular levels, but also by nature of their electron transitions.

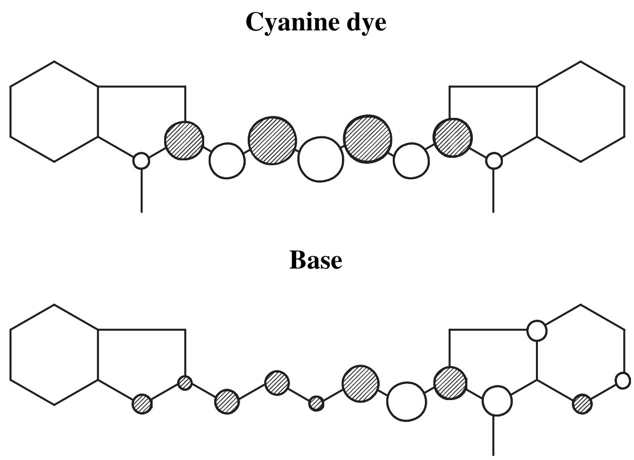


Fig. 9. Diagrams of electron distribution upon excitation: coloured circle – electron density increases; uncoloured circle – electron density decreases.

Table 3
Calculated value δ for the cyanine dyes **7**, **9** and bases **8**, **10**

Compounds	n	Dye	Base
7 (BT), **8** (BT-B)	0	0.2385	0.4091
	1	0.1408	0.8236
	2	0.0959	0.9055
	3	0.0870	1.1197
9 (In), **10** (In-B)	1	0.2258	0.9078
	2	0.1645	0.9765
	3	0.1362	1.0169

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