

INVESTIGATION OF CHARGE WAVES IN THE CHROMOPHORE OF CATION CYANINE DYES USING ^{13}C NMR SPECTROSCOPY

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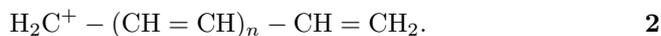
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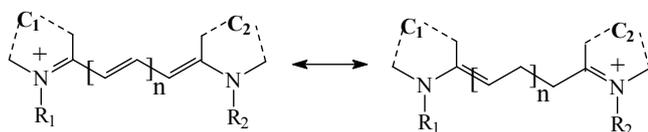
The electron density distribution for a series of symmetric and non-symmetric cation cyanine dyes is investigated on the basis of the data of quantum-chemical calculations and NMR (^{13}C) spectra. It is shown that the calculated atomic charges are in good agreement with the experimental values of chemical shifts. A considerable wave-like alternation of the electron density along the chromophore is found. It is shown that the general electron density distribution represents a superposition of the autolocalized charge and two charge waves generated by the donor finite groups.

was established in [5–7], the total positive charge is autolocalized in the form of a soliton-like wave of alternating partial negative and positive charges instead of being uniformly delocalized along the whole chromophore. According to calculation results, the wavelength in unsubstituted polymethine cations **2** amounts to approximately 15–17 atoms/bonds and does not depend on the length of the conjugated system



1. Introduction

Cyanines belonging to a wider class of polymethine dyes have been well known since 1856, but are still used due to their unique ability to convert light energy (see reviews [1–4] and references cited there). The main cation chromophore of a cyanine dye is presented by a long polymethine chain bounded by two nitrogen atoms:



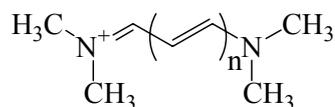
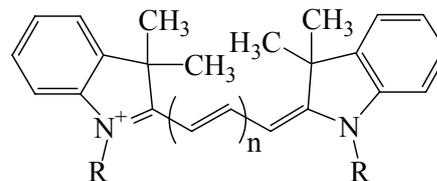
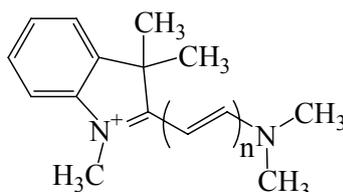
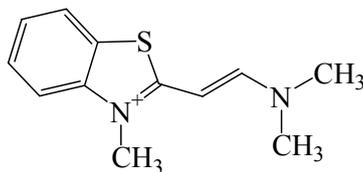
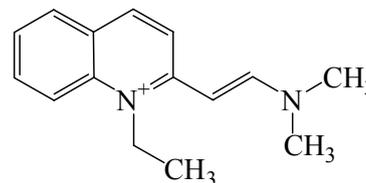
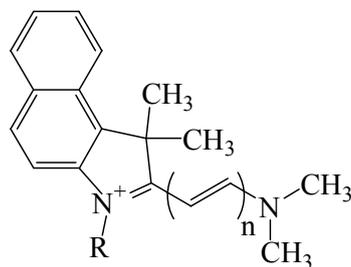
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According to modern ideas, carbon atoms in a conjugated system exist in the sp^2 hybrid state, while $2p_z$ electrons form a common collective π -electron system. As

Simultaneously with the charge wave, a wave of bond lengths, also called a topological (geometrical) soliton or kink, is generated in the π -system of cation **2**. Calculations demonstrate that the bond lengths are practically equalized at the center of the soliton wave and maximally alternate at its edges [5–7].

The introduction of finite groups can result in a significant deformation of the charge wave and in its localization, especially if the conjugated system is extended. It was particularly shown that, at a certain critical number of vinylene groups n (in molecule **1**), the centers of the charge and topological waves shift to one of the chromophore ends [5–9]. Such a shift of the charge wave, for example in cations of polymethine dyes, can result in the violation of a symmetry of the electron structure, which was experimentally detected as an abrupt change of the spectral band in IR spectra of dyes [10, 11].

The passage from symmetric dyes (**1**, $C_1 = C_2$) to cyanines with a non-symmetric chemical structure (**1**, $C_1 \neq C_2$) results in the significant variation of both the charge distribution and the spectral properties [1–


3, $n = 1, 2$

4, $R = \text{CH}_3; n = 1$
 $R = \text{CH}_2\text{CH}_3; n = 2$

5, $n = 1, 2, 3$

6

7

8 $R = \text{CH}_2\text{CH}_3; n = 1$
 $R = \text{CH}_3; n = 3$

3, 12–14]. The quantitative estimation of the degree of asymmetry is traditionally performed, by using a deviation of the absorption maximum calculated according to the formula $D = (\lambda_1 - \lambda_2)/2 - \lambda_{\text{as}}$, where λ_{as} denotes the absorption band maximum of the non-symmetric dye, whereas λ_1 and λ_2 are the band maxima of the corresponding mother symmetric dyes [14]. In the case of typical non-symmetric cyanines, $D > 0$, i.e. the absorption band of a non-symmetric dye shifts toward shorter wavelengths as compared to the mean square of the sum of mother dyes. It was considered that this spectral peculiarity is caused by the al-

ternation of bond lengths along the chromophore arising in the case where the finite groups are not chemically equivalent [12–14]. It is logical to assume that the asymmetry of the chemical structure of cyanines **1** must also result in a shift of the charge and topological waves from the center of the polymethine chain, which must depend on the donor force difference of the both finite groups. Such a violation of the electron density distribution in the chromophore of non-symmetric cyanine dyes can be experimentally detected with the help of nuclear magnetic resonance (NMR) spectra.

Experimental values of the chemical shifts δ in the polymethine chain of the studied dyes

N	Experimental values of the chemical shifts δ , ppm										
	3		4		5			6	7	8	
<i>n</i>	1	2	1	2	1	2	3	1	1	1	3
				172.24			169.6				171
		161.53	173.99	102.76		172.474	99.61				99.22
	162.35	102.73	102.35	153.28	176.73	98.434	150.99	168.53	155.02	177.3	150
	89.81	161.67	149.2	125.21	86.58	156.055	121.7	84.9	88.15	85.35	121.28
	162.35	102.73	102.35	153.28	157.96	106.921	160.33	156.89	157.31	157.5	159.6
		161.53	173.99	102.76		163.199	108.73				108
				172.24			162.25				162.45

2. Main Part

This work presents the results of parallel quantum-chemical and spectral (^{13}C NMR) investigations of the charge distribution in non-symmetric and corresponding symmetric cyanines as a function of the chromophore length (variation of the number of vinylene groups n) and the nature of the finite groups.

The simplest objects chosen for the study were two vinyllogs of symmetric streptocyanines **3** and indocyanines **4** and three vinyllogs of the corresponding non-symmetric hemicyanines **5** representing a combination of dyes **3** and **4**. The effect of the donor force difference was studied by the example of non-symmetric cyanines that can be considered as heteroanalogs of indohemicyanine **5** at $n = 1$. Another way of changing the donor force of the indolenine residual lies in the attachment of an additional benzene cycle: a vinyllogous series of non-symmetric cyanines **8**.

The synthesis of the compounds was described in [12, 15]. The NMR spectra were measured on a Varian GEMINI 2000 spectrometer with frequencies of 400.07 (^1H) and 100.61 (^{13}C) MHz. All one- and two-dimensional experiments were carried out, by using solutions in 0.7 ml DMSO- d_6 at a temperature of 293 K. Tetramethylsilane was used as a standard for calibrating the δ scale. The ^1H and ^{13}C single NMR spectra (with and without decoupling) were obtained using the standard two-pulse sequence with a spectral width of 8 and 30 kHz, 64000 and 128000 data points, respectively. The ^1H - ^1H COSY spectra [16] were obtained in the 2048(F2) \times 512(F1) time data matrix. The NOESY spectra [16] were obtained (in the case of need) with the same parameters as the COSY ones. The mixing times were preliminarily determined from the T_1 measurements for each sample using the generally accepted technique of inversion-reduction. The ^1H - ^{13}C bond was determined with the help of the heteronuclear correlation of the chemical shift (HETCOR) with the 2048(F2) \times 256(F1) time matrix and the

2048(F2) \times 1024(F1) frequency matrix after filling with zeros. The mean value of the constant through one bond J_{CH} was assumed to be equal to 140 Hz. The HETCOR technique used to determine the correlation at large distances had similar parameters, whereas the mean value of the constant through several bonds was equal to 8 Hz.

The quantum-chemical calculations were carried out, by using the Gaussian03 software. The geometry optimization was performed with the help of the DFT B3LYP technique (6-31+G*). Charges at atoms were calculated with the use of natural bond orbitals (NBO). The chemical shifts of ^{13}C signals were calculated in the framework of the GIAO technique [16].

The experimentally found chemical shifts of the carbon (^{13}C) NMR spectra are listed in Table 1. We analyze the charges and the chemical shifts only for carbon atoms belonging to the conjugated system. They can be divided into two groups: 1) atoms in the finite groups; 2) atoms in the polymethine chain. For example, the signals in positions 8–11 (benzene ring) in dyes **4**, **5**, **6–8** lie practically in the same region (109–123 ppm) except for quinohemicyanine **7**, where the signals are somewhat shifted. Protons in the corresponding positions can be considered as aromatic (≈ 7 –7.5 ppm). Due to the polarization under the influence of a nitrogen atom, the signals of the rest of atoms of a benzene ring in dyes **4–8** are usually shifted toward smaller fields. On the contrary, the signals of carbon atoms $\delta_\mu(^{13}\text{C})$ in the chromophore (so-called Kuhn chain) ending with nitrogen atoms are considerably shifted as compared to the aromatic atoms: toward lower fields – for atoms in pair positions and toward stronger fields – for atoms in unpaired positions, which is typical of the chromophores of both cation and anion polymethine dyes [17–22]. This effect is caused by the considerable alternation of the electron density in ions of linear conjugated systems. As one can see from Table, the chemical shifts $\delta_\mu(^{13}\text{C})$ depend on the chromophore length (the number of vinylene groups n), the

chemical structure of the finite groups, and the degree of asymmetry.

As was shown in [5–7], the amplitude of charge alternation Δq_μ and (with regard for the linear correlation between the calculated charges and the chemical shifts) the amplitude of alternation of the chemical signals $\Delta\delta_\mu$ calculated by formulas (1) and (2), respectively, are much more suitable for analyzing the effect of the molecular topology and the asymmetry on the form and the localization of soliton waves than the electron density q_μ at the μ -th atom or the chemical shift $\delta_\mu(^{13}\text{C})$.

$$\Delta q_\mu = (-1)^\mu (q_\mu - q_{\mu+1}), \quad (1)$$

$$\Delta\delta_\mu = (-1)^\mu (\delta_\mu - \delta_{\mu+1}). \quad (2)$$

The wave behavior of the charge distribution and the equilibrium molecular geometry in unsubstituted polymethine cations **2** and their α , ω -disubstituted derivatives with the simplest finite groups were thoroughly investigated in the framework of various quantum-chemical approximations, both semiempirical and non-empirical, with regard for the electron correlation [5–10]. It was shown that the maximum charge alternation is reached at the center of the polymethine chain simultaneously with the maximum equalization of the lengths of the neighboring bonds. The introduction of more complex finite residuals is accompanied by significant changes in the charge distribution, especially in dye molecules with a comparatively short polymethine chain, so that the amplitude of charge alternation in the middle of the chromophore can become even smaller than at its edges. Figure 1 presents the charges and the calculated and experimental chemical shifts for carbon atoms in the polymethine chain of streptocyanine **3** at $n = 2$ and indocyanine **4** at $n = 1$. In this figure, one pays attention, first of all, to the exact synchronism of alternation of the quantities q_μ and $\delta_\mu(^{13}\text{C})$.

It is worth noting that the chemical shifts for the carbon atom neighboring with the nitrogen one and for that at the center of the polymethine chain in streptocyanine **3** ($n = 2$) are practically equal: 161.53 and 161.67 ppm, respectively. In the chromophore of indocarbocyanine **4** ($n = 1$) with a larger donor finite residual, they however considerably differ: 173.99 and 149.2 ppm. In other words, the maximum alternation of the chemical shifts in indocyanines **4** is reached at the both ends of the polymethine chromophore, which completely agrees with the charge distribution (see Fig. 1, *a, b*). Thus, it is possible to propose a parameter of the bond ionicity as the difference between the electron densities at

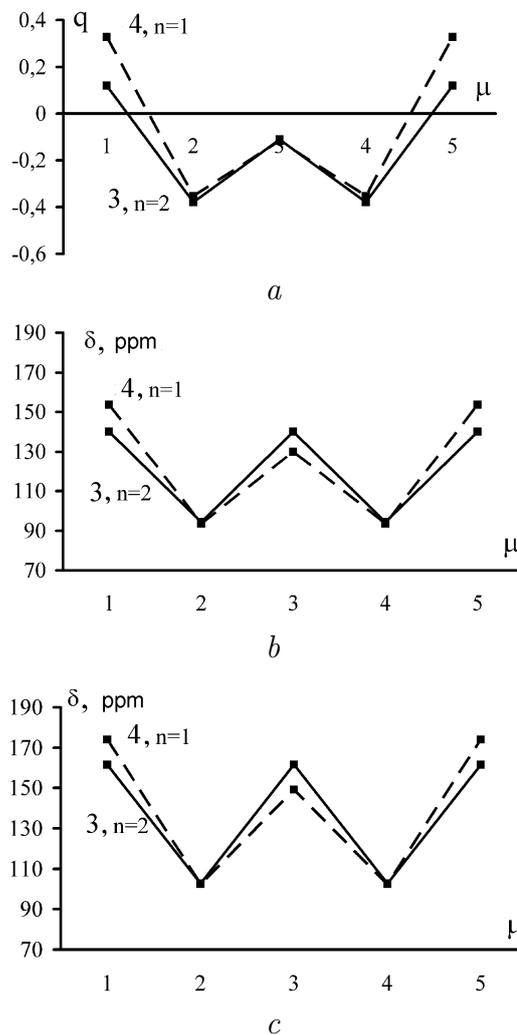


Fig. 1. Charges (B3LYP/3-21G** NBO) (*a*), calculated ^{13}C NMR chemical shifts (B3LYP/3-21G** GIAO) (*b*), and experimental ^{13}C NMR chemical shifts (*c*) of carbon atoms in a conjugated chain of cyanines **3** and **4**

two neighboring atoms. The bond ionicity can be experimentally estimated by the chemical shift difference: $\Delta\delta_\mu = (\delta_\mu - \delta_{\mu+1})$. As one can see from Fig. 1, the ionicity of the first carbon-carbon bond in the chromophore of indocyanines **4** is higher as compared to that of streptocyanines **3**.

The amplitude of charge alternation Δq_μ and the corresponding chemical shifts $\Delta\delta_\mu$ as functions of the chromophore length and the atomic position in the polymethine chain are demonstrated in Fig. 2.

One can see that the degree of alternation of the charges and the chemical shifts at the center of the chromophore regularly decreases with increase in the donor

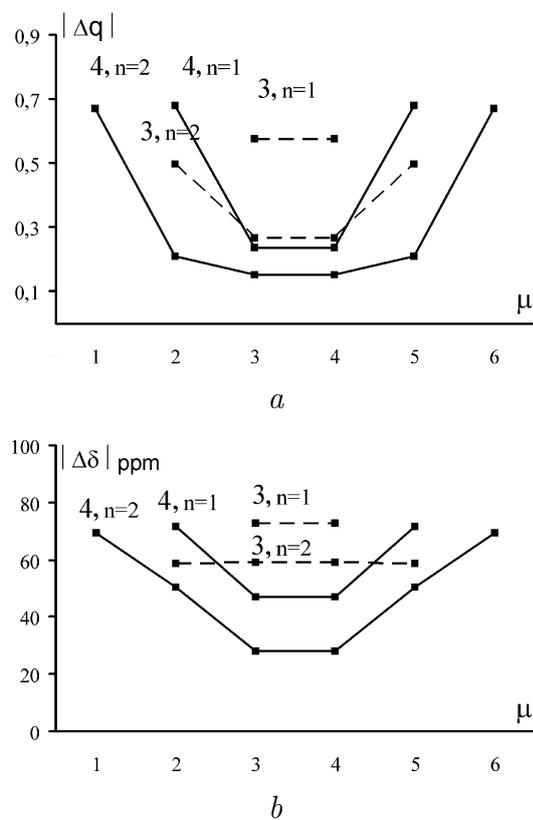


Fig. 2. Alternation of charges (B3LYP/3-21G** NBO) (a) and experimental ^{13}C NMR chemical shifts (b) of carbon atoms in a conjugated chain of cyanines **3** and **4**

force of the finite groups when passing from streptocyanines **3** to indocyanines **4** at the same chain length. The atomic charges and the chemical shifts for these atoms also appear sensitive to the chromophore length. The extension of the chain by introducing a new vinylene group (n changes to 1) is accompanied by the symbatic decrease of the alternation of both the experimental quantity $\Delta\delta_{\mu}(^{13}\text{C})$ and the calculated one – Δq_{μ} . However, in the case of indocyanines **4**, the passage to the higher vinylog ($n = 1 \rightarrow n = 2$) results in an insignificant decrease of the signal difference $\Delta\delta_{\mu}(^{13}\text{C})$ for a pair of extreme atoms: from 71.64 to 69.48 ppm.

With regard for the fact that the charge wave represents an integral object, one can assume that its form must be sensitive to the molecular asymmetry of the charge distribution in non-symmetric cyanines **5–8** containing finite groups with various chemical structures, i.e. various donor forces. The amplitudes of the calculated charges Δq_{μ} and the experimentally measured chemical shifts $\Delta\delta_{\mu}$ as functions of the atomic position

μ for a chromophore of the vinylogous series of non-symmetric dyes **5** and **8** are plotted in Fig. 3. It is logical that the charge waves become non-symmetric, but their integrity is not violated. By analogy with symmetric dyes, the both functions in non-symmetric cyanines have minima getting deeper, as the chromophore is extended. One can see that the amplitude of alternation of the chemical shifts detected for a finite pair of atoms located closer to the heterocyclic residual is larger than at the opposite end of the chromophore close to the dimethylamine group $\text{N}(\text{CH}_3)_2$. It is also true for the amplitude of charge alternation. As was shown in [24], the amplitude of alternation of charges/chemical shifts grows with increase in the donor force. That is why, comparing the values of the parameters Δq_{μ} and $\Delta\delta_{\mu}$ (or the bond ionicity) in the vicinity of the both finite groups, one can state that the indolenine residual in the series of non-symmetric dyes **5** is characterized by a larger donor force than the $\text{N}(\text{CH}_3)_2$ residual. Comparing the alternation of the charges/chemical shifts for the corresponding pairs of atoms in the chromophores of non-symmetric cyanines **5** and **8**, one can see its insignificant increase in the latter case: from 66.99 to 71.78 ppm, which completely agrees with the intensification of the donor properties when passing from indolenine as a finite group (series **5**) to its angularly annealed derivative – the finite group of non-symmetric cyanines **8**.

It is also worth noting that the magnitude of chemical shift $\delta(^{13}\text{C})$ for the carbon atom nearest to the nitrogen atom of the indolenine residual of dye **5** continuously grows when passing to higher vinylogs ($n = 1, 2, 3$): 176.73, 172.47, and 169.60 ppm. At the same time, in the case of the atom bound with the amino group ($\text{N}(\text{CH}_3)_2$), it grows only when introducing the first vinylene group ($n = 1 \rightarrow n = 2$): 157.96 and 163.20 ppm. Thus, if we pass to a dye at $n = 3$, the chemical shift somewhat decreases: 162.25 ppm. In addition, the difference of the values of Δq_{μ} and $\Delta\delta_{\mu}$ for different vinylogs in the both series of non-symmetric cyanine dyes **5** and **8** is more considerable for the atoms located in the middle of the polymethine chain than at its ends (Fig. 3).

The effect made by the variation of the donor ability of one finite group at a fixed another finite group can be considered by the example of a series of hemicyanines with the shortest chain: **5** ($n = 1$), **6**, and **7**. As was shown by Brooker [14], the donor force or basicity of a varying residual continuously grows in the following order: indolenine, benzothiazole, quinoline (dyes **5**, **6**, and **7**, respectively). As one can see from the data given

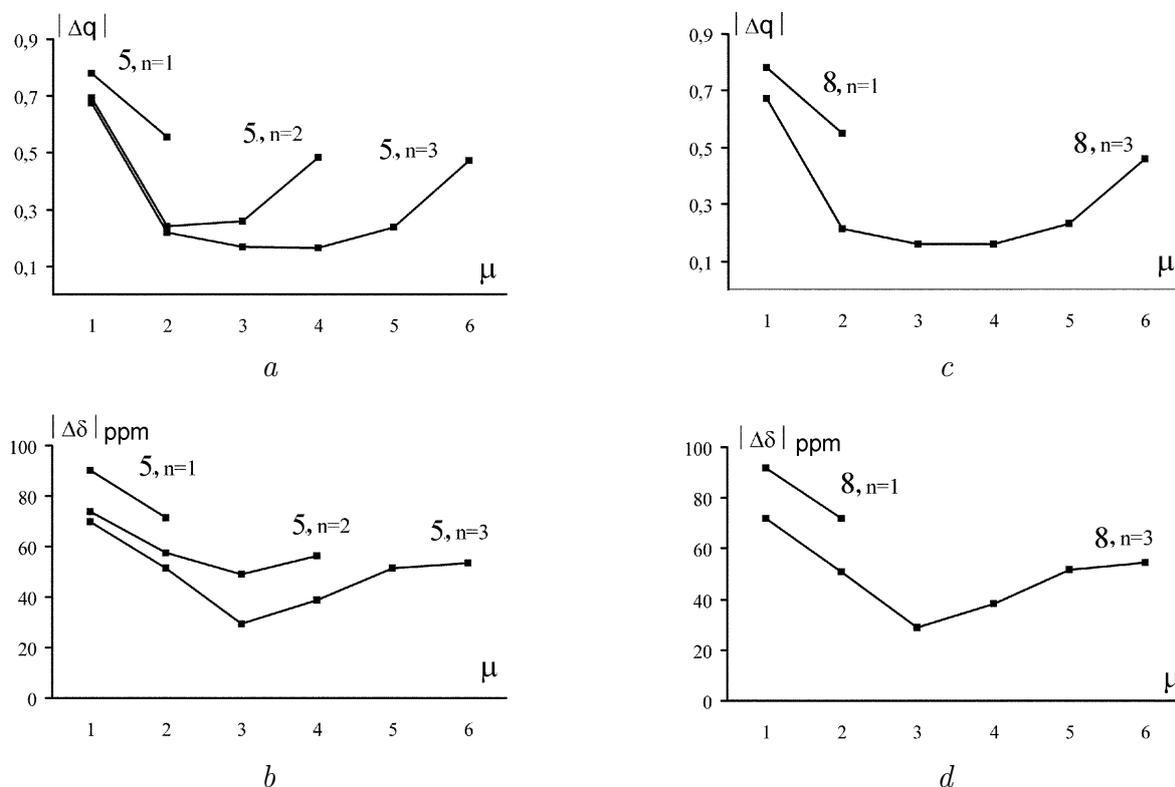


Fig. 3. Alternation of charges (B3LYP/3-21G** NBO) (a, c) and experimental ^{13}C NMR chemical shifts (b, d) of carbon atoms in a conjugated chain of cyanines **5** (a, b) and **8** (c, d)

in Table, the chemical shifts for the both carbon atoms in the polymethine chain are practically insensitive to a change of the chemical structure of non-symmetric dyes **5**, **6**, and **7**. The $\delta(^1\text{H})$ signals in the proton magnetic resonance spectrum also lie practically in the same region. On the contrary, the parameter $\delta(^{13}\text{C})$ for a cited atom that enters the finite heterocycle and is chemically bound with the polymethine chain decreases with increase in the basicity of the finite group in the series of indo-, benzothiazolo-, and quinohemicyanines: 176.73, 168.53, and 155.02 ppm. This results in a significant reduction of the alternation of chemical shifts in the chain, so the parameter $\Delta\delta_\mu$ for the first pair of carbon atoms in the chromophore of hemicyanine **7** with the most basic quinoline residual appears smaller (66.87 ppm) as compared to the value of $\Delta\delta_\mu$ for the next pair of atoms (69.16 ppm).

A decrease of the chemical shift $\delta(^{13}\text{C})$ for the atom of the heterocycle chemically bound with the polymethine chain testifies to the reduction of its partial positive charge and, thus, the shift of the electron density along the chromophore toward the opposite finite group.

The form of the charge waves with minima for the functions $\Delta\delta_\mu = f(\mu)$ and $\Delta q_\mu = f(\mu)$ obtained for indocyanines **3** and their non-symmetric derivatives **5**, as well as the equalization of the alternation amplitude of charges/chemical shifts in the chain of streptocyanines **3**, may seem to conflict with the soliton-like form of the charge waves having a sharp maximum that were obtained for ions of unsubstituted polymethines **2** or model polymethine dyes with the simplest finite groups (see, e.g., review [7]). However, as was earlier shown in [24], the effect of finite groups becomes determinative in the case of molecules with a short polymethine chain, which results in a significant deformation of the charge waves. The perturbation at the ends of the chain induced by the introduction of finite groups generates a proper wave of alternating charges at the both ends of the collective π -electron system, though the amplitude of this wave rapidly attenuates. Thus, the obtained curves $\Delta q_\mu = f(\mu)$ for the polymethine chain of short molecules **3–8** should be interpreted as a superposition of three waves: the soliton wave of charges in the chain generated by the charged π -electron system and two waves

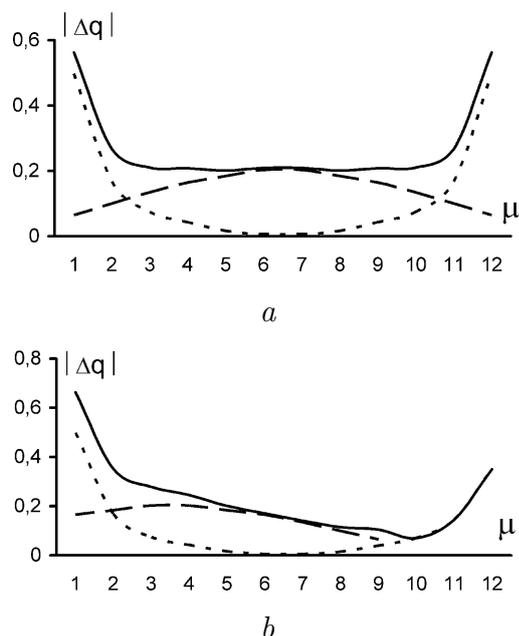


Fig. 4. Diagram of superposition (—) of charge waves (Δq_μ) generated by the chain (- - -) and two finite groups (- - -) in symmetric cyanine **3** ($C_1 = C_2$, $n = 6$) (a) and non-symmetric cyanine **5** ($C_1 \neq C_2$) (b)

arising under the influence of the finite groups. The example of such a superposition of three charge waves in streptocyanine **3** at $n = 6$ is shown in Fig. 4, a. One can see that, due to the superposition of the waves of different origin, the common charge wave has no minimum. In the case of dyes **4** with a still shorter chain, the calculation even yields a decrease in the amplitude of charge alternation, as one can see from Fig. 2, a.

In the case of the model non-symmetric hemicyanine dye **5** at the same chain length ($n = 6$), the general minimum of the wave is shifted from the center of the polymethine chain toward the finite group with less donor property (Fig. 4, b).

3. Conclusions

Thus, the combined experimental and quantum-chemical investigation of the charge distribution in the chromophore of cation symmetric and non-symmetric cyanine dyes has revealed a considerable alternation of the electron density and, respectively, the chemical shifts $\delta(^{13}\text{C})$ along the polymethine chain. The injected charge exists in the form of a wave consisting of a soliton-like wave of autolocalized total positive charge (hole) and two waves-components generated by the donor finite groups. In non-symmetric ion conjugated systems, the charge

wave shifts to the less basic finite group, and the magnitude of this shift depends on the difference between the donor properties of the both finite residuals.

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ДОСЛІДЖЕННЯ ЗАРЯДОВИХ ХВИЛЬ У ХРОМОФОРІ
КАТІОННИХ ЦІАНІНОВИХ БАРВНИКІВ
ЗА ДОПОМОГОЮ ^{13}C ЯМР СПЕКТРОСКОПІЇ

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Р е з ю м е

На основі даних квантово-хімічних розрахунків та спектрів ЯМР (^{13}C) досліджено розподіл електронної густини для серії симетричних та несиметричних катіонних ціанінових барвників. Показано, що розраховані заряди на атомах добре узгоджуються з експериментальними значеннями хімічних зсувів. Знайдено значне хвилеподібне альтернування електронної густини вздовж хромофора. Показано, що загальний розподіл електронної густини є суперпозицією автолокалізованого заряду та двох зарядових хвиль, генерованих донорними кінцевими групами.