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**VIOLATION OF IDEAL POLYMETHINE STATE
IN MEROCYANINES WITH A LONG CHROMOPHORE**

The spectral research of a number of merocyanine dyes, the derivatives of aminocoumarin and the corresponding vinylog series of symmetric anionic polymethine dyes, has been carried out. A special attention is focused on the sensitivity of the absorption curve shape to the solvent polarity, which introduces a substantial correction to the spectral properties of polymethine dyes. It is shown that the analyzed compounds reach an ideal polymethine state, the so-called "cyanine limit", in weakly polar solvents. When changing to solvents with a higher polarity, a considerable growth of the spectral absorption band width is observed, as well as the disappearance of the vibrational transition peak, with the main maximum shifting toward short waves at that. It is found that the emergence of an additional wide short-wave band in the spectra of dyes that absorb in the near IR interval is associated with the violation of the charge distribution symmetry in the polymethine chain. It is also found that, besides the similarity between the absorption spectra of cyanines and corresponding symmetric dyes, the mobility of a charge distribution in the polymethine chromophore for those compounds is possible. Moreover, in strongly polar solvents, they can exist in two forms, which manifests itself in the appearance of an additional absorption band.

Keywords: merocyanine dyes, absorption spectra, quantum chemical calculations, "cyanine limit".

1. Introduction

Merocyanines are non-symmetric neutral linear conjugated systems **1**, which contain a donor and an acceptor end group. They can be interpreted as π -electron systems intermediate between cationic cyanines **2** and anionic polymethine dyes **3** [1–4].

Similarly to symmetric ionic systems **2** and **3**, merocyanines **1** are characterized by narrow and highly intense absorption bands, which determines, first of all, their wide application in domains related to the sunlight conversion [2–4]. Such a similarity of spec-

tral properties for all three types of linear conjugated systems **1–3** is explained by the fact that, at certain parameters, the donor and acceptor characters of end groups can be in the so-called ideal polymethine state, when the lengths of carbon-carbon bonds in the polymethine chain of merocyanine **1** become equal to one another as much as possible; similarly to the bonds in symmetric polymethine dyes **2** and **3**. This is the so-called "cyanine limit" state (see, e.g., works [2–5]). On the other hand, like the spectra of symmetric polymethine dyes **2** and **3**, the spectra of merocyanines **1** are interpreted rather easily and can be used to establish regularities between the molecular and electronic structures, as well as to reveal unexpected deviations

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from those regularities [4]. The chemical structure of linear conjugated systems **1–3** is rather simple and can be changed, in particular, to obtain optimum linear and nonlinear optical properties [3, 6, 7].

One of the most important features of cyanine dyes is the linear dependence of the wavelength at their absorption maximum on the corresponding polymethine chromophore length, i.e. on the number of vinylene groups n in the chain of dyes **1–3**, the so-called “vinylene shift”. For symmetric dyes, this quantity amounts to about 100 nm [3, 6, 7]. For the absorption spectra of merocyanines belonging to the vinylog series and containing some acceptor groups, a similar regularity is also observed, in particular, for indandione [3] or aminocoumarin [8, 9] derivatives. However, analogous researches were carried out for merocyanines with rather a short polymethine chain: $n = 1, 2$. At the same time, it is known that the symmetric ionic dyes with long chromophores, which absorb near 1000 nm, demonstrate a drastic change of the absorption curve shape in polar solvents: in the short-wave spectral section, there emerges an additional band, whose width and intensity depend on the solvent polarity [10–12]. The correlated spectral and quantum chemical researches showed that this phenomenon is related to the symmetry violation in the chromophore of polymethine dyes with a critical chain length. Two forms were found to coexist in the solution: 1) with a symmetric distribution of the electron density along the polymethine chains and 2) with a non-symmetric arrangement of the charge wave (for more details, see review [7] and the references therein).

In view of the similarity between the electronic structures of merocyanines and ionic dyes, it was of interest to study whether a similar spectral phenomenon can be observed for merocyanines with rather long chromophores. In this work, we present the results of the spectral researches of merocyanines, the derivatives of aminocoumarin and strong-donor quinoline, for which we managed to synthesize a series of stable vinylogs.

2. Dye Molecules and Experimental Technique

The dependence of the absorption spectrum shape in the visible and near IR intervals on the solvent polarity was studied for three vinylogs of merocya-

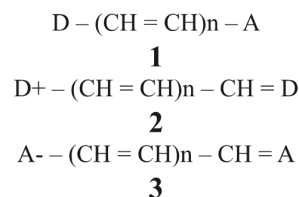


Fig. 1. Structural formulas of merocyanines (**1**), and cationic (**2**) and anionic (**3**) polymethine dyes. Here, n is the number of vinylene groups in the polymethine chain

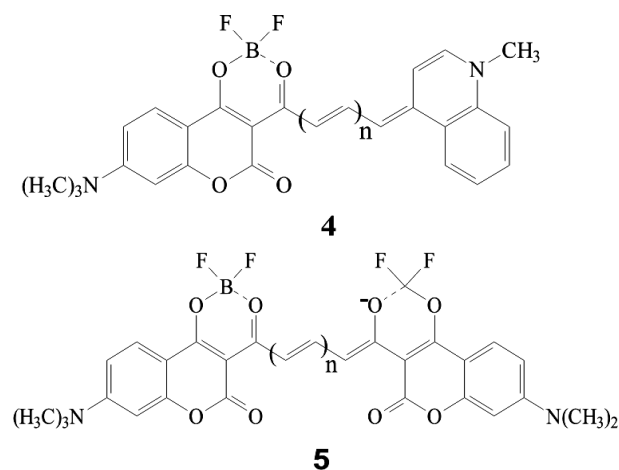


Fig. 2. Chemical formulas of merocyanines **4** and symmetric dyes **5**

nines **4** (with $n = 1, 2$, and 3), the derivatives of aminocoumarin. For the sake of comparison, the spectra of four vinylogs of symmetric anionic dyes with aminocoumarin end remnants were measured under the same conditions: **5** ($n = 1, 2, 3$, and 4) (see Fig. 2). The synthesis of compounds **4** and **5** was described earlier [10]. The structures and compositions of all obtained substances were confirmed with the help of ^1H NMR spectroscopy and elemental analysis. The absorption spectra were registered on a spectrophotometer Shimadzu UV-3100 in chloroform, acetonitrile, dimethylformamide, and acetone of spectral purity at the concentration $C = 10^{-5}$ M. With the help of the software package Origin, the peaks in some absorption spectra were resolved into Gaussian components.

3. Results and Their Discussion

The absorption spectra of three vinylogs of merocyanines **4** and four members in the vinylog series of some symmetric anionic dyes **5** measured in

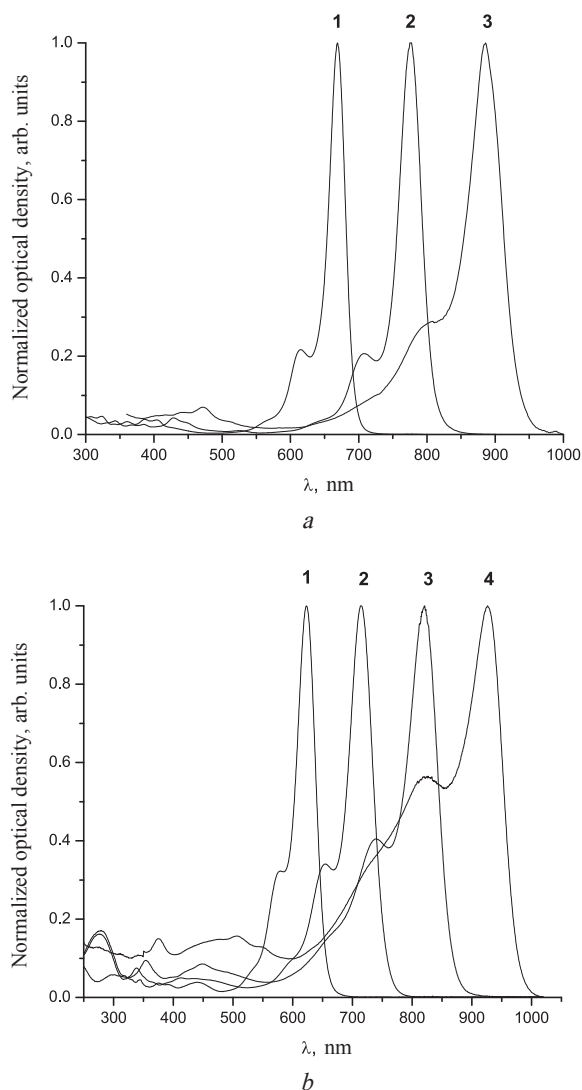


Fig. 3. Absorption spectra of merocyanines **4** (a) and dyes **5** (b) in chloroform

weakly polar chloroform are exhibited in Fig. 3. The corresponding quantitative parameters are summarized in Table. The spectra demonstrate narrow and highly intense absorption bands, which are very similar to one another, in the visible and near IR intervals. The bands monotonically and bathochromically shift as the chromophore is made longer by introducing a new vinylene group $-\text{CH}=\text{CH}-$ (the parameter n grows). In the short-wave section of the spectral band, a characteristic peak is observed at a distance of approximately $1200\text{--}1300\text{ cm}^{-2}$. According to the

theory of color of polymethine dyes (see, e.g., reviews [6, 7, 13–15]), this peak corresponds to the first vibrational transition.

Besides the shape of absorption bands, a characteristic feature of polymethine dyes is the spectral effect of chromophore lengthening, the so-called “vinylene shift”. This is a displacement of the absorption band maximum, when a new vinylene group is introduced:

$$V = \lambda_n - \lambda_{n-1}. \quad (1)$$

The parameter V is approximately identical for cationic and anionic dyes **1** and **2**, and weakly depends on the end groups and the polymethine chain length (for more details, see review [7] and the references therein). As one can see from the data of Table, the vinylene shifts for merocyanines **4** and symmetric anionic dyes **5** are almost identical, especially, for molecules with short chromophores; they are also close to the values of parameter V for cationic dyes **1** [7]. Such a similarity of spectra is interpreted in the literature [3, 5, 13, 16] by the fact that not only neutral form A can adequately describe the electronic structure of merocyanines, but it can also be done, by using form B with separated charges and form C with equalized bond lengths, as is schematically illustrated in Fig. 4.

The authors of works [3, 5, 13, 16] assert that the neutral polyene-like structure A is realized in vacuum (at quantum chemical calculations, when the influence of the environment is not taken into account). At the same time, in the case of balanced donor and acceptor forces of end groups, structure B with equalized bonds dominates; this structure is typical of

Calculation characteristics of electronic transitions in compounds **4** and **5**

Dye	n	λ_{max}	V , nm
4	1	668	
	2	776	108
	3	886	110
5	1	623	
	2	714	91
	3	820	106
	4*	927	107

(*) The dye contains a tri-methylene bridge ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) at the middle of polymethine chain.

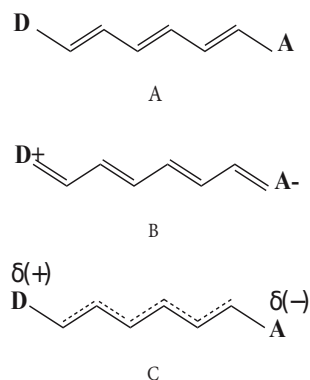


Fig. 4. Representations of a cyanine molecule with the help of resonance structures

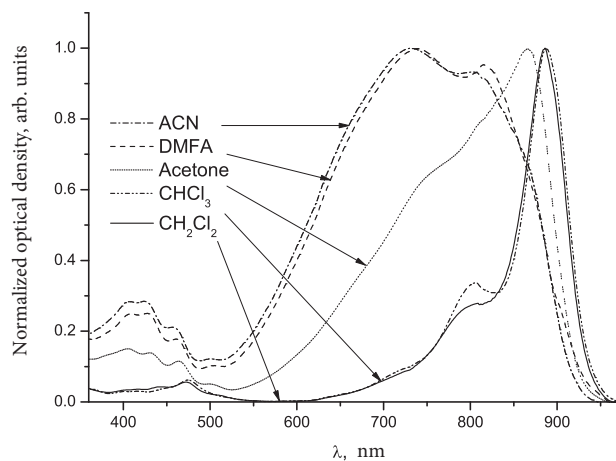


Fig. 5. Absorption spectra of merocyanine **4** with a long chromophore, $n = 3$, in solvents with various polarities

symmetric polymethine dyes: both cationic and anionic. It is owing to the equalizing of bond lengths that the ideal state, the so-called “cyanine limit”, is realized in merocyanines, and the form of their spectral bands becomes similar to that of the spectra of polymethine cyanine dyes, in particular, cyanine dyes with nitrogen-containing heterocyclic end groups.

Hence, the spectral forms for merocyanines **4** and symmetric anionic dyes **5** (Fig. 3) and the comparison of vinylene shifts for both series of compounds **4** and **5** (Table) allow us to draw conclusion that the “cyanine limit” state, which is described by resonance structure B, is attained in merocyanines **4**, the derivatives of aminocoumarin, and strongly donor quinoline in a weakly polar solvent. The registration of spectra of merocyanines **4** in highly polar solvents revealed a

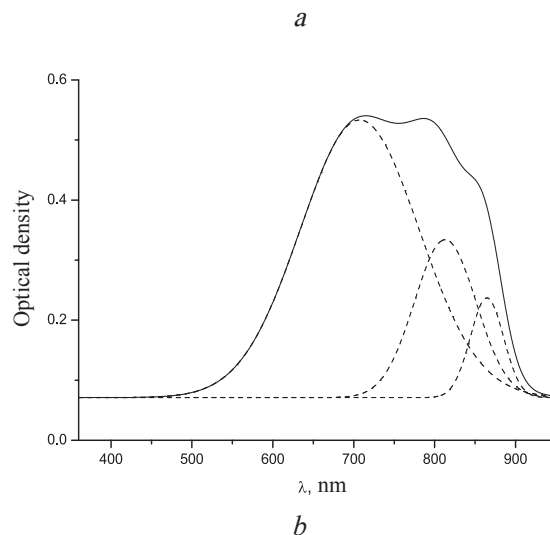
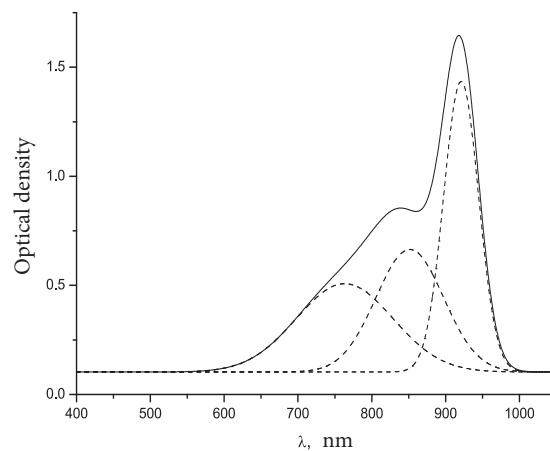


Fig. 6. Spectral absorption bands of dye **5** with $n = 3$ in chloroform (*a*) and dye **4** with $n = 3$ in acetonitrile (*b*) and their resolutions into components

drastic modification in the shape of the long-wave absorption band in the dyes with relatively long polymethine chains. For illustration, Fig. 5 exhibits the absorption spectra of tricarbomerocyanine **4** with $n = 3$.

By comparing the spectra in Fig. 5 and the spectra obtained in weakly polar methylene chloride, which are depicted in Fig. 3, it becomes evident that the change of the solvent even to acetone with enhanced polarity is accompanied by a considerable growth of the spectral band width. The peak of the vibrational transition also disappears. Instead, there appears a shoulder at the short-wave recession section, which is shifted hypochromically, so that it

can hardly be associated with the vibrational structure. The principal maximum also shifts toward short waves.

The further growth of the polarity in such solvents as acetonitrile (ACN) or dimethylformamide (DMFA) changes the spectral curve shape so that the short-wave peak turns out the most intense. In addition, in both solvents, the long-wave peak shifts hypochromically with respect to the corresponding peak in the spectra registered in weakly polar solvents CH_2Cl_2 and CHCl_3 .

This sensitivity of the adsorption curve shape to the solvent polarity was described for higher vinylogs of symmetric polymethine dyes (for more details, see review [7] and the references therein). On the basis of a detailed spectral research and a parallel quantum chemical simulation, it was found that the appearance of the additional wide short-wave band in the spectra of dyes that absorb in the near IR interval is related to the violation of the charge distribution symmetry in the polymethine chromophore. Namely, the charge wave in dyes with long polymethine chains becomes mobile and shifts toward either of the end groups. Two forms can coexist simultaneously in the solution. One of them is symmetric and has rather a small dipole moment, which is directed normally to the chromophore. This form is weakly sensitive to the solvent polarity. The other form is non-symmetric and has a much larger dipole moment directed along the chromophore. As a result, this form is very sensitive to the solvent polarity owing to the dipole-dipole interaction [7]. In work [12] dealing with a detailed spectral and quantum chemical studies of the phenomenon of symmetry violation in thiocyanines (six vinylogs were obtained for them), it was shown that the absorption band for dyes with long chromophores can be resolved into two components, which can be attributed to different forms.

As one can see from Fig. 3, *b*, an analogous modification of the spectral band shape is also observed for symmetric anionic dye **5** with a long chromophore. Accordingly, the absorption curve can be resolved into components that can be associated with the symmetric and non-symmetric forms of dye in the polar solvent (see Fig. 6, *a*). The results of calculations showed that the alternation of neighbor bonds in the non-symmetric form is stronger, i.e. the latter becomes polyene-like.

The corresponding component resolution of the spectral band for merocyanine **4** with a long chromophore in a strongly polar solvent – namely, acetonitrile – is depicted in Fig. 6, *b*. By comparing the both panels of Fig. 6, a conclusion can be drawn that the ideal state “cyanine limit” is violated in merocyanines with long chromophores in strongly polar solvents, so that the dye molecules coexist in two forms: a polymethyne-like form with equalized bonds (resonance structure C) and a polyene-like one with a considerable alternation of neighbor bonds (structure B), similarly to two shapes of symmetric ionic dyes. It is worth noting that the order of single- and double-bond alternation in structure B is opposite to that in neutral form A. A similar change of alternation in polyenes occurs, as was shown in works [17,18], at the transition from the neutral form to their dicationic or dianionic.

4. Conclusions

To summarize, the spectral research of a specially synthesized series of merocyanines, the derivatives of aminocoumarin, and the corresponding vinylogs of symmetric anionic dyes demonstrates that, besides the similarity of absorption spectra for merocyanines and symmetric polymethine dyes, a mobility of the charge distribution in the chromophore and the existence of two forms in strongly polar solvents is possible for the both types, which manifests itself in the appearance of an additional band in their absorption spectra.

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ПОРУШЕННЯ ІДЕАЛЬНОГО ПОЛІМЕТИНОВОГО СТАНУ В МЕРОЦІАНІНАХ З ДОВГИМ ХРОМОФОРОМ

Резюме

Робота присвячена спектральному дослідженню ряду мероціанінових барвників, похідних амінокумарину та відповідних вінілогічних серій симетричних аніонних поліметинових барвників. Особлива увага приділена чутливості форми кривої поглинання до полярності розчинника, що вносить суттєві корективи до спектральних властивостей поліметинових барвників. Показано, що у даних сполук в мало полярних розчинниках досягається ідеальний поліметиновий стан, так званий стан "cyanine limit". При переході до розчинників з вищою полярністю спостерігається значне зростання ширини спектральної смуги поглинання, а також зникання піка коливального переходу. При цьому головний максимум зміщується в бік коротких хвиль. Встановлено, що виникнення додаткової широкої короткохвильової смуги в спектрах барвників, які поглинають в ближній ІЧ області, пов'язано з порушенням симетрії в розподілі заряду в поліметиновому ланцюжку. Знайдено, що крім схожості спектрів поглинання ціанінів й відповідних їм симетричних барвників, для цих сполук можлива мобільність розподілу заряду в поліметиновому хромофорі й існування двох форм в сильно полярних розчинниках, що проявляється в появі додаткової смуги поглинання.