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Nature of electron transitions in polymethine dyes—derivatives of indeno[2,1-*b*]chromene

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Abstract

The nature of the first and the three higher electron transitions in symmetrical and unsymmetrical polymethine dyes containing indeno[2,1-*b*]chromene residues as end groups is discussed. Diagrams of electron density redistribution upon excitation are used for determination of the electron transition localization. It is shown that the first transition in symmetrical dyes and unsymmetrical compounds with pyrilium, thiapyrilium, benz[*c*,*d*]indolium and flavilium residues is localized in the polymethine chain and accompanied by electron transfer at neighboring atoms, whereas the two higher transitions are associated with electron density transfer from the terminal groups to the polymethine chains and hence could be considered as quasi-local transitions. In contrast, in the dyes containing benzothiazolium and indolenium residues as end groups with noticeably small effective lengths, inversion of the polymethine and quasi-local transitions occurs.

Keywords: Pseudoazulene; Polymethine dyes; Absorption spectra; Electron transitions; Quantum-chemical calculations

1. Introduction

Polycondensed π-electron pseudoazulenes containing a heterocyclic subunit are attracting widespread attention due to their unusual properties, particularly the features of their absorption and fluorescence spectra [1–8]. They can exhibit long wavelength absorption, which is considerably sensitive to various changes in the chemical constitution. Another specific spectral property of the pseudoazulenes is the anomalous fact that the emission is caused by $S_2 \rightarrow S_0$ electron transition (see Refs. [9,10] and references therein). In continuation of our previous work with pseudoazulene-containing dyes [11,12] we have synthesized and studied the spectral properties of dyes containing nuclei of the indeno [2,1-*b*]chromene (IC). This polycondensed heterocycle contains isoelectronic to azulene π-system as a main structural component, and hence demonstrates specific spectral features. Although the absorption band was found to be shifted hypsochromically and wider in respect to the original azulene [9], the $S_2 \rightarrow S_0$ nature of the fluorescence remained unchanged [9].

Such an extended π-electron system and comparatively deep color of the IC heterocycle makes it important as an end group in the synthesis of polymethine dyes absorbing in the near-IR spectral region. We, therefore, synthesized a series of the symmetrical and unsymmetrical polymethine dyes based on IC polycondensed conjugated system and studied their spectral properties.

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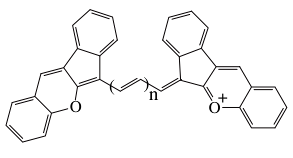
2. Materials and methodology

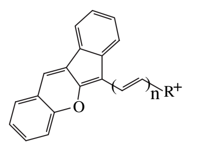
We investigated the dyes with following constitution:

Symmetrical polymethine dyes



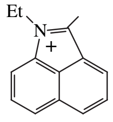
1a,b n = 0 (**a**), 1 (**b**)

Unsymmetrical polymethine dyes

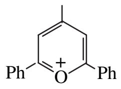


2-8a,b n = 0 (**a**), 1 (**b**)

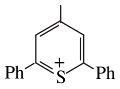
where R is the end group. In the present paper, the following heterocyclic residues were used as end groups:



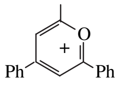
BCDI (Dyes **2**)



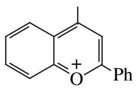
4-Py (**3**)



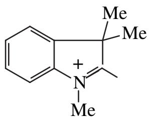
4-TPy (**4**)



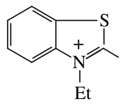
2-Py (**5**)



4-Fl (**6**)



Indo (**7**)



BT (**8**)

The dyes **1a**,**b** were synthesized by the reaction of IC and corresponding IC-containing aldehydes in Ac_2O media in the presence of $HClO_4$. The dyes **2–8** were synthesized by condensation of the corresponding aldehydes with salts of methyl-substituted heterocycles in Ac_2O [13].

Absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100. Spectral grade acetonitrile was used as a solvent for spectral measurements.

To interpret the nature of electron transitions, quantum-chemical calculations were performed. The equilibrium geometry of dye molecules in the ground state was optimized in the AM1 approximation to the gradient of 0.01 kcal/mol. The electron transition characteristics were calculated by the AM1, ZINDO/S and PPP methods, all using π-electron singly excited configurations.

3. Results and discussion

3.1. Symmetrical dyes

Absorption spectra of the two vinylogs of the symmetrical dyes as well as the initial IC in MeCN are presented in Fig. 1. Dyes **1a**,**b** absorb light in comparatively long wavelengths, even on the short polymethine chain: $n = 0$ ($\lambda_{max} = 714$ nm) and $n = 1$ ($\lambda_{max} = 802$ nm), and exhibit relatively narrow bands (Fig. 1) with the shoulder on the short wavelength side ($n = 0$) or with well-pronounced maximum at 736 nm ($n = 1$) which corresponds to the vibronical $0 \rightarrow 0'$ transition with the frequency $1120\ cm^{-1}$. As a typical so-called "polymethine" $\pi \rightarrow \pi^*$ transition, it involved practically only the frontier MOs (HOMO and LUMO) and is accompanied by considerable redistribution of electron density mainly at the carbon atoms within the chain and at those atoms that can be considered as a direct lengthening of the polymethine chromophore (Fig. 2a).

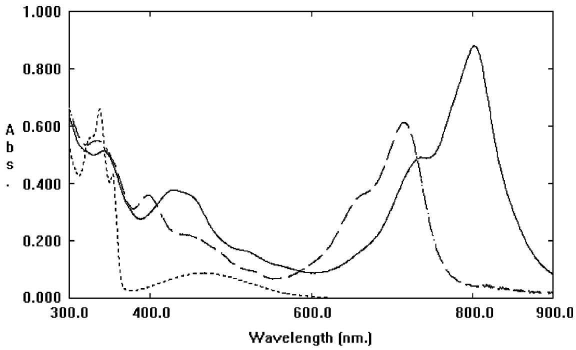
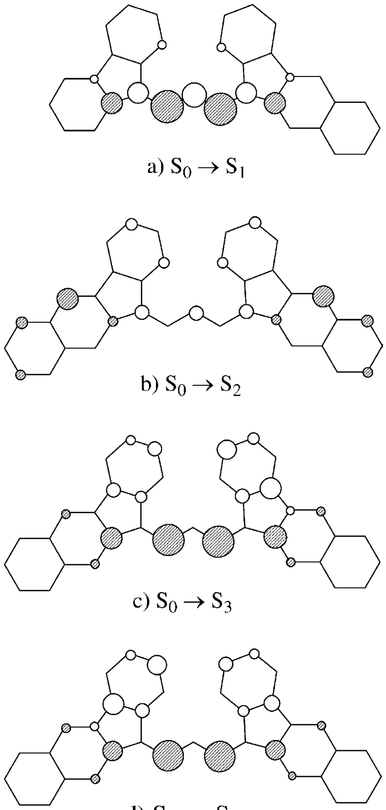


Fig. 1. Absorption spectra of IC (broken line, small dashes) and symmetrical dyes **1a** (broken line, long dashes) and **1b** (solid line).

The calculated wavelengths of the first electron transition, λ^c, in all-valence methods, AM1 and "spectral" ZINDO/S, differ essentially from experimental data: 547 nm (AM1), 568 nm (ZINDO/S) for dye **1a**



a) $S_0 \rightarrow S_1$

b) $S_0 \rightarrow S_2$

c) $S_0 \rightarrow S_3$

d) $S_0 \rightarrow S_4$

Fig. 2. Diagram of electron redistribution at atoms upon excitation in symmetrical dye **1b** (PPP approximation). Blank circles show the decreasing electron density, filled circles show increasing electron density.

Table 1
Experimental data of dyes **1**–**8**

Dye	R	λ_{max} (n = 0), nm	λ_{max} (n = 1), nm	V, nm	ΔV
1	Symm.	714	802	88	–
2	BCDI	710	787	77	19
3	4-Py	683	760	77	30
4	4-Tpy	718	795	77	30
5	2-Py	694	778	82	45
6	4-Fl	707	802	95	1
7	Indo	596	653	57	
		449	502	53	
8	BT	586	624	38	
		447	496	49	

while experimental band maximum, λ_{max}, is equal to 714 nm (Table 1), and 602 nm (AM1), 619 nm (ZINDO/S), while $\lambda_{max} = 802$ for the higher vinylog **1b**. Such divergence between the calculated and experimental values is a typical imperfection for these approximations. The better convergence between calculated and observed results is reached in the π-electron PPP approximation, particularly using the version proposed by Fabian et al. [14] for the calculation of the energy of the first transition in polymethine dyes: 684 and 751 nm for dyes **1a** and **1b**, respectively. Nevertheless, all methods giving the higher transitions should be suitable in the shorter spectral region, 400–500 nm, which agrees with that observed in absorption spectra. Thus, it would be expected that quantum-chemical calculations reflect correctly the nature of the electron transition, the main location of the transition and transferring of the electron density upon excitation.

From Fig. 1 we can see that increasing of the chain length by one vinylene group (dyes **1a** and **1b**) leads to the bathochromic shift of absorption band maximum at 88 nm. Such decreasing of the vinylene shift in respect to the typical value, 100 nm, is likely connected with an additional bathochromic shift of the absorption band of the dye with the shortest chain, **1a**, due to the spatial hindrances.

The comparatively deep absorption of investigated dyes could be caused by two main factors: a greater effective length of the end groups, and an interaction of the frontier levels with the orbitals of π-electron system of the end residues. It was proposed earlier that the quantitative estimation for the influence of topology of the end groups on the energy of first electron transition and relative disposition of the frontier levels by so-called topological indices of the end residues, L and Φ_o is useful. The topological parameter, Φ_o, corresponds to a displacement of electron density from terminal groups to the polymethine chain; it reflects the π-electron donative ability of the end residues and correlates with their basicity. The other parameter, L, gives quantitatively the effective lengthening of a chromophore at the expense of the π-system of end groups and can be expressed by the equivalent number of vinylene groups. Both the topological indices can be mathematically correctly calculated using the topological matrices of the terminal residues [15].

Our calculation gives a relatively large value for the effective lengths of IC residue as an end group ($L = 5.45$), and relatively small π-electron donative ability ($\Phi_o = 36°$).

On the other hand, an additional bathochromic shift of the long wavelength absorption band could be caused by interaction with the higher transitions involving the electron levels of the end groups.

It should be noted that it was more difficult to correctly interpret the higher electron transitions, which is connected with the bad resolving of the spectra in short-wave region. In Fig. 1 it is shown that there are some electron transitions in the spectral region from 600 nm to 400–350 nm, i.e. in the same part where the first absorption band of the initial IC is observed. The existence of several transitions is supported also by analysis of the spectra of unsymmetrical dyes where the higher transitions may manifest themselves even as separated bands of comparative intensities (it will be considered later).

It was considered previously that so-called local or quasi-local transitions should appear in the dyes that contain end groups with an extended π-electron system [16]. Thus the end groups are proposed to be local chromophores while the polymethine chain could be treated as an outer conjugated substituent. In the MO approximation, the quasi-local transition involves necessarily the MO localized mainly at atoms of the end groups; other MO taking part in the transition can be totally delocalized.

The analysis of the results of the quantum-chemical calculations shows that two of the three lowest electron transitions $S_0 \rightarrow S_1$, S_2, S_3 in the symmetrical dyes **1a** and **1b** are quasi-local, while the third transition is connected with only delocalized orbitals: $|\mathrm{HOMO}\rangle \rightarrow |\mathrm{LUMO}+1\rangle$. In the monomethine dye **1a** and trimethine dye **1b**, the two occupied orbitals, $|\mathrm{HOMO}-1\rangle$ and $|\mathrm{HOMO}-2\rangle$, are practically totally localized at end IC residues (Fig. 2). Thus, the quasi-local transitions can be written by the following superpositions:

$$\begin{aligned}\Psi_{\mathrm{loc},1} &= C_1(|\mathrm{HOMO}-1\rangle \rightarrow |\mathrm{LUMO}\rangle) \\ &\quad + C_2(|\mathrm{HOMO}-1\rangle \rightarrow |\mathrm{LUMO}\rangle)\end{aligned}$$

$$\begin{aligned}\Psi_{\mathrm{loc},2} &= C_1(|\mathrm{HOMO}-1\rangle \rightarrow |\mathrm{LUMO}\rangle) \\ &\quad - C_2(|\mathrm{HOMO}-1\rangle \rightarrow |\mathrm{LUMO}\rangle)\end{aligned}$$

where C_1 and C_2 are coefficients, such that $C_1^2 + C_2^2 = 1$.

The redistribution of the electron densities upon these transitions differs considerably from the change in electron densities upon the first electron transitions (Fig. 2). The calculated wavelengths of the quasi-local transitions for both vinylogs are found to be practically degenerated

(407 and 408 nm ($n = 0$), 408 and 409 nm ($n = 1$)) and close to the wavelength of the first transition, 412 nm.

Besides these two pronounced distinctly quasi-local transitions, the calculation predicts one more $\pi \rightarrow \pi^*$-electron transition in the spectral region between 400 and 500 nm. It is accompanied by transferring of the electron density from the polymethine chain and the benzene ring annulated with five-member cycle to chromene heterocycle moiety of the end groups (Fig. 2). The energy of this transition based on ZINDO/S calculations decreases regularly upon increasing of the number of the vinylene groups in the chain, so that its wavelength is equal to 402 ($n = 0$), 412 ($n = 1$), 420 ($n = 2$), 433 ($n = 3$) and 448 nm ($n = 4$). In contrast, the energies of both the quasi-local transitions remain practically the same. Such close energies of these three electron transitions suggest that different methods could give different nature (quasi-local or delocalized) of the higher, $S_0 \rightarrow S_2$, S_3, S_4, transitions. Nonetheless, all approximations predicted for the symmetrical dyes **1a** and **1b** the existence of two specific electron transitions that are localized mainly in the end groups; they should be somewhat similar to the first transition in the IC, and corresponding bands should lie in the region 400–500 nm. It is possible that the actual splitting of the quasi-local transitions could be relatively great although the calculations predict that they are practically degenerated.

One can consequentially assume that one of the two local transitions should disappear in unsymmetrical dyes **2–8** which contain only one IC residue as an end group.

3.2. Unsymmetrical dyes

It is convenient to divide unsymmetrical dyes **2–8** with the pseudoazulene as one terminal group into two groups depending on the magnitude of an effective length L of the second end residue R.

1. Dyes **2–6**: the parameter L for the residue R is comparable to the effective length of the IC end group. The symmetrical dyes based on corresponding heterocycles, $R^+{-}(CH{=}CH)_n{-}R$, absorb in approximately the same spectral region as the symmetrical dyes **1a**,**b**: 550–650 nm ($n = 0$) or 670–760 nm ($n = 1$).
2. Dyes **7a**,**b** and **8a**,**b**: these contain benzothiazolium and indolenium residues as the end groups with a noticeably smaller parameter, L, than the effective length of the IC. It is known that, for example, symmetrical indocarbocyanine absorbs at 542 nm and thiacarbocyanine at 552 nm [17]. Such considerable difference in the magnitude of index L for both the end groups leads to considerable changes in absorption spectra, which will be considered in Section 3.3.

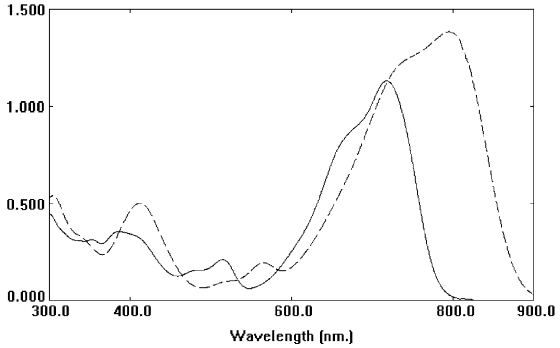


Fig. 3. Spectra of absorption of dyes **4**: $n = 0$ (solid line) and $n = 1$ (broken line). These spectra are typical for unsymmetrical dyes with large effective length of group R.

Herein the nature of the electron transitions in the dyes **2–6** is discussed. Absorption spectra (Fig. 3) are mostly similar to the spectra of symmetrical dyes **1a** and **1b** although a vibronical structure of the long wavelength bands is more pronounced. Also, the bands corresponding to the higher transitions can be more separated, for example, in dyes **4a**,**b** (Fig. 3). One can suggest that the nature of the first electron transition in these unsymmetrical molecules should be the same as that in symmetrical polymethines **1a**,**b**. In fact, Fig. 4 shows that the diagram of the electron redistribution upon the $S_0 \rightarrow S_1$ transition in the unsymmetrical dye **4b** containing the 4-TP residue is similar to the corresponding diagram for the symmetrical dye **1b**.

The end groups in unsymmetrical dyes differ substantially by their basicity, which could be quantitatively estimated using the topological index Φ_o [15]. The difference in basicities of both residues causes the alternation of the CC-bond lengths in the polymethine chain and hence a deviation D of the band maximum which can be described using following equation [17]:

$$D = (\lambda_1 + \lambda_2)/2 - \lambda_{un}, \tag{1}$$

where λ_1 and λ_2 are the band maxima of both the corresponding symmetrical dyes, while λ_{un} is the maximum of absorption in unsymmetrical dye. It was shown that parameter D increases quadratically upon going to the higher vinylogs. Then the deviation of the vinylene shift can be given as $\Delta V = (V_1 + V_2)/2 - V_{un}$, where indices are the same as Formulae (1); taking into consideration the lengthening of the chromophore it should be more sensitive to asymmetry of the dye molecule. Table 1 presents the vinylene shifts of the dyes **1–6** as well as the deviations ΔV for them. One could infer that the values of ΔV for the higher vinylogs were more suitable for estimation of the asymmetry degree of the unsymmetrical dyes.

The analysis of the calculation has shown that the occupied orbital, $|\mathrm{HOMO} - 1\rangle$, is localized mainly in the IC residue, similar to symmetrical dyes **1a**,**b**, while

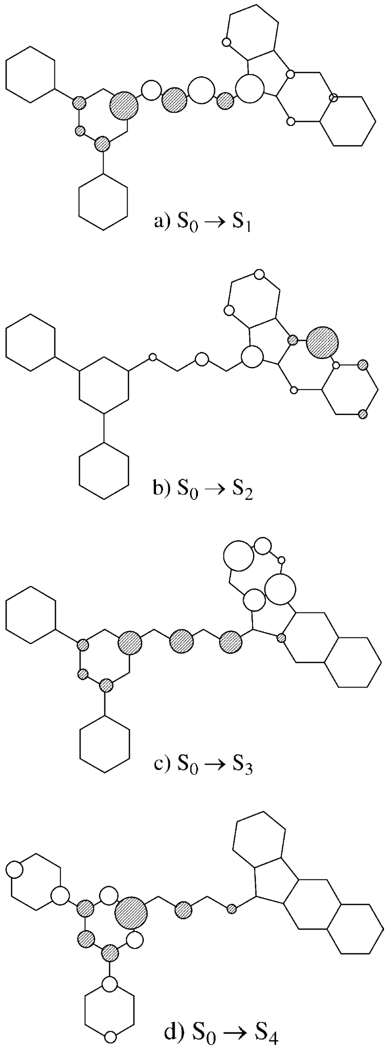


Fig. 4. Diagram of electron redistribution at atoms upon excitation in unsymmetrical dye **4b** (PPP approximation).

the $|\mathrm{HOMO}-2\rangle$ could be located in the other end group. According to this, one of the higher transitions involving the local MO should be located in the IC residue as it is obtained for dye **4b** (Fig. 4). The fourth transition $S_0 \rightarrow S_4$ turns out to be mainly concentrated in the thiapyrilium nucleus, whereas the third transition $S_0 \rightarrow S_3$ involved only the delocalized levels: $|\mathrm{HOMO}\rangle$ first of all $|\mathrm{LUMO}+1\rangle$.

It is to be noted that the calculated wavelength of the transition located in the IC residue remains practically the same in all unsymmetrical dyes, 401–402 nm, while the other two higher electron transitions are more sensitive to a topology of the varied end group R, for example 405 and 372 nm (**2b**), 405 and 384 nm (**3b**), 490 and 392 nm (**4b**). A more exact correlation between the calculated energies of the higher electron transitions and the observed absorption bands is difficult due to the poor resolution of the spectral bands in this region, 400–600 nm.

3.3. Inversion of polymethine and local transitions

Finally, the nature of the electron transitions in the unsymmetrical dyes **7a**,**b** and **8a**,**b** when effective lengths of the end group R and the IC nucleus differ significantly, $L = 3.06$ for benzothiazolium and $L = 2.76$ for indolenium [18], will be discussed. In these cases both shapes and intensities of the first and second bands of the absorption spectra change substantially (Fig. 5). One can see that the long wavelength band becomes wide with pronounced vibronic structure, especially in the dyes with the longer chain, **7b** and **8b** ($n = 1$). Thus, the first spectral band would begin to take the shape of the absorption band of the initial IC heterocycle and not that of the usual band of the typical polymethine dyes. Meanwhile, the "polymethine" shape follows from Fig. 5 to manifest itself for the second spectral band, positioned approximately at 450 nm ($n = 0$) or 500 nm ($n = 1$). The typical narrow and relative intensive absorption band with usual vibronic shoulder or even the separated maximum is observed for all four unsymmetrical dyes of this series: **7a**, **7b**, **8a**, **8b**. Such substantial transformation of the long wavelength and next spectral bands is found to be reflected on the magnitude of the vinylene shifts of the first and second maxima. It is shown in Table 1 that bathochromic effect upon the lengthening of the chromophore decreases considerably for long wavelength maximum, 57 nm (**7a** → **7b**) and 38 nm (**8a** → **8b**), while the vinylene shifts of the second band are nearer (53 nm for the dyes **7a** → **7b**) or even greater (49 nm for the dyes **8a** → **8b**) than the corresponding values for the first band.

Similar spectral effect, observed in the unsymmetrical dyes containing the end groups with considerable difference in their effective lengths, is called inversion of the electron transitions of the different nature: polymethine and quasi-local [16]. Our investigation has shown that the inversion manifests itself especially in unsymmetrical dyes that are derivatives of the IC.

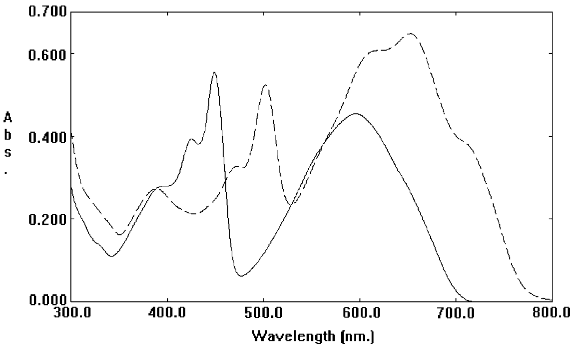


Fig. 5. Spectra of absorption of dyes **7**: $n = 0$ (solid line) and $n = 1$ (broken line). These spectra are typical for unsymmetrical dyes with small effective length of group R.

4. Conclusion

Thus, the polymethine dyes containing the indeno [2,1-*b*]chromene as one or two terminal groups display some features in their absorption spectra. The symmetrical dyes exhibit deep absorption (near IR) due to a great effective length of such end group and an additional interaction of the polymethine chromophore with the quasi-local chromophores of both the residues.

Two higher transitions are accompanied by transferring of electron density from the indeno[2,1-*b*]chromene and pyrilium and thiapyrilium residues to the polymethine chain and have relatively low energies.

Also, in unsymmetrical dyes containing indolenine or benzothiazole end group with a small effective length, the inversion of the polymethine and quasi-local transitions occurs, which leads to the substantial change of the shape of the first and second absorption bands.

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