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Dyes and Pigments 63 (2004) 323–332

www.elsevier.com/locate/dyepig

Electronic properties of polymethine systems. 6. Bond order and bond length changes upon excitation

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Received 3 October 2002; received in revised form 12 January 2004; accepted 24 January 2004

Abstract

The dependence of bond order and bond length changes upon the excitation on the molecular topology of linear conjugated systems has been investigated using quantum-chemical methods. It has been found that the molecular geometry and π-bond orders in the excited state of polymethine dyes (odd ionic π-systems) and substituted polyenes (even neutral π-systems) containing residues with their localized MOs differ significantly from that in the typical π-systems having a totally delocalized HOMO and LUMO. Also, the extraordinary π-bond order changes upon excitation have been shown to exist in relatively long polymethine dyes when the symmetry breaking occurs. These results are consistent with spectral data.

Keywords: Conjugated systems; Electron transition; Quantum-chemical calculation; Symmetry breaking

1. Introduction

The wide application of polymethine dyes and related polyenes is derived from their ability to absorb and strongly emit light in the visible and near IR regions of the electromagnetic spectrum. In addition to their traditional use in optical sensitizers, laser media, mode-lock compounds, and polymerization [1–5], these dyes can be employed as fluorescent probes, and molecular wires, in non-linear optics and light concentrators [6–8]. These applications require specific molecular features for a given compound to be effective. For instance, the absorption or fluorescence bandwidth, the excited state lifetime, Stoke's shift, and quantum yield are key considerations in the design of fluorescent sensors. These properties are known to be closely related to electronic and geometrical changes in dye molecules in the excited state [9,10]. During the lifetime of their excited states, bond lengths, bond angles and geometries of polymethine dyes or polyene dyes could change.

The present study pertains to the use of MO calculation to study bond order and bond length changes in the first singlet excited state (S_1) of linear polymethine compounds and the influence of these changes on spectral bandwidth and Stoke's shift in fluorescence spectra.

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0143-7208/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2004.01.006

1.1. Methodology of quantum-chemical calculations

The general formula for linear conjugated systems can be written by formula **1**

$$[G_1 \overset{\text{- - - -}}{=\!=} (CH)_n \overset{\text{- - - -}}{=\!=} G_2]^Z \quad z = 0,\ \pm 1,\ \pm 2 \qquad \mathbf{1}$$

Here G_1 and G_2 are end groups of arbitrary chemical constitution conjugated with the polymethine chain.

Symmetrical linear conjugated systems ($G_1 = G_2$) with a closed electron shell are divided into two types that have distinct electronic and spectral properties [11]. The type containing an even number of CH-groups in the polymethine chain, α,ω-diheterosubstituted polyenes (**2**), are marked by a high degree of alternation π-bond order (and length) in the ground state (S_0) and S_1 excited state, while π-electron densities at the carbon atoms within the polymethine chain are practically equivalent

$$[G \overset{\text{- - - -}}{=\!=} (CH \overset{\text{- - - -}}{=\!=} CH)_n \overset{\text{- - - -}}{=\!=} G]^Z$$

$$z = 0,\ +2,\ -2 \qquad \mathbf{2}$$

As a rule, heterosubstituted polyenes can exist in reduced and oxidized forms, which differ by two π-electrons [12,13].

By contrast, ionic linear conjugated systems with odd numbers of π-centers in polymethine chain traditionally known as polymethine dyes (**3**), are characterized by equivalent carbon–carbon bonds and the essential alternation of atomic charges [14]

$$[G \overset{\text{- - - -}}{=\!=} (CH \overset{\text{- - - -}}{=\!=} CH)_n \overset{\text{- - - -}}{=\!=} CH \overset{\text{- - - -}}{=\!=} G]^{\pm} \qquad \mathbf{3}$$

The electronic structure in S_0 and S_1 states and the spectral properties of polymethine dyes and heterosubstituted polyenes are determined principally by the delocalized π-electrons, while the localized σ-electrons form the molecular core [11,14]. Promoting π-electrons from HOMO to LUMO generates the lowest singlet excited state (vertical or Frank–Condon state with the same molecular geometry) and the relaxed state with the excited state equilibrium geometry (emitting state).

The main types of electronic transitions in symmetrical structure **1** are: (1) transitions involving delocalized MOs; (2) transitions involving delocalized MOs and orbitals localized in end groups; and (3) transitions involving the localized (or quasi-localized) MOs [11]. The first type has been called polymethine electron transition. It involves the MOs, which are delocalized at the carbon atoms of chain methine groups and the associated wavelength of polymethine electron transitions increases linearly on lengthening the chain. If conjugated system contains end groups that have an extensive conjugated system, they form the so-called localized or quasi-localized MOs, which are mainly localized within end groups. Electronic transitions that involve the quasi-localized level had been referred to as quasi-localized electronic transitions. The third type of transition is found in a donor–acceptor conjugated system or in long polymethine dyes when the loss of symmetry occurs. It is accompanied by considerable intramolecular charge transfer [11].

In contrast to the S_0, molecules in excited states are short lived, and hence cannot reach a global energy minimum, but only a local minimum [14,15].

It is known [14,15] that the conjugated systems in the emitting excited state can have distorted molecular geometries that affect bond lengths, bond angles, molecular planarity and cause disruption of π-conjugation. In this work, only bond length changes were considered, as it was assumed that geometrical perturbations in the emitting excited state of linear conjugated systems cause the normal Stoke's shift in the fluorescence spectra [14], while other conformational transformations require more time and lead to anormal effects in fluorescence spectra. On the other hand, conformation changes in molecules with linear conjugated systems mainly determine the fluorescence quantum yield.

The good correlation between the π-bond order ($P_{\mu\nu}$) in the ground state and the carbon–carbon bond length ($R_{\mu\nu}$) is found to exist in conjugated molecules [16]. This is shown by Eq. (1), where $a = 0.154$ nm and $b = -0.014$ nm

$$R_{\mu\nu} = a + bP_{\mu\nu} \qquad (1)$$

It is also possible that Eq. (1) is correct for π-electron systems in excited states. It can be used to perform excited state geometry optimizations using a procedure that is similar to the ground state calculation, but using the excited state density matrix. Another problem is connected with accuracy of the calculated transition energies. Traditionally, the *p*th excited state wave function Ψ_p is presented as an expansion in the terms of the single excited configurations Φ_{i-j} (approximation of configurational interaction) [17]. This is shown in Eq. (2), where $T_{p,i-j}$ are coefficients

$$\Psi_p = \sum T_{p,i-j}\Phi_{i-j} \tag{2}$$

There are versions of molecular models that are parametrized with spectral investigation in mind, e.g. CNDO/S, ZINDO/S. We found that the electron transition energies obtained for linear conjugated systems using the AM1 method correlated well with results using ZINDO/S.

However, it has been found that the calculated energies for the Frank–Condon state in a vinylogous series of polymethine dyes and polyenes differ increasingly from experimental data (absorption spectra) upon lengthening the polymethine chain, so that correlation between calculated and experimental transition energies is only 30–50% [18]. These results are caused by using the limited configurational interaction approximations. For complex molecules, the configurational interaction is usually based on single $\pi\rightarrow\pi^*$ excited configurations. On the other hand, the all-valence $(\sigma+\pi)$ quantum-chemical approximations significantly overestimate the bond and atomic π-occupancy (AM1, ZINDO/S) and hence the MOs obtained using the all-valence SCF procedure for the S_0 density matrix are inadequate for configurational interaction expansion.

Increasing the number of configurations involved leads to an improvement in the correlation between calculated and experimental data, but it requires considerable increase in the number of excited configurations (single, double, etc.) and computer time, without significantly increasing the calculation accuracy. In addition, it should be taken into consideration that standard configurational interaction approximations were parameterized using a limited number of configurations (e.g. 16–25) [19]. Thus, the use of large numbers of configurational interaction leads to electron interaction in the excited state that must be taken into account twice.

With regard to quantum-chemical calculation of Stoke's shifts, one must calculate energies (E_t) of the excited state using the ground state equilibrium geometry ($E_t^{(o)}$) and using the excited state equilibrium geometry ($E_t^{(*)}$). The Stoke's shift (Δ_s) is the difference between the resultant values ($E_t^{(o)}-E_t^{(*)}$).

The geometry optimization for the both states should be performed by a similar procedure and with the same accuracy. We have found that reliable results can be obtained using the following approach:

1. Calculation of the optimized geometry using MMP2 molecular mechanics approximations, using π-bond orders consistent with the S_0 and the S_1.
2. Calculation of electron transitions $E_t^{(o)}$ and $E_t^{(*)}$ using PPP approximations for the 25 lowest single excited configurations and standard atomic and bond parameters [19].

This simplified approach, of course, does not produce the fine geometric features, such as the loss of symmetry in the rather long linear conjugated systems, molecules which are obtained by using the AM1 method for pyridopolycarbocyanines [20] or polyene dications [21]. However, the accuracy of the approach is sufficient to show the dependence of the Stoke's shift on the molecular topology of linear conjugated systems and on electron shell occupancy in a systematic way. Nevertheless, the long polymethine dyes should be considered only in the all-valence semiempirical methods.

2. Results and discussion

2.1. Delocalized electron transitions

The typical electron transitions in the polymethine dyes containing the comparative short chain involve the frontier MOs which are totally delocalized within whole dye molecule. It was established that the transition energy and other transition characteristics depend appreciably on the carbon–carbon bond π-orders or lengths in the chromophore [11].

In the present study, the alternation of bond lengths within polymethine chain of the simplest polymethine dyes, polymethines **4**, streptocyanines **5** and oxonoles **6** as well as the simplest polyenes in the neutral (**7a**–**9a**) and ionic (**7b**–**9b**) forms in the ground and emitting states was investigated

$\mathrm{H_2C^-{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}CH_2}$ **4**

$\mathrm{H_2N{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}^{+}NH_2}$ **5**

$\mathrm{O^-{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}O}$ **6**

$\mathrm{H_2C{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}CH_2}$ **7a**

$\mathrm{H_2C^-{-}(CH{=}CH)_{\mathit{n}}{-}{}^{-}CH_2}$ **7b**

$\mathrm{H_2N{-}(CH{=}CH)_{\mathit{n}}{-}NH_2}$ **8a**

$\mathrm{H_2N^+{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}^{+}NH_2}$ **8b**

$\mathrm{O{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}O}$ **9a**

$\mathrm{O^-{-}(CH{=}CH)_{\mathit{n}}{-}O^-}$ **9b**

Calculations obtained in both AM1 and MMP2 approximations have shown that the maximum alternation of the π-bond orders and hence alternation of bond lengths are reached for the polymethine chain of the unsubstituted polyenes **7a**, while the maximum bond equalization of π-bond orders is observed in the dyes **5**. It is because these compounds correspond to the ideal polyene and the ideal polymethine. These results agree with the previous investigation of dependence of the electron distribution on end group constitution [11,22]. Introducing the end groups produces a displacement of the MO nodes, which can be estimated quantitatively using the topological index Φ_o (so that $0 \le \Phi_o \le 90°$). For the model end groups of the dyes **4**–**6**, their parameters Φ_o are the following: $\Phi_o = 0°$ for the $\mathrm{CH_2{=}CH}$-residue, $\Phi_o = 34°$ for the $\mathrm{H_2N^+{=}CH}$-residue and $\Phi_o = 63°$ for O=CH-group.

As AM1 calculations for streptocyanines **5** with $n \ge 7$ gave unsymmetric structures, while MMP2 gave symmetric structures, we have limited our consideration to molecules having $n \le 6$.

It is convenient to estimate quantitatively the degree of bond alternation in polymethine chain for a vinylogous series of linear conjugated systems by taking the average of differences in the lengths of neighboring carbon–carbon bonds. This estimation is achieved using parameter ρ, in Eq. (3) [23]), where m is the total number of bonds involved, and i covers the range of 1 to $m-1$

$$\rho = \frac{1}{m-1}\sum_i |l_i - l_{i-1}| \tag{3}$$

The calculated ρ values for the linear conjugated systems **4**–**9** are presented in Fig. 1. These results indicated that alternation of bond lengths (ρ) for the emitting excited state is invariably less than the ρ values for S_0, regardless of the molecule type (polymethine or polyene), the total charge or topology of end groups. However, the differences between ρ values for the emitting state and for S_0 were greater in polyenes than in polymethine dyes. In addition, the parameter ρ in the polyenes is more sensitive to variations in the end group index Φ_o.

Based on our calculation, the geometrical changes upon excitation can be defined by a change in the multi-dimensional vector $\Delta(R)$, which corresponds to the distance between the bond length vectors. In this regard, the vector length $\delta(R)$ is given by Eq. (4), where R_i^* and R_i^o are the ith bond lengths in the emitting excited state and the ground state, respectively

$$\delta(R) = \sqrt{\sum (R_i^o - R_i^*)^2} \tag{4}$$

Eq. (4) is similar to that used to describe the vibronic structure of the spectral band [24,25].

The dependence of δ values, using MMP2 data, on the number of the vinylene groups in polymethine dyes and heterosubstituted polyenes is shown in Fig. 2. These results show that increasing the polymethine chain length leads to a decrease in δ values. The largest δ value corresponds to dyes **4**, when deviation of electron structure from ideal polymethine ($\Phi_o = 45°$) is minimum. The calculation of the substituted polyenes with considerable alternation of bond orders gives the increase in δ

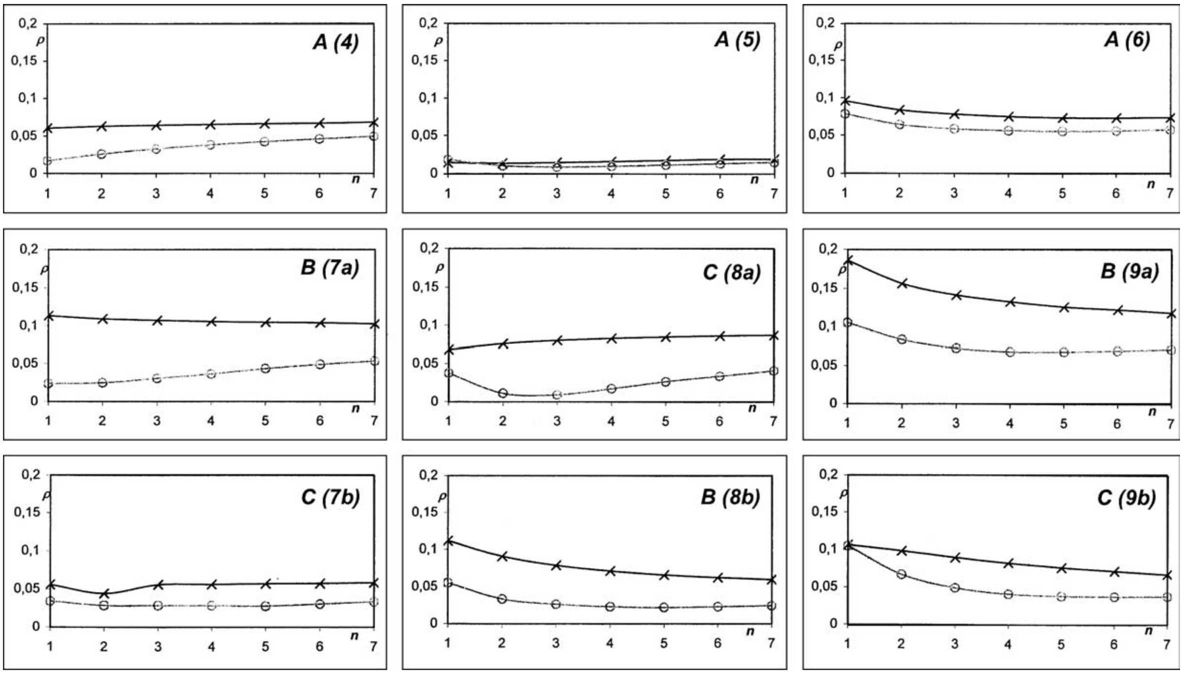


Fig. 1. Parameter ρ of ground (×) and excited states (o) for vinylogous series of polymethine dyes **4–6** (A(**4**), A(**5**), A(**6**)) and polyenes in the neutral form **7a–9a** (B(**7a**), B(**8a**), B(**9a**)) and ionic form **7b–9b** (C(**7b**), C(**8b**), C(**9b**)).

value. However, unlike polymethine dyes **4–6**, polyenes **7–9** are less sensitive to the nature of the end groups. In this regard, the results in Fig. 2 show that end group topology has a greater effect in the ionic polyene form.

It follows from Fig. 2A that the greatest effect of the change of δ value in conjugated systems with $G = -CH{=}CH_2$ is obtained for the polyene **7a** when $\Phi_o = 0°$. Increasing the Φ_o value in hetero-analogues **8** and **9** (Fig. 2B, C) causes a decrease in the amplitude of alternation of bond lengths (decrease in δ values). As a result, differences in δ values for the α,ω-diaminopolyenes **8a** or diketones **9a** and their ionic forms are lower than in the case of the classic polyenes **7a** and **7b**.

The same trends are found in the Stoke's shifts ($\Delta_s = E_t^{(o)} - E_t^{(*)}$), calculated for the vinylogues of linear conjugated systems (Fig. 3). In the polymethine dyes, chain lengthening is accompanied by a significant decrease in the Stoke's shifts. The calculated Δ_s is greatest for polymethine dyes **4** (oxonoles).

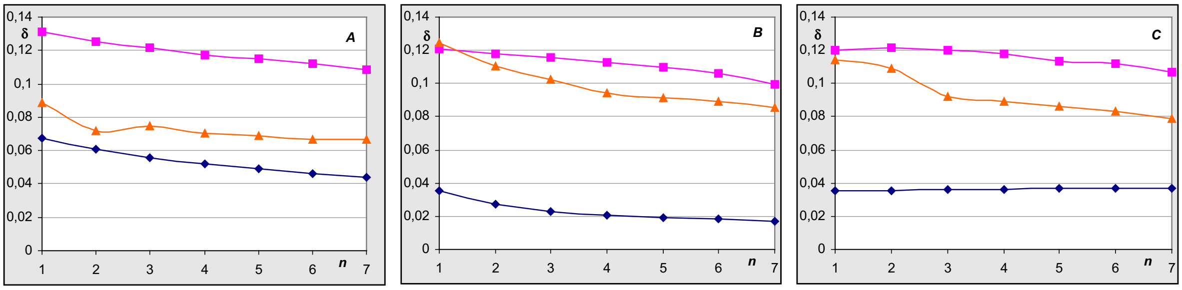


Fig. 2. δ values for polymethine dyes (—◆—), neutral polyenes (—■—) and ionic polyenes (—▲—), calculated molecules **1**, where $G = (-CH{=}CH_2)$ (A), $G = ({=}CH{-}NH_2)$ (B), $G = (-CH{=}O)$ (C).

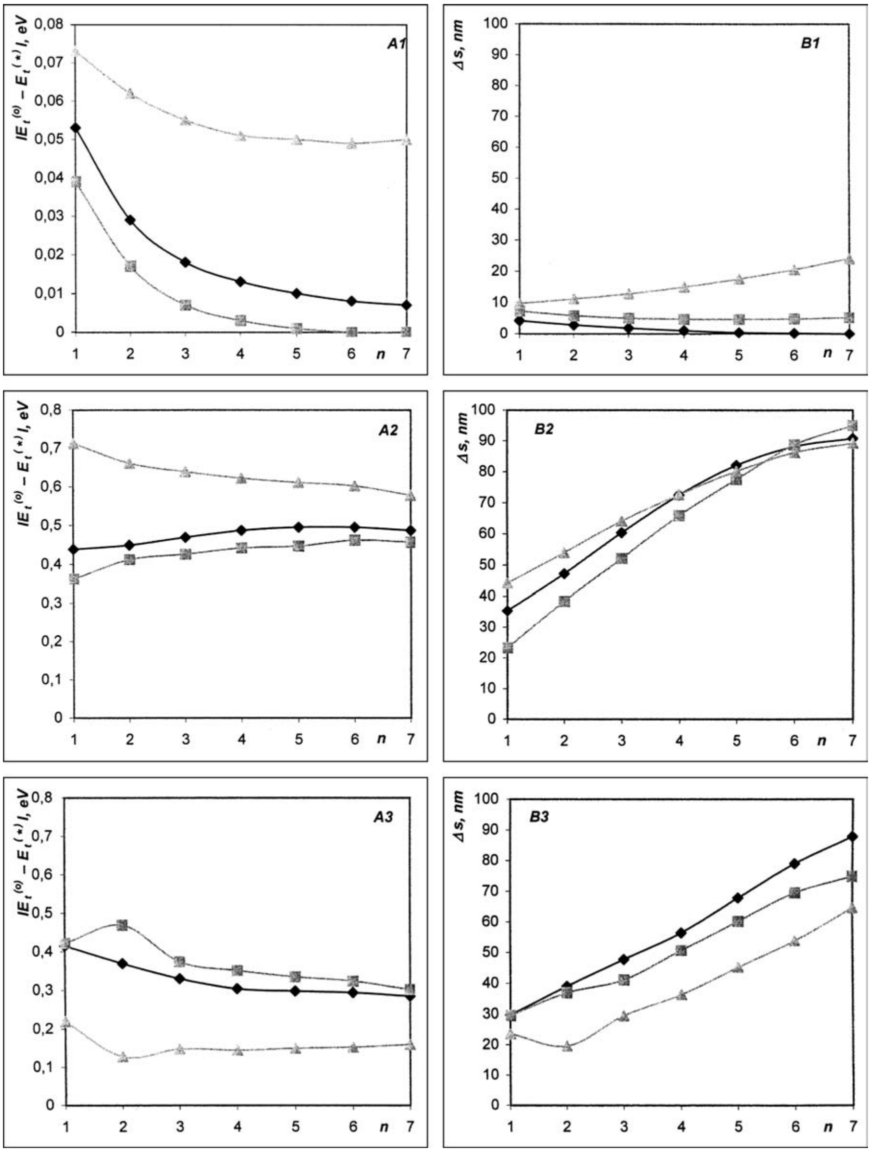
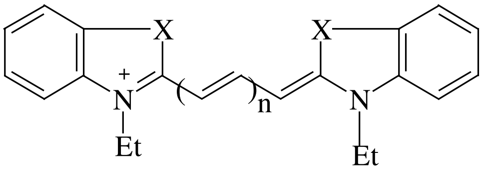


Fig. 3. Stock's shifts in eV (A1–A3) and in nm (B1–B3) of vinylogous series molecules **1**, where G = (–CH=CH$_2$) (—◆—), G = (=CH–NH$_2$) (—■—), G = (–CH=O) (—▲—), where A1 and B1 are polymethine dyes, A2 and B2 are neutral polyenes and A3 and B3 are ionic polyenes.

This was true for cyanine dyes **10**, where X = S, CMe$_2$, O, NEt [26] (Table 1)



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The Stoke's shift decreases systematically as the number of vinylene groups increases. In addition, a small Δ_s is observed for the indo- and thiapolycarbocyanines, with end groups of middle basicity (**10**, X = CMe$_2$, S), while decreasing Φ_o values in oxacyanines (X = O) or quinocyanines (X = NEt) are responsible for the observed increasing Stoke's shifts.

Table 1
Spectral characteristics of the PMDs **10** [26]

X	Φ_o	n	λ_{max}^{abs}, nm	λ_{max}^{fl}, nm	Δ_s, nm	Δ_s, cm^{-1}
S	44°	1	559	575	16	498
		2	656	676.5	20.5	461
		3	762.5	790	27.5	456
		4	875	910	35	440
CMe$_2$	41°	1	547	564	17	551
		2	642	661	19	447
		3	742	766	24	422
		4	855	880	25	332
		5	963	988	25	263
O	37°	1	485	500	15	619
		2	580	610	30	848
		3	682	710	28	580
NEt	64°	1	490	516	26	1028
		3	691	715	24	485

A complex relationship between the calculated Stoke's shifts and either molecular topology or electron shell occupancy is found for heterosubstituted polyenes **7–9**. Although calculations involving the quasi-ideal polyenes **6** predict an energy increase of Δ_s values, the gradient $\partial\Delta_s/\partial n$ is so low that its effect on wavelength increases progressively. One could note, that increasing Φ_o values in heterosubstituted **8** or **9** decrease the calculated Stoke's shifts, when compared with unsubstituted polyenes **7**. However, the chain lengthening in the heterosubstituted polyenes **8a** and **9a** is accompanied by an increase in Δ_s in contrast to the unsubstituted polyene **7a** (Fig. 3A). For the ionic polyenes forms (**7b**, **8b** and **9b**), chain lengthening leads to a substantial reduction in Δ_s, the gradient $\partial\Delta_s/\partial n$ being dependent on the end group topology (Fig. 3).

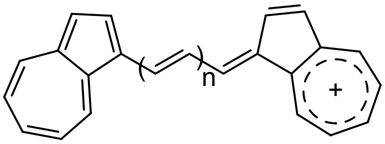
Taking Eq. (1) into consideration for π-electron systems, Eq. (4) could be rewritten as Eq. (5),

$$\delta(p) = \sum (p_i^* - p_i^o)^2 \tag{5}$$

where p_i^* and p_i^o are the ith π-bond order in the Frank–Condon excited and ground states for the same equilibrium geometry, respectively. The $\delta(p_i)$ value, has been used [27] to investigate the correlation between absorption bandwidths and bond order changes following excitations in polymethine dyes. It was found for many types of polymethine dyes, increasing the polymethine chain length leads to a decrease in $\delta(p)$, which is consistent with a decrease in absorption bandwidth.

2.2. Transitions involving the localized MOs

The quasi-localized electronic transitions involving localized MOs in the linear conjugated systems containing end groups with an extensive π-system are known [11]. This would involve structures of polymethine dyes with the azulene residues (**11** and **12**). It has been found that electrons in both frontier MOs in dyes **11** are delocalized,



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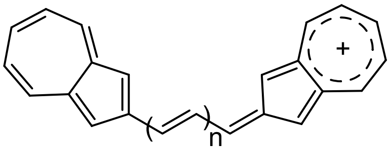


12

while the LUMO and the next empty MO in the shorter type **12** polymethines are almost completely localized on the atoms of the azulene nuclei and that their energies practically coincide with the LUMO energy of the azulene molecule [28]. As a result, the first and second electronic transitions appear to be the localized electronic transition. In the first approximation, positions of the quasi-localized levels do not depend on the chain length, while the positions of the delocalized levels are directly related to the number of vinylene groups in the chain [11,14,22]. Thus, this inversion of the quasi-localized and delocalized levels and the inversion of the localized electronic transition and polymethine transition could take place at the same chain length. This behavior should also characterize the dependence of the bond length parameters: ρ and δ, on the value of n. The calculated data in Fig. 4 show that the ρ values of 1,1′-diazulenepolymethine **11** in the S_0 increase with the increasing number of vinylene groups,

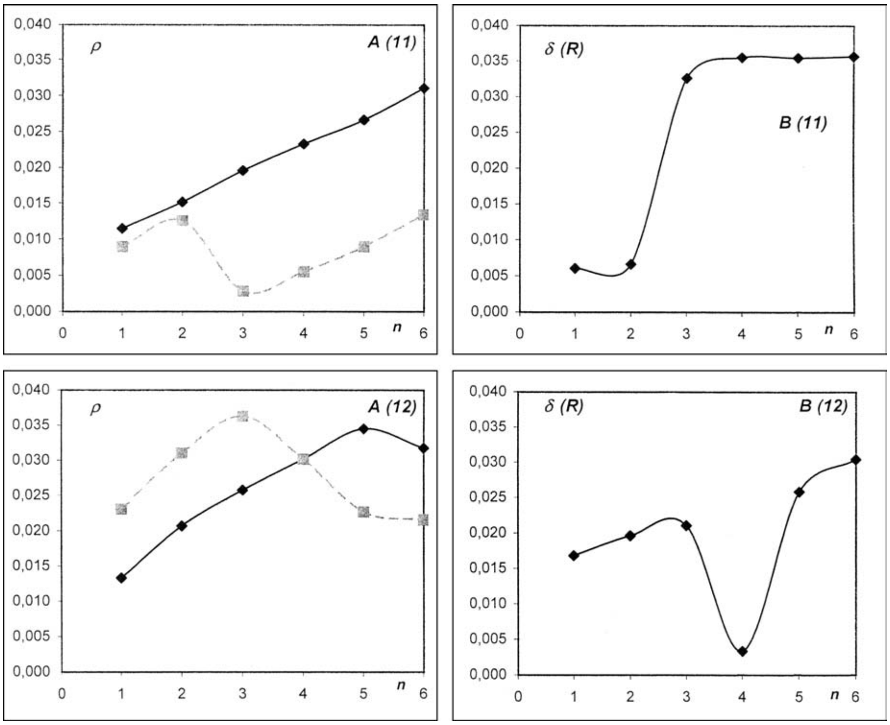


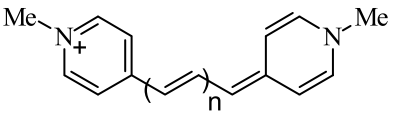
Fig. 4. Alternation of bond lengths (A(**11**), A(**12**)) in ground (—♦—) and excited (—■—) states and $\delta(R)$ values (B(**11**), B(**12**)) for vinylogous series of polymethine dyes **11** and **12**.

while the changes in the parameter ρ for the simplest polymethine dyes and heterosubstituted polyenes (**4–9**) are relatively small (compare Figs. 1 and 4). The ρ values in the emitting state for the **11** dyes with shorter chain ($n = 1, 2$) are close to values in the ground state. Lengthening chain to the heptamethine ($n = 3$) dye is accompanied by a considerable increase in ρ value for the emitting state. It is also clear that the parameter ρ values in the excited state for the shorter type **12** dyes ($n = 1–3$) are lower than the ground state values (Fig. 4, A (**12**)). In this case, the $S_0 \rightarrow S_1$ transition mainly involves the azulene residues. In the case of the dyes **12** with $n = 4$, the inversion of localized electronic transition and polymethine transition occurs, and the parameter ρ in the ground and the emitting excited state is practically the same. Further chain length increases give ρ values similar to those in the polymethines **4–6**.

Due to the dependence of the parameter ρ on the chain length considered above, $\delta(R)$ values also change. It increases sharply for dyes **11** upon changing from $n = 2$ to $n = 3$ (Fig. 4, B(**11**)), while the curve $\delta(R) = f(n)$ for the polymethine dyes **12** has a critical point when $n = 4$ (Fig. 4, B(**12**)) and when $\delta(R) \approx 0$.

2.3. Transitions involving polymethine dyes with breaking symmetry

The dependence of the parameter ρ on increasing chain length is further demonstrated in the relative long polymethines. It has been established using spectral methods and quantum-chemical calculations that the symmetry of pyridocyanines **13** is broken when $n = 6$ [20]. In the present study, AM1 calculations



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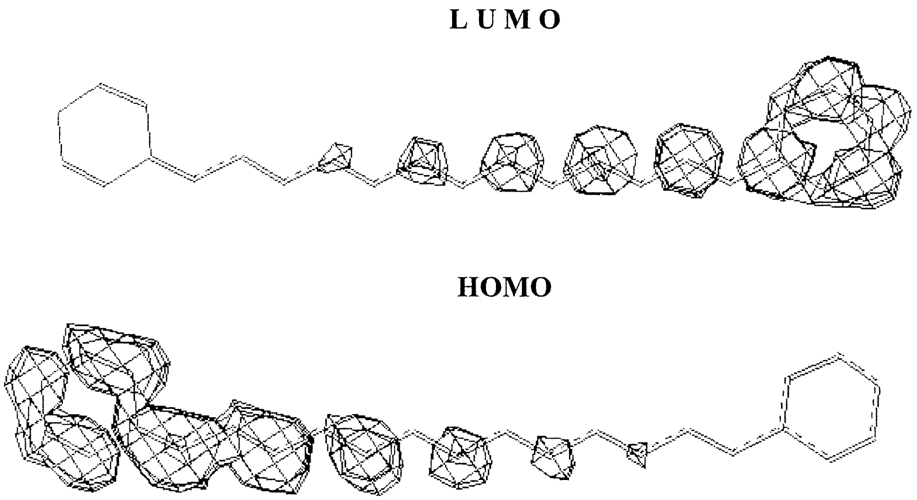

Fig. 5. Frontier MO localization ($C^2_{i\mu}$) for the polymethine dyes **13** ($n = 6$).

indicate that the LUMO is restricted to atoms on one half of the dye molecule while the HOMO involves opposite end of the molecular structure (Fig. 5). Thus, for polymethine dyes **13** with $n = 6$, inner molecular electron transitions are realized. Such transitions will be accompanied by the corresponding changes in the π-bond populations.

In Fig. 6 $\delta(p)$ values calculated from the ground state geometry of type **13** dyes are shown. It can be seen that lengthening of chain leads to a decrease in the $\delta(p)$ values for symmetrical dye molecules ($n < 5$), that is characteristic for typical polymethine dyes. However, when $n > 5$, sharp increase in bond order occurs because the first transition becomes inner molecular electron transition instead of the polymethine transition. This change in the nature of the first transition should manifest itself in the shape of absorption band. In our case, the longwave band in spectrum of hexacarbocyanine **13** ($n = 6$) appears to be quite broad, while the corresponding bands for dyes **13** ($n = 1$–4) are rather narrow.

These results indicate that changes in bond order and bond length depend not only on odd or even methine group number in the polymethine length of the linear conjugated systems, molecular charge and nature of end group, but also on the type of electronic transition.

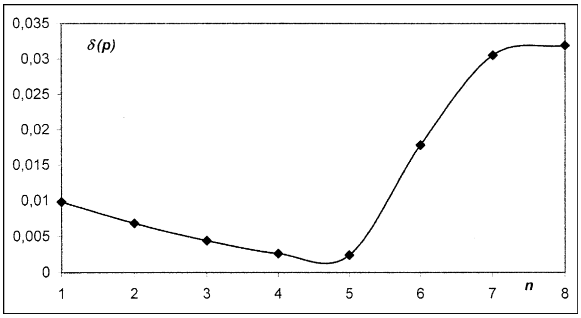

Fig. 6. $\delta(p)$ values for polymethine dyes **13**.

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