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Electronic Properties of Polymethine Systems. 3. Polymethine and Quasi-local Electron Transitions

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ABSTRACT

The nature of the first and the higher electron transitions in linear polymethine systems containing complex conjugated terminal groups are discussed. For determination of the electron transition localization, diagrams of electron density changes on excitation and the values of the atomic localities are used. It is shown that the first transition of normal polymethines is localized within the polymethine chromophore; higher transitions are associated with excitation within local chromophores. In contrast, in polyenes and polymethines containing deeply coloured nuclei, inversion of the polymethine and quasi-local transitions occurs.

1 INTRODUCTION

In previous papers[1,2] the frontier levels and relative stability of linear polymethine systems (LPMS) (**1**) have been analysed

$$G_1\text{—}(CH)_m\text{—}G_2$$

This present study is concerned with a consideration of the excited states of LPMSs.

As a general rule, the frontier MOs of normal LPMSs without a complex end group (EG) are delocalized within the whole molecule; we will refer to these as MO polymethines. Accordingly, the electron transition between the polymethine levels can be regarded as a polymethine electron transition (PET). The lowest PET between the frontier levels has a large moment μ directed along the polymethine chain (PC). On lengthening the PC, the first PET moment increases in proportion to the number of vinylene groups in the chain. The moments of higher PETS are essentially less. In the case of symmetrical heteropolyenes (HOP) having symmetry C_i, the second PET is forbidden.

If the LPMSs have EGs with an extensive conjugated system, then there appear the so called local or quasi-local MOs, which are mainly localized within EGs. The electron transition with the participation of the quasi-local level will be referred to here as a quasi-local electron transition (LET). In colour theory terms, those EGs G_1 and G_2 can be regarded as local chromophores.

In this paper we shall consider the nature of PET and LET in detail.

2 INTERACTION AND LOCALITY OF ELECTRON TRANSITIONS

The appearance of LETs in the visible region of the spectrum occurs if the quasi-local level is disposed near the Fermi level of π-electrons. So far as polymethine and local chromophores overlap and belong to the same conjugated system of the molecule, they can interact effectively. It is necessary to note, however, that this interaction is essentially distinguished by chromophore interaction within bis-dyes (**2**):[3-5]

$$G_1{-}(CH)_m{-}G_2{-}M{-}G_3{-}(CH)_n{-}G_4$$

(**2**)

where M is a bridge.

The orbital approximation is convenient for the description of those phenomena (Fig. 1). Thus, bis-dye has two independent PETs between two pairs of polymethine levels of two parent dyes (Fig. 1(a)). Then the chromophore interaction leads to the absorption band maxima of the parent dyes splitting and changing their intensities. It has been found by Kiprianov and Dyadyusha[3] that the intensities of the long-wavelength and short-wavelength maxima depend on the angle Θ between the axis of the interacting chromophores: $I_-/I_+ = \mathrm{tg}^2\,(\Theta/2)$. Unlike the above, the interaction of local and polymethine chromophores is described by means of three electron levels, viz. two polymethine levels and a quasi-local level (Figs 1(b)–1(e)). Thus, the LET considered in this paper involve one quasi-local MO and one polymethine MO. The degree of MO locality determines the degree of electron transition locality.

In a first approximation, the quasi-local level position does not depend on the PC length and the LPMS type; it is sensitive only to the EG

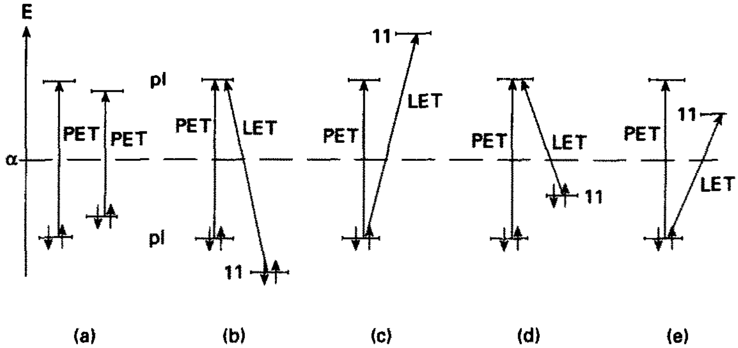


Fig. 1. Disposition of polymethine levels (pl) and quasi-local ones (11) and also polymethine electron transitions (PET) and quasi-local transitions (LET).

topology. On the contrary, the position of the polymethine level is directly related to the number of methine groups in the PC.[1]

As a rule PET and LET interact, and then excited states are described by means of expansion:

$$|S_1\rangle = C_1|\mathrm{PET}\rangle + C_2|\mathrm{LET}\rangle; \; |S_2\rangle = C_1|\mathrm{PET}\rangle - C_2|\mathrm{LET}\rangle \qquad (1)$$

where C_1 and C_2 are expansion coefficients.

The shape of the absorption spectrum of LPMSs containing complex conjugated EGs depends on the mutual dispositions of the polymethine and the quasi-local energy levels.

It is convenient to use electron redistribution diagrams for analysis of the electron transition locality. These diagrams demonstrate the electron density changes Δq_μ at atoms, or bond order changes $\Delta p_{\mu\nu}$ occurring on electron transition:

$$\Delta q_\mu = q^*_\mu - q^0_\mu \qquad \text{or} \qquad \Delta p_{\mu\nu} = q^*_{\mu\nu} - p^0_{\mu\nu} \qquad (2)$$

The values Δq_μ and $\Delta p_{\mu\nu}$ characterize the sensitivity of the electron transition to changes in chemical structure. In perturbation theory, the correction to the transition energy is calculated as follows:

$$\Delta E = -\Delta q_\mu \delta\alpha_\mu \qquad \Delta E = -2\Delta p_{\mu\nu}\delta\beta_{\mu\nu} \qquad (3)$$

where $\delta\alpha_\mu$ and $\delta\beta_{\mu\nu}$ are corrections to the Coulomb and resonance integrals which quantitatively characterize the structural changes. Typical diagrams are shown in Figs 2–4.

Another method consists in using the transition density matrix (TDM) D.[6,7] The element of the TDM are constructed as follows:

$$D^{(p)}_{\mu\nu} = \sum_{i-j} T_{p,i-j}(C_{\mu i}C_{\nu j} + C_{\mu j}C_{\nu i}) \qquad (4)$$

where $T_{p,i\text{-}j}$ is the coefficient of configuration $\Phi_{i\text{-}j}$ in the expansion of the excited state function: $\Psi_p = \Sigma\, T_{p,i\text{-}j}\Phi_{i\text{-}j}$; and indices i and j are numbers of the single occupied MOs in the corresponding configuration.

The atomic localities are determined by the diagonal elements of the matrix D^2: $L_\mu = D^2_{\mu\mu}$. In a one-electron approximation, we obtain:

$$L_\mu = (C^2_{i\mu} + C^2_{j\mu})/2 \tag{5}$$

Insofar as the squared coefficient $C^2_{i\mu}$ is a measure of the probability that the electron on the ith MO is situated near the μth atom, the value L_μ demonstrates the probability of the transition of an electron at the μth atom on excitation.

By summing values L_μ in a fragment of the molecule, we can obtain an electron transition in a part of molecule; summing L_μ in the whole molecule gives:

$$\Sigma L_\mu = 1$$

There is a simple relation between the electron density change matrix $\Delta P = P^* - P^o$ and the TDM D:

$$\Delta P = -D^2(P^0 - E), \qquad |\Delta P| = D^2 \tag{6}$$

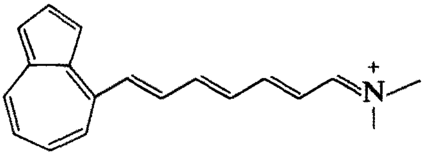
where P^* is the electron density matrix of the excited state, P^0 is that of the ground state, and E is a matrix specific as follows: $E_{\mu\mu} = 1$, $E_{\mu\nu} = 0$.

It follows from formulae (6) that the modulus of electron density changes $|\Delta q_\mu|$ corresponds to the atom locality L_μ.

We now consider the possible cases of interaction between the polymethine and the local chromophores. The calculations were carried out in the PPP approximation, with the same atom and bond parameters as those previously used,[8] and the excited state function constructed as an expansion of the lowest 25 electron configurations.

3 ELECTRON TRANSITIONS IN USUAL PMD

In normal PMDs the quasi-local level is more distant from the Fermi level than both frontier polymethine levels (Figs 2(b), 2(c)). As the simplest model, the hypothetic unsymmetrical dye 3, having one azulene nucleus, can be considered.



(3)

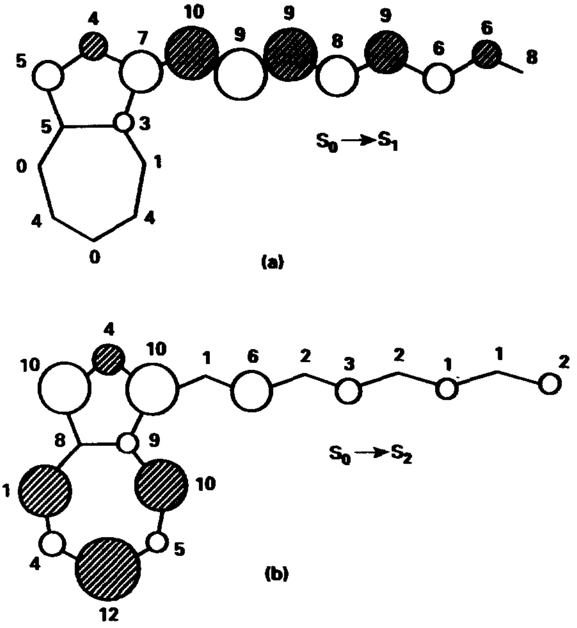
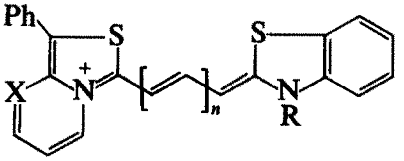


Fig. 2. Electron density changes (▨, ○) and atomic localities $L\mu$ (%) of dye **3**; ○, electron density increases upon excitation; ○, electron density decreases.

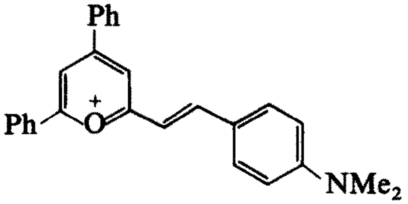
This end group has a small effective length (L = 3·69) and topology index $\Phi_o = 27°$.[1,8,9] The dye with an azulene nucleus has a relatively low electron donor ability, π_o, but azulene itself is a deeply coloured conjugated system having λ_{max}^{575} nm.[10,11] The energies of its Hückel frontier MOs are $\varepsilon_e = \alpha - 0{\cdot}40\beta$, $\varepsilon_g = \alpha + 0{\cdot}48\beta$. Calculations for dye 3 in the HMO approximation gives the energy of the three levels nearest to the Fermi levels: $\varepsilon_u = \alpha + 0{\cdot}36\beta$, $\varepsilon_{u+1} = \alpha - 0{\cdot}19\beta$, $\varepsilon_{u+2} = \alpha - 0{\cdot}40\beta$, where u is a number of HMOs. It follows from the calculation that the MO φ_{u+2} is almost completely (98%) localised at the atoms of the azulene nucleus. Thus, this orbital is a quasi-local one; its energy practically coincides with the LUMO energy of the azulene molecules. As a result, the second transition in the unsymmetric dye **3** can be regarded as an LET.

More accurate calculation in the PPP approximation gives the following wavelengths of electron transitions: λ_1 = 625 nm, λ_2 = 567 nm. The electron redistribution diagrams and other electron characteristics are shown in Fig. 2. The first transition $S_o \rightarrow S_1$ is mainly localized at the atoms of the polymethine chromophore. The PET is 65% localized in the PC and 35% in the EG. The transition moment μ_1 is directed along the polymethine chromophore. Figure 2(a) demonstrates that the second transition is mainly localised in the azulene nucleus and at atoms which are disposed in vinylogous positions relative to the end group atom connected with the PC. Values of L_μ are greater at the azulene atoms. The moment μ_2 is directed along the local chromophore and it is smaller than the PET moment μ_1.

An analogous situation is realized in dyes (**4**) containing thiazolopyridinium or thiazolopyrimidinium nuclei, and in the unsymmetric pyrylostyryls (**5**).



(**4**) $n = 0$–2
X = CH, N

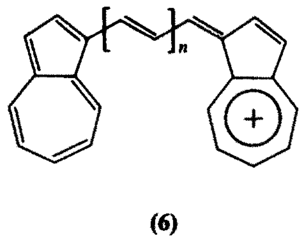


(**5**) X = H, OMe, OEt

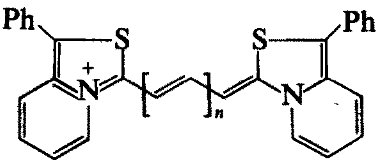
Two intense absorption bands are observed in the visible and near IR regions for polymethine dyes (**5**).[12,13] The long-wavelength band is typical of usual polymethine dyes. Lengthening of the PC leads to a maximum shift of about 110–115 nm. The vinylene shift of the short-wavelength band is essentially less (30–40 nm), and the band intensity decreases.

The pyrylostyryls (**5**) have two maxima, at 400–500 nm and at 570–650 nm.[14] Quantum chemical calculation shows that the second transition is mainly localized at the atoms of the diphenylpyrylium nucleus.

The symmetrical PMDs (**6**, **7**) have two identical local chromophores. If they exhibit no interaction, their LET energies should practically coincide.



(**6**)



$n = 0, 1,2$

(**7**)

The long-wavelength maxima of α,ω-di(1-azulenyl)monomethine(**6**) ($n = 0$) lie in the visible region of the spectrum: $\lambda_{max} = 603$ nm.[15] The calculated wavelengths and vinylene shifts of the first three electron transitions are given in Table 1; Table 2 gives the atom localities L_μ; electron redistribution diagrams are depicted in Fig. 3. The first transition $S_0 \to S_1$ is seen, from Fig. 3(a), to be of polymethine nature. Some atoms of the five-membered ring contribute to the PET; they can be regarded as an extension of the polymethine chromophore. In contrast, the second

TABLE 1

Calculated Electron Transition Characteristics of Dyes **6** and **7** (PPP Approximation, in nm)

Dye	*n*	λ_1	*V*	λ_2	*V*	λ_3	*V*
6	1	607		562		560	
	2	675	68	577	15	576	16
	3	748	73	590	13	589	13
7	0	667		490		423	
	1	726	59	498	8	437	14
	2	797	73	512	14	458	21

($S_0 \rightarrow S_2$) and the third ($S_0 \rightarrow S_3$) transitions are accompanied by changes in the electron density, mainly at the atoms of the end groups (Fig. 3(b)). The atoms in the β-position, and those in the vinylogous ones, contribute to LETs. The PC can then be regarded as a conjugated substituent of a local chromophore. Table 2 shows that the atom localities L_μ of the first PET are considerably greater than those of LETs $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$. For example, the PET $S_0 \rightarrow S_1$ in polymethine (**6**) ($n = 3$) is 60% localized at the chain atoms, and LETs are 89% localised within the azulene nuclei. The energies of the second and the third transitions are seen from Table 1 to practically coincide. It is thus apparent that LETs do not interact with each other. However, lengthening of the PC leads to a

TABLE 2

Atomic Localities $L\mu$ of Symmetric Dyes **6** and **8** ($n = 3$)

Atom μ	*1-Azulenylpolymethine*			*2-Azulenylpolymethine*		
	S_1	S_2	S_3	S_1	S_2	S_3
1	0·05	0·05	0·05	0·08	0·08	0·03
2	0·02	0·03	0·03	0·00	0·00	0·04
3	0·03	0·05	0·05	0·08	0·08	0·04
4	0·03	0·04	0·04	0·03	0·03	0·01
5	0·00	0·05	0·05	0·04	0·04	0·02
6	0·03	0·03	0·03	0·03	0·03	0·00
7	0·00	0·06	0·06	0·04	0·04	0·03
8	0·03	0·03	0·03	0·03	0·03	0·00
9	0·01	0·05	0·05	0·04	0·04	0·02
10	0·03	0·04	0·04	0·03	0·03	0·01
11	0·08	0·00	0·00	0·04	0·04	0·10
12	0·06	0·04	0·04	0·01	0·01	0·07
13	0·08	0·01	0·01	0·05	0·05	0·09
14	0·07	0·03	0·03	0·01	0·01	0·08

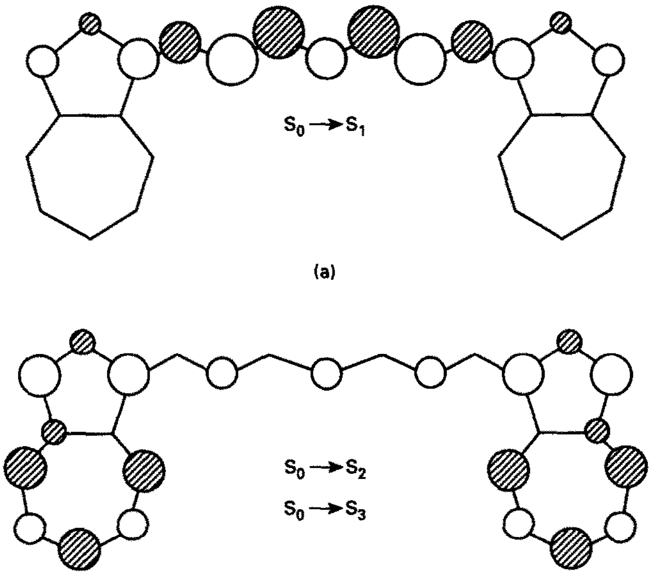


Fig. 3. Electron redistribution diagrams of dye **6** (n = 3).

decrease in LET energies, due to the participation of some chain atoms in local chromophores.

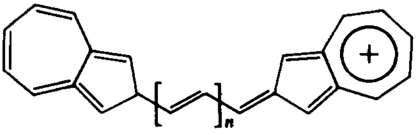
The essential interaction is realized in PMDs (7); as seen from Table 1, the energies of the second and third transitions differ significantly. Experimental data confirm the calculations; the short-wavelength absorption band of the carbocyanine (7, n = 1) and the dicarbocyanine (n = 2) have two maxima.[16]

The calculation also predicts the decrease in LET moments μ_2 and μ_3. In fact, the short-waveband intensity falls if the number of vinylene groups increases. The short-wavelength band often disappears in long PMDs.

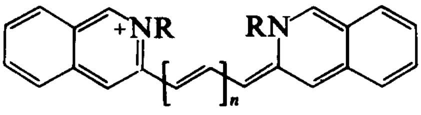
4 INVERSION OF POLYMETHINE AND LOCAL TRANSITIONS

If a local level lies closer to the Fermi level than that of the polymethine levels (Fig. 1(d,e)), then the LET has a lower energy than PET, i.e. inversion of PET and LET occurs. This change in the nature of the first and the next higher electron transitions is realized, provided the polymethine levels are strongly shifted up or down, and the inter-level distance is relatively great. There is a large energy gap in the PMD having a short PC and small effective length of EGs. On the other hand, the maximum shift of polymethine levels with the same distance between them is achieved when the topology index π_0 takes on its limiting values: O° or 90°. Then one of polymethine levels is a nonbonding one, and, as a result, the electron donor ability π_0 is 0° or 90°, as far as $\Phi_0 = \pi$ for PMDs.[1]

As an illustration, we can consider the α,ω-di(2-azulenyl)polymethine (**8**).



(8)



(9)

As an end group, the azulene residue has a topology index $\Phi_0 = 0°$ if the PC is connected to the carbon atom in position 2; the effective length L is 3·50. The local level of azulene with the energy $\varepsilon = \alpha - 0{\cdot}40\beta$ maintains an unchanged disposition as far as the corresponding MO has a node at the atom connected with the PC.

Calculated data are presented in Table 3 and in Fig. 4. Analysis of the atomic localities L_μ (Table 1) and diagrams of the electron density redistribution (Fig. 4) in PMD (**8**) having short PC permit the conclusion that the first two electron transitions are mainly localized in the azulene end groups. The local transitions are accompanied by electron density transfer from the end groups to the PC, in contrast to dyes **6** (Fig. 3(b)).

Polymethine nature manifests itself only in the third transition (Fig. 3(b)). It follows from Table 2 that the LET in heptamethine (n = 3) is 60% localised within the local chromophore and the PET is 80%

TABLE 3

Calculated Electron Transition Characteristics of Dyes **8** and **9** (PPP Approximation, in nm)

Dye	*n*	λ_1	*V*	λ_2	*V*	λ_3	*V*
8	0	737		692		470	
	1	734	−3	712	20	536	66
	2	715	−19	712	0	600	64
	3	706	−9	704	−8	664	64
	4	740	36	684	−20	675	11
	5	798	58	683	−1	660	−15
9	0	600		520		423	
	1	650	50	574	54	496	73
	2	710	60	617	43	557	61
	3	773	63	648	31	602	45
	4	836	73	671	23	634	32
	5	901	65	690	19	658	24

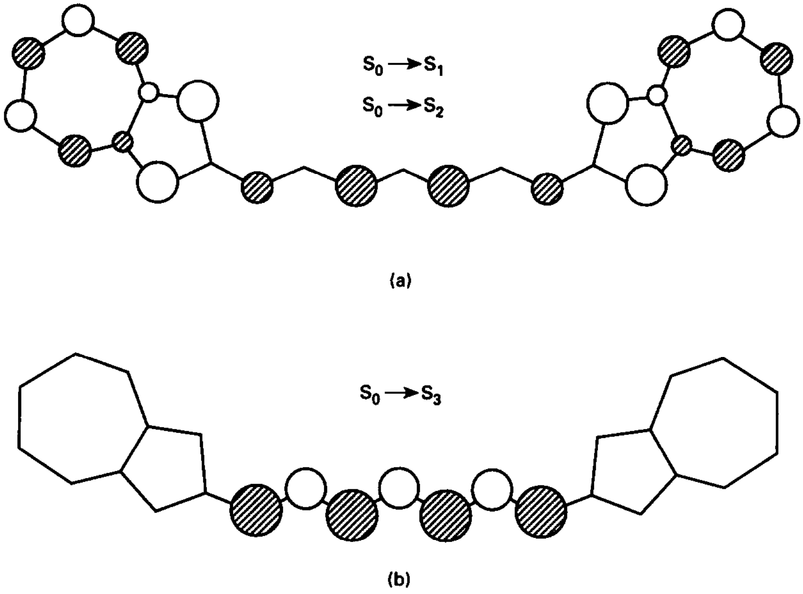


Fig. 4. Electron redistribution diagrams of dye **8** (n = 3).

localised within the polymethine chromophore. An increase in the number of vinylene groups in the PC causes the polymethine levels to gradually approach the Fermi level, while the local levels are not sensitive to lengthening of the PC. As a result, if the PC is long enough, the two polymethine levels can approach closer to the Fermi level than the quasi-local level of the azulene residue. Then the PET energy is less than the LET energy, i.e. the first and higher transitions change their nature,

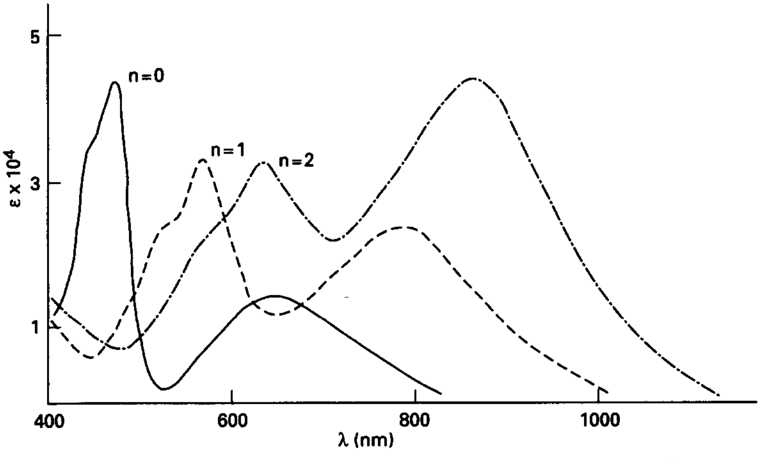
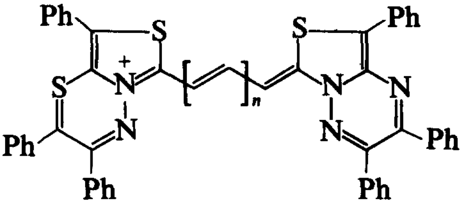


Fig. 5. Absorption spectra of dyes **10** (in acetonitrile).[19]

or opposite inversion occurs. The vinylene shift of the first and third electron transitions are seen, from Table 3, to be substantially changed if $n > 3$. Analysis of the electron density redistribution and the localities L_μ shows that the first transition of the longchain dyes (**8**) ($n > 4$) is a polymethine one. Therefore, it is more correct to calculate the vinylene shift by comparing λ_1 of a nonamethine dye ($n = 4$) and λ_3 of heptamethine dye ($n = 3$): i.e. $V = 76$ nm. This is close to the value calculated for normal dyes in the PPP approximation.[17] On further PC lengthening, the energy of the first transition essentially decreases, $V = 58$ nm.

As another example, the PMDs (**9**) having iso-quinoline residues with high basicity ($\Phi_0 = 80°$), can be considered. Dyes **9** demonstrate a transition inversion if the PC is short. On the other hand, the first electron transition is of a polymethine nature if the chain is long enough ($n > 4$). 3-Quinocarbocyanine (**9**) ($n = 1$) has been described by Brooker;[18] it has a broad long-wavelength absorption band which is not typical of polymethine dyes. this seems to correspond to a quasi-local transition in the end group chromophore.

Experimentally, the inversion of the electron transitions has been observed in thiazolo[3,4-a][1,2,4]triazine dye (**10**).[19]



(10)

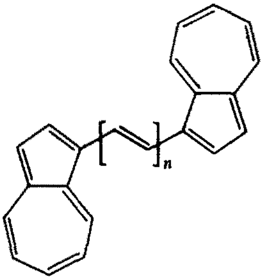
It is apparent from Fig. 5 that the short-wavelength band shape is typical of polymethines. It is narrower and more intense than the long-wavelength absorption band. Evidently, the lowest electron transition is a LET and the second transition is of a polymethine nature.

5 QUASI-LOCAL TRANSITION IN POLYENES

Local level position is much the same for polyenes and polymethines, i.e. it is independent of the PMC type. Two important factors influence the polymethine level disposition. First, the electron levels of a polyene are shifted approximately at $\pi\beta/(4(n+L))$ relative to those of the polymethine with the same end groups.[1,2] The levels are shifted up if the number of π-electrons exceeds that in the corresponding polymethine, and down in the opposite case. Secondly, the distance between the highest occupied polymethine level and the lowest unoccupied level essentially increases due to bond alternation. As a result, inversion of PET and LET is more probable in a polyene, especially if the PC is short. Additionally, the bond alternation causes the frontier polymethine levels of the polyene to approach the Fermi level more slowly.

The maximum shift of the polymethine levels depends on the end groups. For polyenes, the following relationship between the electron donor ability π_0 and the topology holds: $\Phi_0 : {}^1\pi_0 \equiv \Phi_0 \pm 45°$. This is the reason why the maximum level shift occurs in HP having EGs with $\Phi_0 = 45°$, unlike PMDs, having a nonbonding MO if $\Phi_0 = 0°$ or $90°$.

As an example, we have studied the nature of the electron transitions in α,ω-di(1-azulenyl)polyenes (**11**) having the same end groups as the polymethine dyes (**6**).



(11)

In this case, the electron donor ability π_0 of the electron-balanced form is rather high: $\varphi_0 = 72°$. Polyenes **11** and their isomers have two typical absorption bands in the visible and near IR regions of the spectrum, a broad long-wavelength band and comparatively narrow shortwave adsorption.[11,12] It follows from the calculations that two lowest transitions are caused by excitation within local chromophores. Thus, Table 4 shows that the moments of the two first transitions μ_1 and μ_2 are relatively small, while the third transition moment μ_3 is essentially greater. Chain lengthening by one vinylene group brings practically no changes in the energy of the first and the second transitions in the polyene. Further addition of vinylene groups leads to a negative vinylene shift (−8 nm). Evidently, this phenomenon is connected with the weakening of the interaction between local chromophores, which is most pronounced in polyenes with a short PC.

The energy of the third transition decreases gradually with lengthening of the PC (Table 4) and the vinylene shift is 30–35 nm. The moment μ_3 is directed along the polymethine chromophore, if one takes account of the EGs. This indicates that the third transition is a polymethine one.

In conclusion, it should be emphasized that the energy gaps in polyenes are greater than in polymethines; as a result, the inversions of polymethine and quasi-local electron transitions occur more often for polyenes.

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